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APPLICATION OF DENDRONIZED-METAL COMPLEXES ON SILICA AS CATALYSTS FOR ORGANIC SYNTHESIS

RATANA CHANTHATEYANONTH

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ABSTRACT

This thesis describes a variety of synthetic attempts to prepare dendrimer-metal complexes anchored to silica. The new complexes were obtained by immobilization of a tridentate diphosphinoaryl ligand (PCP-type) palladium(II) complex onto silica and silica supported dendrimers which combine the advantages of heterogeneous and homogeneous catalysts. They are thermally stable and they are also stable towards oxygen and moisture.

These complexes show high catalytic activity for the Heck reaction of aryl iodides with styrene and *n*-butyl acrylate, resulting in high yields of stilbene and cinnamate ester. They are also active in the reactions of a variety of aryl bromides with *n*-butyl and methyl acrylate, providing para-substituted cinnamate esters in good yields.

These complexes are also effective catalysts for the cyclocarbonylation reaction of 2-allylphenol yielding five- or seven-membered ring lactones in good selectivity and in high yields.

In addition, these complexes can be recycled by simple filtration in air and reused with little to moderate loss of activity. In both kinds of reactions, the dendritic systems show higher activity compared to the non-dendritic systems.

ABBREVIATIONS

Ac	Acetyl
BOC	*tert*-butoxycarbonyl
br	broad
n-Bu	*normal*-butyl
°C	degree Celsius
δ	chemical shift relative to tetramethylsilane
CH_2Cl_2	dichloromethane
dppb	1,4-bis(diphenylphosphino)butane
d	doublet
DCC	dicyclohexylcarbodiimide
DMAP	4-(dimethylamino)pyridine
DMF	dimethylformamide
EI	electron impact
equiv.	Equivalent
Et	ethyl group
Et_3N	triethylamine
EtOAc	ethyl acetate
EtOH	ethanol
g	grams
GC	gas chromatography

H	hours
Hz	Hertz
ICP	inductive coupling plasma
J	coupling constant, in Hz
L	ligand
m	multiplet
M	metal
M	molar
M^+	parent molecular ion
Me	methyl group
MeOH	methanol
mg	milligrams
min	minute
mL	milliliters
mol	mole
mp	melting point
mmol	millimoles
MS	mass spectrometry
NMP	*N*-methyl-pyrrolidinone
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge thermal ellipsoid plot
PAMAM	polyamidoamine
Ph	phenyl group

%	percent
ppm	parts per million
psi	pound per square inch
r.t.	room temperature
s	singlet
t	triplet
TADDOL	α,α,α’,α’ – tetraaryl-1,3-dioxolane-4,5-dimethanol
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TON	the turnover number

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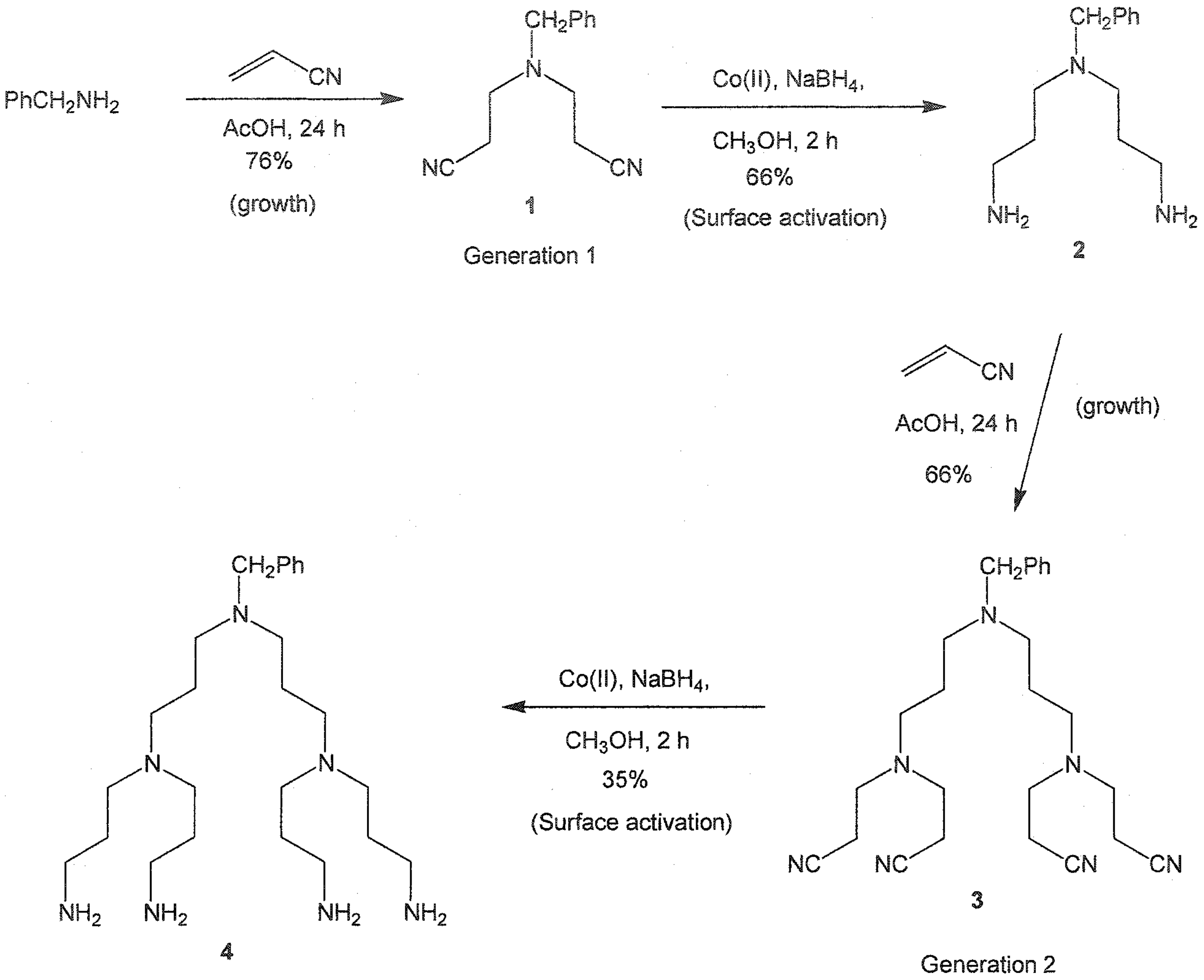
1

Introduction

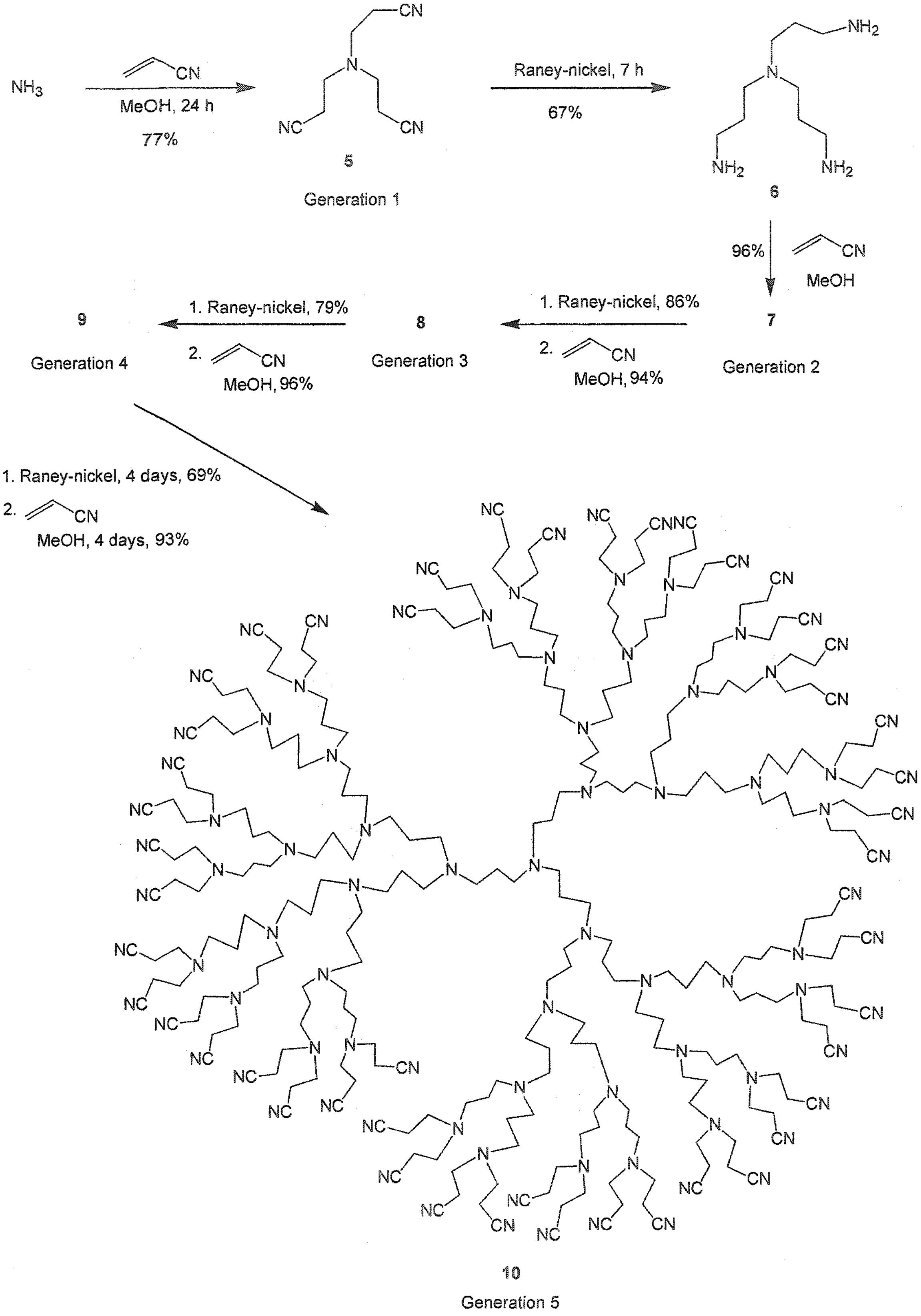
1.1 General Introduction

Dendrimers are macromolecules, which possess tree-like structures, and have attracted great interest in the last 25 years.(1) The first example of the successful synthesis of dendrimers was described in 1978 by Vögtle and co-workers (Scheme 1.1).(2) The synthesis, which consisted of Michael addition of acrylonitrile followed by reduction of the nitrile group, is expensive and has a low-yielding reduction step. Consequently, dendrimers were not seriously considered for use in industry until the cost issue was addressed by Tomalia and co-workers in 1985.(3) They synthesized dendrimers by using strategies which involved time-sequenced propagation techniques. However, this process required a longer reaction time for each successive generation. In 1993, the first example of the synthesis of a fifth generation dendrimer was prepared in high yield. This was accomplished by increasing the reaction time for the Michael addition of acrylonitrile from 24 h to 4 days and that of the reduction step from 7 h to 4 days (Scheme 1.2).(4:5)

An advantage in the construction of dendrimers is the ease with which molecular size and shape can be control. The highly branched structure of dendrimers can be adjusted to modify their physical, electronic and optical properties. There are therefore many applications of dendrimers in medicine(6-8) and catalysis.(9-21)



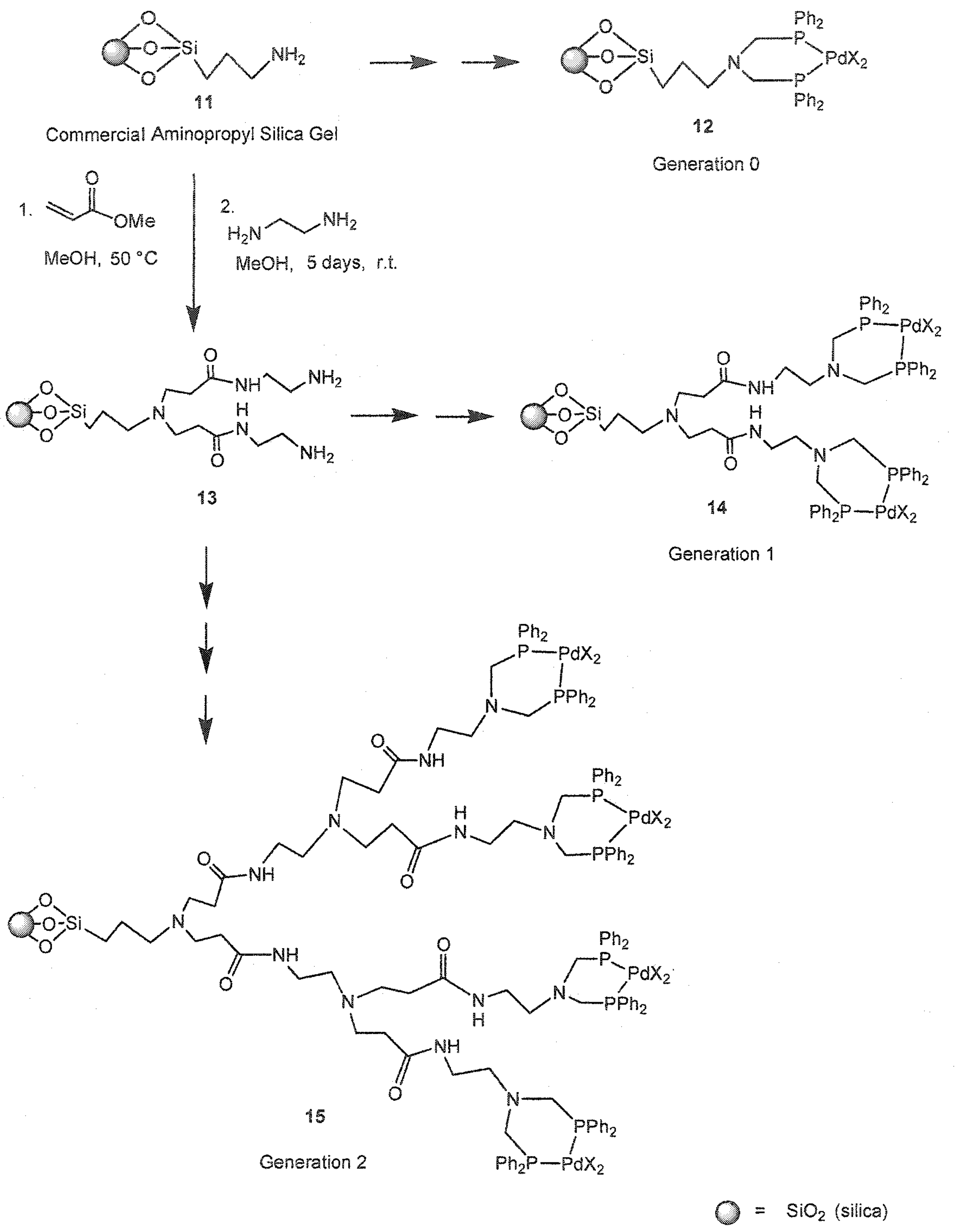
Scheme 1.1 The First Synthesis of a Dendrimer



Scheme 1.2 The First Synthesis of a Fifth Generation Dendrimer

Homogeneous catalysis is widely used in organic chemistry, as the pre-catalysts are usually commercially available and well defined.(22;23) Some catalysts exhibit high selectivity and activity(24-26) and some are useful for stereoselective synthesis.(27;28) However, product separation and, especially, catalyst recovery can be difficult to achieve in an efficient manner. Heterogeneous catalysts, on the other hand, can be easily separated and recycled.(29) Therefore, heterogeneous catalysis forms are more economical and environmentally friendly, which makes then particularly attractive in industrial applications.(30;31) Nonetheless, heterogeneous processes are usually of lower reactivity than homogeneous ones.

Dendrimers containing metals have been reported as catalysts and some of these have advantages when compared with monomeric, homogeneous and heterogeneous catalysts (see section 1.3). In effect, they retain the properties observed for the homogeneous system while allowing for simple separation from the reaction mixture.(10;12;16;18-20) Our strategy is to synthesize dendrimers, which have a metal complex attached to a surface, as analogues of homogeneous catalysts. Recently, it was shown that a dendrimer palladium complex immobilized on silica is catalytically active for several reactions.(32-35) For example, palladium complexed to heterogeneous polyaminoamidodiphonated dendrimers built on a silica gel core support (PPh_2-PAMAM-SiO_2) are effective catalysts for the Heck(32) and carbonylation reactions (Scheme 1.3).(35)



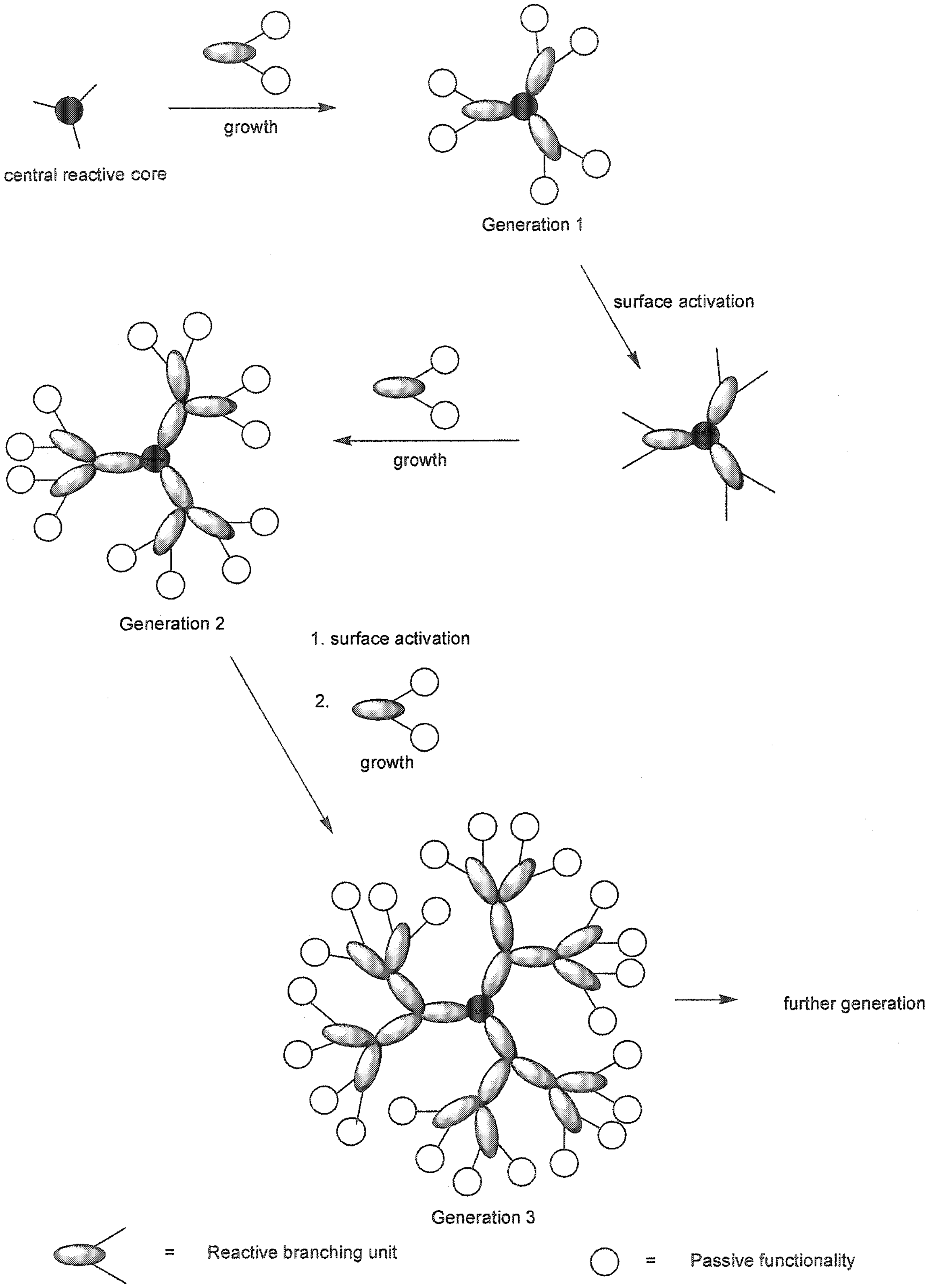
Scheme 1.3 Palladium Complexes to a Dendrimer Built on Silica Gel Used as Catalysts for the Heck ($X = CH_3$) and Carbonylation ($X = Cl$) Reactions

The Heck reaction is recognized as one of important reactions in organic chemistry for C-C bond formation (see section 1.4).(36;37) It is known that a pincer complex, a tridentate compound which consists of two metallacycles that share a metal-carbon bond, has a more robust metal-carbon bond than its simple complex analog (see section 1.4).(24;38) In addition, it is known that diphosphines are good ligands for palladium-catalyzed Heck reactions.(24;39;40)

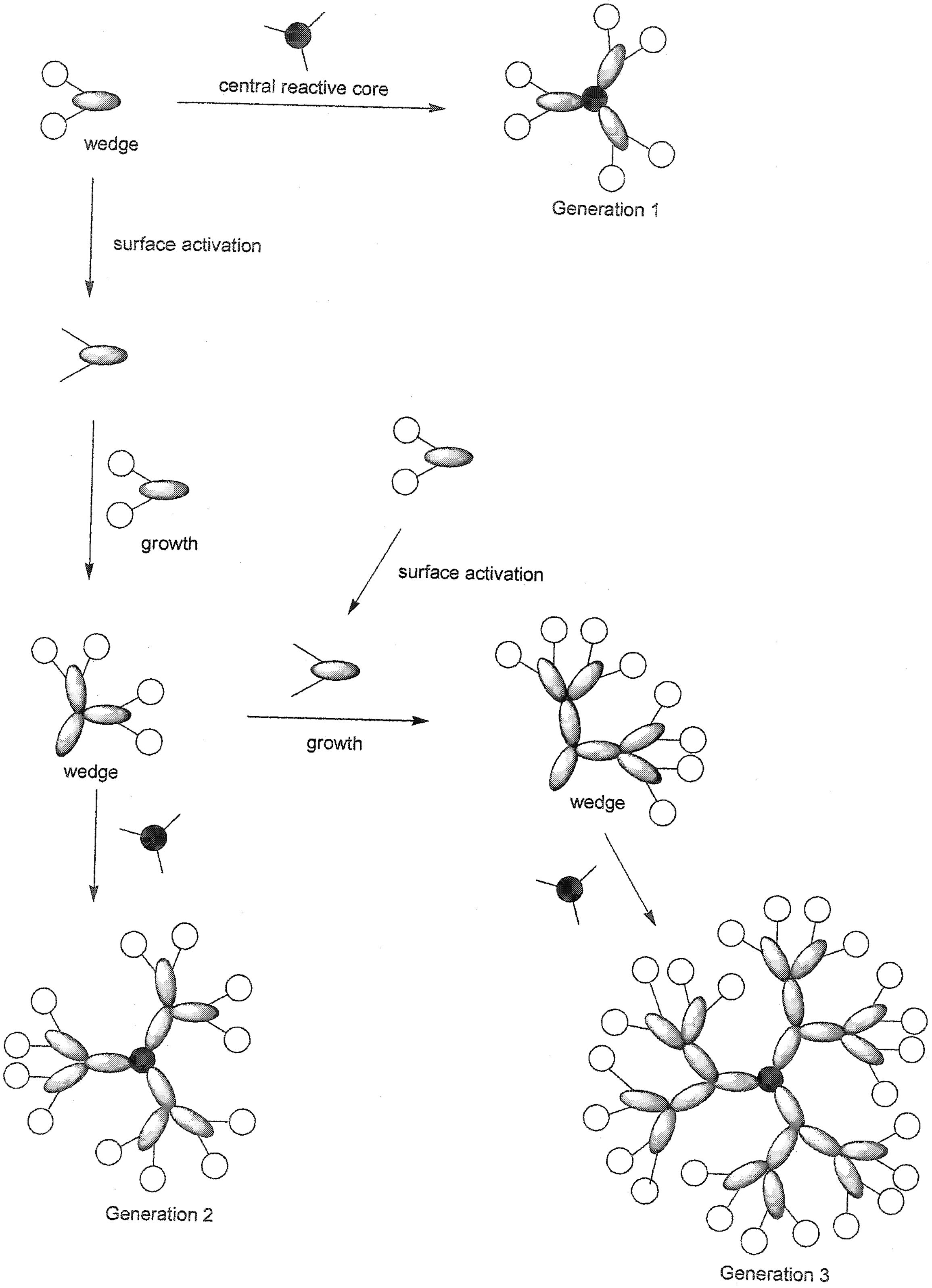
Carbonylation involves the direct insertion of carbon monoxide into an organic substrate (see section 1.5). This reaction usually occurs in the presence of a transition-metal complex as the catalyst. Palladium catalysts are especially useful for carbonylation reactions leading to amides,(41-44) acids,(45;46) ketones,(47) esters,(35;48;49) lactones,(50-53) and others.(54;55) One of the most interesting applications of the carbonylation reaction is intramolecular cyclocarbonylation, which creates heterocyclic compounds such as five-, six- and seven-membered lactones in moderate to high yields (see section 1.5).(50;51;53) Some of these products are pharmacologically active or are used as intermediates to synthesize biologically active compounds(56) or polyesters,(57;58) and are usually difficult to prepare by conventional synthetic methods.

1.2 Dendrimer Synthesis

An efficient method for the synthesis of dendrimers is by repetition of similar steps. Each additional repetitive cycle leads to a new "generation" of dendrimer.(59) There are two strategies to prepare dendrimers: divergent(60) and convergent.(61) The divergent method begins with a core monomer and proceeds outward (Scheme 1.4). The convergent method, on the other hand, builds the dendrimer from the end groups inward (Scheme 1.5).



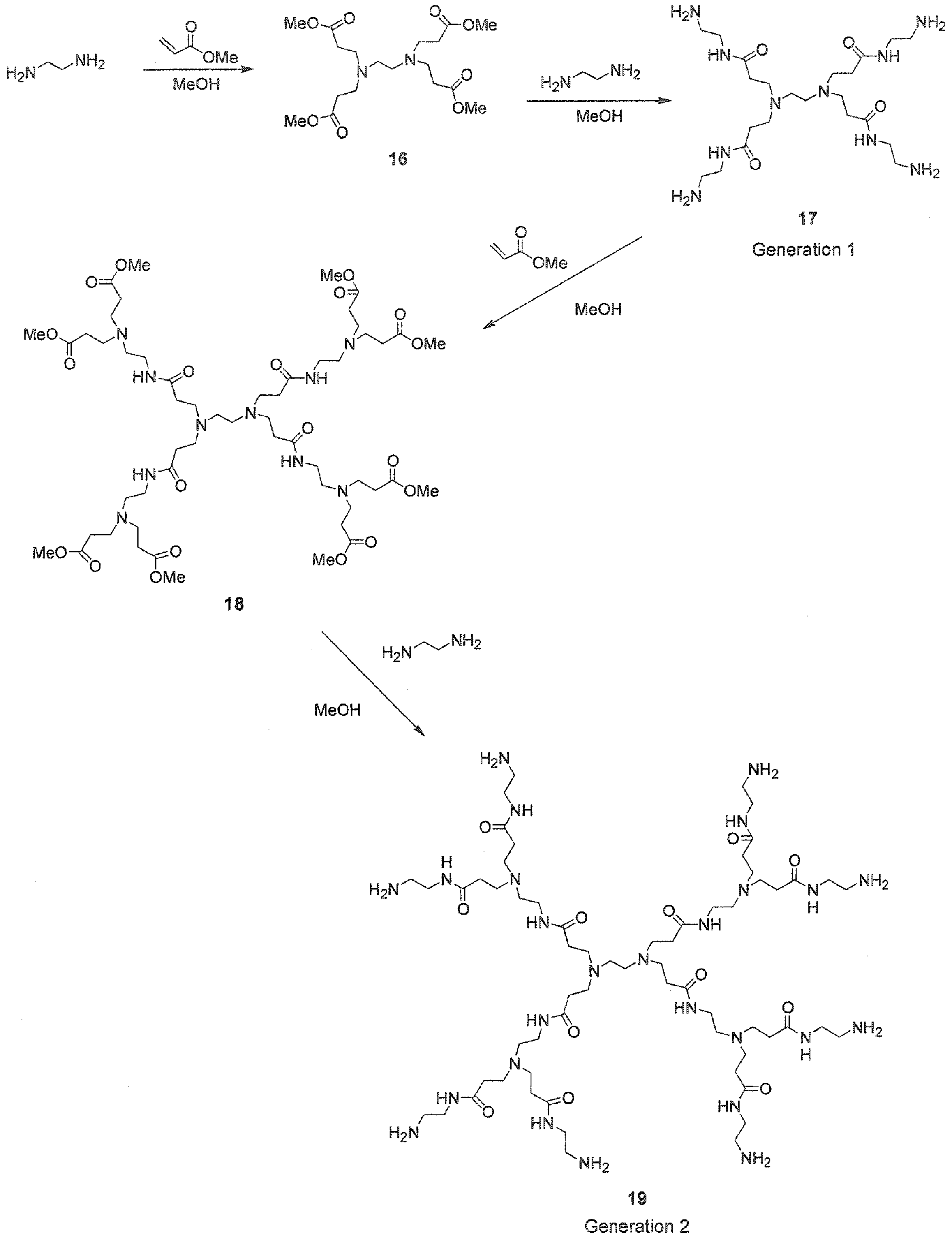
Scheme 1.4 Divergent Synthesis



Scheme 1.5 Convergent Synthesis

1.2.1 Divergent Synthesis

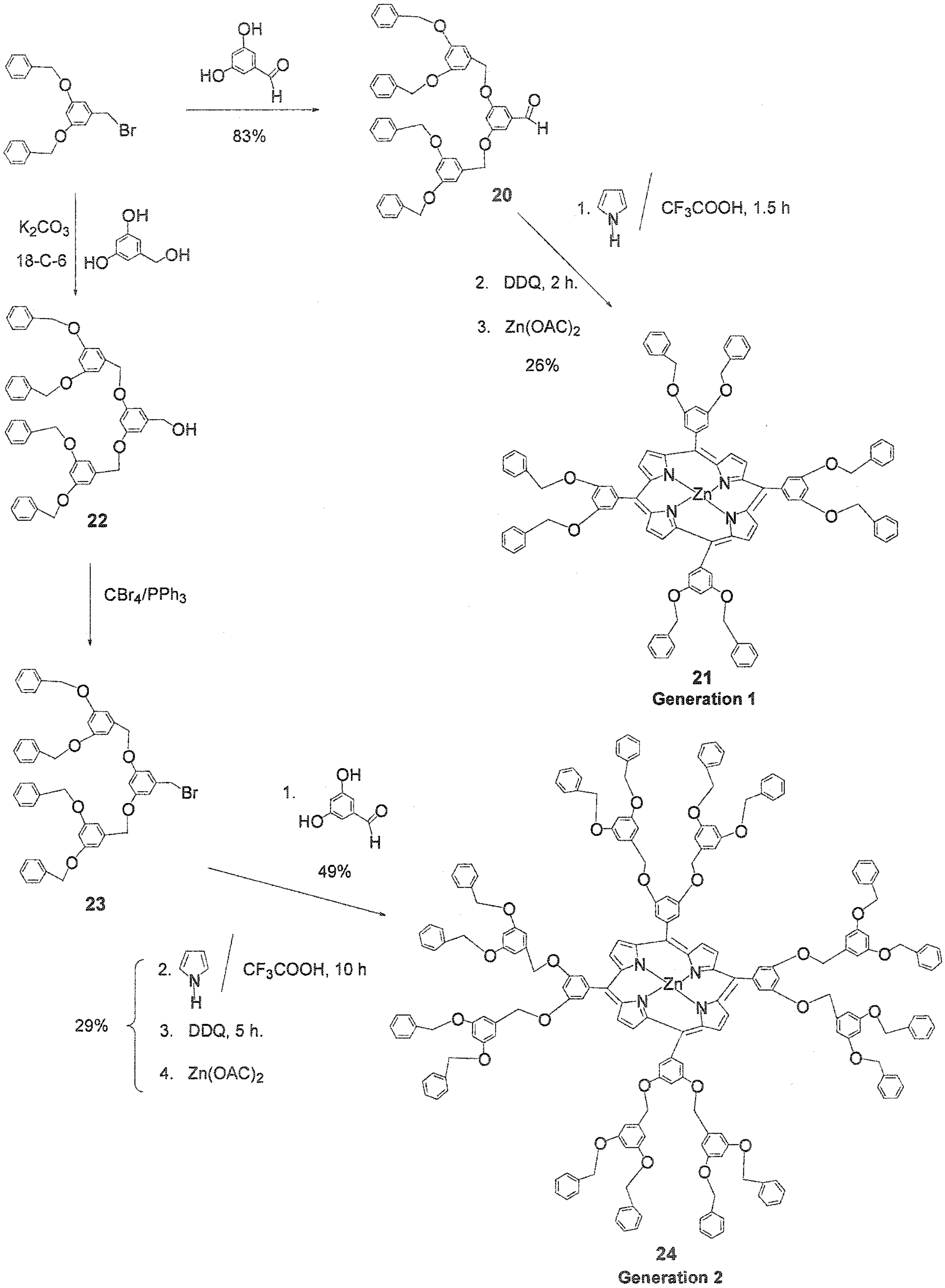
Originally, dendrimers were synthesized by using a divergent method.(2;3) This designation comes from the way in which the dendrimers radiate outward from the reactive core molecule and continue to diverge into space. As shown in Scheme 1.4, the synthesis of the first-generation dendrimer involves a facile reaction of the monomer with the core. Once all of the reactive sites on the core are used up, the reaction halts. Next, the end groups must be activated before any further monomer can be added. These two steps, called growth and surface activation, can be repeated to prepare higher generations. An advantage of the divergent approach to dendrimer synthesis is the ability to modify different generations. The chemical and physical properties of dendrimers can thus be fine-tuned by changing the end groups. Ideally, the structure and molecular weight of a dendrimer can be precisely controlled. The divergent method is successful for the preparation of many dendrimers, but the latter are virtually impossible to isolate in pure form because of incomplete growth steps and side reactions, particularly at higher generations. This type of synthesis relies on efficient reactions in multiple sites of the molecule in order to assure low polydispersities. As mentioned previously in section 1.1, Tomalia and co-workers introduced time sequenced propagation techniques to synthesize dendrimers, and polyamidoamine (PAMAM) dendrimers were prepared in excellent yields (98-100%) (Scheme 1.6).(3) However, details of the completed synthesis were not reported in their paper.



Scheme 1.6 Tomalia's Divergent Synthesis of PAMAM

1.2.2 Convergent Synthesis

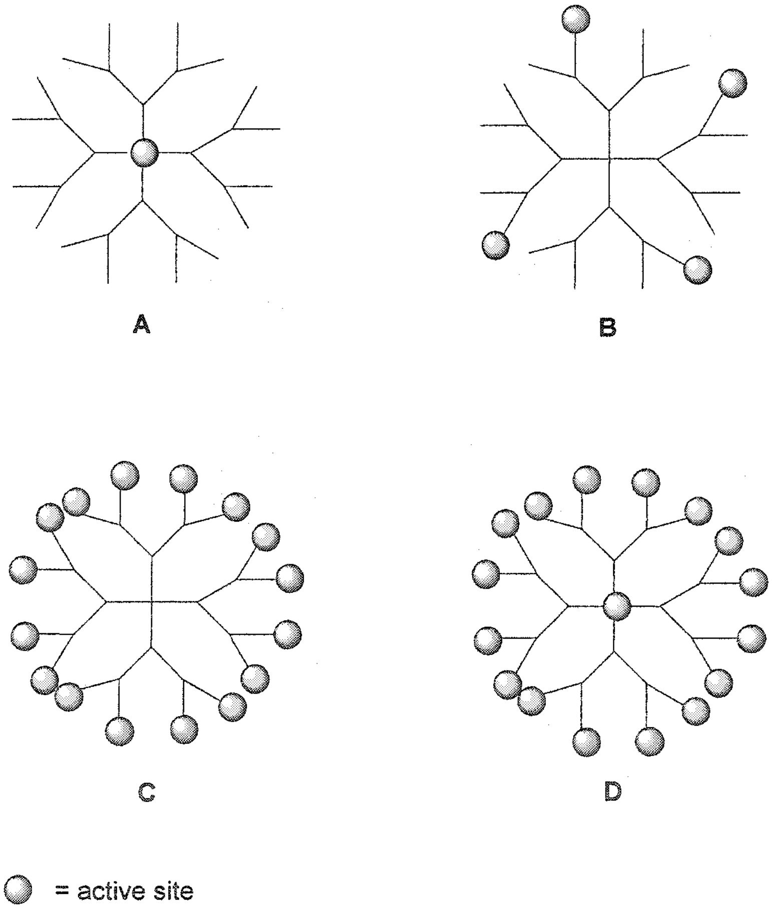
In the convergent synthesis, the dendrimers are constructed from the outside-in. The reaction starts at the outer surface of the future dendrimer and continues growing inwards through stepwise addition of monomers. Once the growing segments reach the desired size, a core unit is then connected, resulting in the formation of a dendrimer (Scheme 1.5). The segments, before the final connection to the core, are described as "wedges." Ordinarily, three to four wedges connect to the core. The advantage of this method is that, at any stage of the wedge synthesis, only two simultaneous reactions are required, producing the next dendrimer generation. Almost perfect dendrimer structures can be obtained, which is infrequent in the case of the divergent method. A convergent synthesis of dendrimers was first introduced in 1990 by Hawker and Fréchet.(62) Fréchet-type dendrimers(63) contain very small amounts of impurities when compared with divergently grown dendrimers (Scheme 1.7). Nevertheless, the synthesis of higher generations gives lower yields and can result in serious steric problems. Consequently, a lot more starting material is lost as compared to divergent strategy.



Scheme 1.7 Fréchet-type Dendrimers

1.3 Dendrimers in Catalysis

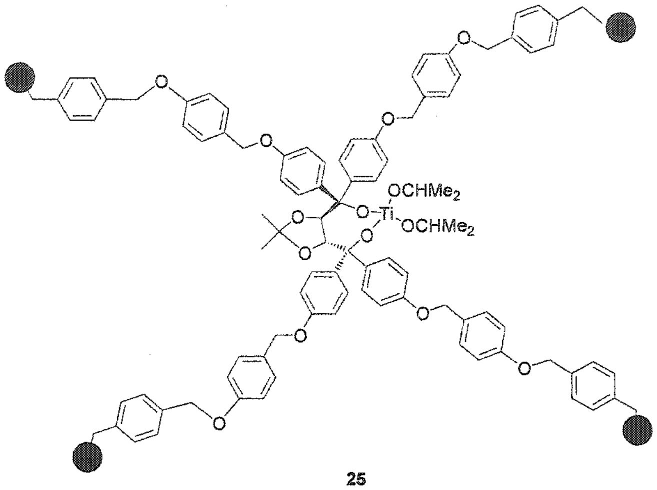
The combination of dendrimers and organometallic chemistry has resulted in the development of metallodendrimers. Dendrimers can be synthesized with the metallic-containing component at an exact location (e.g. at the core or at the periphery of the dendrimers (Figure 1.1)).(64) Many metals such as ruthenium,(65) rhodium,(66) copper,(67) cobalt,(68) nickel,(10) titanium,(69) platinum,(70) or palladium(24;71;72) have been complexed to dendrimers.



A- active site at the core, **B**- actives sites at some portion of the periphery, **C**- active site at the periphery, **D**- actives sites both at the core and periphery.

Figure 1.1 Active Sites in Dendrimers

An advantage of having a metal at the core of a dendrimer is the better control of steric effects in the active site. For example, Seebach *et al.*(69) prepared α,α,α',α' – tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) type titanium(IV) catalysts (**25** and **26**) (Figure 1.2), which were used for the enantioselective nucleophilic addition of diethyl zinc to benzaldehyde (eq. 1.1). It is interesting that the catalyst revealed similar activities and selectivities to its monomeric analogue (**27**) (Figure 1.3). The catalyst could also be recycled by filtration and reused. However, only dendrimers of low generation number (zero, one and two) act as catalysts.



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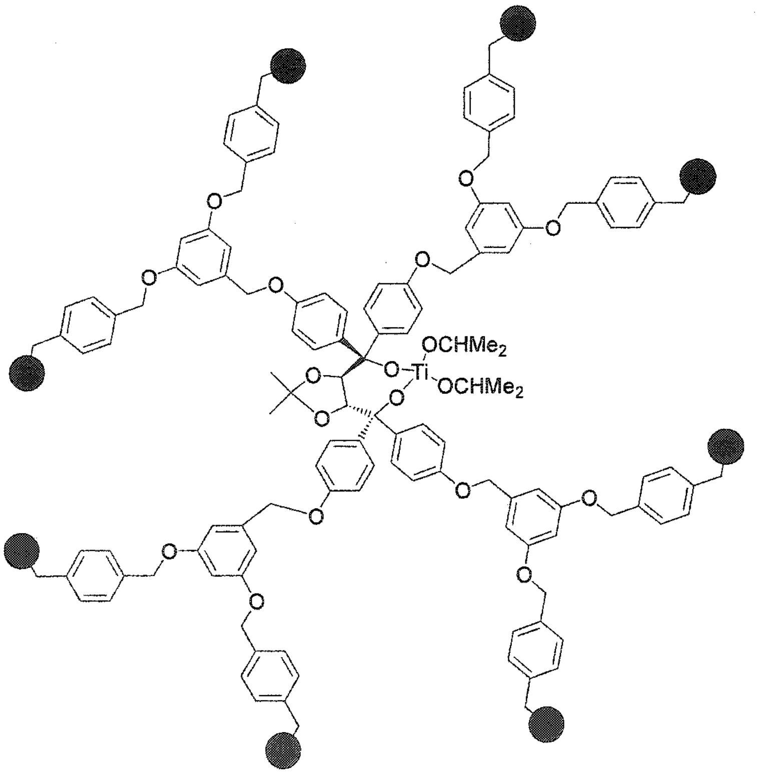
Generation Zero

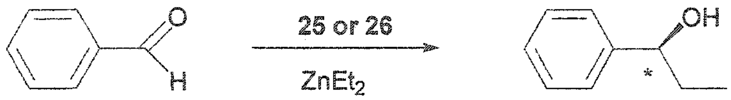


● = Polystyrene backbone

26

Generation one

Figure 1.2 TADDOL Titanium(IV) Dendrimers



eq. 1.1

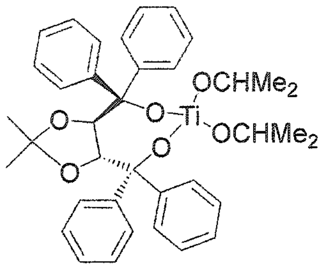


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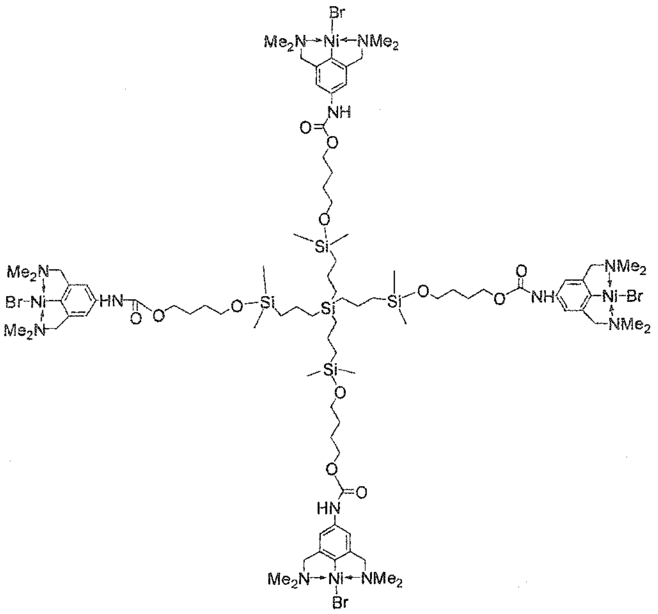
Figure 1.3 Homogeneous TADDOL Titanium(IV) Complex

The metal sites at the periphery of the dendrimer can react directly with the substrate. Therefore, the reaction rate is faster than when the metal is located at the core. A metal at the periphery of the dendrimer can also be prepared with many kinds of ligands. For instance, van Koten *et al.* synthesized carbosilane dendrimers with nickel at the periphery (**28** and **29**, Figure 1.4). These were successfully used as a catalyst for the Kharasch addition (eq. 1.2)(10) and the catalysts could be recycled with moderate loss of activity. However, the reactivities of the dendrimeric catalysts were lower than that of the non-dendritic analogue **30** (Figure 1.5).



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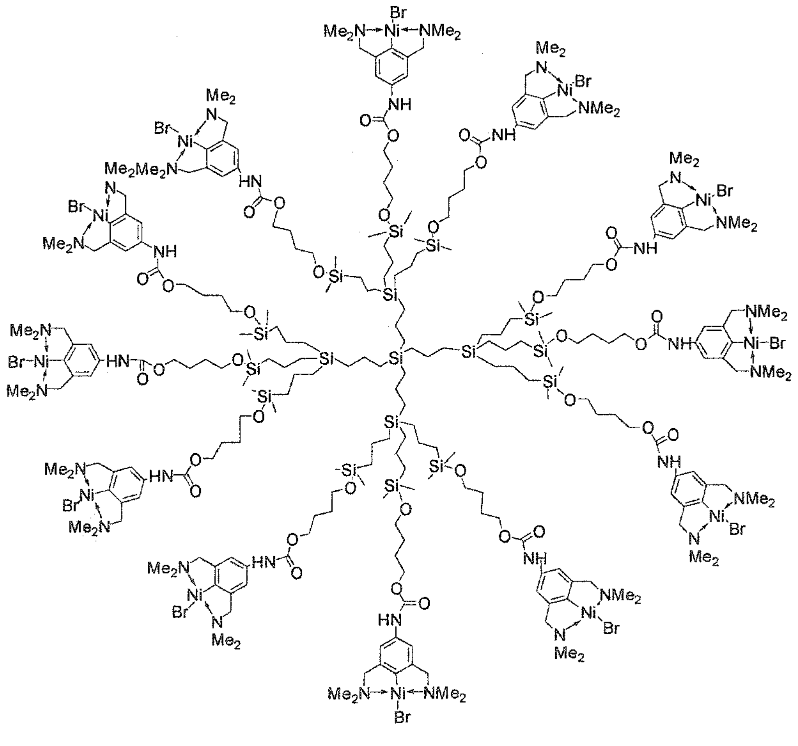
Generation zero



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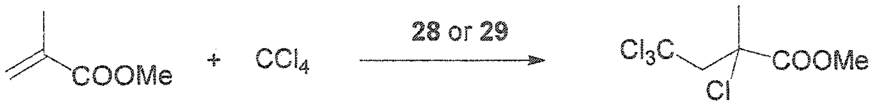
Generation one

Figure 1.4 Nickel Containing Carbosilane Dendrimers



eq. 1.2

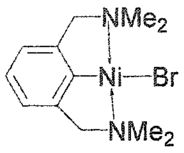


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Figure 1.5 Mononuclear Arylnickel Complex

In 1997, Reetz *et al.* synthesized a phosphinated dendrimer (**31**) (Figure 1.6). After coordination with [Pd(CH_3)$_2$(tmeda)] at the periphery and probable elimination of tetramethylethylenediamine (TMEDA), the resulting complex was used as a catalyst for the Heck reaction (eq. 1.3).(12) It is noteworthy that this catalyst showed high thermal stability and could be precipitated and reused after the reaction.

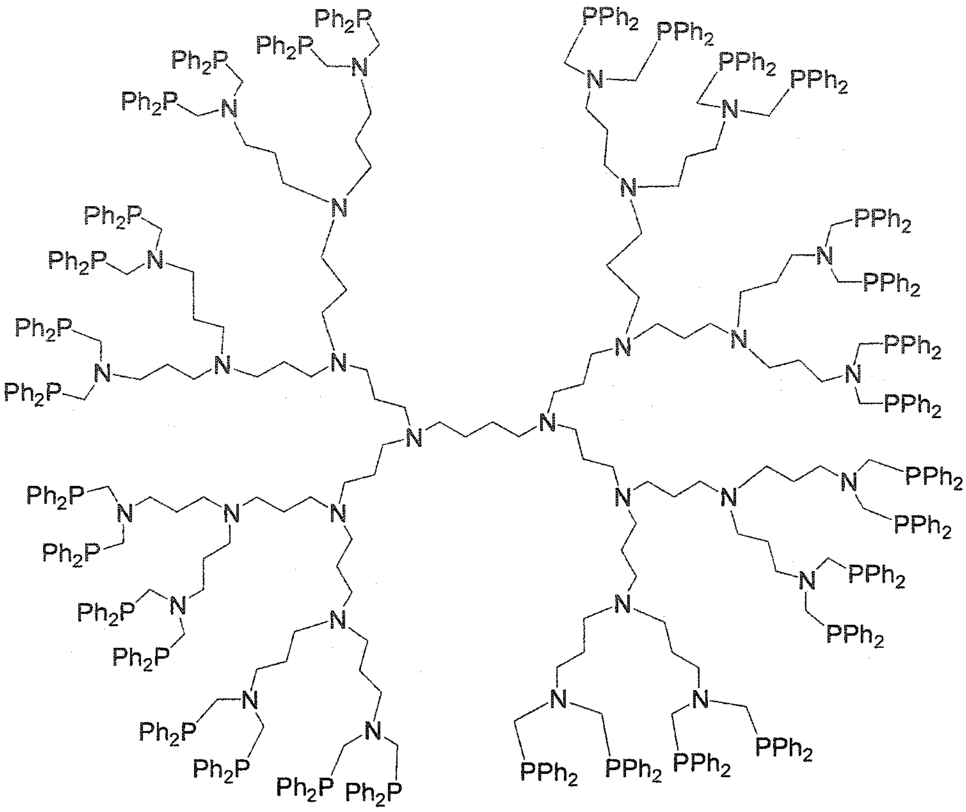

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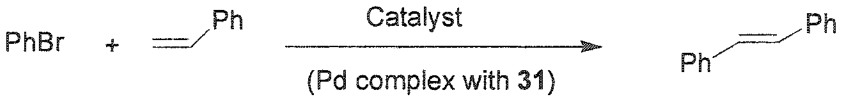
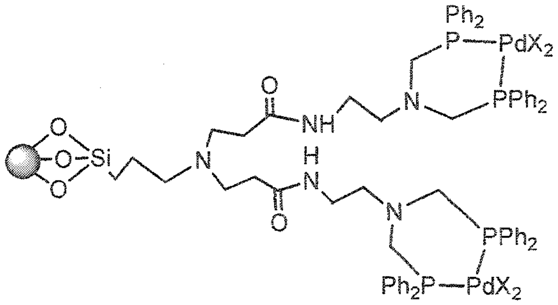
Figure 1.6 Phosphinated Dendrimer



eq. 1.3

Recently, another phosphinated poly(amidoamine) dendrimer (PAMAM) was built on silica gel, and its palladium complexes were found to be active catalysts for the Heck and carbonylation reactions (Figure 1.7; also see Scheme 1.5 in section 1.1).(34;35)



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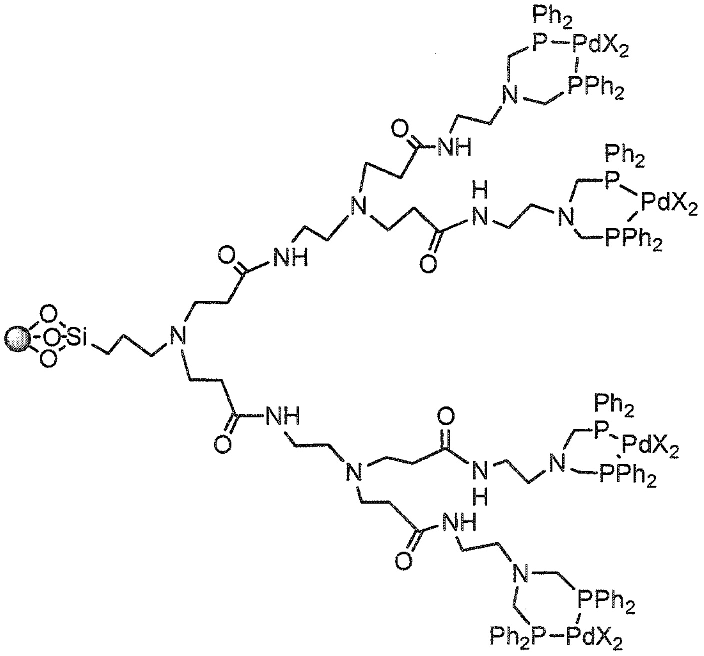
Generation 1



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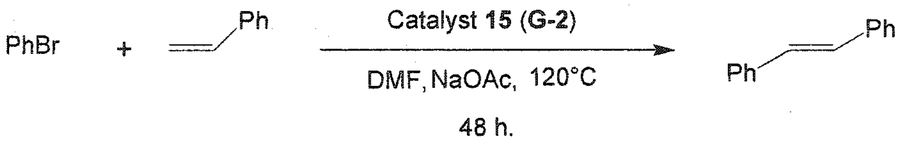
Generation 2

Figure 1.7 Palladium Complexes to a Dendrimer Built on Silica Gel Used as Catalysts for the Heck (X = CH_3) and Carbonylation (X = Cl) Reactions

The catalyst was easily recycled, but the reactivity decreased (Tables 1.1, 1.2 and eq. 1.4 and 1.5). The possibility of metal leaching was examined for both reactions using different methods. For the Heck reaction, the catalyst was filtered as per usual, and additional starting materials were added to the reaction solution. According to gas chromatography (GC) analysis, there was no further reaction. However, this does not prove that there was no leaching. If palladium decomposed to palladium metal, then there would be no further reaction. In the case of the carbonylation reaction, an Inductively-Coupled Plasma (ICP) analysis was used to determine the content of palladium in the catalyst before and after the first cycle. It was found that the extent of leaching of palladium was 6-10%.

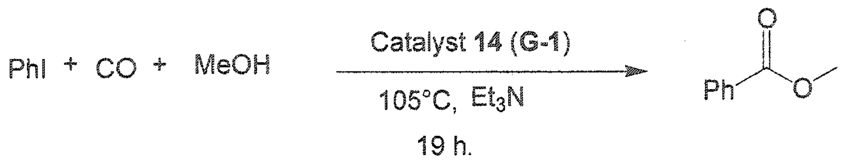


eq. 1.4

Table 1.1. Heck reaction of bromobenzene and styrene catalyzed by **15** (**G-2**).[a]

Run No.	Yield (%)[b]
1	59
2	45

[a]Reactions were conducted using 100 mg of catalyst ***15*** *($1.1x10^{-2}$ mmol), 6 mmol of bromobenzene and 6.6 mmol of styrene in DMF. [b]Determined by GC.*



eq. 1.5

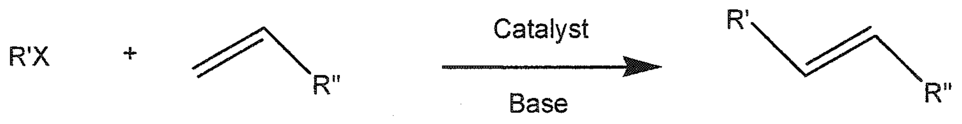
Table 1.2. Catalytic carbonylation of iodobenzene by **14** **(G-1)**;[a]

Run No.	Yield (%)[b]
1	100
2	92
3	77
4	71
5	76

[a] *Reactions were conducted using 25 mg of* ***14*** *(2.0×10^{-2} mmol) and 1.5 mmol of* iodobenzene *for 19 h in MeOH at 100 psi and 105 °C.* [b] *Determined by GC.*

1.4 The Heck Reaction

The Heck reaction usually involves carbon-carbon bond formation by the olefination of aryl halides in the presence of a palladium catalyst and a tertiary amine (eq. 1.5).(40) It provides a convenient route to substituted olefins, dienes, and other unsaturated compounds, some of which are of practical use (e.g. pharmaceuticals, dyes, and UV screens).

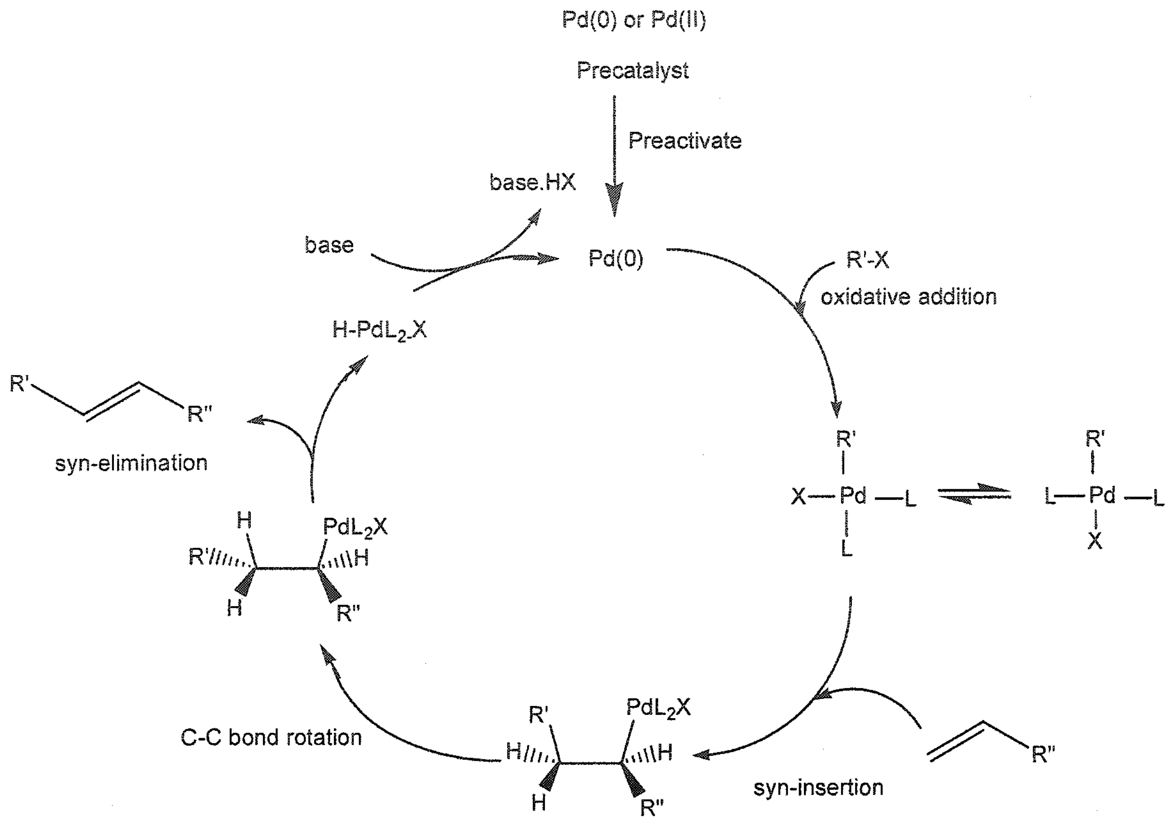


eq. 1.5

R'' = aryl or vinyl
X = halide, triflate

The usual catalytic cycle proposed for the Heck reaction is illustrated in Scheme 1.8. The catalytically active complex is assumed to be a coordinated 14-or 16-electron unsaturated palladium(0) species. Tetrakis(triphenylphosphane)palladium(0) is a frequently used catalyst precursor. In solution, it generates a 16-electron tris-(triphenylphosphine)palladium(0) complex. Bis(triphenylphosphine)palladium(0), the catalytically active species, is generated after the loss of a second phosphine ligand. Palladium(II) complexes such as palladium acetate or bis(triphenylphosphine)palladium dichloride can be reduced to palladium(0) in the catalytic cycle. Usually, the reduction of

Pd(II) to Pd(0) occurs in phosphine-assisted catalytic cycles.(73-75) It has been found that the more electrophilic the phosphorus, the higher the rate of reaction.(75) The oxidative addition step is the rate-determining step for the reaction. The R″ substituents of the olefin do not appreciably affect the oxidative addition, but the strengths of the R′-X and M-X bonds have a significant impact on the oxidative addition step. The order of reactivity for R′-X is I >> OTf > Br >> Cl.(76) Usually, the addition of the Pd complex to the olefin is regioselective, and the palladium binds to the atom with the higher electron density. However, in some cases, the electronic effect of substituents has a smaller influence than steric effects.(77) The R′ group is delivered from the same face as the palladium (syn-insertion). Then, it is converted into the product by a β-hydride elimination, which is also a syn-process (palladium and hydrogen are on the same face). The catalyst is reformed after HX elimination in the presence of a base.



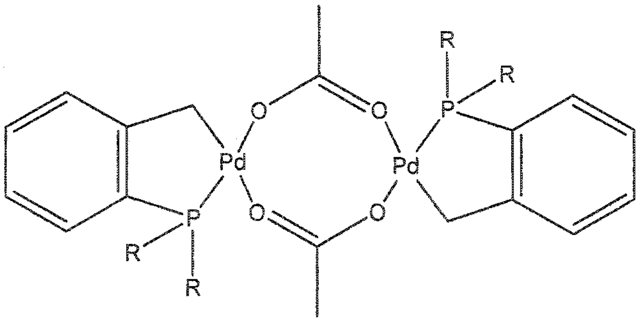
Scheme 1.8 The Heck Catalytic Cycle

Palladium(0) complexes require no more than two strongly bound ligands to complete the catalytic cycle. Thus, there is considerable restriction on the choice of ligands and their concentration in the reaction. Phosphine-free palladium complexes are good catalysts for the Heck reaction but their stability is not sufficient for longer reaction times. Single phosphine catalysts are very reactive and much more stable than phosphine-free complexes. A drawback of monodentate phosphine-mediated catalysis is the extremely low concentration of the reactive dicoordinated Pd(0) complex, which is due to its low equilibrium constants (eq. 1.7 and 1.8). The concentration of active species decreases substantially in the presence of excess ligands.

$$\mathrm{PdL_4} \rightleftharpoons \mathrm{PdL_3} + \mathrm{L} \qquad K_1 >> 1\ \mathrm{M} \qquad \text{eq. 1.7}$$

$$\mathrm{PdL_3} \rightleftharpoons \mathrm{PdL_2} + \mathrm{L} \qquad K_1 << 1\ \mathrm{M} \qquad \text{eq. 1.8}$$

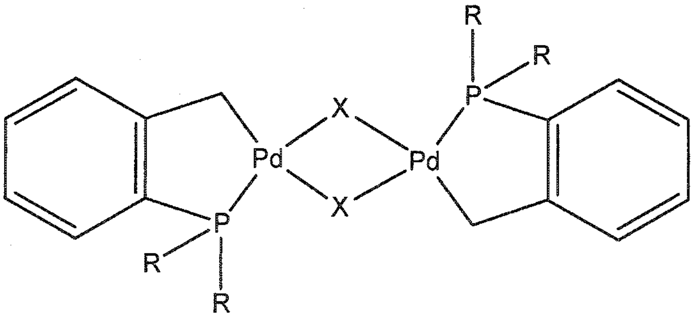
In 1995, Herrmann and coworkers prepared the palladacycle, $Pd_2(P(o\text{-}Tol)_3)_2(\mu\text{-}OAc)_2$ (**32**), which is known as Herrmann's catalyst (*hc*) (Figure 1.8).(78) It is an effective catalyst for the Heck reaction of aryl bromides. However, it is less reactive for iodoarenes, which suggests that the reaction pathway might include the cleavage of a palladacycle. Indeed, Herrmann and coworkers found that complex **33** was formed during the reaction (Figure 1.9). In 1984, complex **33**, X = I, was characterized and found not to be a catalyst for the reaction.(79) However, Herrmann and coworkers discovered that complex **33**, X = Br, is a catalyst as well as **32**. Herrmann and coworkers also found that the active species were palladacycles and there was no evidence of the cleavage of the P-C bond or reduction of **32**. Therefore, they believed that the Pd(II)/Pd(IV) system was more likely involved than the Pd(II)/Pd(0) system but no mechanism was proposed.



32

R = *o*-Tol

Figure 1.8 Herrmann's Catalyst

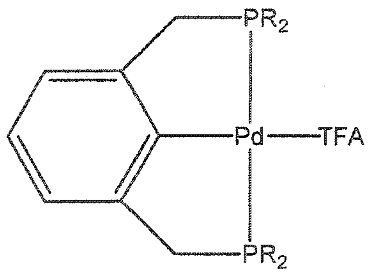


33

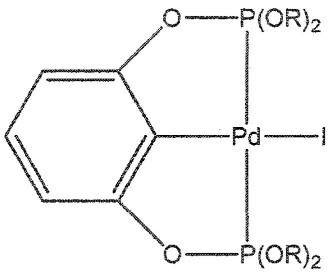
R = *o*-Tol, X = Br or I

Figure 1.9 The Cyclometalated Halide Complexes

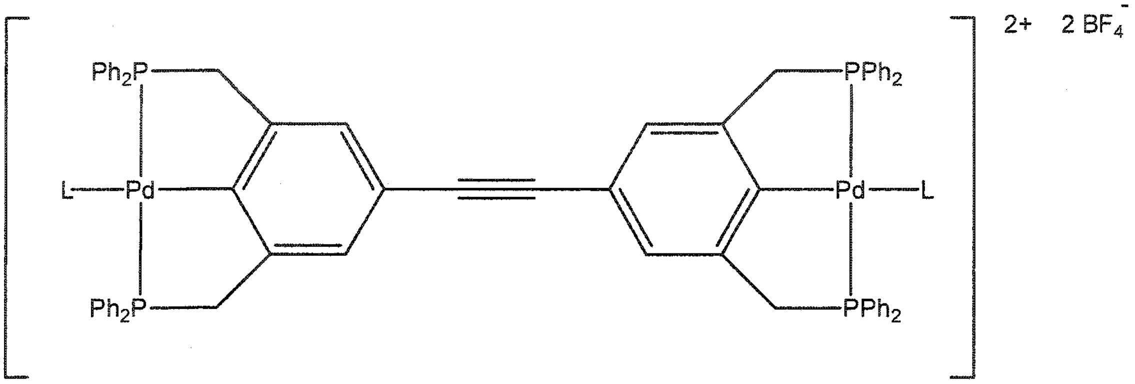
PCP–type palladium complexes are tridentate pincer ligands in which phosphenyl substituents, CH_2PR_2, coordinate to the palladium centre, resulting in two five-membered ring metallacycles sharing the Pd-C bond (Figure 1.10).(24;39;40)



34, R = ^{i}Pr



35, R = *p*-C_6H_4OMe

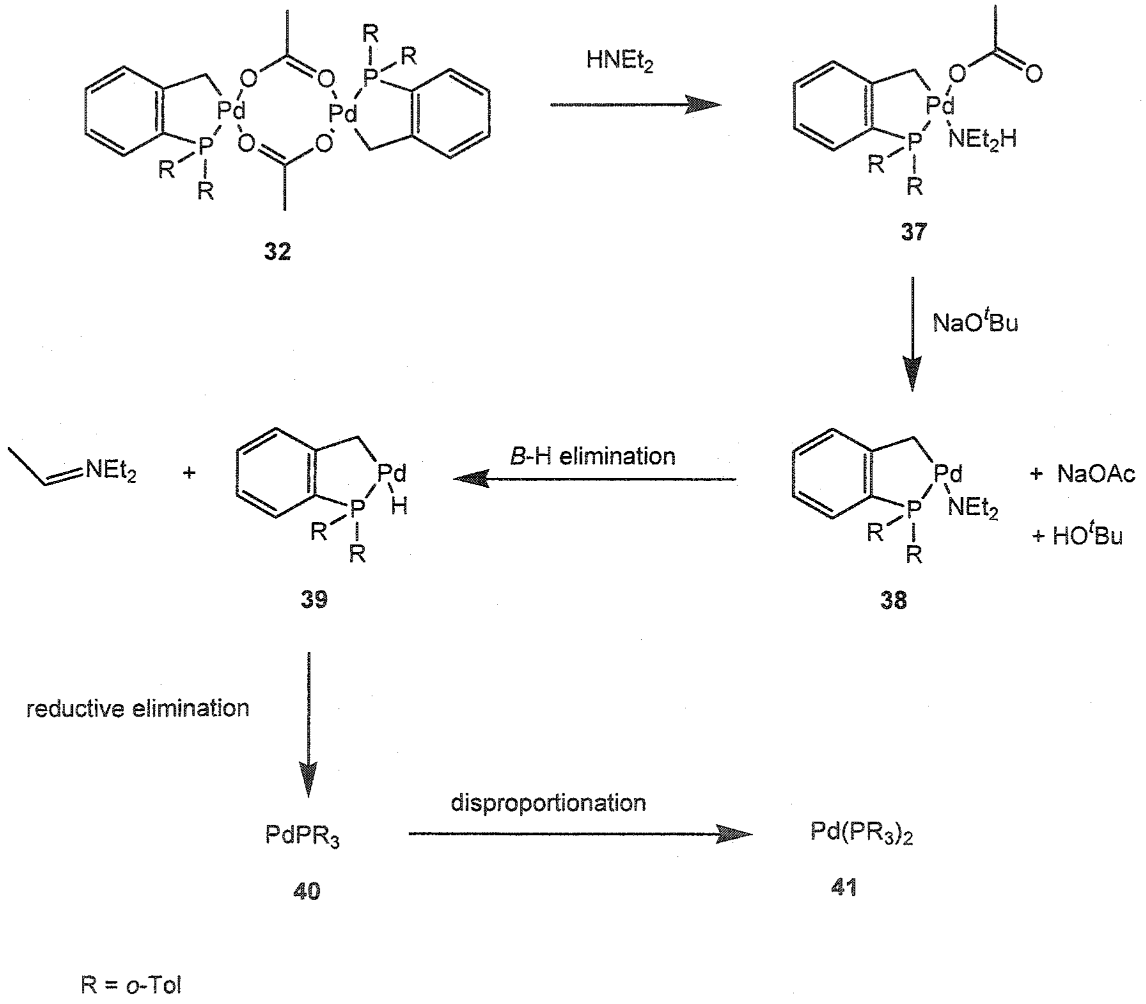


36, L = MeCN

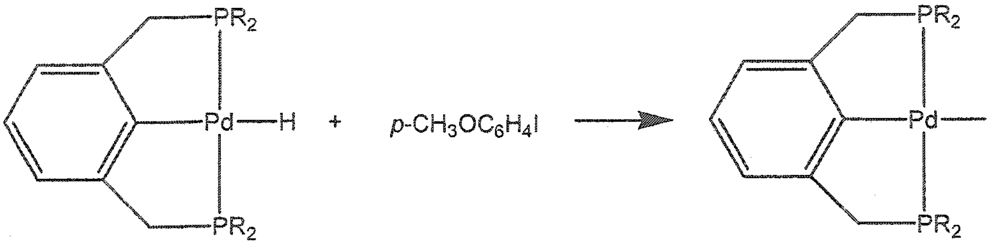
Figure 1.10 Palladium Complex with PCP Type Ligands

Complexes **34**, **35** and **36** are highly active catalysts for the Heck reaction of iodobenzene with styrene and butyl or methyl acrylate. The mechanism was not studied in detail but there is some evidence that the major pathway for the Heck reaction catalyzed by **34** and **35** is the Pd(II)/Pd(IV) system, not the Pd(II)/Pd(0) system. Milstein and co-workers found that **34** was recovered unchanged, after the reaction was carried out for several days at 140-160 °C.(24) Consequently, the catalysts show high turnover numbers (from

108,000 to 528,700 mol product/mol Pd for **34** and from 142,900 to 980,000 mol product/mol Pd for **35**), which implies that the dual chelation is important here.(24;39) Also, since it had already been reported by Hartwig and co-workers that the palladium(II) complex **32** can be reduced to Pd(0) via a palladium(II) hydride (Scheme 1.9),(80) the reaction of the hydride complex **42** was investigated with *p*-iodoanisole (eq. 1.9).



Scheme 1.9 Postulated Mechanism for the Synthesis of Complex 41



42, R = ^{i}Pr

43, R = ^{i}Pr

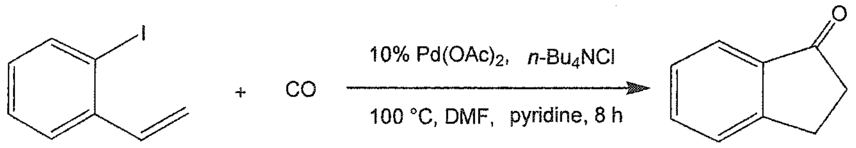
+ $CH_3OC_6H_5$

eq. 1.9

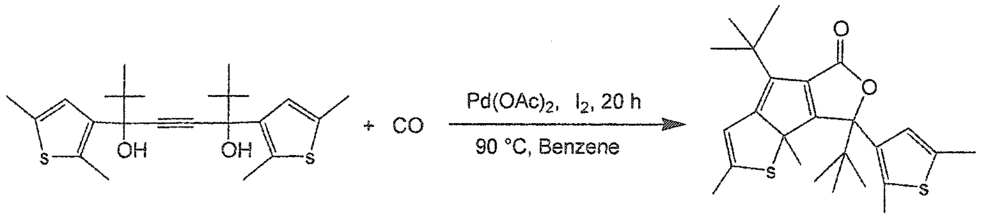
This reaction afforded complex **43** and anisole quantitatively products, which were not observed in the Heck reaction catalyzed by **34**. However, another possibility is that dechelation of the bis-palladacycle may occur at high temperatures, and after the Heck reaction is complete, the PCP is formed again. It is air which may help to regenerate the PCP palladacycle, as Pd(0) must be reoxidized to Pd(II) to enable the formation of the palladacycle. Nonetheless, the mechanism is currently the subject of debate.

1.5 Carbonylation Reactions

Reactions in which carbon monoxide is introduced into an organic molecule, alone or with other components such as alcohols or amines, are called carbonylation reactions. From 1938 to 1957, many carbonylation methods were found by Reppe and coworkers, several of which led to industrial processes.(81-83) Most carbonylation reactions require a catalyst in order to proceed. A variety of transition metals, such as Ni, Pd, Ru and Rh, are effective catalysts for the synthesis of molecules containing carbonyl functionalities(35;41-53) such as ketone **45** (eq. 1.10)(49) and lactone **47** (eq. 1.11).(54)

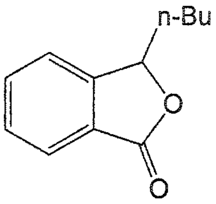


44 **45** eq. 1.10



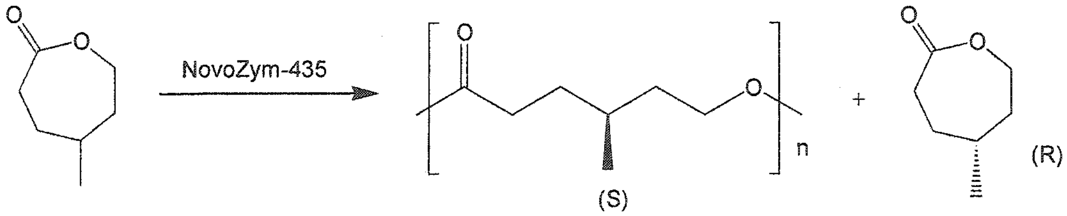
46 **47** eq. 1.11

Some medium-ring lactones are of potential value as biologically active compounds (e.g. Figure 1.11)(56) or polyesters (eq. 1.12).(57;58) Transition metal-catalyzed intramolecular cyclocarbonylation reactions of unsaturated alcohols lead to the formation of lactones. Murray and co-workers have synthesized methylene lactones (**53**) from the palladium-catalyzed cyclocarbonylation of acetylenic alcohols (**52**) under mild conditions (eq. 1.13).(84) This reaction, however, needs $SnCl_2$ as a cocatalyst.



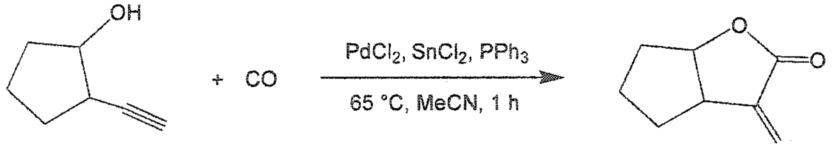
48

Figure 1.11 3-*n*-Butyl Phthalide



49 **50** **51**

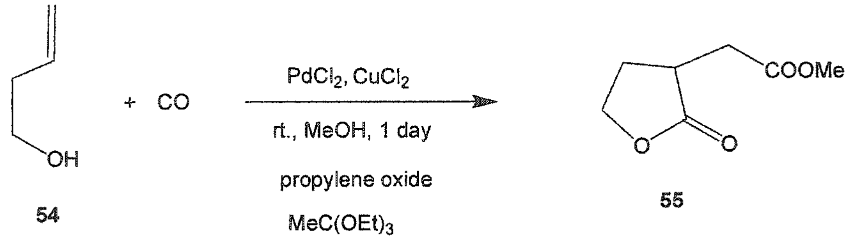
eq. 1.12



52 **53**

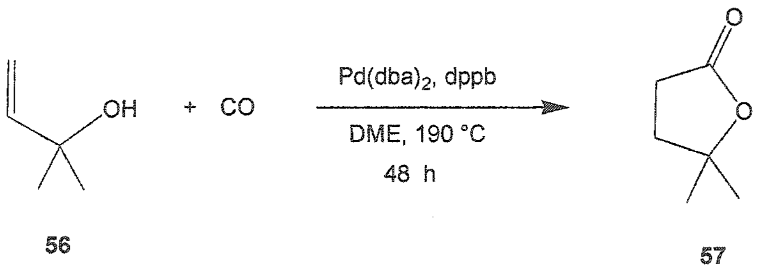
eq. 1.13

Tamaru and co-workers found that a lactone ester (**55**) was formed at room temperature by the palladium-catalyzed dicarbonylation of 3-buten-1-ol (**54**) when propylene oxide and cupric chloride were used in conjunction with a palladium catalyst (eq. 1.14).(85)

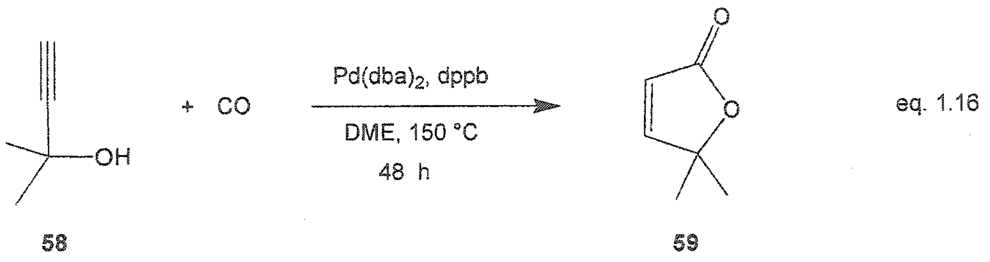


eq. 1.14

El Ali and Alper reported that allylic alcohol (**56**) (eq. 1.15) or alkynol (**58**) (eq. 1.16) reacted in the absence of cupric chloride to form lactones (**57** and **59**) in good yields.(86)



eq. 1.15



Most lactones synthesized by this method are monocyclic five-membered ring compounds. Six- and seven-membered rings are usually difficult to prepare selectively. Alper, van Leeuwen and coworkers have found that phosphine ligands can influence the rate of the carbonylation reactions,(87-89) with the rate increasing in the order of 1,2-bisphosphine (dppe) << 1,3- bisphosphine (dppp) < 1,4- bisphosphine (dppb). In the latter case, the increased reactivity is due to a flexible seven-membered ring chelate. El Ali and co-workers prepared five-, six- and seven-membered ring bicyclic lactones (**61**, **62** and **63**) by the palladium-catalyzed cyclocarbonylation of allylic alcohol (**60**), using the hydridoaquopalladium complex, trans-$[(Cy_3P)_2Pd(H)(H_2O)]BF_4$ (**64**)(90) as the catalyst (eq. 1.17 and Table 1.3).(50) This catalyst was employed for the carbonylation of allenic alcohols to give vinylacrylic acids.(91)

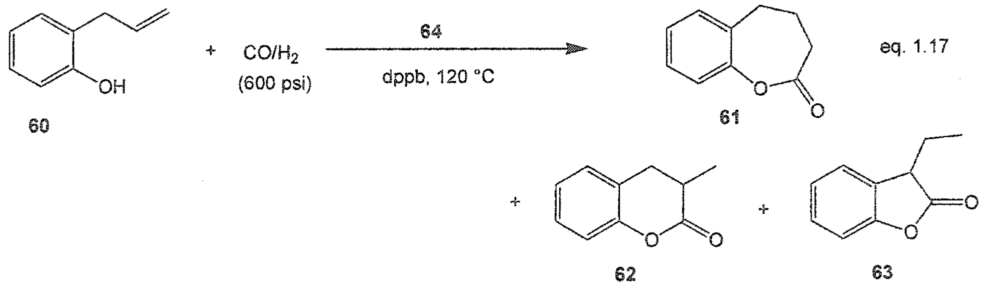


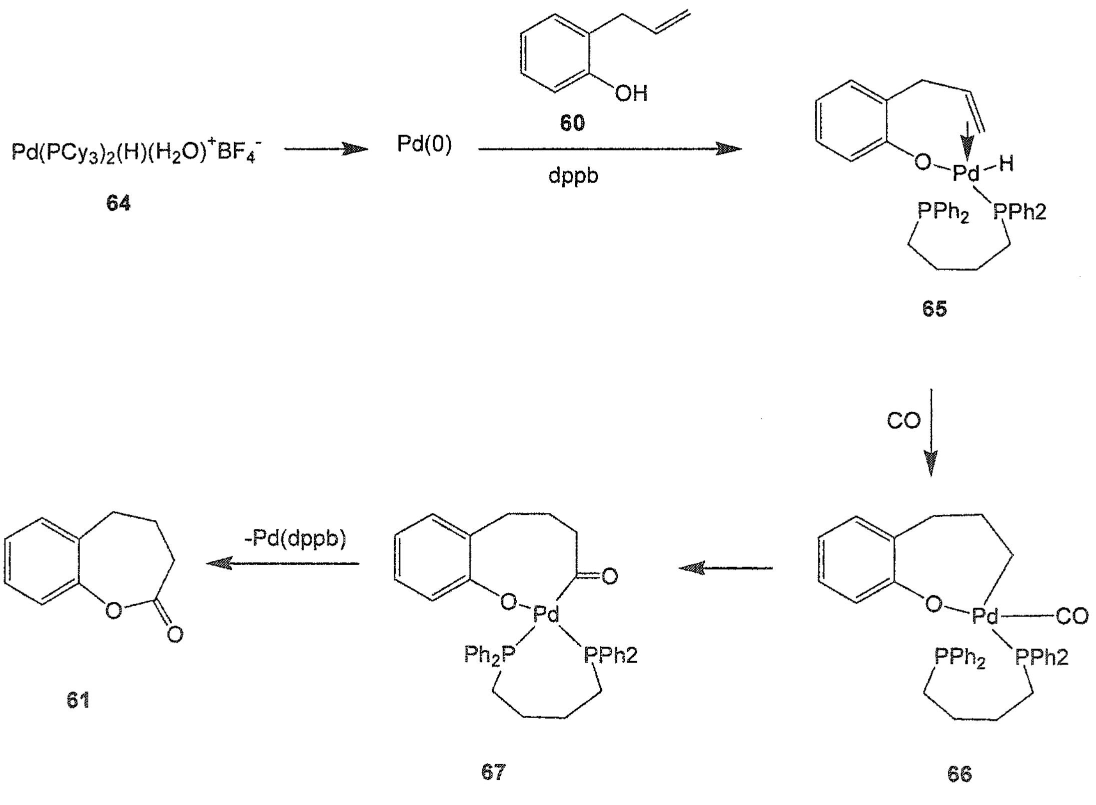
Table 1.3. Catalytic cyclocarbonylation of 2-allylphenol by **64.**[a]

Entry	Time (h)	P_{CO}, psi	P_{H2}, psi	Solvent	Conversion (%)[b]	Product Distribution,[c] %		
						61	**62**	**63**
1	16	300	300	Toluene	93	92	7	1
2	16	300	300	CH_2Cl_2	97	52	21	27
3	16	100	500	CH_2Cl_2	98	6	18	76
4	16	500	100	CH_2Cl_2	48	16	70	14
5	16	600	-	Toluene	trace	-	-	-
6	16	600	-	CH_2Cl_2	trace	-	-	-

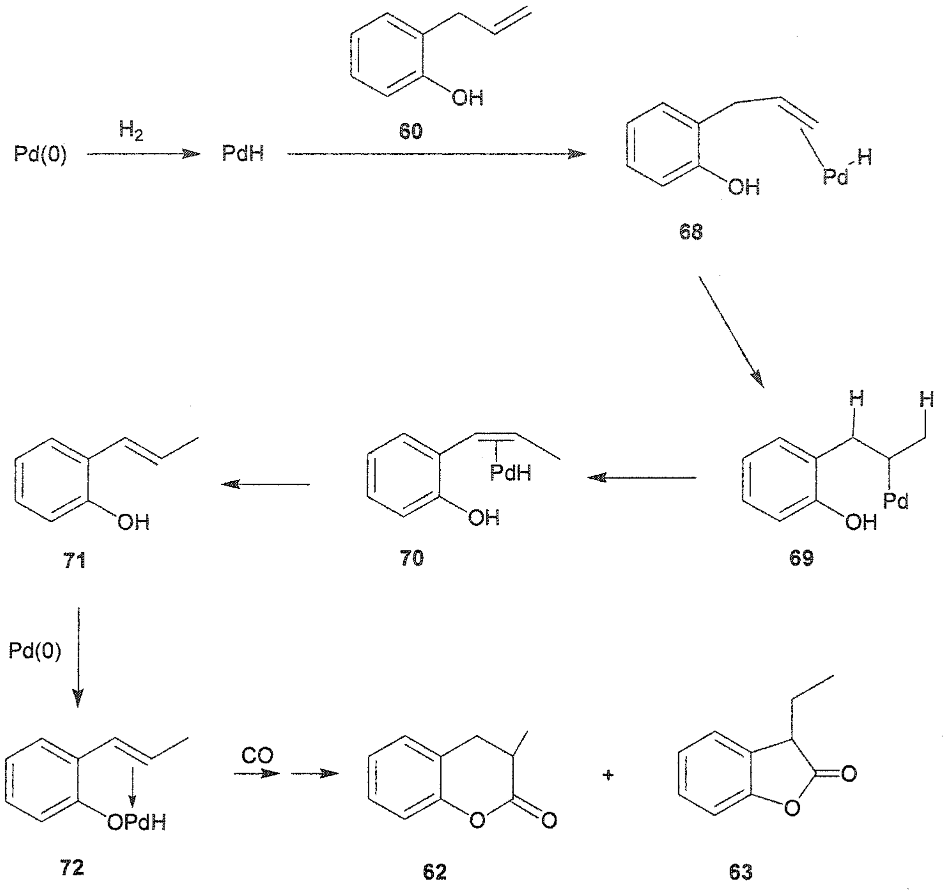
[a] *Reactions were conducted using (1.0x10^{-2} mmol) of **64**, 0.04 mmol of dppb and 1mmol of 2-allylphenol.*

[b and c] *Determined by NMR and GC*

The distribution of five-, six-, or seven-membered ring bicyclic products is controlled by the relative pressures of carbon monoxide and hydrogen, as well as by the solvent. For example, when using a 1/1 mixture of CO/H_2 and toluene as the solvent, the seven-membered ring lactone was obtained in excellent yield (entry 1, Table 1.3). However, only moderate selectivity for the seven-membered ring lactone resulted when CH_2Cl_2 was used in place of toluene (entry 2, Table 1.3). When a 1/5 mixture of CO/H_2 was used for the reaction in CH_2Cl_2, the five-membered ring lactone was formed as the major product (entry 3, Table 1.3). The six-membered ring lactone was obtained in high yield when the mixture of CO/H_2 was changed to 5/1 (entry 4, Table 1.3). The absence of H_2 for the reactions, in either toluene or CH_2Cl_2, led to only traces of lactones and the starting material was recovered (entries 5 and 6, Table 1.3). It was also found that other bidentate phosphine ligands such as dppe and dppp, or monodentate phosphine ligands such as triphenylphosphine, provided less than 10% yield of the lactones and poor regioselectvity. No reaction occured in the absence of dppb. The authors also proposed mechanisms for these carbonylation reactions (Schemes 1.10 and 1.11).



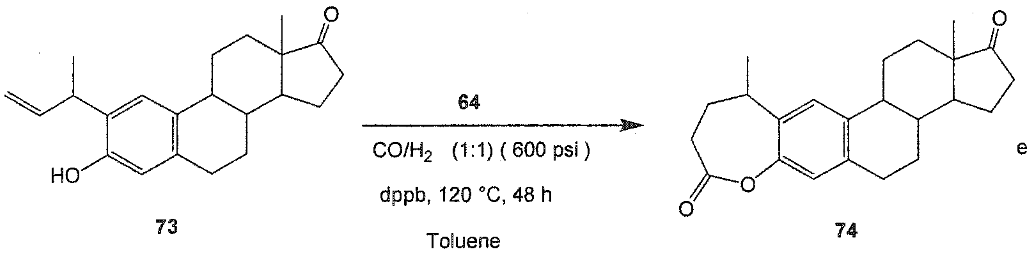
Scheme 1.10 Proposed Mechanism for the Cyclocarbonylation of 2-Allylphenol to Form the Seven-membered Ring Lactone.



Scheme 1.11 Proposed Mechanism for the Cyclocarbonylation of 2-Allylphenol to Form the Six-and Five-membered Ring Lactones.

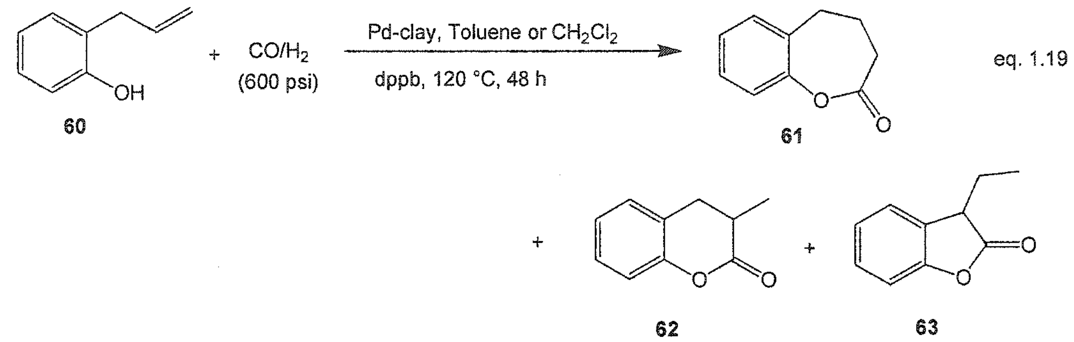
In the formation of the seven-membered ring lactone, an oxidative addition of palladium (0) (generated from **64**) to the OH bond, and the coordination of olefin to Pd (which was coordinated with dppb as a monodentate ligand) gave **65**. This was followed by the intramolecular hydropalladation and coordination of carbon monoxide, to give **66**. Carbonyl insertion with dppb becoming a bidentate ligand, afforded **67**. The seven-membered ring lactone was generated by subsequent reductive elimination. In the case of the five- and six-membered ring bicyclic products, Pd(0) reacted with hydrogen to provide a palladium hydride, which coordinated with the olefin to form **68**. Isomerization to **70** occurred via an addition-elimination pathway (**69**). Decomplexation generated **71**. The five- and six-membered ring lactones were obtained by oxidative addition of Pd(0) to **71** to form **72**, with subsequent steps being analogous to those in Scheme 1.10.

Polycyclic lactone (**74**) was also formed in high yield. The seven-membered ring product was the sole specie when the reaction was run in toluene (eq. 1.18).(50)

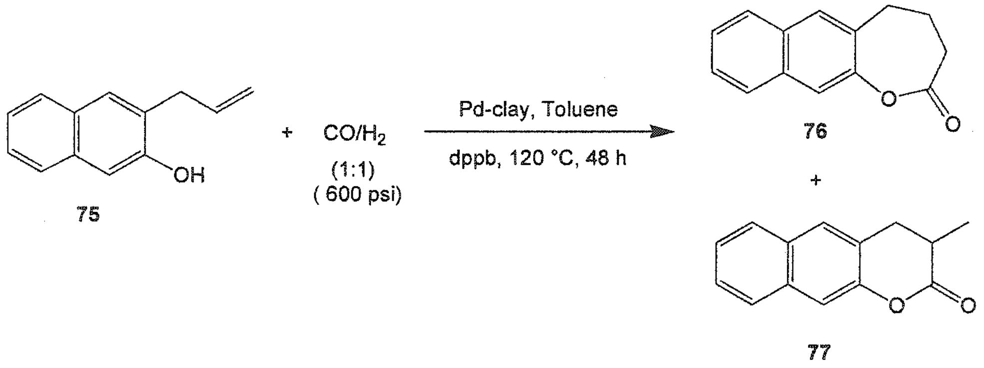


eq. 1.18

Orejon and Alper also successfully prepared five-, six-, and seven-membered ring bicyclic and polycyclic lactones (eq. 1.19 and eq. 1.20) from allylic alcohols by using palladium-montmorillonite (Pd-clay) as a catalyst.(51) Most of their results were similar to the homogeneous system and seven-membered ring lactones were obtained as the major products. However, there were some differences between the two systems. For example, using CH_2Cl_2 as the solvent for the heterogeneous process, the major product was the five-membered ring lactone, and the isomerization product, 2-propenylyphenol, was also obtained in up to 27% yield. Six-membered ring lactones were also formed, but as minor products. In addition, at higher temperatures, the selectivity for the seven-membered ring product decreased, behaviour opposite to that observed in the homogeneous catalytic system.

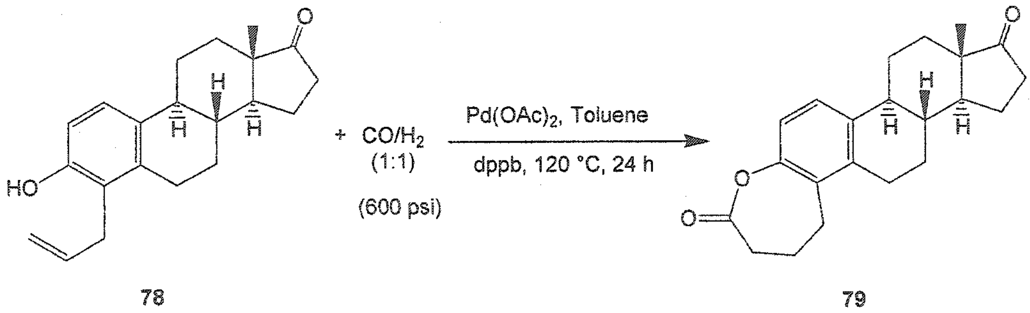


eq. 1.19



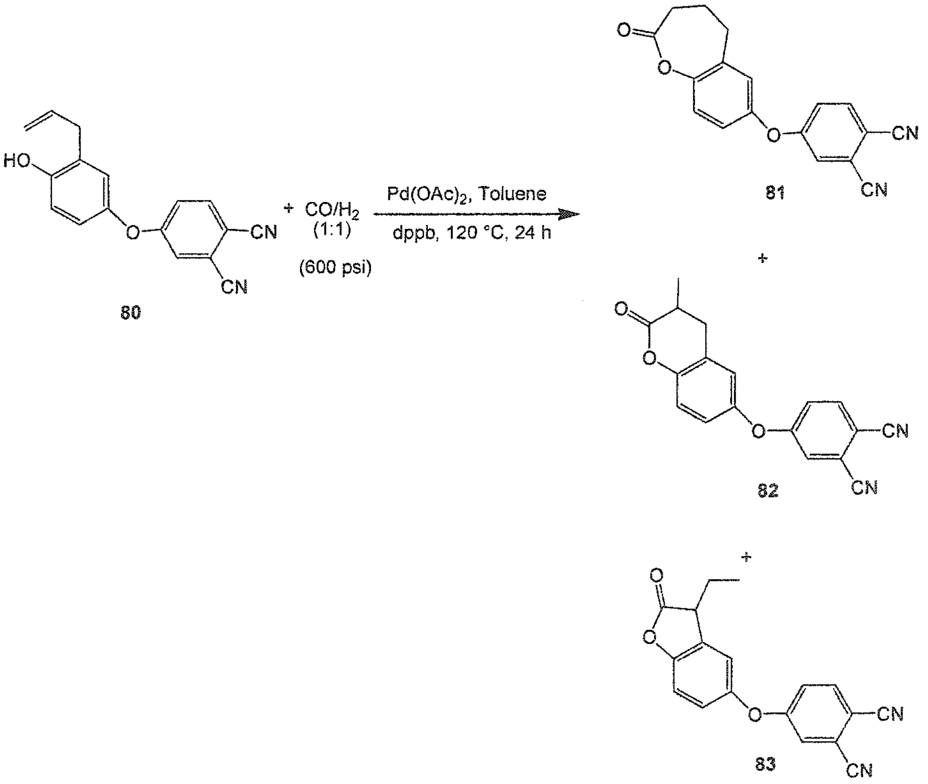
eq. 1.20

Troisi and coworkers described an analogous method to prepare the steroid lactone (**79**) by using palladium acetate as a catalyst for the cyclocarbonylation reaction (eq. 1.21).(92)



eq. 1.21

Recently, Vasapollo and coworkers investigated the cyclocarbonylation reactions of a substrate which contains cyano groups by using the same homogeneous system as Troisi's (eq. 1.22).(53) The conversions were excellent (89-95%), and the seven-membered ring lactone **81** was formed in good yield (85-90%), even when toluene was replaced by CH_2Cl_2. However, when excess hydrogen (CO/H_2 = 100/500 psi) was used, only 45% conversion was obtained.



eq. 1.22

1.6 Research Objectives

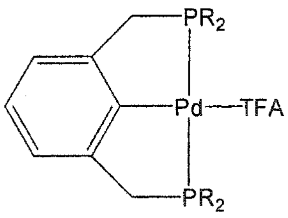
The inspiration for this work is the development of dendrimer metal catalysts built on silica, which are simple to recycle and minimize chemical waste. In addition, palladium complexes stabilized by phosphines on dendrimers are known to be good catalysts for the Heck and carbonylation reactions. However, metal leaching in both reactions is still a problem, which needs to be addressed. Therefore, the object of this work is to prepare dendrimers built on silica which are stable and are good catalysts for both the Heck and carbonylation reactions. In addition, they should exhibit good recyclable properties.

2

Synthesis of Silica-supported Heterogeneous Polyamino-amidodiphosphinated Dendrimers

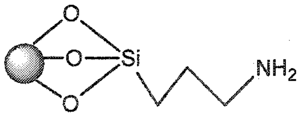
2.1 Introduction

As noted in Chapter One, pincer PCP-type palladium(II) complexes display high stability and excellent catalytic activity for the Heck reaction. The present chapter describes the immobilization of a PCP-type palladium(II) complex **34,** R = Ph (Figure 2.1) onto a commercial aminopropyl silica gel (**11**, Figure 2.2). The supported complex was prepared under relatively mild conditions,(93) compared with the preparation of complex **34,** R = ^{i}Pr (Figure 1.9, Section 1.4).(24)



34

Figure 2.1 Palladium catalyst with PCP types Ligands (R = ^{i}Pr, Ph)



11

Figure 2.2 Commercial Aminopropyl Silica Gel

This chapter describes a variety of synthetic attempts to produce this product, leading eventually to the preparation of a silica supported PCP-type palladium(II) complex (**A**) (Figure 2.3). Subsequently, generation one (**G-1**) (**B**) and generation two (**G-2**) (**C**) polyaminoamido (PAMAM) dendrimers were also synthesized (Figures 2.4 and 2.5). A similar dendrimer, but with a 6-carbon spacer group, was also synthesized as another generation one complex (**G-1**) (**D**), to compare the reactivity with that of (**G-1**) (**B**) (Figure 2.6).

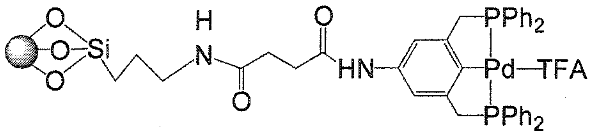


Figure 2.3 A silica supported PCP-type palladium(II) complex (A)

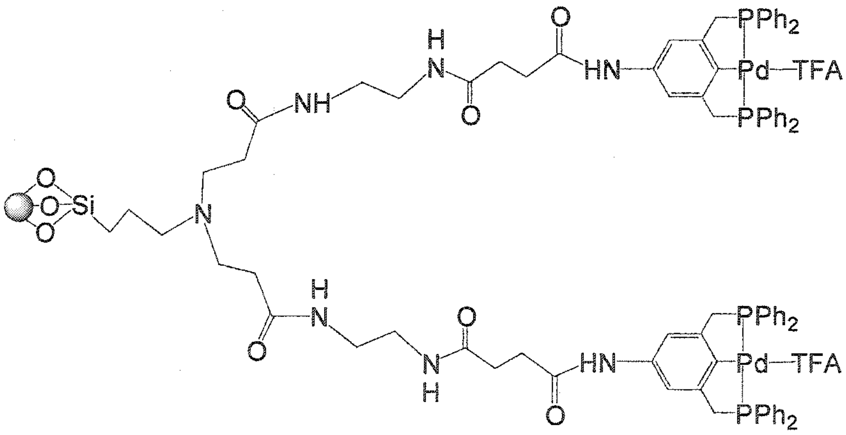


Figure 2.4 Generation One Dendrimer (G-1) (B)

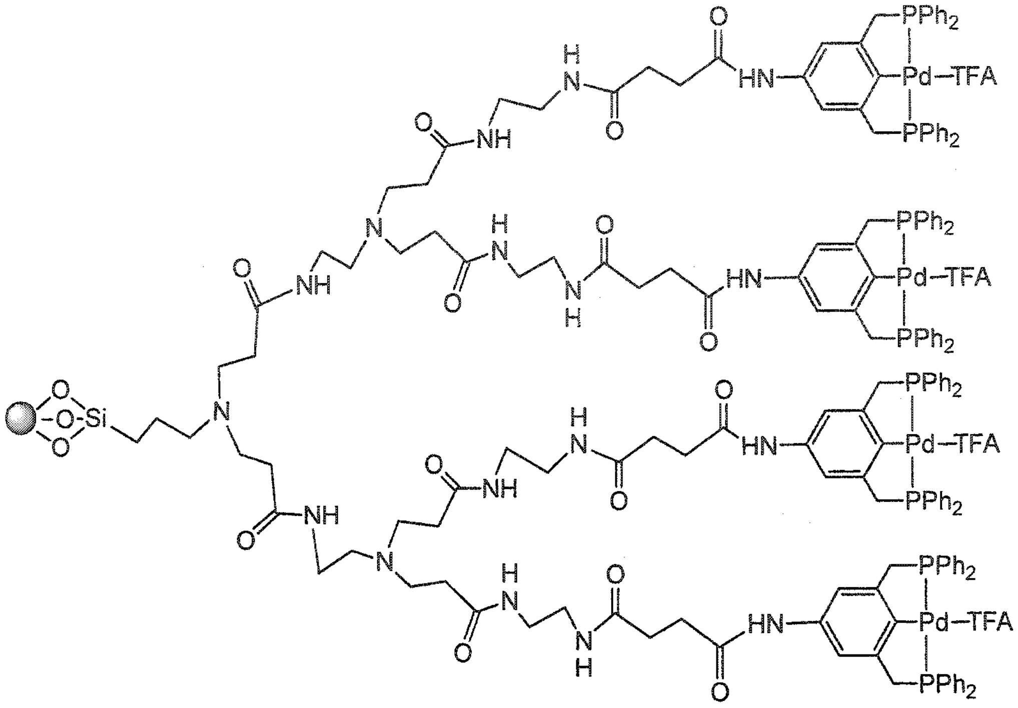


Figure 2.5 Generation Two Dendrimer (G-2) (C)

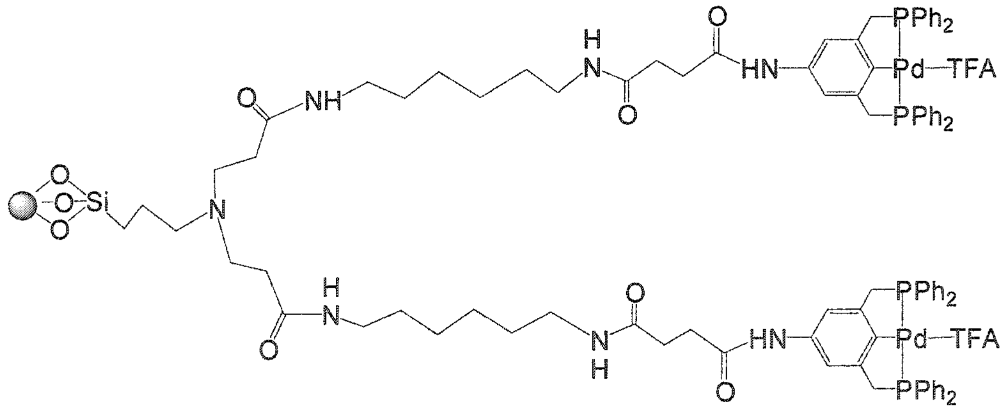
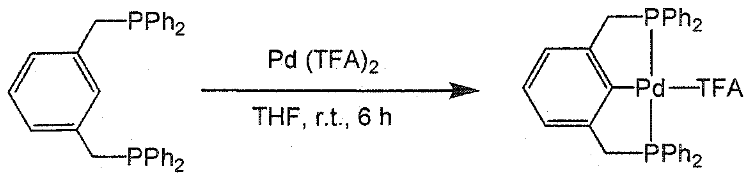


Figure 2.6 Generation One Dendrimer (G-1) (D)

Model complex **34,** R = Ph was synthesized by reaction of 1,3-bis-(diphenylphosphanylmethyl)benzene with palladium(II) trifluoroacetate [Pd(TFA)$_2$] at room temperature (eq. 2.1). By contrast, the preparation of complex **34,** R = ^{i}Pr required heating in refluxing tetrahydrofuran (THF). The accessibility of **34,** R = Ph at room temperature (vs. the high temperature required for **34,** R = ^{i}Pr) could be due to the geometry of the resulting complex, thus placing the C-H bond in a position where the cyclometallation could occur in an easy manner. Crystals, which were suitable for X-ray analysis, were obtained for **34,** R = Ph (Figure 2.7).



34, R = Ph

eq. 2.1

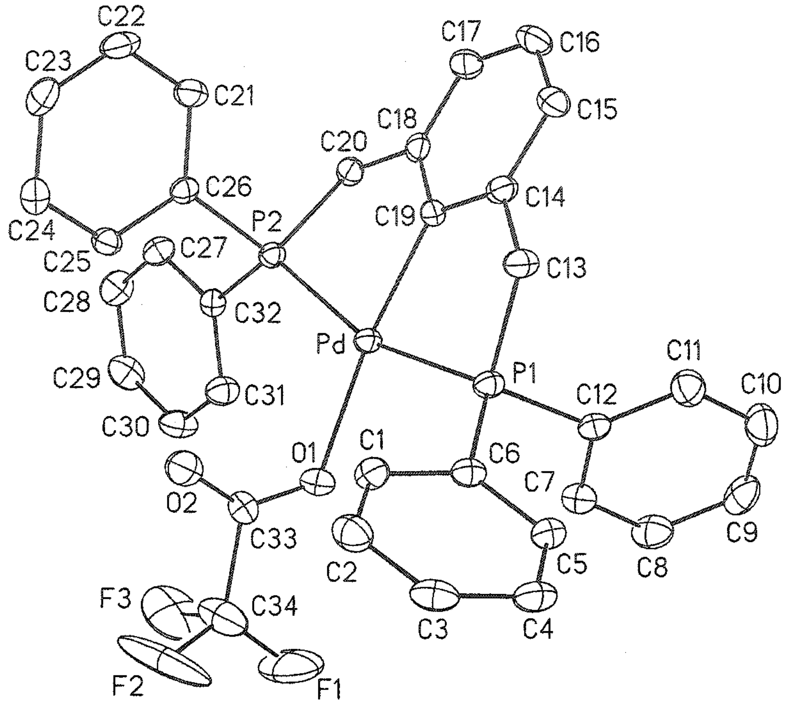
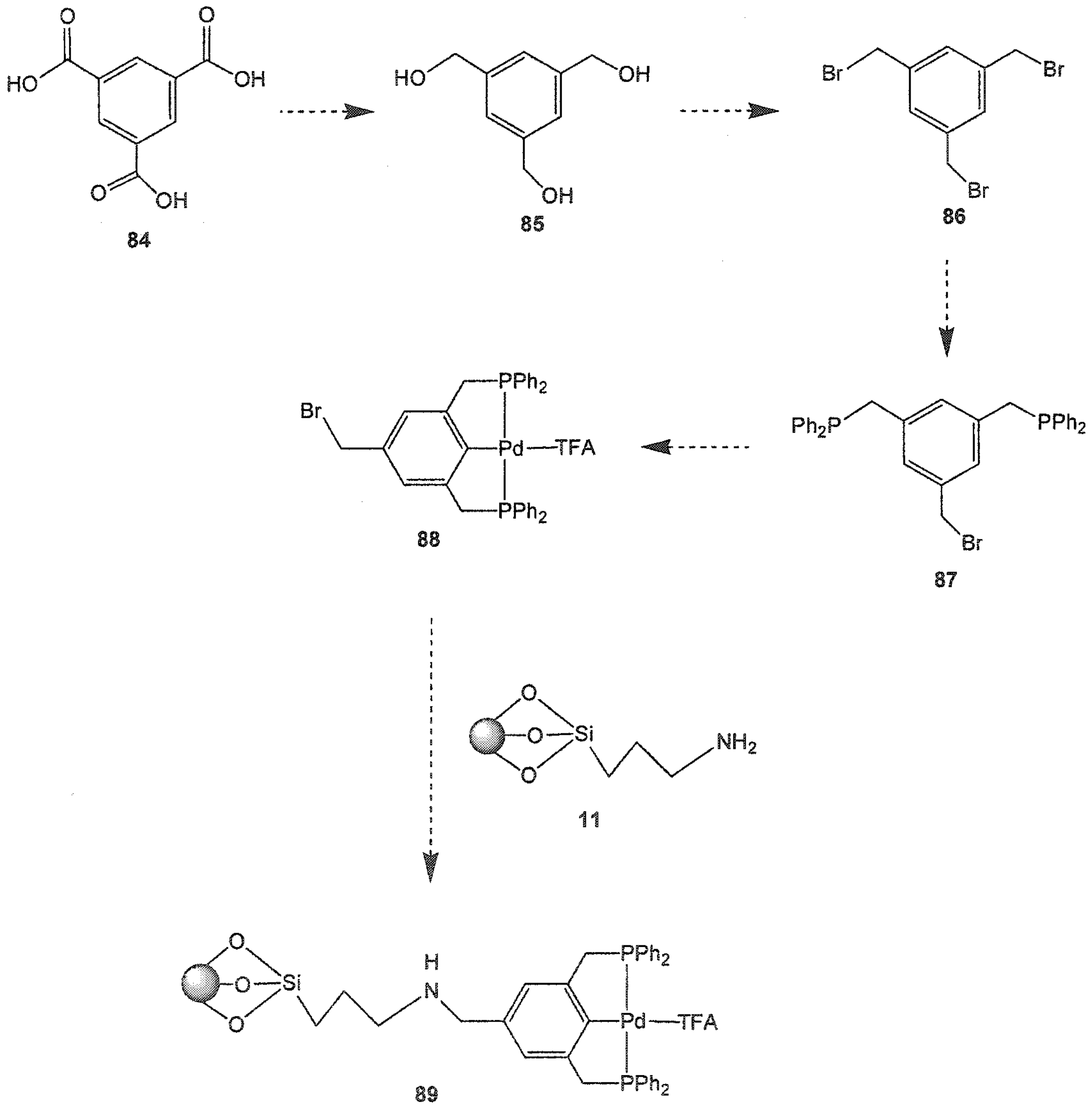


Figure 2.7 ORTEP Diagram of Complex 34, R = Ph (hydrogen atoms omitted for clarity).

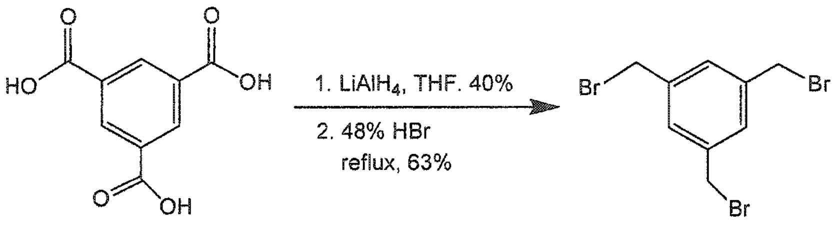
2.2 The First Synthetic Approach Towards a Silica Supported PCP-type Palladium(II) Complex

The preparation of a silica supported PCP-type palladium(II) complex was first attempted following the reaction sequence illustrated in Scheme 2.1.



Scheme 2.1 First Synthetic Approach Towards a Silica Supported PCP-type Palladium(II) Complex

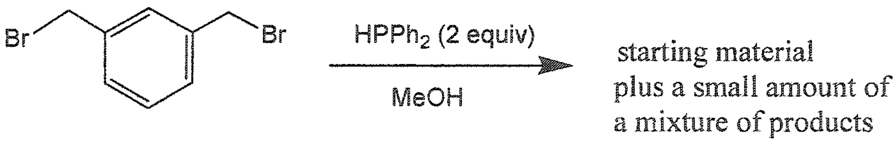
1,3,5-Trisbromomethylbenzene (**86**) was prepared according to the procedure described in the literature, from a commercially available starting material, benzene-1,3,5-tricarboxylic acid (**84**), by reduction with lithium aluminium hydride and then refluxing with 48% hydrobromic acid (eq. 2.2).(94)



84 **86**

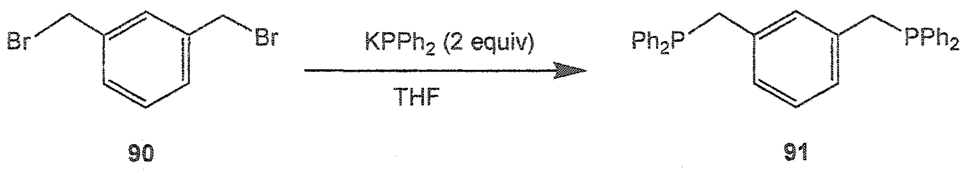
eq. 2.2

Before the synthesis of 3,5-bis(diphenylphosphanylmethyl)bromomethylbenzene (**87**) was attempted, the reactivity of 1,3-bis(bromomethyl)benzene (**90**) was studied by treatment with diphenylphosphine and potassium diphenylphosphide (eq. 2.3 and 2.4).



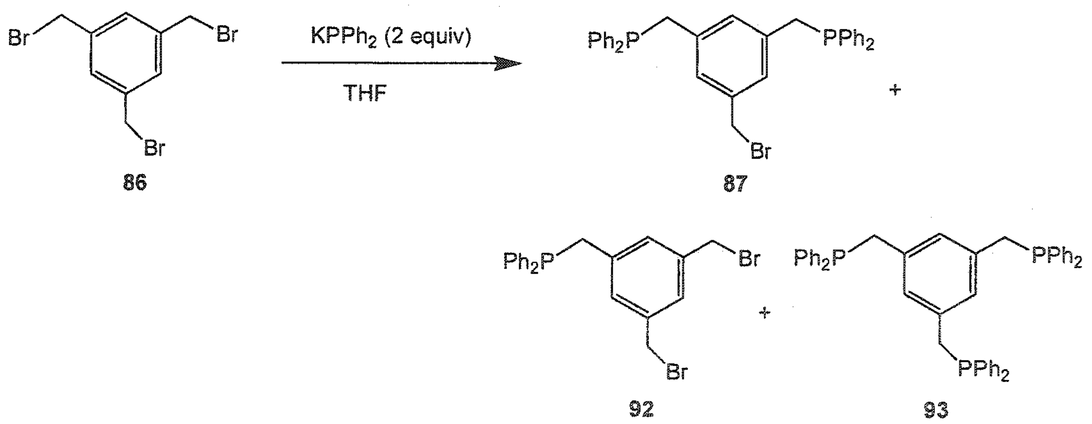
90

eq. 2.3



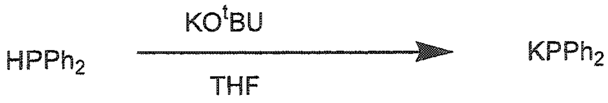
eq. 2.4

It was found that the diphenylphosphine showed little reactivity with **90** at room temperature (24 h.) or at reflux (15 h.), affording a mixture of products, which could not be purified. On the other hand, **90** reacted with the potassium diphenylphosphide and gave only 1,3-bis[(diphenylphosphinoylmethyl)benzene (**91**). Unfortunately, when potassium diphenylphosphide was reacted with **86**, a mixture was obtained, which could not be purified. FAB mass spectroscopy showed masses for the phosphine oxide analogs of compounds **87**, **92** and **93**, so we believe that the product mixture might consist of **87**, **92** and **93** (eq. 2.5).



eq. 2.5

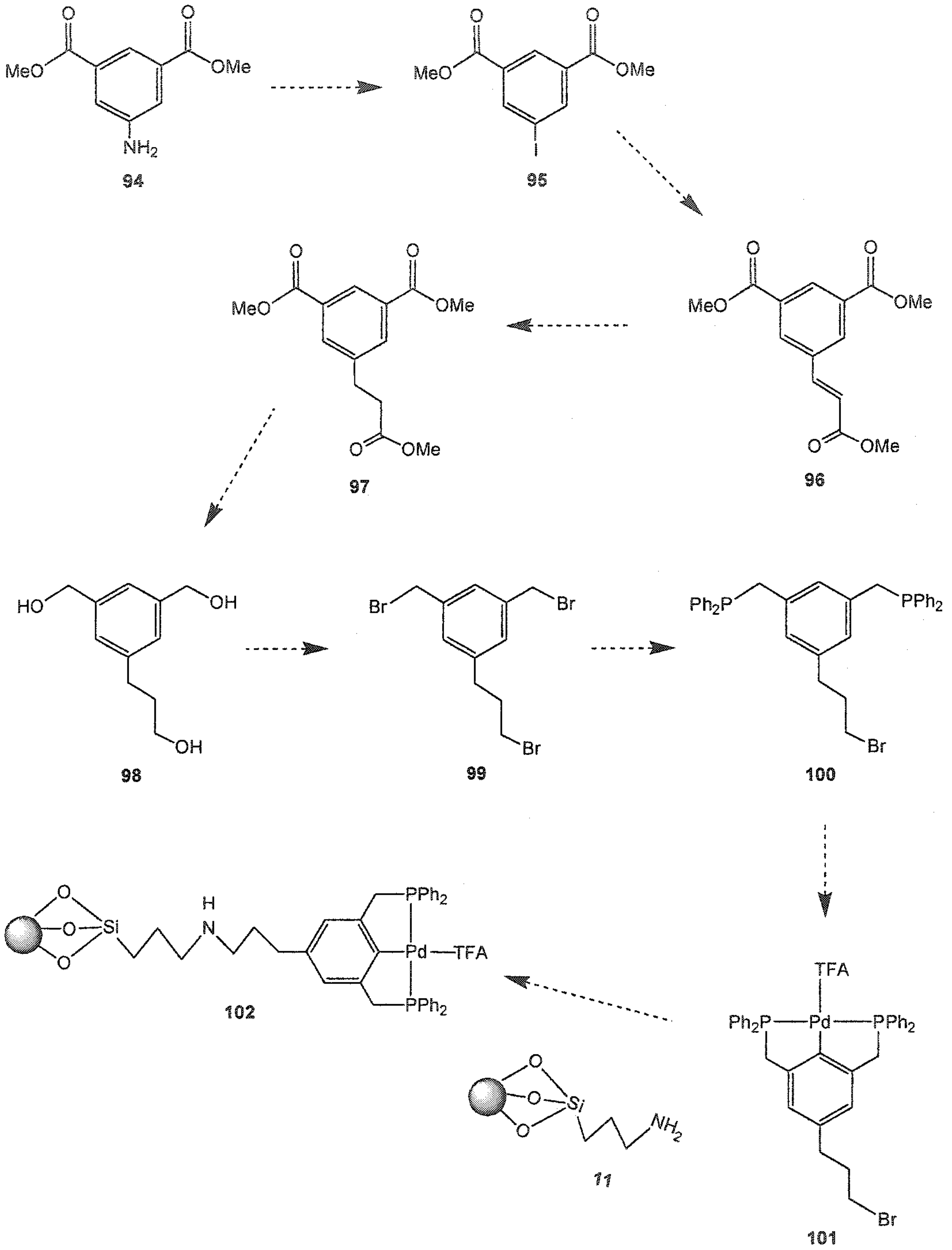
This finding might be a result of the reaction of the potassium diphenylphosphide with **86**, **87** and **92** at almost the same rate. A potential problem in the above approach was uncertainty concerning the precise concentration of potassium diphenylphosphide. Therefore, potassium diphenylphosphide was prepared from diphenylphosphine using potassium tertiary butoxide (eq. 2.6). Unfortunately, similar results were obtained.



$$HPPh_2 \xrightarrow[THF]{KO^tBU} KPPh_2 \qquad \text{eq. 2.6}$$

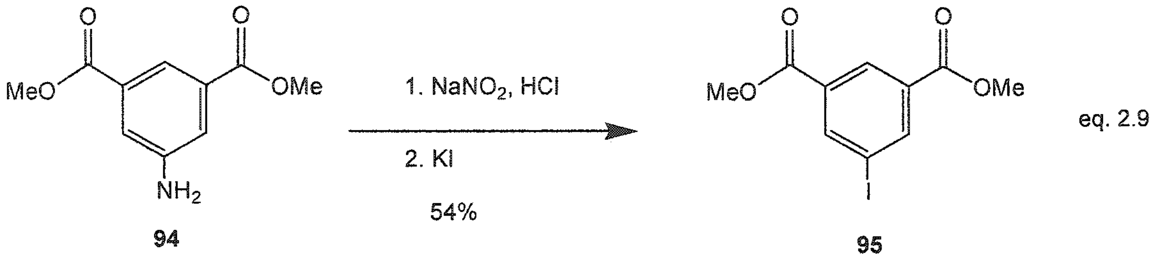
2.3 The Second Synthetic Approach Towards a Silica Supported PCP-type Palladium(II) Complex

As in the first approach, a mixture of products was obtained from the reaction of potassium diphenylphosphide and **86**, which has three equivalent bromides. At this point, the non-equivalent tribromide, 1,3-bisbromomethyl-5-(3-bromopropyl)benzene (**99**) was employed, instead of **86**. Another synthetic pathway to a silica supported PCP-type palladium(II) complex was proposed and it was hoped that the reaction of compound **99** in which one bromine was not at the benzylic position with potassium diphenylphosphide would provide only 1,3-bis(diphenylphosphanylmethyl)-5-(3-bromopropyl)benzene (**100**) as the product (Scheme 2.2).

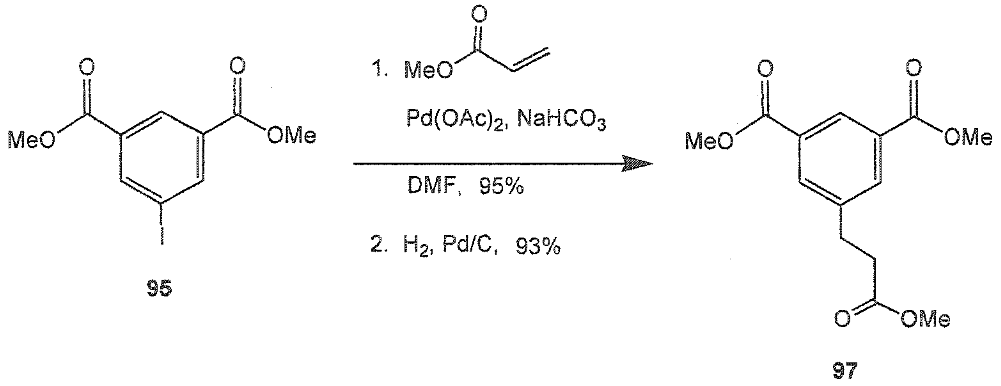


Scheme 2.2 Second Synthetic Approach Towards a Silica Supported PCP-type Palladium(II) Complex.

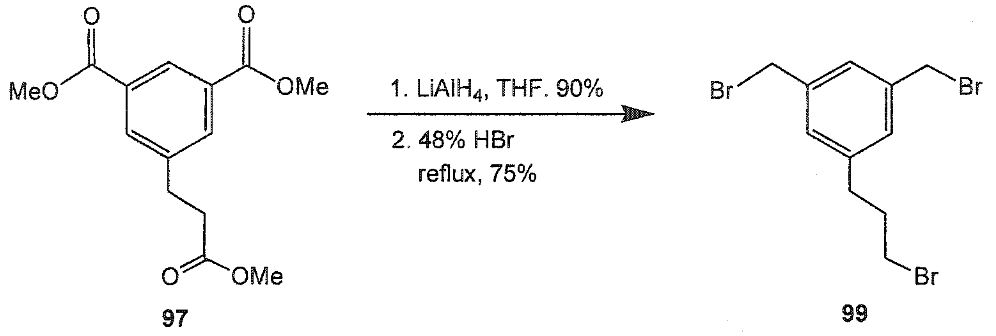
Compound **99** was prepared in 5 steps; first, the commercially available dimethyl-5-aminoisophthalate (**94**) was converted to 5-iodoisophthalic acid dimethyl ester (**95**) in 54% yield, under conditions similar to those for the preparation of iodobenzene from aniline, using sodium nitrite in concentrated hydrochloric acid and potassium iodide (eq. 2.9).(95)



Compound **97** was then synthesized in high yield by Heck reaction of compound **95** with methyl acrylate under modified standard Heck conditions, followed by hydrogenation (eq. 2.10). Finally, compound **99** was isolated in good yield by reduction of **97** with lithium aluminium hydride, and then refluxing with 48% hydrobromic acid under similar conditions to those used for the preparation of **86** (eq.2.11).

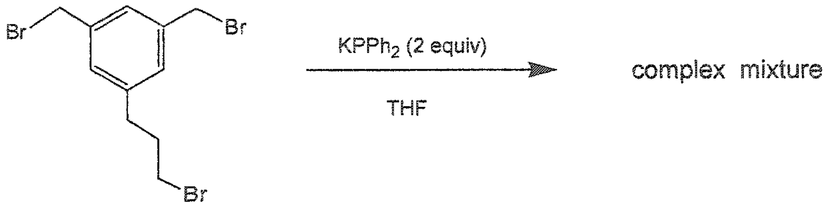


eq. 2.10



eq. 2.11

Many attempts were made at preparing compound **100**. Potassium diphenylphosphide was tried first, and since it was purchased as a solution in tetrahydrofuran (THF), only the reaction temperature was varied to try to obtain compound **100** selectively (eq. 2.12 and Table 2.1). It was found that there was no reaction at temperatures at 0 °C, and potassium diphenylphosphide reacted completely with **99** at 22 °C for 10 h. (entry 1, Table 2.1). A longer reaction time was attempted at temperatures between 0 and 22 °C (entry 2, Table 2.1). Finally, the reaction was attempted between 0 and 18 °C (entry 3, Table 2.1) but unfortunately, in these three reactions, unidentified mixtures of products were formed.



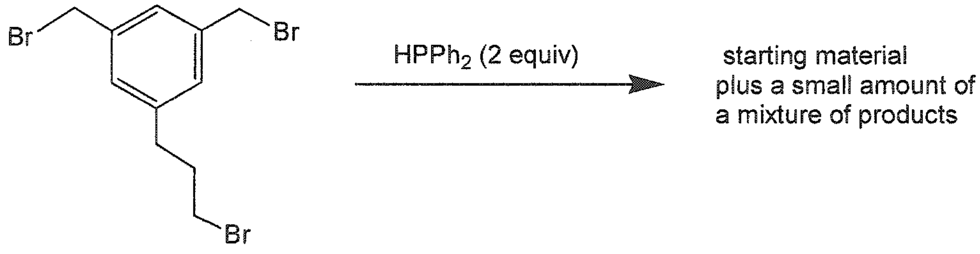
99

eq. 2.12

Table 2.1. Reaction of **99** with potassium diphenylphosphide

Entry	Temperature (°C)	Time (h)
1	-78	5
	0	4
	22	10
2	0	4
	5	2
	10	4
	15	2
	22	12
3	0	2
	5	4
	10	4
	18	2

This observation suggested that the reactivity of the three bromines in dissimilar positions was similar and it was therefore difficult to selectively prepare **100**. Diphenylphosphine was also used in attempting to prepare **100**. Since diphenylphosphine previously showed low reactivity with 1,3-bis(bromomethyl)bezene (**90**), different conditions were used here (eq. 2.13 and Table 2.2). It was found that side reactions occurred at reaction temperatures of 50 °C or 60 °C, more than at 22 °C (entries 1 and 2, Table 2.2). Therefore, a longer time (5 days) at 22 °C was tried, using a polar solvent (MeOH) or a non-polar solvent (benzene) (entries 1 and 2, Table 2.2). The non-polar solvent provided less side products but unfortunately, in all cases, the starting material was recovered in nearly quantitative yield.



99

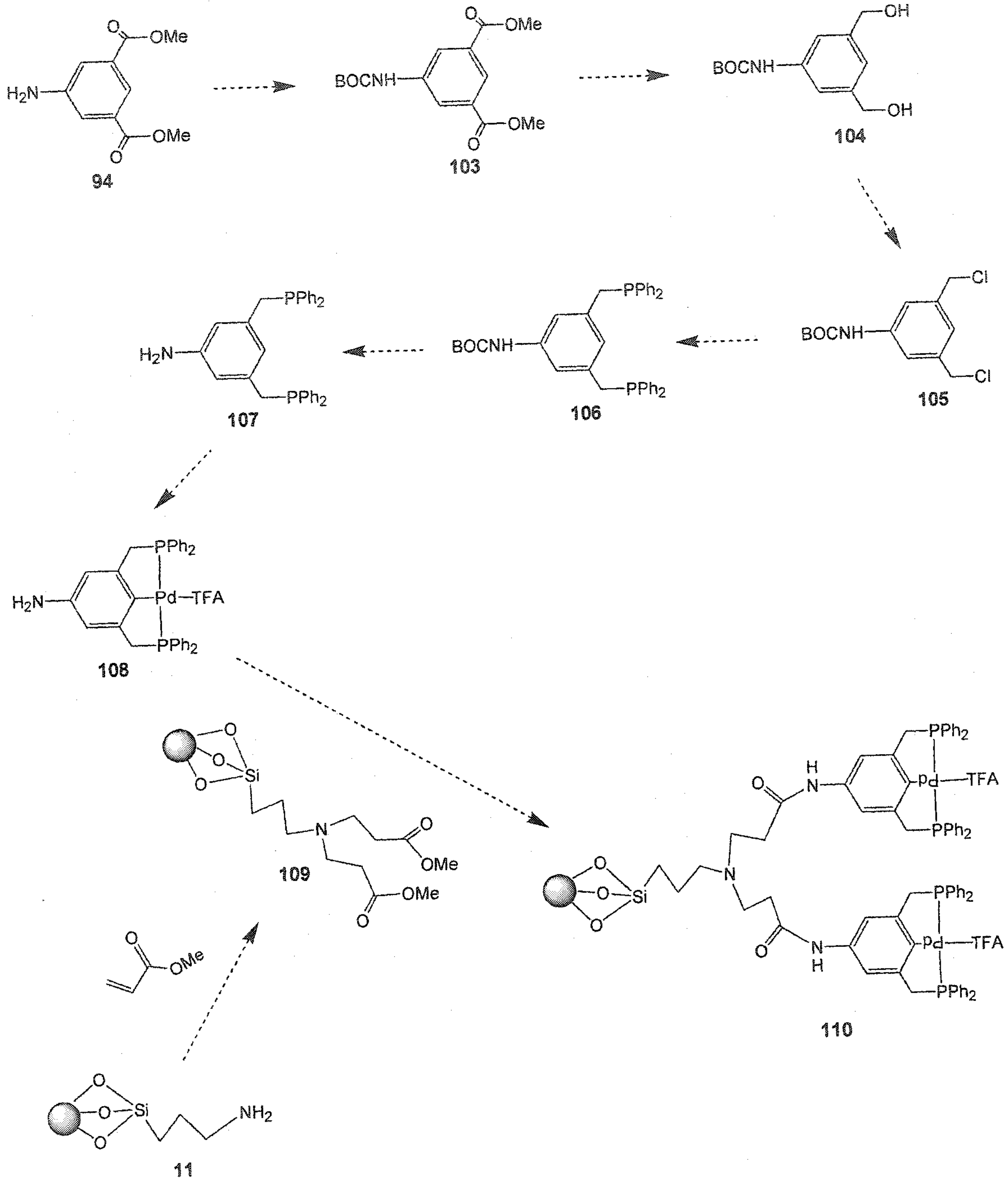
eq. 2.13

Table 2.2. Reaction of **99** with diphenylphosphine

Entry	Solvent	Temperature (°C)	Time (h)
1	THF	22	18
		50	12
2	acetone	22	2
		60	3
3	MeOH	22	120
4	Benzene	22	120

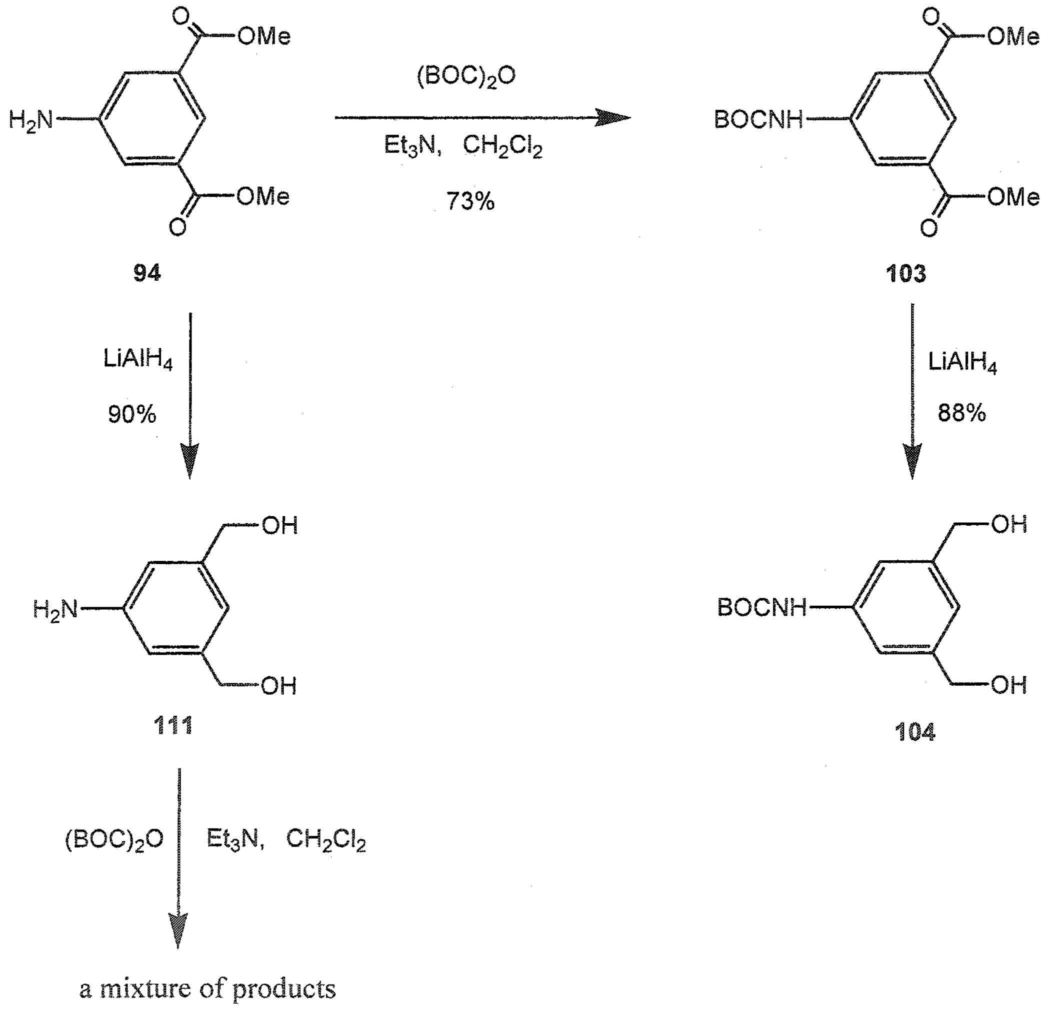
2.4 The Third Synthetic Approach Towards a Silica Supported PCP-type Palladium(II) Complex

At this stage, we considered another pathway to synthesize a silica supported PCP-type palladium(II) complex (see Scheme 2.3). Dimethyl-5-aminoisophthalate (**94**) was again used as the substrate, but the key step was the protection of the amino group with *t*-butoxycarbonyl (BOC) before reaction with potassium diphenylphosphide.



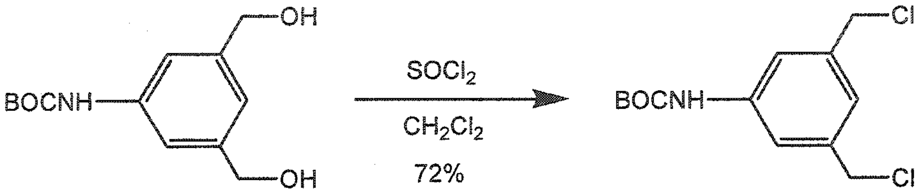
Scheme 2.3 **Third Synthetic Approach Towards a Silica Supported PCP-type Palladium(II) Complex**

N-[3,5-bis(hydroxymethyl)phenyl]-2,2-dimethylpropionamide (**104**) was synthesized in good yield by first protecting the amino group of **94** using a modified procedure described in the literature,(96) followed by reduction with $LiAlH_4$. Effecting reduction before protecting the amino group with BOC was also attempted, to compare the methods, but it was found to give a mixture of products (Scheme 2.4).



Scheme 2.4 Preparation of Compound 104

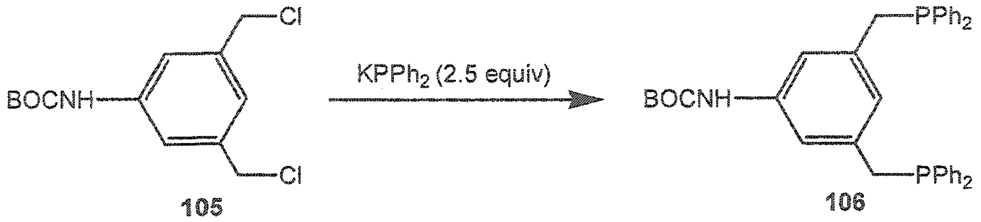
Treatment of **104** with thionyl chloride furnished a dichloride **105** in 72% yield (eq. 2.14).



104 **105**

eq. 2.14

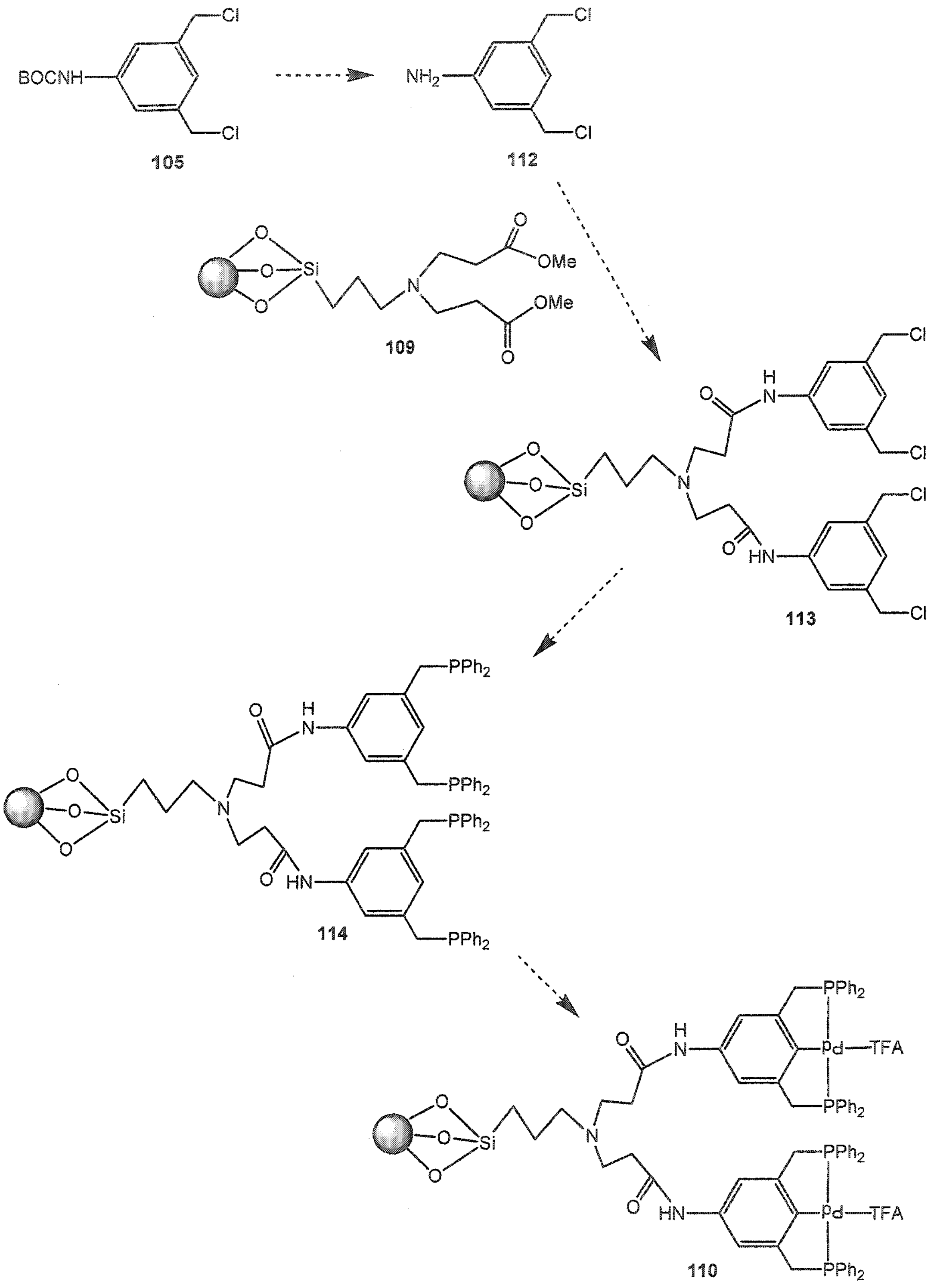
The reaction of **105** with potassium diphenylphosphide provided *N*-[3,5-bis(diphenylphosphanylmethyl)phenyl]-2,2-dimethylpropionamide (**106**) as expected, but unfortunately, the reaction required at least 2.5 equivalents of potassium diphenylphosphide (eq. 2.15). Excess potassium diphenylphosphide, which formed diphenylphosphine during working-up, created difficulty in the purification step. Subsequently, several unsuccessful attempts were made to remove the diphenylphosphide and diphenylphosphine from the product, by trying to dissolve the mixture in different solvents such as MeOH, hexane and pentane or a mixture of these solvents. In addition, product **106** was bound to silica when column chromatography was used for the purification.



eq. 2.15

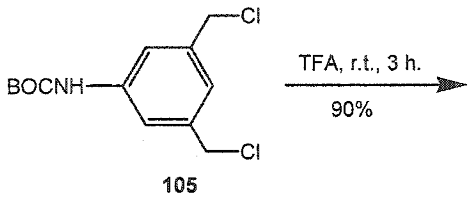
2.5 The Fourth Synthetic Approach Towards a Silica Supported PCP-type Palladium(II) Complex

In order to solve the purification problem, we decided to change our strategy by cleaving the protecting group off and then connecting the substrate to the silica before reaction with the potassium diphenylphosphide, as in Scheme 2.5.

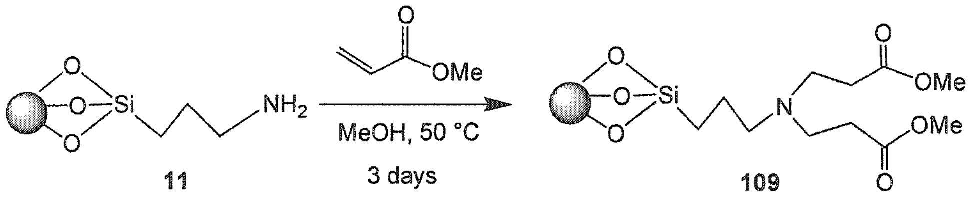


Scheme 2.5 Fourth Synthetic Approach Towards a Silica Supported PCP-type Palladium(II) Complex.

The reaction of **105** with trifluoroacetic acid (TFA) gave 3,5-bis(chloromethyl)-phenylamine (**112**) in 90% yield (eq. 2.16). However, it was found that **112** decomposed at room temperature, and thus it was used immediately for the next step. Silica gel **109** was synthesized according to the procedure described in the literature, from commercially available aminopropyl silica gel (**11**) (eq. 2.17).(66)



eq. 2.16

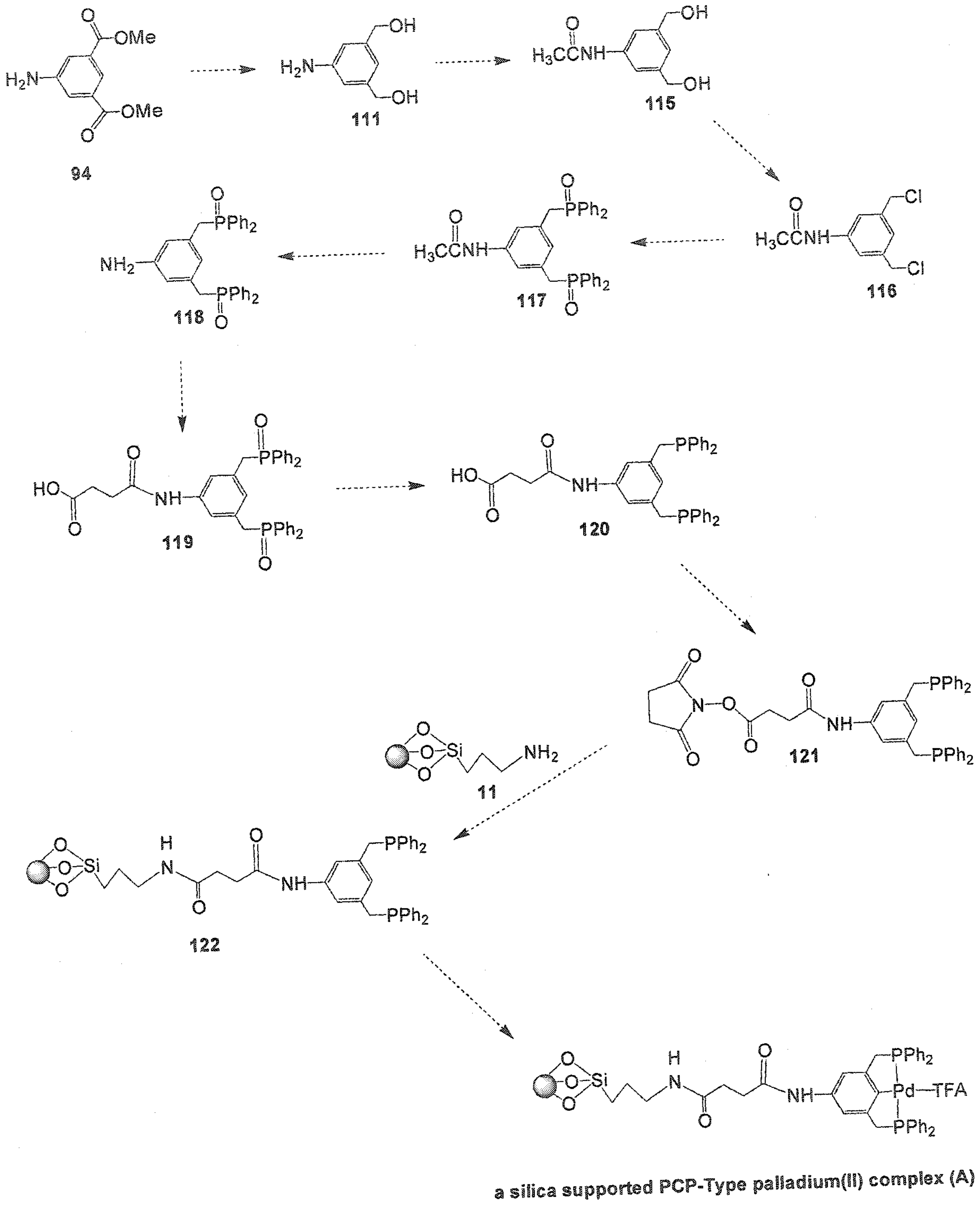


eq. 2.17

The reaction of **109** with **112** under a modified literature procedure(64) gave recovered starting material **109**, and decomposed **112**. This suggested that the reaction was so slow that compound **112** decomposed before possible reaction with **109**.

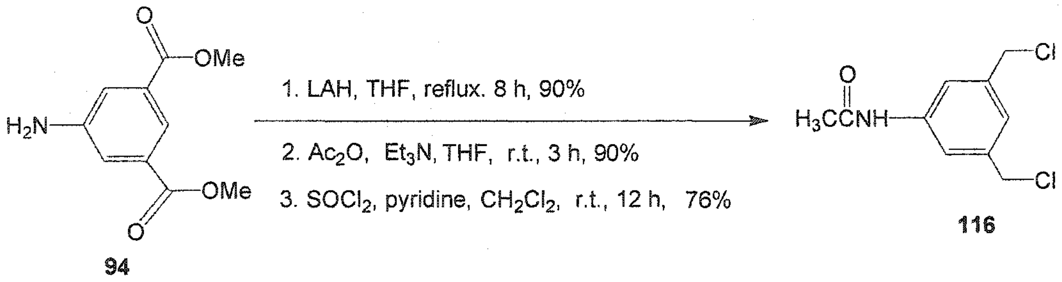
2.6 Synthesis of a Silica Supported PCP-type Palladium(II) Complex (A)

As noted, the phosphine compound is technically difficult to handle for purification because of its sensitivity to air. Therefore, the next route to synthesize the silica supported PCP-type palladium(II) complex was based on protecting the phosphine compound as phosphine oxide, which is stable and not sensitive to air (Scheme 2.6).



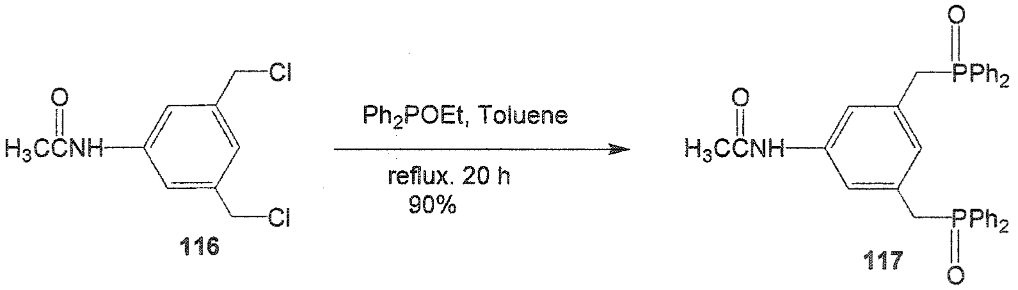
Scheme 2.6 Synthesis of a Silica Supported PCP-type Palladium(II) Complex (A)

N-acetyl-3,5-bis(chloromethyl)aniline (**116**) was prepared in 3 steps (reduction, acetylation and chlorination) according to the procedure described in the literature, starting from commercially available 5-aminoisophthalic acid dimethyl ester (eq. 2.18).(97)



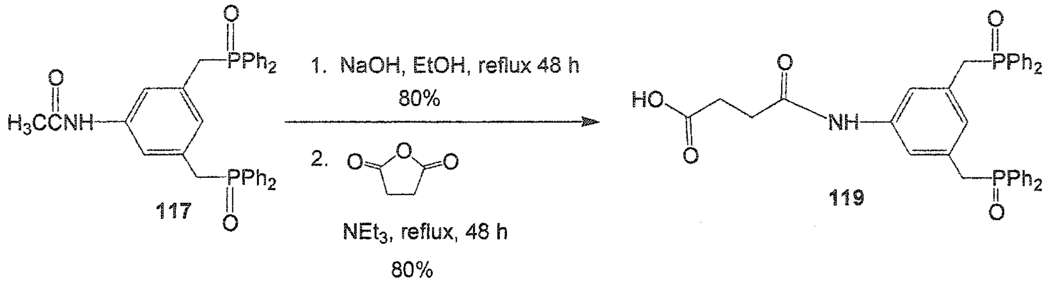
eq. 2.18

The *N*-[3,5-bis(diphenylphosphinoylmethyl)phenyl]acetamide (**117**) was synthesized by an Arbuzov-type reaction of **116** (eq. 2.19). In contrast with the diphosphine analogue, **117** is air stable



eq. 2.19

The subsequent deprotection and reaction with succinic anhydride afforded *N*-[3,5-bis(diphenylphosphinoylmethyl)phenyl]succinamic acid (**119**) (eq. 2.20). Compound **119** was characterized by ^{1}H NMR, ^{13}C NMR, $^{31}P\{H\}$NMR, and X-ray crystallography (Figure 2.8).



eq. 2.19

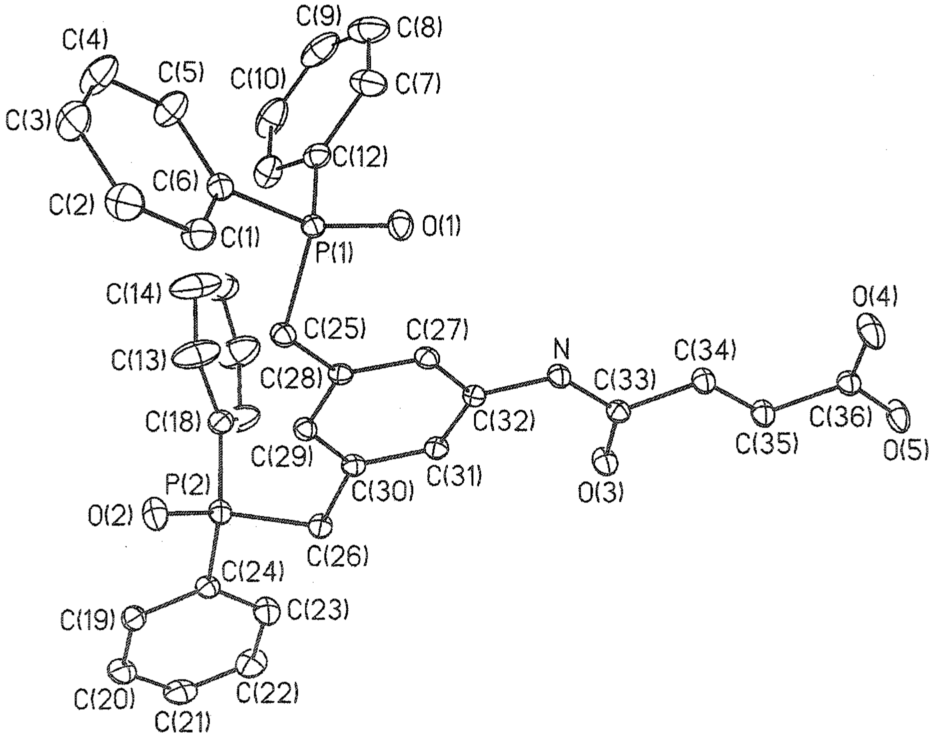
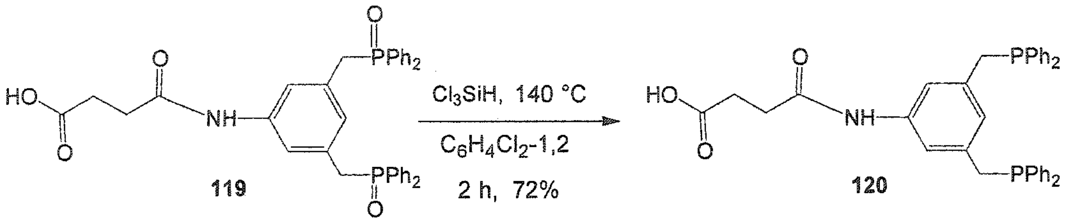


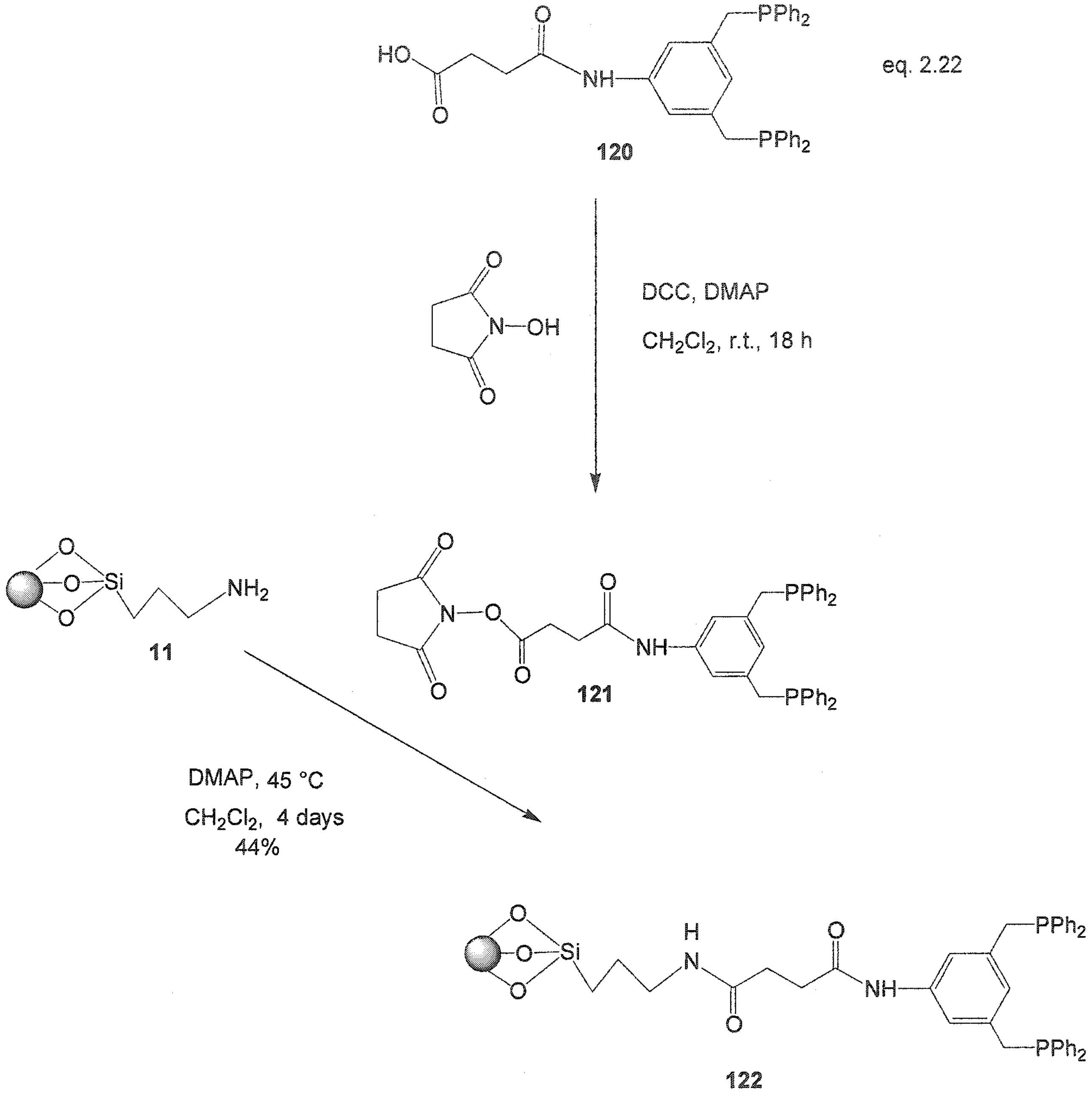
Figure 2.8 ORTEP Diagram of *N*-[3,5-Bis(diphenylphosphinoylmethyl)phenyl]-succinamic Acid (119) (hydrogen atoms omitted for clarity)

Reduction of **119** with $HSiCl_3$ afforded the diphosphine compound (**120**) in 72% yield (eq. 2.21).



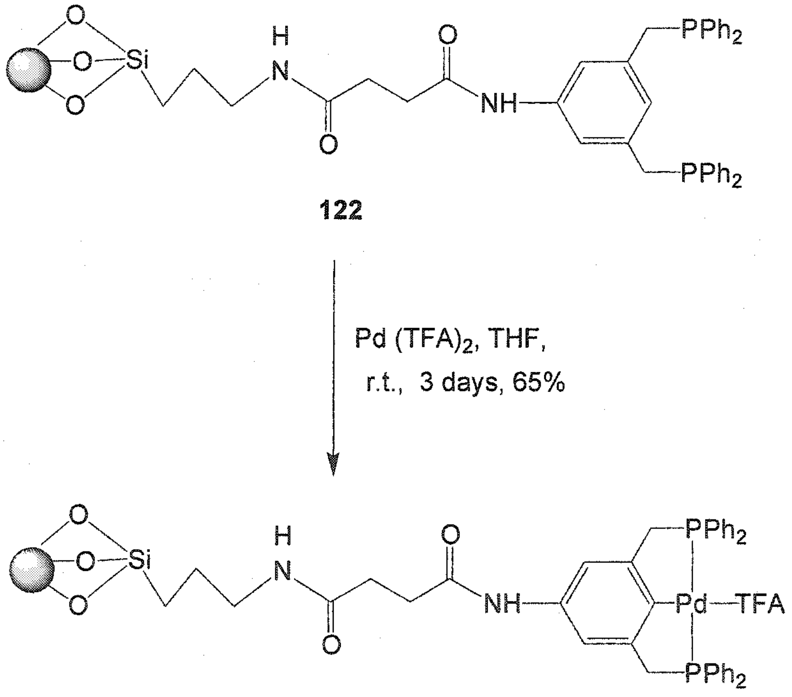
eq. 2.21

Reaction of **120** with *N*-hydroxysuccinimide and DCC gave the *N*-hydroxysuccinimide ester (**121**) which, when treated with commercial aminopropyl silica gel (**11**), afforded the supported ligand (**122**) (eq. 2.22). CP/MAS ^{31}PNMR was used as a tool for the determination of the successful binding to the silica, as the chemical shift values are very sensitive to small changes in the microenvironment. The CP/MAS ^{31}P NMR spectrum of **122** showed a signal at -10.9 ppm and a small signal (phosphine oxide) at 27.1 ppm, whereas the ^{31}P NMR solution spectrum of compound **120** gave a signal at -9.0 ppm (phosphine oxide at 34.7 ppm). As well, the CP/MAS ^{13}C NMR spectrum of **122** shows signals due to aromatic carbons. The percentage of phosphorus, as determined by ICP analysis, was 1.59% (entry 1, Table 2.3, see page 80). The amine content of the commercial aminopropyl silica gel (**11**) used was 0.9 mmol/g. The theoretical percentage of phosphorus was 3.58-3.65% (phosphine oxide formation may occur during the ICP process, which will lower theoretical percentage of phosphorus) (entry 1, Table 2.3, see page 80).



eq. 2.22

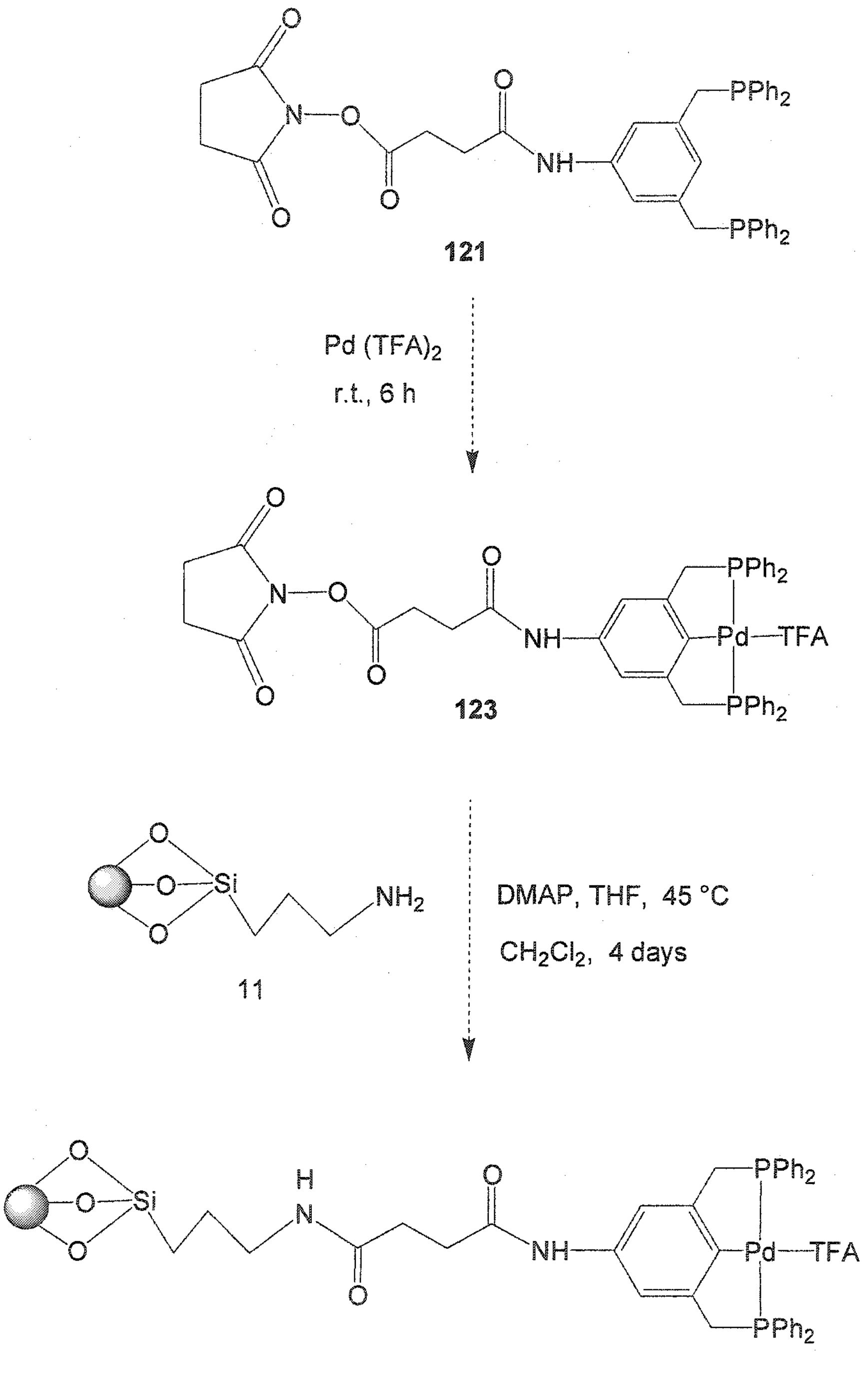
$Pd(TFA)_2$ was then reacted with **122** to form a silica supported PCP-type palladium(II) complex (**A**) (eq. 2.23) in 65% yield (entry 1, Table 2.3, see page 80). A phosphine/palladium ratio of 4/1 was used to avoid the formation of other complexes along with the PCP palladium(II) complex, such as palladium bound to the amino groups of the aminopropyl silica gel. The ^{31}P NMR spectra of complexes **A** and **34** showed peaks at 37.9 ppm and at 37.2 ppm, respectively (there is also a low intensity signal in the NMR of **A**, at 28.7 ppm due to phosphine oxide impurity) (It has already been reported that the ^{31}PNMR chemical shifts of the silica-bound late transition metal species which are coordinated with phosphine donors are similar to those of their molecular precursors).(98) The percentage of palladium in **A**, determined by ICP, was 1.67% and the theoretical percentage of palladium was 2.58% (entry 1, Table 2.3, see page 80).



eq. 2.23

a silica supported PCP-type palladium(II) complex (**A**)

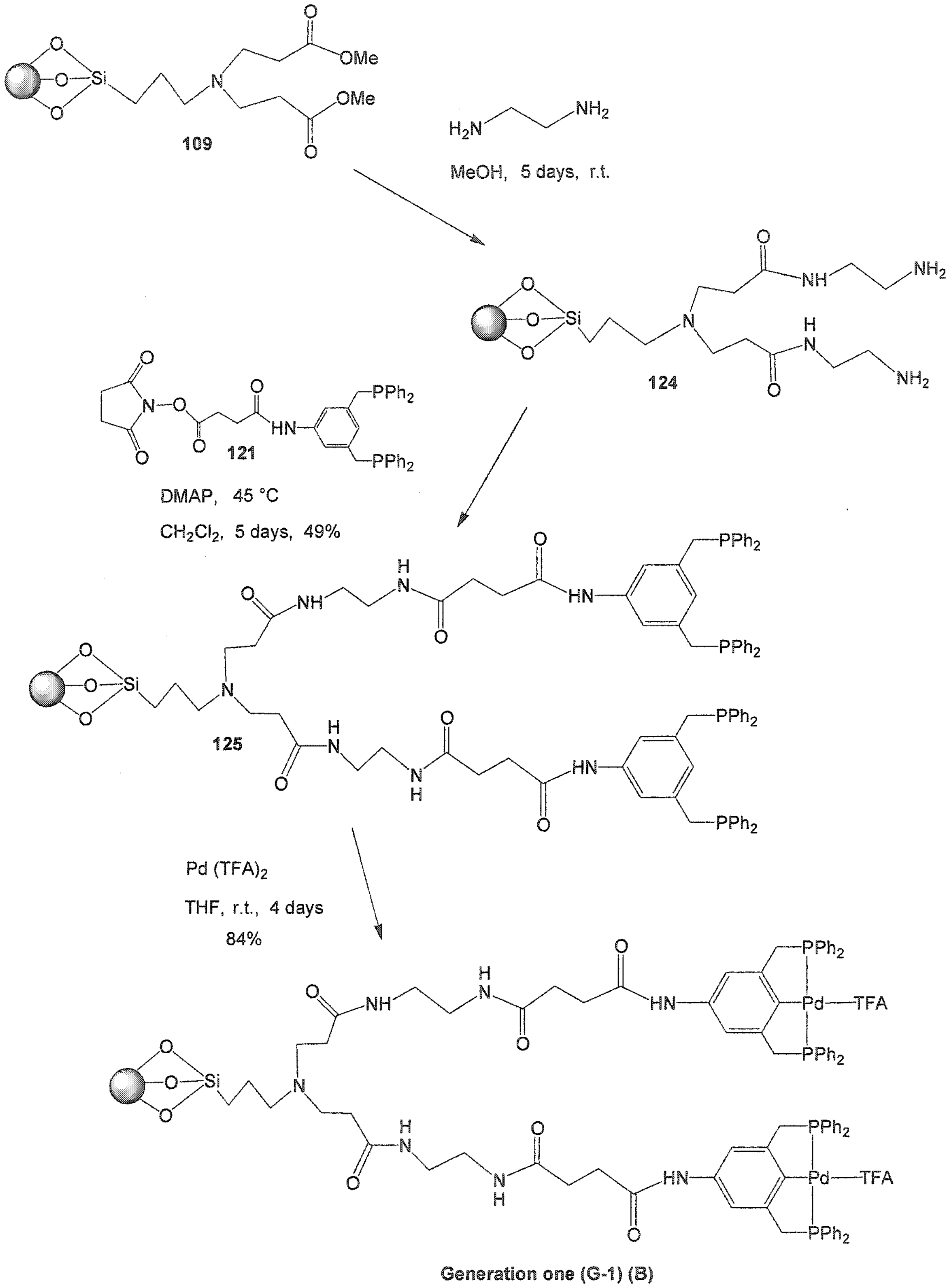
Another preparation of complex **A** was also attempted, by effecting cyclometallation of the phosphine ligands with the Pd complex prior to binding with silica (Scheme 2.7). However, due to the reactivity of the *N*-hydroxysuccinimide ester, problems were encountered in the purification of the Pd complex (**123**) obtained by this route. In the previous method, the purification of the silica bound ligand was simpler.



Scheme 2.7 An Alternative Synthetic Approach Towards A

2.7 Synthesis of a Generation one Dendrimer (G-1) (B) Silica Supported PCP-type Palladium(II) Complex

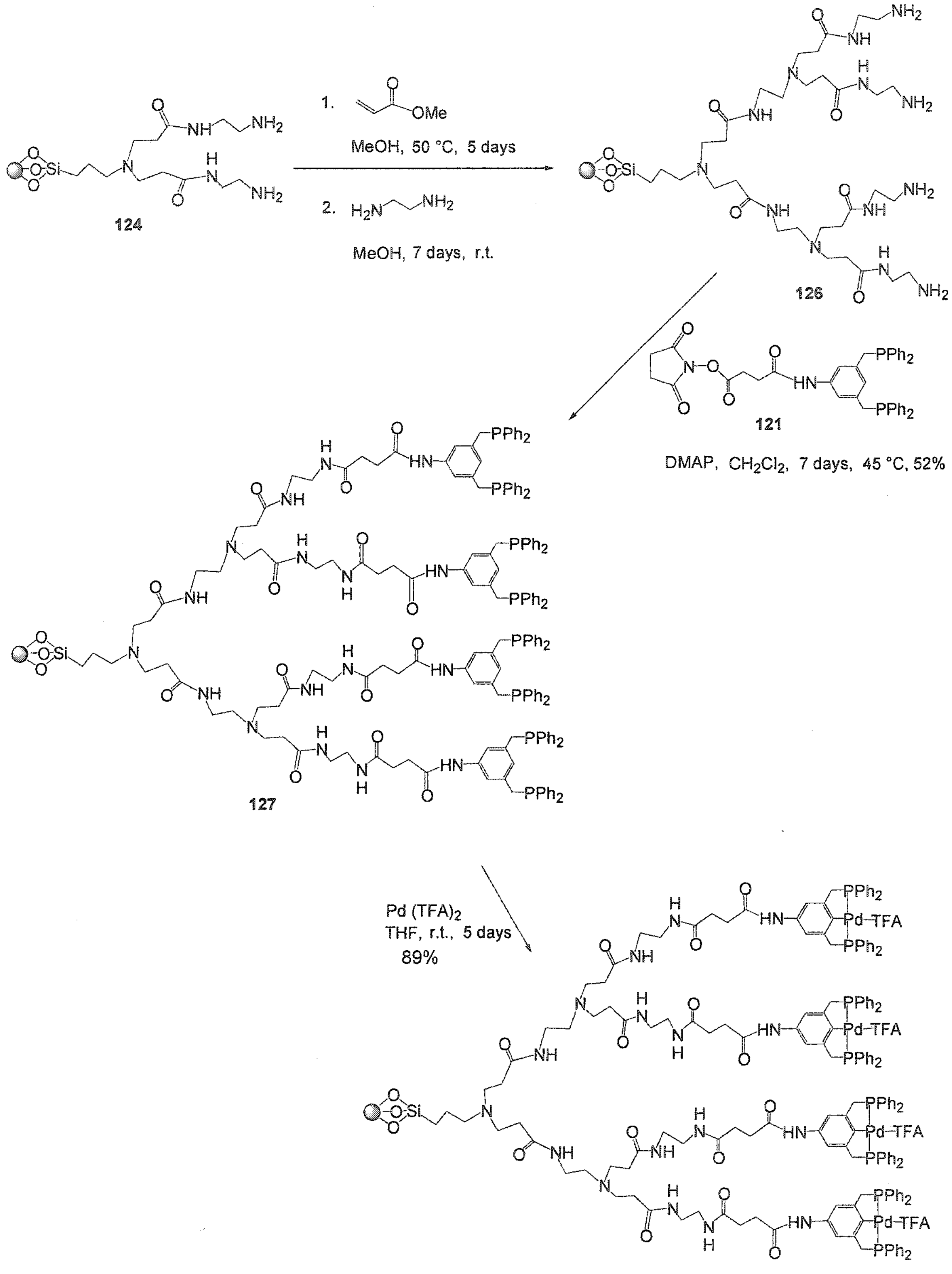
After the successful synthesis of **A**, a generation one dendrimer (**G-1**) (**B**) with a phosphine/palladium ratio of 4/1 was prepared by a similar strategy, illustrated in Scheme 2.8. Silica gels **109** (see page 64) and **124** were prepared according to the procedure described in the literature.(66) Compound **121** was prepared as described on page 71. The CP/MAS ^{31}P NMR and ^{13}C NMR spectra of **125** were similar to those of **122**; the CP/MAS ^{31}P NMR spectrum showed a signal at -8.6 ppm and a small signal (phosphine oxide) at 27.9 ppm, and the ^{13}C NMR CP/MAS spectrum displayed signals for aromatic carbons. As well, the CP/MAS ^{31}P NMR spectrum of **B** was similar to that of **A**, showing a signal at 38.7 ppm and a small signal at 29.3 ppm (phosphine oxide impurity). The percentages of phosphorus and palladium, determined by ICP analysis, were 2.37% and 3.22%, respectively, and the theoretical percentages of phosphorus and palladium were 4.81-4.93% and 3.82, respectively (entry 2, Table 2.3, see page 80).



Scheme 2.8 Synthesis of a Generation One Dendrimer (G-1) (B) Silica Supported PCP-type Palladium(II) Complex

2.8 Synthesis of a Generation Two Dendrimer (G-2) (C) Silica Supported PCP-type Palladium(II) Complex

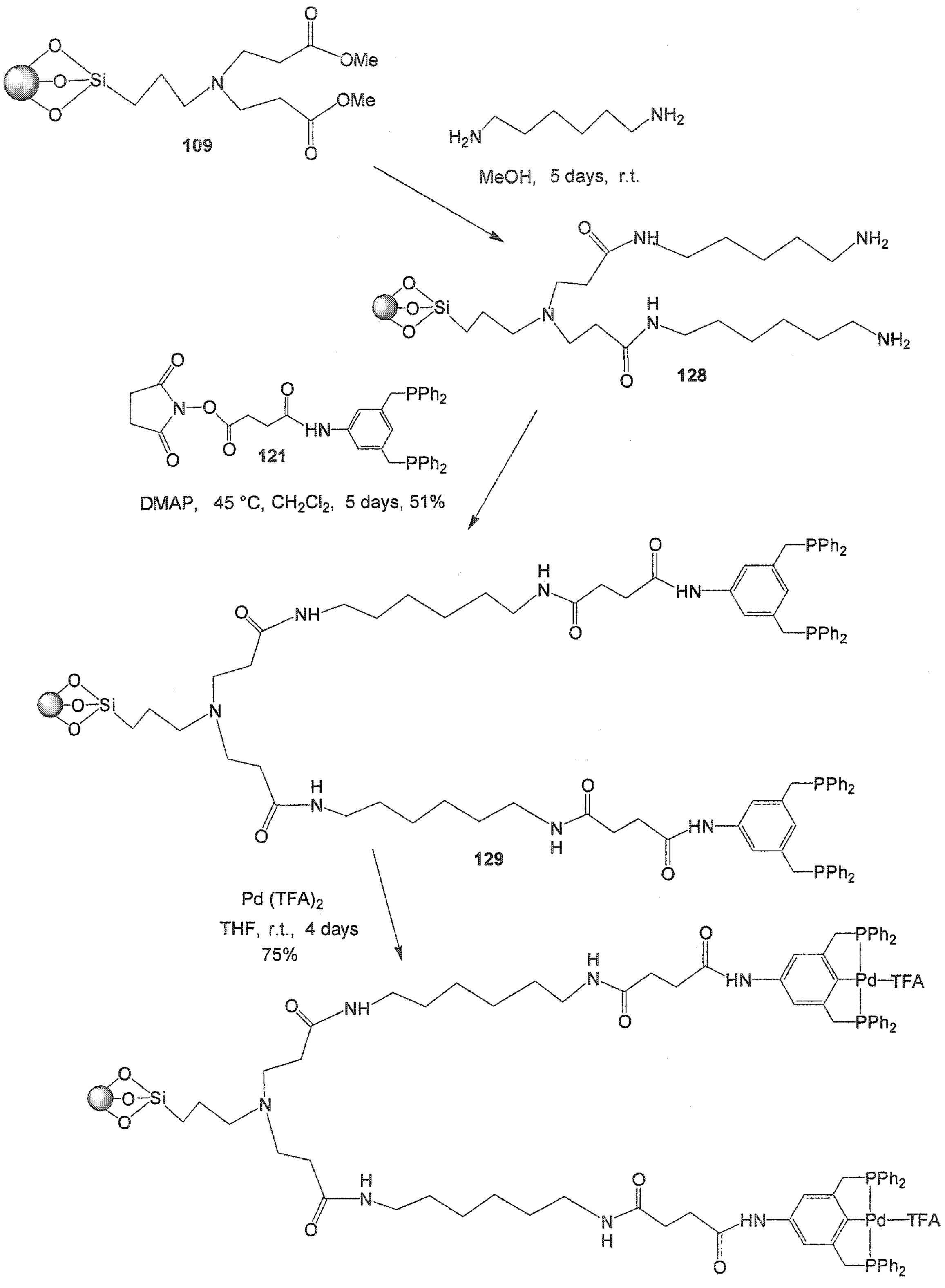
After the successful synthesis of **A** and **B**, a generation two dendrimer (**G-2**) (**C**) with a phosphine/palladium ratio of 4/1 was prepared using a similar strategy (Scheme 2.9). Silica gel **124** and **126** were prepared according to the procedure described in the literature.(66) The CP/MAS ^{31}P NMR and ^{13}C NMR spectra of **127** were similar to those of **122** and **125**, showing a signal at -11.3 ppm and a small signal (phosphine oxide) at 27.1 ppm, and the ^{13}C NMR CP/MAS spectrum displayed signals for aromatic carbons. The CP/MAS ^{31}P NMR spectrum of **C** was similar to that of **A** and **B**, showing a signal at 36.3. The percentages of phosphorus and palladium, determined by ICP analysis, were 3.0 % and 4.29%, respectively and the theoretical percentages of phosphorus and palladium were 5.81-5.99% and 4.84 respectively (entry 3, Table 2.3, see page 80).



Scheme 2.9 Synthesis of a Generation Two Dendrimer (G-2) (C) Silica Supported PCP-type Palladium(II) Complex

2.9 Synthesis of a Generation One Dendrimer (G-1) (D) Silica Supported PCP-type Palladium(II) Complex

After the successful synthesis of **A**, **B**, and **C**, a generation one dendrimer (**G-1**) (**D**) with a phosphine/palladium ratio of 4/1 was prepared by a similar strategy (Scheme 2.10). Silica gel **128** was prepared under the same conditions as that of **124** but the 1,2-diaminoethane was replaced with 1,6-diamino hexane. The CP/MAS ^{31}P NMR and ^{13}C NMR spectra of **129** were similar to those of **122**, **125** and **127**; the CP/MAS ^{31}P NMR spectrum showed a signal at –11.2 ppm and the ^{13}C NMR CP/MAS spectrum displayed signals for aromatic carbons. Also, the CP/MAS ^{31}P NMR spectrum of **D** was similar to that of **A**, **B** and **C**, showing a signal at 35.6 ppm. The percentages of phosphorus and palladium, determined by ICP analysis, were 2.33% and 2.84%, respectively and the theoretical percentages of phosphorus and palladium were 4.61-4.72% and 3.81%, respectively (entry 4, Table 2.3, see page 80).



Scheme 2.10 Synthesis of a Generation One (G-1) (D) Silica Supported PCP-type Palladium(II) Complex

Table 2.3. Phosphorus and palladium contents of **A**, **B**, **C** and **D**.

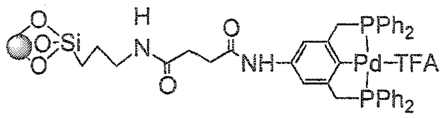
Entry	Catalyst	ICP result % P	Theoretical amount % P		Yield % P	ICP result % Pd	Theoretical amount % Pd	Yield % Pd
			Free Phosphine	Phosphine oxide				
1	**A**	1.59	3.65	3.58	44	1.67	2.58	65
2	**B**	2.37	4.93	4.81	48-49	3.22	3.82	84
3	**C**	3.0	5.99	5.81	50-52	4.29	4.84	89
4	**D**	2.33	4.72	4.61	49-51	2.84	3.81	75

3

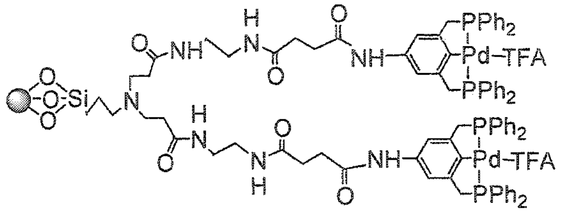
*The Catalytic Activities of **A**, **B**, C and **D***

3.1 Introduction

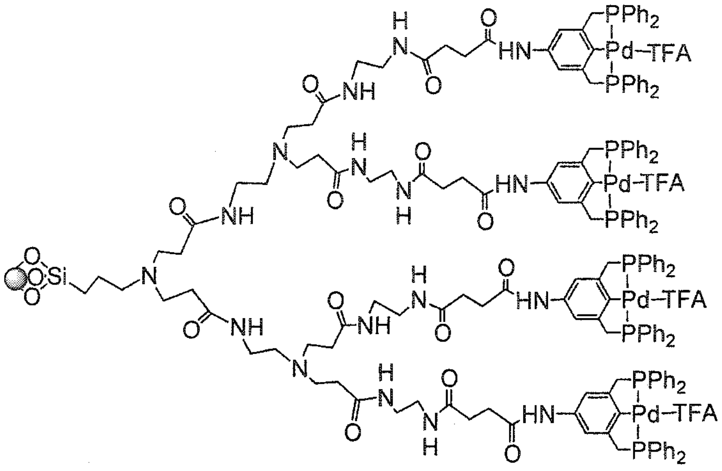
The following chapter describes catalytic activities of generation zero dendrimer (**G-0**) (**A**), generation one dendrimer (**G-1**) (**B**), generation two dendrimer (**G-2**) (**C**) with a 2-carbon spacer and generation one dendrimer with a 6-carbon spacer group, (**G-1**) (**D**) (Figure 3.1) for the Heck and intramolecular cyclocarbonylation reactions. A study of catalyst recycling was also undertaken. It was found that **A** (**G-0**), **B** (**G-1**), **C** (**G-2**) and **D** (**G-1**) were efficient catalysts for the Heck and intramolecular cyclocarbonylation reactions. The successful immobilization of a PCP-type palladium(II) complex onto silica under mild conditions represents a strategy that combines the advantages of heterogeneous and homogeneous catalysts. It was found that these catalysts were thermally stable up to 170 °C and stable towards moisture and oxygen. The catalytic reactions carried out with careful exclusion of moisture and air gave the same yield as those carried out without any special precautions. Therefore, all catalytic reactions were performed without special effort to remove moisture or air. In addition, the catalysts could be recycled by simple filtration in air and reused with only a moderate loss of activity. Since the amount of the each recycle catalyst was not enough to run a CP/MAS ^{31}P NMR, ICP analysis was used to examine the possibility of leaching of the catalyst after the recycles in some reactions.



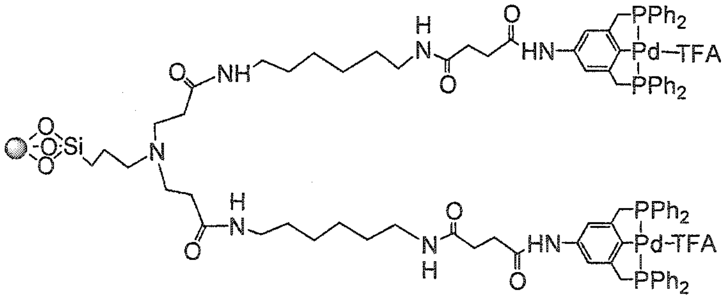
Generation zero (**G-0**) (**A**)



Generation one (**G-1**) (**B**)



Generation two (**G-2**) (**C**)

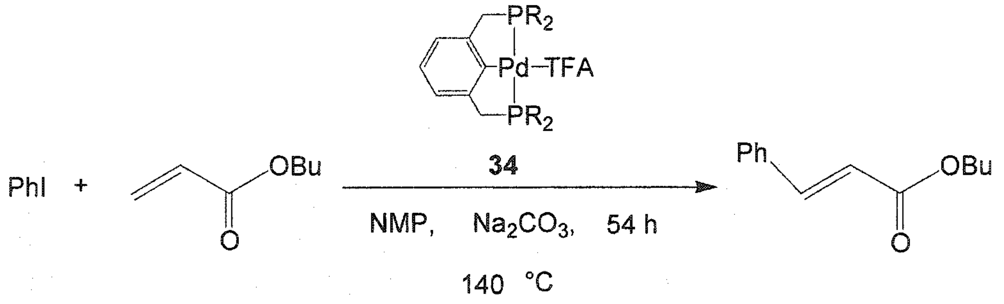


Generation one (**G-1**) (**D**)

Figure 3.1 Catalysts A(G-0), B(G-1), C(G-2) and D(G-1)

3.2 The Heck Reaction

Complex **34**, R = Ph was a good catalyst for the Heck reaction of iodobenzene and *n*-butyl acrylate using the same conditions of those reported for complex **34**, R = ^{i}Pr.(24) (eq. 3.1 and Table 3.1).



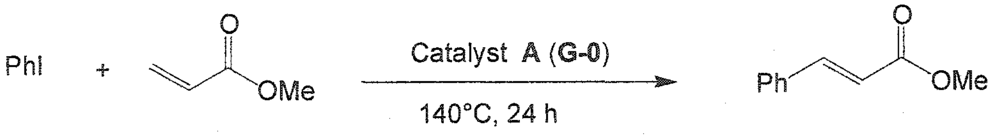
eq. 3.1

Table 3.1. Heck reaction of iodobenzene and *n*-butyl acrylate catalyzed by **34**, R = Ph.[a]

Conversion (%)[b]	TON (mol of product/mol of Pd)
>99	68300[c]

[a] *Reaction was conducted using 0.1 mg (1.45x10-4 mmol) of catalyst 34, 10 mmol of iodobenzene and 12 mmol of n-butyl acrylate in NMP.* [b] *Determined by GC.* [c] *The TON was at least the number specified as the reaction was already complete at 54 hours*

The silica-PCP-type palladium(II) complex **A** (**G-0**) was then investigated as a catalyst for the Heck reaction. It was found that the coupling reaction of iodobenzene and methyl acrylate at 140 °C, using either sodium carbonate (Na_2CO_3) or triethylamine (NEt_3) as the base, in *N*-methyl-pyrrolidinone (NMP) or dimethylformamide (DMF) provided complete conversion (eq. 3.2 and Table 3.2).



eq. 3.2

Table 3.2. Heck reaction of iodobenzene and methyl acrylate catalyzed by **A** (**G-0**).[a]

Entry	Base	Solvent	Conversion (%)[b]	TON (mol of product/mol of Pd)
1	Na_2CO_3	NMP	>99 (82)[c]	1020[d]
2	NEt_3	DMF	>99 (89)[c]	1020[d]

[a]Reactions were conducted using 25 mg ($3.9x10^{-3}$ mmol) of catalyst A, 4 mmol of iodobenzene and 4.8 mmol of methyl acrylate. [b]Determined by GC. [c]Isolated yield. [d]The TON was at least the number specified as the reaction was already complete at 24 hours.

Since the Heck reaction of iodobenzene and methyl acrylate catalyzed by **A** was quite facile, it would be difficult to fully optimize the conditions from this reaction. The slower coupling of bromobenzene and methyl acrylate catalyzed by **A** was investigated instead (eq. 3.3 and Table 3.3).

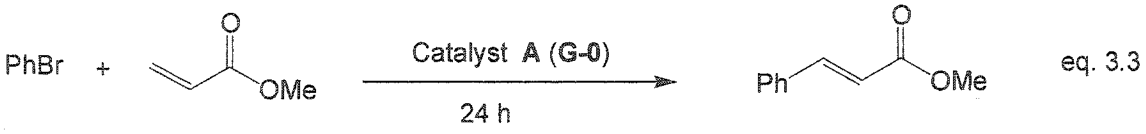
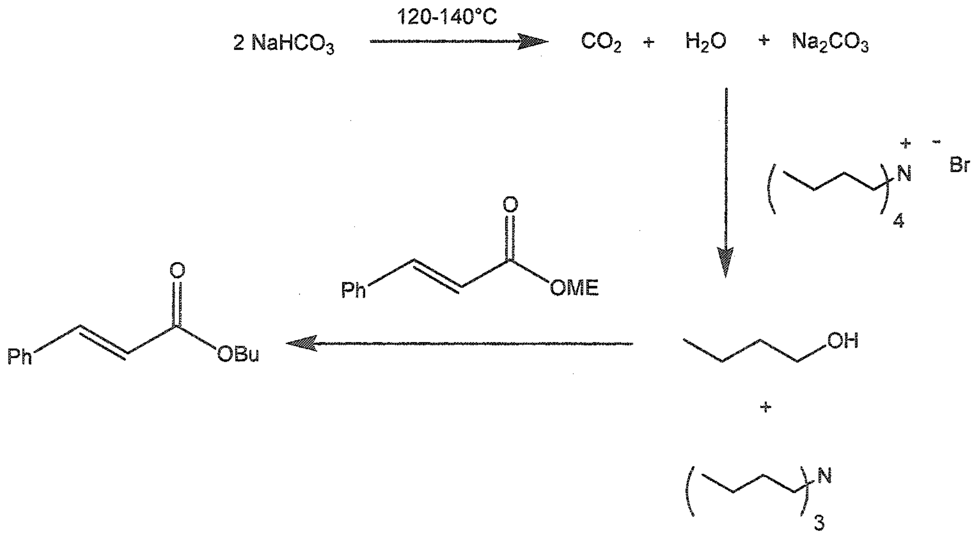


Table 3.3. Heck reaction of bromobenzene and methyl acrylate catalyzed by **A (G-0)**.[a]

Entry	Temperature (°C)	Base	Solvent	n-Bu_4NBr (mol%)[b]	Conversion (%)[c]	Methyl cinnamate (%)[c]	Butyl cinnamate (%)[c]
1	120	NEt_3	DMF	-	15	15	-
2	140	NEt_3	DMF	-	24	24	-
3	140	NaOAc	DMF	-	30	30	-
4	140	NaOAc	DMF	50	45	45	-
5	140	NaOAc	NMP	50	44	44	-
6	140	$NaHCO_3$	DMF	50	32	31	1
7	140	$NaHCO_3$	NMP	50	50	47	3
8	120	$NaHCO_3$	NMP	50	40	39	1
9	140	Na_2CO_3	DMF	-	32	32	-
10	140	Na_2CO_3	NMP	-	36	32	-

[a] *Reactions were conducted using 25 mg ($3.9x10^{-3}$ mmol) of catalyst A, 2 mmol of bromobenzene and 2.4 mmol of methyl acrylate for 24 hours.* [b] *mol % n-Bu_4NBr refer to aryl bromide.* [c] *Determined by GC, based on bromobenzene and the product.*

Firstly, the effect of base was studied. Sodium acetate (NaOAc), sodium bicarbonate ($NaHCO_3$) and Na_2CO_3 provided better results than NEt_3 (Table 3.3). Higher conversions were obtained when the temperature was raised from 120 °C to 140 °C (entries 1 and 2 and 7 and 8, Table 3.3). On the case of solvent effect, it was found that the reactions in NMP were better than in DMF (entries 6 and 7, Table 3.3) but there was no solvent effect when NaOAc was the base (entries 4 and 5, Table 3.3). Tetrabutyl ammonium bromide (Bu_4NBr) as an additive was considered and this improved the yields of the reactions (entries 4, 5 and 7, Table 3.3). However, in the case of $NaHCO_3$ as a base, a trace of butyl cinnamate was also detected as a by-product (entries 6, 7 and 8, Table 3.3), which might be due to the decomposition of sodium bicarbonate at high temperature (120-140 °C) (Scheme 3.1). It was also found that under the same conditions in entry 7, butyl cinnamate was form 46% yield when the reaction was 48 hours.

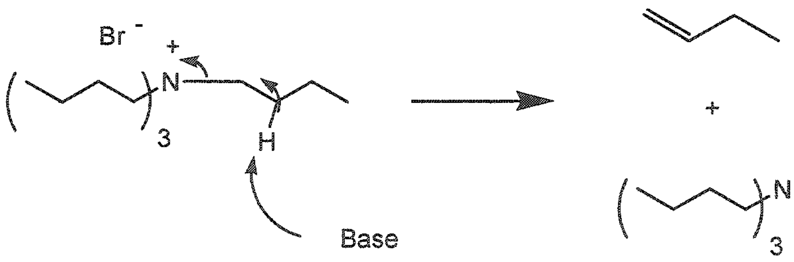


Scheme 3.1 Postulated Mechanism for Synthesis of Butyl Cinnamate

Bu_4NBr was not added when Na_2CO_3 was the base. This is due to the fact that Na_2CO_3 is a stronger base than $NaHCO_3$ and NaOAc (Table 3.4). Na_2CO_3 can deprotonate Bu_4NBr providing the Hoffman elimination by product(eq. 3.4).(99)

Table 3.4. The pH of 0.10 M solution of bases

Base	pH
$NaHCO_3$	8.4
NaOAc	8.4
Na_2CO_3	11.6



eq. 3.4

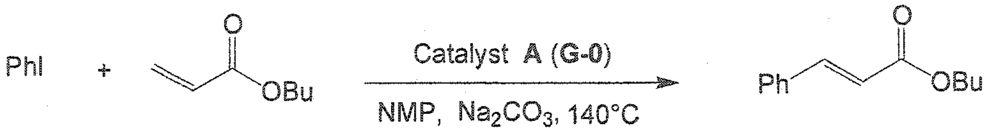
The recyclability of the catalyst was then studied, using either NaOAc or Na_2CO_3 as the base, NMP as solvent at a temperature of 140 °C (entry 5 and 10 in Table 3.3). It was found that under the conditions of entry 5, Table 3.3, the catalyst **A** (**G-0**) lost activity on recycling but under the conditions of entry 10, Table 3.3, catalyst **A** (**G-0**) could be more effectively recycled (Table 3.5).

Table 3.5. Heck reaction of bromobenzene and methyl acrylate catalyzed by **A** (**G-0**).[a]

Base	Run No	n-Bu_4NBr (mol%)[b]	Conversion (%)[c]
NaOAc	2	50	38
NaOAc	3	50	23
Na_2CO_3	2	-	37
Na_2CO_3	3	-	34

[a] *Reactions were conducted using 25 mg ($3.9x10^{-3}$ mmol) of catalyst A, 2 mmol of bromobenzen and 2.4 mmol of n-methyl acrylate in NMP for 24 hours at 140 °C.* [b] *mol % n-Bu_4NBr refer to aryl bromide.* [c] *Determined by GC, based on bromobenzene and the product.*

Therefore, the best conditions were similar to those reported for complex **34**, R = ^{i}Pr.(22) The reaction of iodobenzene and *n*-butyl acrylate was carried out at 140 °C, using sodium carbonate as the base, in NMP (eq. 3.5 and Table 3.6).



eq. 3.5

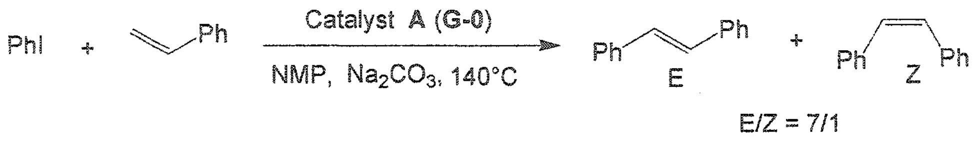
Table 3.6. Heck reaction of iodobenzene and *n*-butyl acrylate catalyzed by A (**G-0**).[a]

Run No.	Time (h)	Conversion (%)[b]	TON (mol of product/mol of Pd)
1	3	88	2710
1	6	>99 (90)[c]	3050
2	6	84 (75)[c]	2590
3	6	70	-[d]

[a] *Reactions were conducted using 25 mg (3.9x10⁻³ mmol) of catalyst A, 12 mmol of iodobenzene and 14.4 mmol of n-butyl acrylate in NMP for 24 hours at 140 °C.* [b] *Determined by GC, based on bromobenzene and the product..* [c] *Isolated yield.* [d] *Palladium loading was not measured.*

High TON was obtained (3050 mol of product/mol of Pd), and the catalyst was recycled three times with only moderate loss of activity.

Lower reactivity resulted when the substrate was changed from *n*-butyl acrylate to styrene (TON = 2620 mol of product/mol of Pd) (eq. 3.6 and Table 3.7). A mixture of E/Z stilbene were formed in a ratio of 7/1.



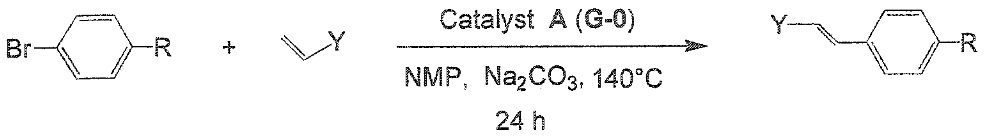
eq. 3.6

Table 3.7. Heck reaction of iodobenzene and styrene catalyzed by **A** (**G-0**).[a]

Run No.	Time (h)	Conversion (%)[b]	TON (mol of product/mol of Pd)
1	6	44	1350
1	15	72	2220
1	30	85	2620
2	30	80	-[c]

[a]Reactions were conducted using 25 mg ($3.9x10^{-3}$ mmol) of catalyst A, 12 mmol of iodobenzene and 14.4 mmol of styrene in NMP for 24 hours at 140 °C. [b]Determined by GC, based on bromobenzene and the product. [c]Palladium loading was not measured.

Bromobenzene and several *p*-substituted bromobenzenes were also used as substrates with methyl or *n*-butyl acrylate. Good activities and recycling properties of catalyst **A** (**G-0**) were observed here (eq. 3.7, and Tables 3.8 and 3.9). However, a higher loading of catalyst (1.6×10^{-2} mmol of Pd, 100 mg of catalyst) was necessary for these reactions. A *p*-substituent on the benzene ring has no significant effect on the reaction. Chlorobenzene was found to react poorly with the acrylate (TON = 16 mol of product/mol of Pd). The rate-determining step of the reaction may involve oxidative addition.



eq. 3.7

Table 3.8. Heck reaction of bromobenzene and *para*-substituted bromobenzenes, and *n*-butyl or methyl acrylate catalyzed by **A** (**G-0**).[a]

Entry	R Group	Y Group	Run No.	Conversion (%)[b]	TON (mol of product/ mol of Pd)
1	H	C(O)O^{n}Bu	1	86	108
2	OMe	C(O)OMe	1	95	119
3	OMe	C(O)O^{n}Bu	1	90	113
4	C(O)OMe	C(O)O^{n}Bu	1	>99	124
5	Me	C(O)O^{n}Bu	1	>99	124

[a]Reactions were conducted using 100 mg ($1.6x10^{-2}$ mmol) of catalyst A, 2 mmol of para substituted bromobenzenes and 2.4 mmol of n-butyl or methyl acrylate for 24 h in NMP at 140 ℃. [b]Determined by GC, based on bromobenzene and the product or by NMR.

Table 3.9. Heck reaction of bromobenzene and *para*-substituted bromobenzenes, and *n*-butyl or methyl acrylate catalyzed by **A** (**G-0**);[a] a recycling study.

Entry	R Group	Y Group	Run No.	Conversion (%)[b]
1	H	C(O)O^{n}Bu	2	86
2			3	79
3			4	70
4			5	79
5	OMe	C(O)OMe	2	92
6			3	94
7	OMe	C(O)O^{n}Bu	2	81
8			3	83
9	C(O)OMe	C(O)O^{n}Bu	2	98
10			3	94
11	Me	C(O)O^{n}Bu	2	85
12			3	58

[a] *Reactions were conducted using 100 mg ($1.6x10^{-2}$ mmol) of catalyst A, 2 mmol of para substituted bromobenzenes and 2.4 mmol of n-butyl or methyl acrylate for 24 h in NMP at 140 °C.* [b] *Determined by GC, based on bromobenzene and the product or by NMR.*

The possibility of leaching of the catalyst was examined by ICP analysis to determine the palladium content of the catalyst after the recycles. ICP analysis showed that the total palladium content was 0.89, 1.14, 1.45 mass% Pd (entries 2-4, Table 3.10) after the catalyst was used 5 times (entry 4, Table 3.9) and 3 times (entries 8 and 10, Table 3.9). In the case of 4-bromotoluene, a lower conversion was found after the reaction was run three times (entry 12, Table 3.9) (58% conversion). ICP analysis showed that there was only 0.7 mass% Pd after the catalyst was used 3 times (entry 5, Table 3.10). The metal leaching might be due to the gradual decomposition of the complex, brought on by the harsh reaction conditions (140 °C for several days). Oxidation of the metal center, which would cause the PCP ligand to become more labile, may also account for some of the leaching. It is likely that oxidation accounts for some of the leaching. The extent of oxidation influences the proportion of leaching.

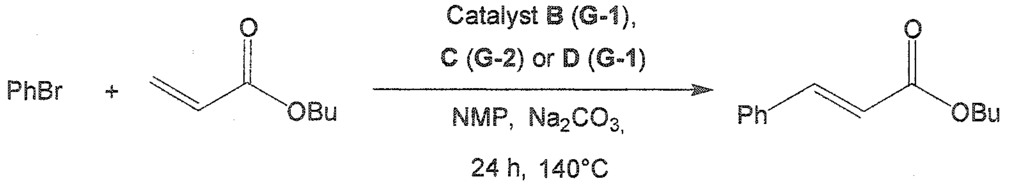
Table 3.10. Palladium contents.

Entry	Reaction No[a]	Run No	ICP result % Pd	% Pd leaching
1	A[b]	0	1.67	-
2	4	5	0.89	47
3	8	3	1.14	32
4	10	3	1.45	13
5	12	3	0.7	58

[a]Entries from Table 3.9. [b]Catalyst before the reaction

Since one of these reactions showed low conversion on the third run (entry 12, Table 3.9) and that ICP analysis showed high % palladium leaching out, a control experiment was carried out using a palladium-silica system catalyst. This catalyst was obtained by stirring Pd(TFA)$_2$ and silica (10% by weight of palladium to silica) in THF. This system displayed poor stability as it decomposed to black Pd particles during a 20 h reaction and could not be recycled without significant loss of activity (99% conversion for the first run, 68% conversion for the second and 29% conversion for the third run). By contrast, complex A, which shows no visible decomposition after 3 days in solution, is considerably more stable. These results suggest that complexation of the PCP ligand significantly enhances the stability of Pd catalysts. However, there may be a small portion palladium that is only bound to the silica. To determine if Pd-PCP catalyst is not immobilized onto the silica, it will not be able to recycle effectively. Conditions were identical to those for the Pd(TFA)$_2$ experiment described above, except that complex **34** was used as the catalyst (R = Ph, 2% by weight of palladium to silica). Conversion dropped dramatically after each run: from >99% conversion for the first run, to 75% for the second, and finally to 38% for the third run.

After **A (G-0)** was found to be a good catalyst for the Heck reaction, **B (G-1)**, **C (G-2)** and **D (G-1)** were then examined for their catalytic ability for the Heck reaction of bromobenzene and *n*-butyl acrylate. High activities and good recycling properties were found (eq. 3.8, and Tables 3.11 and 3.12) with **B (G-1)** being more active than **A (G-0)**. Generation one dendrimer, but with a 6-carbon spacer group, **D (G-1)**, is more active than **B (G-1)**. Also, **C (G-2)** is more active than **B (G-1)** and **D (G-1)**. This might be due to the fact that the catalyst active site is moving further from the silica surface by increasing the chain length of the ligand and therefore the complex behaves more like a homogeneous-like catalyst.



eq. 3.8

Table 3.11. Heck reaction of bromobenzene and *n*-butyl acrylate catalyzed by **B (G-1)**, **C (G-2)**, or **D (G-1)**.[a]

Catalyst	Run No.	Conversion (%)[b]	TON (mol of product/mol of Pd)
B (G-1)	1	>99	132
C (G-2)	1	94	188
D (G-1)	1	>99	152

*[a]Reactions were conducted using 50 mg of catalyst **B** (1.5x10^{-2} mmol) or **D** (1.3x10^{-2} mmol), or 25 mg of catalyst **C** (1.0x10^{-2} mmol), 2 mmol of bromobenzene and 2.4 mmol of n-butyl acrylate for 24 h in NMP at 140 °C.* *[b]Determined by GC, based on bromobenzene and the product.*

Table 3.12. Heck reaction of bromobenzene and *n*-butyl acrylate catalyzed by **B** (G-1), **C** (G-2), or **D** (G-1);[a] a recycling study.

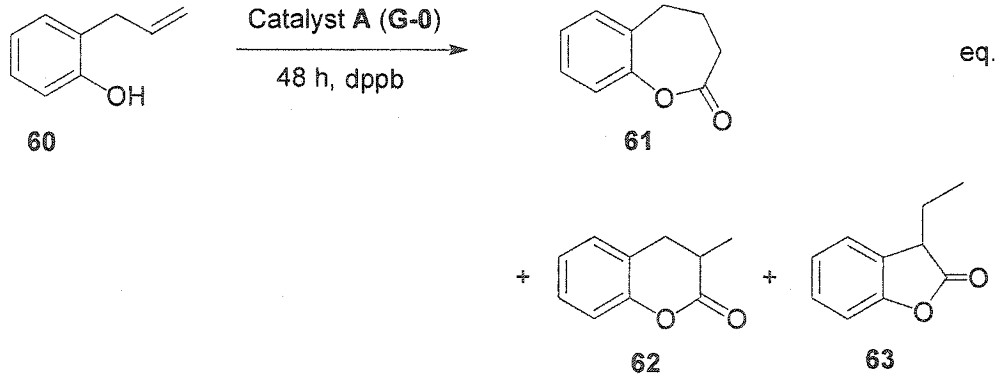
Catalyst	Run No.	Conversion (%)[b]
B (G-1)	2	>99
	3	98
	4	94
	5	82
C (G-2)	2	>99
	3	96
	4	96
	5	81
D (G-1)	2	99
	3	>99
	4	>99
	5	96

[a] *Reactions were conducted using 50 mg of catalyst* ***B*** *($1.5x10^{-2}$ mmol) or* ***D*** *($1.3x10^{-2}$ mmol) or 25 mg of catalyst* ***C*** *($1.0x10^{-2}$ mmol), 2 mmol of bromobenzene and 2.4 mmol of n-butyl acrylate for 24 h in NMP at 140 °C.* [b] *Determined by GC, based on bromobenzene and the product.*

The mechanism of **A (G-0)**, **B (G-1)**, **C (G-2)** and **D (G-1)** for the Heck reactions is expected to rely on homogeneous PCP complexes; Milstein and coworkers have suggested that the catalysis cycle may involve a Pd(II)/Pd(IV) cycle, not a classical Pd (0) cycle.(24) The investigation is still in progress.(24) A critical obstacle in this mechanistic work is that, as of yet, no intermediate palladium complexes have been conclusively identified.

3.3 The Cyclocarbonylation Reaction

Based on the positive the results described in the previous section, the catalytic activity of **A** (**G-0**) for the intramolecular cyclocarbonylation of 2-allylphenol (**60**) was investigated. First, 2-allylphenol was treated with a 1/1 mixture of CO/H_2 (total pressure 600 psi) and 1,4-bis(diphenylphosphino)butane (dppb) in toluene at 120 °C for 48 h to form the corresponding lactone in 93% conversion and in good selectivity for the seven-membered ring lactone (**61**) (entry 1, Table 3.13). Small amounts of six- and five-membered ring lactones (**62** and **63**) were also formed. Various conditions were used to obtain a better conversion and increased selectivity, including changing the relative pressures of carbon monoxide and hydrogen, temperature, and solvent (eq. 3.9). The results are summarized in Table 3.13.



eq. 3.9

Table 3.13. Catalytic cyclocarbonylation of 2-allylphenol by A (G-0).[a]

Entry	Temperature (°C)	P_{CO}, psi	P_{H2}, psi	Solvent	Conversion (%)[b]	Product Distribution (%)[c]			TON (mol of product/ mol of Pd)
						61	**62**	**63**	
1	120	300	300	Toluene	93	78	11	11	116
2	140	300	300	Toluene	>99	24	24	52	124
3	120	300	300	CH_2Cl_2	>99	28	25	47	124
4	120	100	500	Toluene	>99	77	8	15	124
5	**140**	**100**	**500**	**CH_2Cl_2**	**>99**	**5**	**13**	**82**	**124**
6	120	200	0	Toluene	11	91	5	4	14
7	120	400	0	Toluene	63	86	13	1	79
8	100	400	0	Toluene	3	86	7	7	4
9	**140**	**400**	**0**	**Toluene**	**98**	**86**	**11**	**5**	**123**
10	130	400	0	Toluene	92	83	14	3	115
11	120	600	0	Toluene	90	82	15	3	113
12	140	600	0	Toluene	96	78	16	6	120
13	**120**	**500**	**100**	**Toluene**	**>99**	**83**	**10**	7	**124**

[a] *Reactions were conducted using 50 mg (0.8x10^{-2} mmol) of A, 0.04 mmol of dppb and 1mmol of 2-allylphenol for 48h.* [b and c] *Determined by NMR and GC.*

The reaction conversions improved by increasing the temperature to 140 °C or by using CH_2Cl_2 instead of toluene, however, there was only moderate selectivity for the five-membered ring lactone (entries 2 and 3, Table 3.13). Using a 1/5 mixture of CO/H_2 (total pressure 600 psi), the conversion and the selectivity for the five-membered ring lactone was increased as compared to entry 1 (entry 4, Table 3.13). At this point, using a 1/5 mixture of CO/H_2 (total pressure 600 psi) in CH_2Cl_2, at 140 °C, the five-membered ring lactone should be formed in good yield and in high selectivity and indeed it formed 82% selectivity with >99% conversion (entry 5, Table 3.13). The selectivity for the seven-membered ring lactone increased in the absence of hydrogen (entries 6-11, Table 3.13) but traces of lactones were obtained at lower temperature (100 °C) or at lower pressure (200 psi) (entries 6 and 8, Table 3.13). The best conversion and selectivity for the 7-membered ring lactone was obtained when the pressure of CO was 400 psi in toluene at 140 °C (entry 9, Table 3.13). Lower conversions were obtained at temperatures of 120 or 130°C (entries 7 and 10, Table 3.13). At higher pressures of CO (600 psi instead of 400 psi), lower conversions and selectivity were obtained (entries 11 and 12, Table 3.13). The seven-membered ring lactone was also obtained in good conversion, and in high selectivity with a 5/1 mixture of CO/H_2 (total pressure 600 psi) in toluene at 120 °C (entry 13, Table 3.13).

The recyclability of the catalyst was studied using the most favorable conditions (entries 5, 9 and 13,Table 3.13). It was found that under the conditions of entry 5, Table 3.13, the catalyst **A** (**G-0**) decomposed gradually. Low conversion and moderate selectivity for the seven-membered ring lactone were observed in the third run (Table 3.14).

Table 3.14. Catalytic cyclocarbonylation of 2-allylphenol by **A (G-0)**;[a] a recycling study.

Run No	Conversion (%)[b]	Product Distribution (%)[c]		
		61	**62**	**63**
2	97	7	21	72
3	38	54	36	10

[a] Reactions were conducted using 50 mg of A (0.8x10^{-2} mmol), 0.04 mmol of dppb and 1 mmol of 2-allylphenol for 48 h in CH_2Cl_2 using a 1:5 mixture of CO/H_2 (total pressure 600 psi) at 140 °C. [b] and [c] Determined by NMR and GC

Using the conditions of entry 9, Table 3.13, the catalyst **A (G-0)** was also decomposed in the third run (Table 3.15). This suggested that at temperature 140 °C, diphosphine ligands PCP complexes to palladium might be exchanged with dppb and finally decomposed to Pd(0).

Table 3.15. Catalytic cyclocarbonylation of 2-allylphenol by **A** (**G-0**);[a] a recycling study using only CO.

Run No	Conversion (%)[b]	Product Distribution (%)[c]		
		61	**62**	**63**
2	96	88	9	3
3	11	86	14	0

[a]Reactions were conducted using 50 mg of A (0.8x10^{-2} mmol), 0.04 mmol of dppb and 1 mmol of 2-allylphenol for 48 h in Toluene, using 400 psi of CO at 140 °C. [b and c]Determined by NMR and GC.

Nevertheless, these conditions are still of interest since the homogeneous hydridoaquopalladium complex trans-$[(Cy_3P)_2Pd(H)(H_2O)]BF_4$ (**64**), in the absence of hydrogen, gave only traces of lactones.(50) In addition, heterogeneous Pd-clay, in the absence of hydrogen, afforded only 37% lactones with high selectivity for the seven-membered ring product.(51) Investigation of the catalytic reactivities of catalysts **B** (**G-1**), **C** (**G-2**), and **D** (**G-1**) under these conditions were conducted. Similar results were obtained to those obtained for catalyst **A** (**G-O**): the reactions worked well for the first and second runs but the catalyst decomposed after that (Tables 3.16 and 3.17). The activities of **B** (**G-1**), **C** (**G-2**), and **D** (**G-1**) in the cyclocarbonylation reaction are similar to those observed for the Heck reaction. The catalyst containing a 6-carbon spacer group, (**G-1**) (**D**), was more active than **B** (**G-1**) and **C** (**G-2**) which in turn was more active than **B** (**G-1**) and **D** (**G-1**).

Table 3.16. Catalytic cyclocarbonylation of 2-allylphenol by **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**);[a] using only CO.

Catalyst	Conversion (%)[b]	Product Distribution (%)[c]			TON (mol of product/mol of Pd)
		61	**62**	**63**	
B	97	89	9	2	121
C	91	84	11	5	182
D	98	82	8	10	140

*[a]Reactions were conducted using 25 mg of catalyst **B** ($0.8x10^{-2}$ mmol) or **D** ($0.7x10^{-2}$ mmol), or 25 mg of catalyst **C** ($1.0x10^{-2}$ mmol), 0.04 mmol of dppb, and 1 mmol of 2-allylphenol for **B** or **D**, or 2 mmol of 2-allylphenol for **C** for 48 h in toluene, using 400 psi of CO at 140 °C. [b and c]Determined by NMR.*

Table 3.17. Catalytic cyclocarbonylation of 2-allylphenol by **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**);[a] a recycling study using only CO.

Catalyst	Run No	Conversion (%)[b]	Product Distribution (%)[c]		
			61	**62**	**63**
B	2	96	87	9	4
	3	75	90	8	2
C	2	91	84	11	5
	3	69	86	11	3
D	2	88	89	6	5
	3	46	86	11	3

[a] *Reactions were conducted using 25 mg of catalyst* ***B*** *($0.8x10^{-2}$ mmol) or* ***D*** *($0.7x10^{-2}$ mmol), or 25 mg of catalyst* ***C*** *($1.0x10^{-2}$ mmol), 0.04 mmol of dppb, and 1 mmol of 2-allylphenol for* ***B*** *or* ***D****, or 2 mmol of 2-allylphenol for* ***C*** *for 48 h in toluene, using 400 psi of CO at 140 °C.* [b and c] *Determined by NMR.*

It was found that catalyst **A** (**G-O**) could be recycled five times, under the conditions of entry 13, Table 3.13 (5/1 mixture of CO/H_2, total pressure 600 psi, in toluene at 120 °C) (Table 3.18).

Table 3.18. Catalytic cyclocarbonylation of 2-allylphenol by **A** (**G-0**);[a] a recycling study using 5:1 CO/H_2.

Run No	Conversion (%)[b]	Product Distribution (%)[c]		
		61	**62**	**63**
2	93	80	13	7
3	>99	87	9	4
4	91	81	14	5
5	98	80	11	9

[a]*Reactions were conducted using 50 mg of A (0.8x10^{-2} mmol), 0.04 mmol of dppb and 1 mmol of 2-allylphenol for 48 h in Toluene, using a 5:1 mixture of CO/H_2 (total pressure 600 psi) at 120 °C.* [b and c]*Determined by NMR and GC*

When catalyst **A** (**G-0**) was replaced by **B** (**G-1**), **C** (**G-2**), or **D** (**G-1**) under the same conditions, similar conversions and selectivities were obtained. The reactivities of **B** (**G-1**), **C** (**G-2**), and **D** (**G-1**) corresponded to those mentioned previously (Tables 3.19 and 3.20).

Table 3.19. Catalytic cyclocarbonylation of 2-allylphenol by **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**).[a]

Catalyst	Conversion (%)[b]	Product Distribution (%)[c]			TON (mol of product/mol of Pd)
		61	**62**	**63**	
B	97	85	10	5	121
C	98	89	10	1	196
D	98	80	12	8	140

[a] *Reactions were conducted using 25 mg of catalyst* ***B*** *($0.8x10^{-2}$ mmol) or* ***D*** *($0.7x10^{-2}$ mmol), or 25 mg of catalyst* ***C*** *($1.0x10^{-2}$ mmol), 0.04 mmol of dppb, and 1 mmol of 2-allylphenol for* ***B*** *or* ***D****, or 2 mmol of 2-allylphenol for* ***C*** *for 48 h in toluene, using a 5:1 mixture of CO/H_2 (total pressure 600 psi) at 120 °C.* [b and c] *Determined by NMR.*

Table 3.20. Catalytic cyclocarbonylation of 2-allylphenol by **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**).[a]

Catalyst	Run No	Conversion (%)[b]	Product Distribution (%)[c]		
			61	**62**	**63**
B	2	85	89	10	1
	3	97	85	11	4
C	2	97	82	11	7
	3	92	88	10	2
D	2	87	86	11	3
	3	>99	86	8	6

[a] *Reactions were conducted using 25 mg of catalyst **B** ($0.8x10^{-2}$ mmol) or **D** ($0.7x10^{-2}$ mmol), or 25 mg of catalyst **C** ($1.0x10^{-2}$ mmol), 0.04 mmol of dppb, and 1 mmol of 2-allylphenol for **B** or **D**, or 2 mmol of 2-allylphenol for **C** for 48 h in toluene, using a 5:1 mixture of CO/H_2 (total pressure 600 psi) at 120 °C.* [b and c] *Determined by NMR.*

As mentioned previously, the catalyst A (G-0) gave different yields and selectivities for the cyclocarbonylation of 2-allylphenol compared with the homogeneous hydridoaquopalladium catalyst trans-$[(Cy_3P)_2Pd(H)(H_2O)]BF_4$ (**64**) under the similar conditions (50) (Table 3.21), The differences suggest that the catalytic mechanism for A differs from that of **64**.

Table 3.21. Catalytic cyclocarbonylation of 2-allylphenol by **A** (**G-0**) or **64**.[a]

Entry	Catalyst	Temperature (°C)	P_{CO}, psi	P_{H2}, psi	Solvent	Conversion (%)[b]	Product Distribution (%)[c]		
							61	**62**	**63**
1	**A**	120	300	300	CH_2Cl_2	>99	28	25	47
2	**64**	120	300	300	CH_2Cl_2	97	52	21	27
3	**A**	120	600	-	Toluene	90	82	15	3
4	**64**	120	600	-	Toluene	trace	-	-	-

*[a] Reactions were conducted using (1.0x10^{-2} mmol) of **64** or 50 mg (0.8x10^{-2} mmol) of **A**, 0.04 mmol of dppb and 1mmol of 2-allylphenol. [b and c] Determined by NMR and GC*

The substrate effect for the cyclocarbonylation reaction was studied by replacing 2-allylphenol with 2-allyl-6-methylphenol (**130**, R_1 = Me and R_2 = H) or 2-allyl-4-chlorophenol (**130**, R_1 = H and R_2 = Cl) and using **A** (**G-0**) as the catalyst (eq. 3.10). This might provide some insight into the mechanism for the cyclocarbonylation reaction. The results were similar to 2-allylphenol (**130**, R_1 = H and R_2 = H) and the catalyst could be recycled three times (Tables 3.22 and 3.23). Therefore, the cyclocarbonylation was not significantly sensitive to the steric and/or electronic effects.

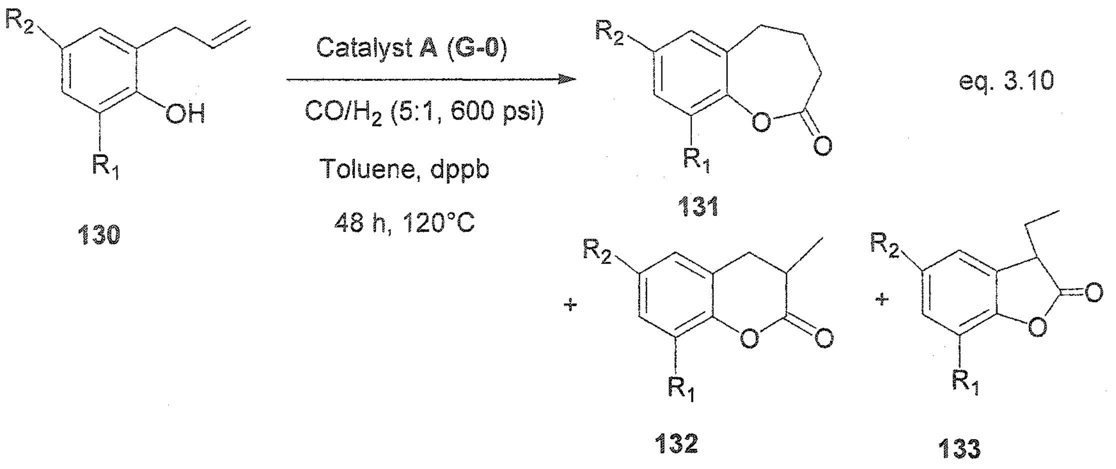


Table 3.22. Catalytic cyclocarbonylation of 2-allylphenols by **A** (**G-0**).[a]

En-try	R_1 Group	R_2 Group	Run No.	Conversion (%)[b]	Product Distribution (%)[c]			TON (mol of product/mol of Pd)
					131	**132**	**133**	
1	Me	H	1	>99	88	11	1	124
2	H	Cl	1	98	81	9	10	123
3	H	H	1	>99	83	10	7	124

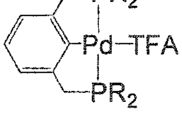
[a] *Reactions were conducted using 50 mg ($0.8x10^{-2}$ mmol) of A, 0.04 mmol of dppb and 1 mmol of 2-allylphenols for 48 hours in toluene, using a 5:1 mixture of CO/H_2 (total pressure 600 psi) at 120 ℃.*
[b and c] *Determined by NMR and GC.*

Table 3.23. Catalytic cyclocarbonylation of 2-allylphenols by A (**G-0**);[a] using 5:1 CO/H_2; a recycling study.

Entry	R_1 Group	R_2 Group	Run No.	Conversion (%)[b]	Product Distribution (%)[c]		
					131	**132**	**133**
1	Me	H	2	96	91	9	0
2			3	>99	88	11	1
3	H	Cl	2	90	88	9	3
4			3	97	84	11	5
5	H	H	2	93	80	13	7
6			3	>99	87	9	4

[a] *Reactions were conducted using 50 mg (0.8x10^{-2} mmol) of A, 0.04 mmol of dppb and 1 mmol of 2-allylphenols for 48 hours in toluene, using a 5:1 mixture of CO/H_2 (total pressure 600 psi) and at 120 °C.*
[b and c] *Determined by NMR and GC*

At this point, investigation of the reactions catalyzed by homogeneous PCP complex could be useful for understanding the catalytic activity of complexes **A-D**. Complex **34,** R = Ph was also examined as a catalyst for the cyclocarbonylation reaction of 2-allylphenol to compare the results with those obtained by using catalysts **A**, **B**, **C** and **D** under similar conditions (Table 3.24).

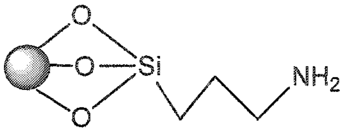


34

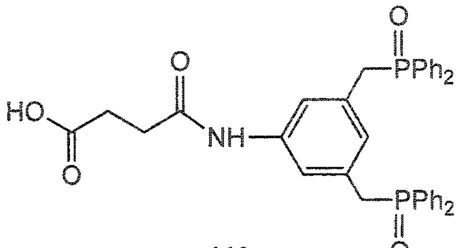
Table 3.24. Catalytic cyclocarbonylation of 2-allylphenol by **34**, R = Ph, **A**, **B**, **C**, or **D**[a]

Entry	Catalyst	Temperature (°C)	dppb, mmol	P_{CO}, psi	P_{H2}, psi	Silica (**11**) (mg)	**119**, mmol	Conversion (%)[b]	Product Distribution (%)[c]		
									61	**62**	**63**
1	**34**	120	-	500	100	-	-	25	48	26	26
2	**A**	120	-	500	100	-	-	trace	-	-	-
3	**34**	120	0.04	500	100	-	-	99	48	20	32
4	**A**	120	0.04	500	100	-	-	>99	83	10	7
5	**B**	120	0.04	500	100	-	-	97	85	10	5
6	**C**	120	0.04	500	100	-	-	98	89	10	1
7	**D**	120	0.04	500	100	-	-	98	80	12	8
8	**34**	120	0.04	400	-	-	-	93	57	28	15
9	**A**	120	0.04	400	-	-	-	98	86	11	5
10	**B**	120	0.04	400	-	-	-	97	89	9	2
11	**C**	120	0.04	400	-	-	-	91	84	11	5
12	**D**	120	0.04	400	-	-	-	98	82	8	10
13	**34**	120	0.04	500	100	50	-	99	54	18	28
14	**34**	120	0.04	500	100	-	0.03	95	59	21	20

[a] *Reactions were conducted using 7 mg (1.5x10^{-2} mmol) of catalyst **34** or 50 mg (0.8x10^{-2} mmol) of **A**, 25 mg of catalyst **B** (0.8x10^{-2} mmol) or **D** (0.7x10^{-2} mmol), or 25 mg of catalyst **C** (1.0x10^{-2} mmol) and 1mmol of 2-allylphenol for 48 h in toluene.* [b and c] *Determined by NMR and GC.*



Aminopropyl silica gel (11)



119

It was found that in the absence of dppb, lactones were formed in low conversion (entry 1, Table 3.24). Traces of lactones were obtained for the heterogeneous catalyst **A** (**G-0**). Lactones were synthesized in higher conversions when dppb was added but only with moderate selectivity for the seven-membered ring lactone (entry 3, Table 3.24). This is significantly different from the case of **A** (**G-0**), **B** (**G-1**), **C** (**G-2**), or **D** (**G-1**) (entries 4-7, Table 3.24). Running the reaction in the absence of hydrogen for **34,** R = Ph, gave lactones in high conversion, comparable to the case when catalysts **A** (**G-0**), **B** (**G-1**), **C** (**G-2**), or **D** (**G-1**) were used but the selectivity for the seven-membered ring lactone was still moderate (entries 8-12, Table 3.24). Attempting to find out what affected the selectivity, aminopropyl silica gel (**11**) or compound **119** were added to the reaction but no significant change in the selectivity was noticed (entries 13 and 14, Table 3.24). Therefore, aminopropyl silica gel or phosphine oxide impurity did not effect the selectivity. It is possible that the difference in selectivities is due, in part, to the substantial difference in size between heterogeneous catalysts **A** (**G-0**), **B** (**G-1**), **C** (**G-2**), or **D** (**G-1**) and complex **34**, R = Ph.

Substitution of bidentate (dppb) by monodentate (PPh_3) ligand afforded a significant decrease in conversion (entries 1 and 2, Table 3.25). This result was also different from that of catalyst **64**, which provided less than 10% conversion. Increasing the amount of monodentate (PPh_3) ligand to 0.08 mmol, the conversion was increased with good selectivity for the seven-membered ring lactone (entry 3, Table 3.25). Also, reducing the amount of dppb to 0.02 mmol, the conversion was reduced (entry 4, Table 3.25). Therefore, higher conversions are favored by use of larger amounts of phosphine. While there is a loss of activity on going from the bidentate phosphine (dppb) to the monodentate ligand (PPh_3), this effect can be attenuated by using higher concentrations of the latter (twice the amount (mmols) of PPh_3 was needed in order to rival the performance of dppb system, since the latter contains two P's per molecule, while PPh_3 only contains only one).

Table 3.25. Catalytic cyclocarbonylation of 2-allylphenol by **A**.[a]

Entry	dppb, mmol	PPh_3, mmol	Conversion (%)[b]	Product Distribution (%)[c]		
				61	**62**	**63**
1	-	0.04	54	63	28	9
2	0.04	-	>99	83	10	7
3	-	0.08	86	84	12	4
4	0.02	-	81	85	14	1

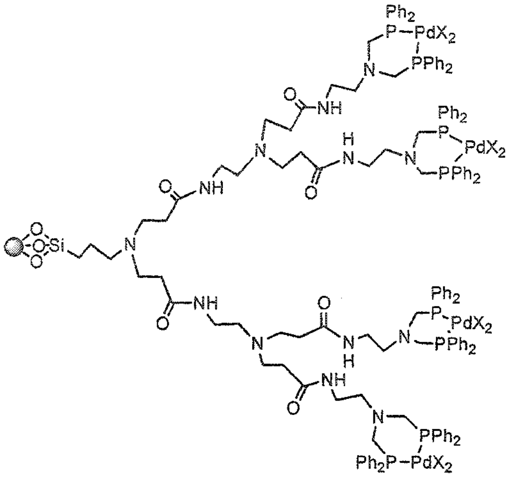
[a]Reactions were conducted using 50 mg of A ($0.8x10^{-2}$ mmol), and 1 mmol of 2-allylphenol for 48 h in Toluene, using a 5:1 mixture of CO/H_2 (total pressure 600 psi) at 120 °C. [b and c]Determined by NMR and GC.

Typically temperatures of 120 °C and addition of phosphine ligands are required which suggest that there is exchange of phosphine ligands between dppb or PPh_3 and PCP. However, the mechanism cannot be concluded yet. Further mechanistic studies of the reactions catalyzed by homogeneous PCP complex would be useful. The possibility of leaching of the catalyst was not examined since the amount of catalyst remaining after 3 or 5 recycles was insufficient for ICP analysis.

4

Conclusions

The foregoing describes new catalytic systems obtained by immobilization of a PCP-type palladium(II) complex onto silica and silica supported dendrimers, which combine the advantages of heterogeneous and homogeneous catalysts. These complexes are stable towards oxygen and moisture. They show high catalytic activity for the Heck reaction of aryl iodides with styrene and *n*-butyl acrylate, resulting in high yields of stilbene and cinnamate ester. The new complexes are also active in the reactions of a variety of aryl bromides with *n*-butyl and methyl acrylate, providing para-substituted cinnamate esters in good yields. These complexes are also effective catalysts for the cyclocarbonylation reaction of 2-allylphenol yielding five- or seven-membered ring lactones in good selectivity and in high yields. In addition, they can be recycled by simple filtration in air and reused with little or moderate loss of activity. In both kinds of reactions, the dendritic systems show higher activity than the non-dendritic systems. The problem of metal leaching, while still a concern, is nevertheless improved compared with the behavior of catalyst **15** (**G-2**) (Figure 4.1), for which metal leaching was found to range from 6-10% after the first run.



15

Generation 2

Figure 4.1 Palladium Complexes to a Dendrimer Built on Silica Gel Used as Catalysts for the Heck (X = CH_3) and Carbonylation (X = Cl) Reactions

5

Experimental Section

5.1 General Considerations

Chemicals were purchased from Aldrich, Strem and Lancaster Chemical companies were used without further purification. The aminopropyl silica gel (**11**) was purchased from Fluka (particle size is 35-70 nm, surface area is 305 m^2/g, pore volume is 0.70 cm^3/g, average pore diameter is 7.68 nm, and amine content is 0.9 mmol/g). 1,3,5-Trishydroxymethylbenzene (**85**),(94) 1,3,5-trisbromomethylbenzene (**86**),(94) 1,3-bis[(diphenylphosphinoylmethyl)-benzene (**91**),(93) 3,5-bis(hydroxymethyl)-aniline (**111**),(97) *N*-acetyl-3,5-bis(hydroxymethyl)aniline (**115**),(98) *N*-acetyl-3,5-bis-(chloromethyl)aniline (**116**)(98) and all PAMAM-SiO_2 dendrimer compounds **109**, **124**, **126**, and **128**(66) were prepared according to the procedure described in the literatures.

All reactions were carried out under an atmosphere of nitrogen. All manipulations of air-sensitive materials were carried out using standard Schlenk techniques. During work-up procedures 'drying' refers to drying an organic phase with magnesium sulfate ($MgSO_4$) and 'concentration *in vacuo*' refers to concentration using a Büchi R-114 Rotavapor.

Solvents were purified and dried following standard procedures.(100) Brine refers to a saturated aqueous solution of sodium chloride.

Column chromatography was performed using Silicycle silica gel 60, 230-400 mesh.

Melting points were determined in capillary tubes using a Fisher-Johns melting point apparatus and values are uncorrected.

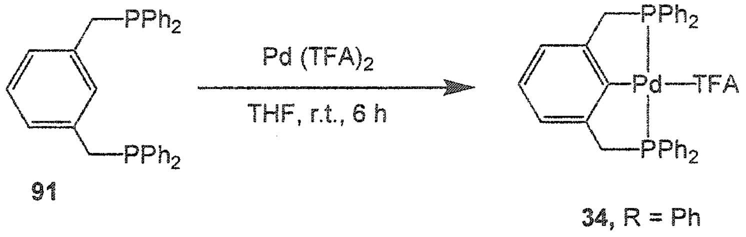
Solution NMR spectra were recorded at 20.5 °C, unless otherwise indicated, on a Varian Gemini-200 (^{1}H at 199.97 MHz and ^{13}C{^{1}H} at 50.28 MHz) or a Bruker 300 NMR spectrometer (^{1}H at 300.13 MHz, ^{13}C{^{1}H} at 75.48 MHz and ^{31}P{^{1}H} at 121.49 MHz). ^{1}H and ^{13}C NMR spectra are reported in ppm and the residual non-deuterated solvent in the deuterated solvents served as a reference. ^{31}P chemical shifts are reported in ppm relative to the external standard 85% H_3PO_4. The ^{13}C and ^{31}P CP/MAS (cross polarization/magic angle spinning) NMR spectra, frequency 50.32 MHz and 81.00 MHz respectively, were recorded on a Bruker ASX-200 spectrometer. Solid samples were prepared by transfer of the relevant material to a 5 mm o.d. pyrex NMR tube and connected to a high vacuum stopcock in a M. Braun GmbH glovebox. The sample was then removed from the drybox, placed under high vacuum and, without breaking vacuum, sealed off at 30 mm lengths. The tubes were then placed in zirconia rotors used in the Bruker ASX-200 instrument.

Gas chromatography was carried out using a Hewlett Packard HP 5890 Series II chromatograph. GC yields are determined with reference to authentic products and reactants.

High-pressure reactions were conducted in stainless steel autoclaves fitted with a screw cap from Parr Instruments. The reactions with carbon monoxide were carried out in a fume hood with CO detectors installed nearby.

ICP analyses were carried out by Galbraith Laboratories, Knoxville, TN. or by The Institute for National Measurement Standards Chemical Metrology at the National Research Council, Ottawa.

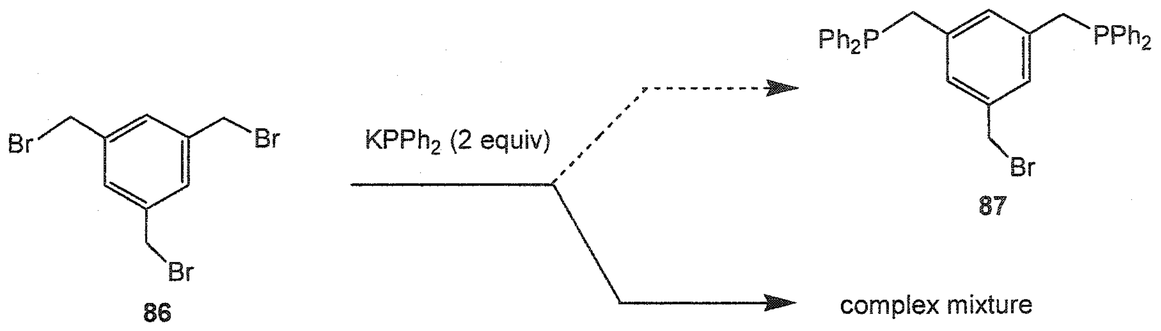
5.2 Synthesis of Complex 34, R = Ph



A solution of 1,3-bis[(diphenylphosphinoylmethyl)benzene (**91**) (0.56 g, 1.2 mmol) and Pd(TFA)$_2$ (0.2 g, 0.6 mmol) in THF (15 mL) was stirred at room temperature for 6 hours. Evaporation to dryness gave yellowish crystals. Yield: 0.76 g (92%). Mp 148 °C (dec.); ^{1}H NMR (300.13 MHz, CDCl$_3$) δ (ppm) 7.76-7.62 (m, 10H, Ar*H*), 7.51-7.33 (m, 11 H, Ar*H*), 7.08-6.95 (m, 2H, Ar*H*), 3.86 (t, J = 4.5 Hz, 4H, PhC*H*$_2$); ^{13}C{^{1}H} (50 MHz, CDCl$_3$) δ (ppm) 144.9, 133.4, 133.3, 133.2, 133.1, 131.8, 131.7, 131.4, 131.2, 129.3, 129.2, 129.0, 128.6, 126.8, 124.0, 123.9 (Ar*C*), 41.7, (PhCH$_2$); ^{31}P NMR (121 MHz, CDCl$_3$) δ (ppm) 37.2; Electrospray MS for $C_{34}H_{23}O_2P_2PdF_3$ 620 (M-CF_3^+).

Note: In each PPh$_2$ unit, the two phenyl groups are equivalent. Also, the two PPh$_2$ groups are equivalent. Total Ar carbons = 4 (Ph) + 4 (bridging/metallated group) = 4 + 4 = 8. However, each carbon atom appears as a doublet due to coupling with ^{31}P (I = 1/2 and natural abundance = 100%). Total Ar carbons = 8 X 2 = 16. Each phosphorus atom appears as a singlet because natural abundance of ^{13}C (I = 1/2) is 1.11%. The NMR resonances are broadened because the palladium nucleus is NMR active, having $I > ½$. (^{105}Pd I = 5/2 and natural abundance = 22.2%).

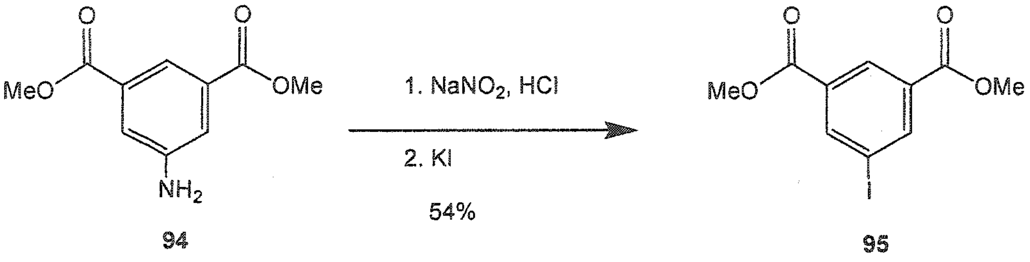
5.3 Attempted Synthesis of 3,5-Bis(diphenylphosphanylmethyl)bromomethylbenzene (87)



A red solution of potassium diphenylphosphide (0.36 g, 1.6 mmol) in THF (3.2 mL) was added dropwise to a solution of 1,3,5-trisbromomethylbenzene (**86**) (0.29 g, 0.8 mmol) in THF (10 mL) at –78 °C. After the addition was complete, the solution was kept at that temperature for 4 hours before being allowed to warm up to room temperature and then stirred further at room temperature for 12 hours. The solvent was evaporated *in vacuo*. The resulting residue was extracted with toluene. The solvent was then evaporated under reduced pressure affording a mixture (0.4 g).

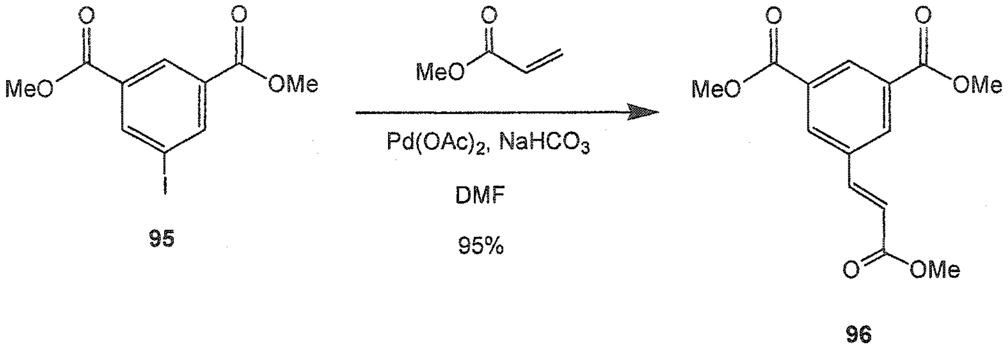
Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum.

5.4 Synthesis of 5-Iodoisophthalic Acid Dimethyl Ester (95)



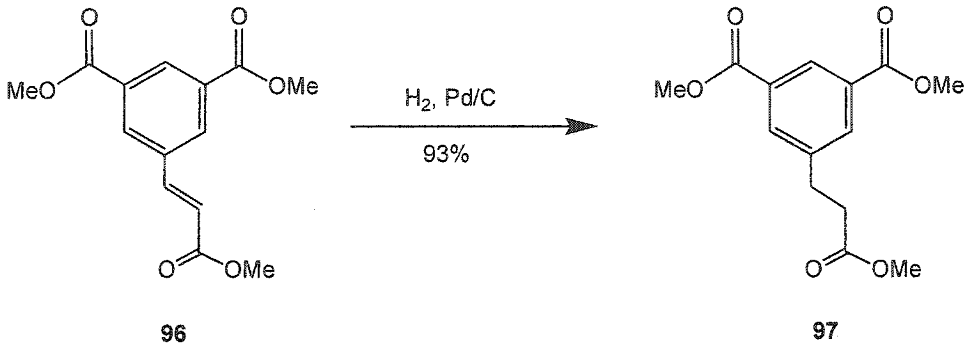
A modified literature procedure was used.[95] A solution of sodium nitrite (1.9 g, 29.7 mmol) in water (10 mL) was added dropwise to a solution of dimethyl-5-aminoisophthalate **(94)** (5.7 g, 27.3 mmol) in 5% HCl (60 mL) at 0-5 °C. After the addition was complete, the solution was kept at that temperature, stirred for 1 hour, followed by slow addition of potassium iodide (4.6 g, 27.7 mmol) in water (5 mL). The mixture was allowed to warm to room temperature, stirred for an additional 1 hour, and the solution was then heated to 65 °C for 2 hours. The reaction mixture was cooled to room temperature and basified by 10% NaOH, and extracted with EtOAc. The crude 5-iodoisophthalic acid dimethyl ester **(95)** was shaken with a little sodium metabisulphite solution until a pale yellow color was obtained. Column chromatography on silica gel (elution with 19:1 hexane-ethyl acetate) gave an off-white solid. Yield: 4.7 g (54%). Mp 139-140 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.59 (s, 1H, Ar*H*), 8.52 (s, 2H, Ar*H*), 3.93 (s, 6H, CH_3O); $^{13}C\{^1H\}$ (50 MHz, $CDCl_3$) δ (ppm) 165.2 (*C*=O), 142.9, 132.7, 130.3, 94.0 (Ar*C*), 53.2 (*C*H_3O); EI MS for $C_{10}H_9O_4I$ 320 (M^+).

5.5 Synthesis of 5-(2-Methoxycarbonylvinyl)isophthalic Acid Dimethyl Ester (96)



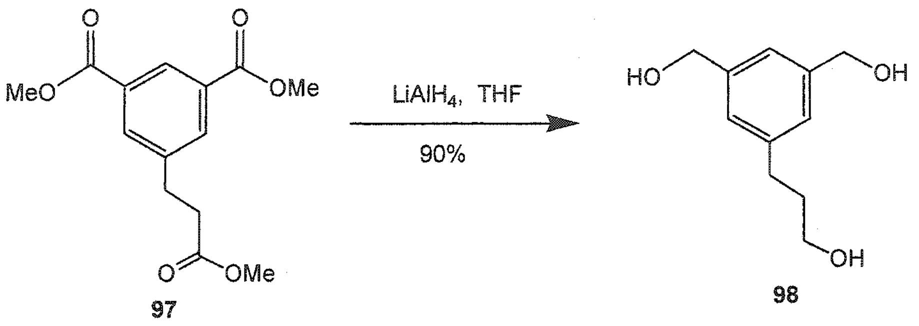
A solution of **95** (7.5 g, 23.4 mmol), methyl acrylate (20.2 g, 0.23 mol), sodium bicarbonate (4.9 g, 58.3 mmol), palladium acetate (0.5 g, 2.3 mmol), and tetra-*n*-butylammonium chloride (6.5 g, 23.4 mmol) in 100 mL of dimethylformamide (DMF) was stirred at room temperature under nitrogen for 48 hours. Water (150 mL) was added and the mixture was extracted several times with diethyl ether, and the combined organic phase was washed with saturated NaCl aqueous solution and water, dried ($MgSO_4$), filtered and evaporated *in vacuo* to yield a white solid. Yield: 6.2 g (95%). Mp 158-159 °C; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.63 (s, 1H, Ar*H*), 8.34 (s, 2H, Ar*H*), 7.73 (d, J = 18 Hz, 1H, CH=C*H*Ar), 6.56 (d, J = 18 Hz, 1H, CH=C*H*COOMe), 3.96 (s, 6H, CH_3O), 3.81 (s, 3H, CH_3O); $^{13}C\{^1H\}$ (50 MHz, $CDCl_3$) δ (ppm) 167.3, 166.2, 143.1, 135.9, 133.4, 132.3, 132.0, 121.0, 53.2, 52.5; EI MS for $C_{14}H_{14}O_6$ 278 (M^+).

5.6 Synthesis of 5-(2-Methoxycarbonylethyl)isophthalic Acid Dimethyl Ester (97)



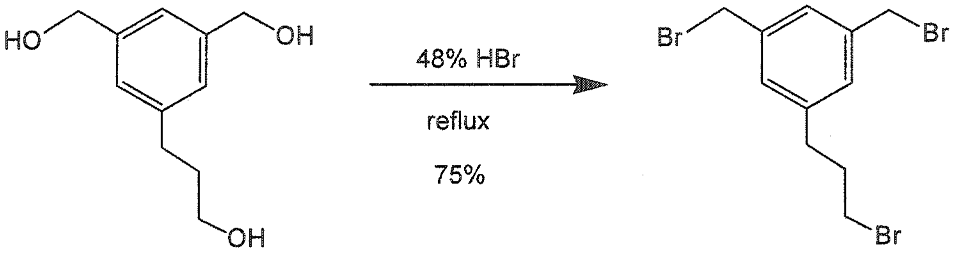
A mixture of **96** (3.2 g, 11.5 mmol) and 10% palladium on charcoal (0.8 g, 0.8 mmol) in EtOAc (120 mL) were placed in a stainless steel autoclave with a glass liner equipped with a stirring bar. The autoclave was charged with hydrogen gas (400 psi) and the mixture was stirred at room temperature for 20 hours. The catalyst was filtered off and the solvent was removed *in vacuo* to give a white solid. Yield: 3.0 g (93%). Mp 65-66 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.51 (s, 1H, Ar*H*), 8.03 (s, 2H, Ar*H*), 3.91 (s, 6H, CH_3O), 3.65 (s, 3H, CH_3O), 3.03 (t, J = 8 Hz, 2H, CH_2Ar), 2.65 (t, J = 8 Hz, 2H, CH_2COOMe); $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$) δ (ppm) 173.1 (*C*=O), 166.6 (Ar*C*=O), 141.8, 134.1, 131.2, 129.2 (Ar*C*), 52.7 (CH_3O), 52.1 (CH_3O), 35.5 (CH_2COOMe), 30.8 (CH_2Ar); EI MS for $C_{14}H_{16}O_6$ 280 (M^+).

5.7 Synthesis of 3-[3,5-Bis(hydroxymethylphenyl)]-propan-1-ol (98)



A solution of **97** (4.9 g, 17.5 mmol) in THF (100 mL) was added dropwise to a suspension of lithium aluminium hydride (1.3 g, 34.2 mmol) in THF (120 mL) at 0 °C. After the addition was complete, the mixture was refluxed for 30 minutes. The reaction mixture was cooled to 0 °C before water (2.5 mL) and 15% NaOH (9.5 mL) were carefully added. The precipitate formed was removed by filtration through celite and the solvent was evaporated under reduced pressure, affording compound **98** as a pale yellow liquid. Yield: 3.1 g (90%). ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ (ppm) 7.03 (s, 1H, Ar*H*), 6.94 (s, 2H, Ar*H*), 5.19-5.01 (m, 2H, O*H*), 4.52-4.35 (m, 5H, ArC*H*$_2$O and O*H*), 3.49-3.28 (m, 2H, C*H*$_2$O), 2.67-2.41 (m, 2H, C*H*$_2$Ar), 1.85-1.58 (m, 2H, $CH_2C\mathit{H}_2CH_2$); $^{13}C\{^1H\}$ (50 MHz, $(CD_3)_2SO$) δ (ppm) 140.8, 140.3, 123.5, 120.7 (Ar*C*), 61.7 (ArCH_2O), 58.9 (*C*H_2O), 32.9 ($CH_2CH_2CH_2$), 30.3 (*C*H_2Ar); EI MS for $C_{11}H_{16}O_3$ 178 (M- H_2O^+).

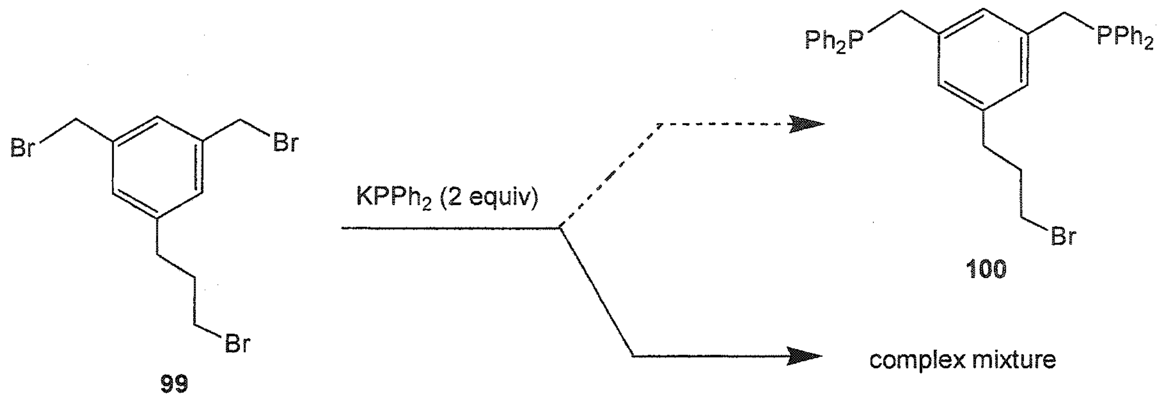
5.8 Synthesis of 1,3-Bis(bromomethyl)-5-(3-bromopropyl)benzene (99)



98 99

A solution of **98** (1.1 g, 5.6 mmol) in 48% HBr (40 mL) was heated to reflux for 12 hours. The reaction solution was cooled to 0 °C, and added to cold water (100mL), and the mixture was extracted with EtOAc several times. The combined organic phase was washed with saturated NaCl solution and water, dried ($MgSO_4$), filtered and evaporated *in vacuo*. Column chromatography on silica gel (elution with 9:1 hexane-ethyl acetate) afforded a white solid. Yield: 1.6 g (75%). Mp 45-46 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.26 (s, 1H, Ar*H*), 7.12 (s, 2H, Ar*H*), 4.44 (s, 4H, ArC*H*$_2$Br), 3.39 (t, J = 6 Hz, 2H, C*H*$_2$Br), 2.77 (t, J = 8 Hz, 2H, C*H*$_2$Ar), 2.11-2.08 (m, 2H, CH_2C*H*$_2$$CH_2$); ^{13}C{^{1}H} (50 MHz, $CDCl_3$) δ (ppm) 142.6, 139.2, 129.9, 128.1 (Ar*C*), 34.4 ($CH_2CH_2CH_2$), 34.3 (*C*H_2Ar), 33.5 (*C*H_2Br), 30.3; EI MS for $C_{11}H_{13}Br_3$ 384 (M^+).

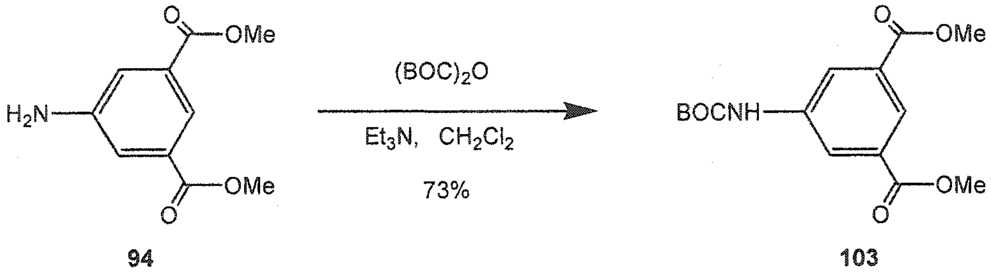
5.9 Attempted Synthesis of 1,3-Bis(diphenylphosphanylmethyl)-5-(3-bromopropyl)benzene (100)



A red solution of potassium diphenylphosphide (0.11 g, 0.5 mmol) in THF (1.0 mL) was added dropwise to a solution of **99** (0.1 g, 0.26 mmol) in THF (3 mL) at 0 °C. After the addition was complete, the solution was stirred at 0 °C for 4 hours, allowed to warm to 5 °C for 2 hours, 10 °C for 4 hours, 15 °C for 2 hours and room temperature 12 hours. The solvent was removed *in vacuo*. The resulting residue was extracted with toluene. The solvent was then evaporated under reduced pressure affording a mixture (0.1 g).

Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum.

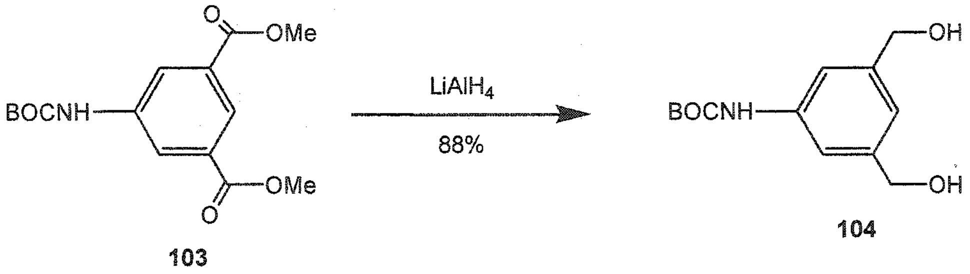
5.10 Synthesis of 5-(2,2-Dimethylpropionylamino)-isophthalic Acid Dimethyl Ester (103)



94 **103**

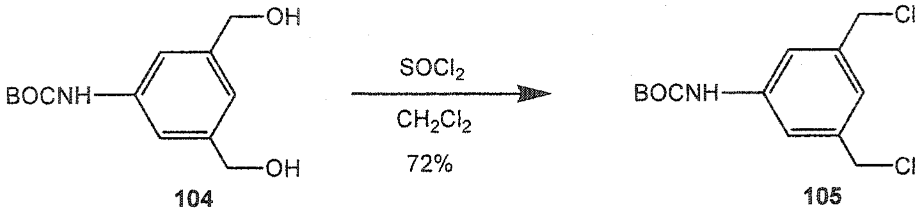
Di-tert-butyldicarbonate (8.7 g, 39.9 mmol) was added to a mixture of **94** (5.5 g, 26.3 mmol) and triethylamine (7.3 g, 72.2 mmol) in CH_2Cl_2 (125 mL) at room temperature. The mixture was stirred at room temperature for 1 hour, and then refluxed for 12 hours. The mixture was diluted with a 10% sodium bicarbonate solution (50 mL), and then extracted with CH_2Cl_2 several times. The combined organic phase was washed with brine, dried ($MgSO_4$), filtered and evaporated *in vacuo.* Column chromatography on silica gel (elution with CH_2Cl_2) gave a white solid. Yield: 5.9 g (73%). Mp 112 °C (dec); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.36-8.27 (m, 3H, Ar*H*), 7.08 (s, 1H, N*H*), 3.92 (s, 6H, CH_3O), 1.55 (s, 9H, CH_3C); $^{13}C\{^1H\}$ (50 MHz, $CDCl_3$) δ (ppm) 166.8 (Ar*C*=O), 153.2 (NH*C*=O), 134.0, 131.8, 125.5, 124.0 (Ar*C*), 81.8 (CH_3C), 53.1 (CH_3O), 28.9 (CH_3C); EI MS for $C_{18}H_{17}NO_6$ 309 (M^+).

5.11 Synthesis of *N*-[3,5-Bis(hydroxymethyl)phenyl]-2,2-dimethylpropionamide (104)



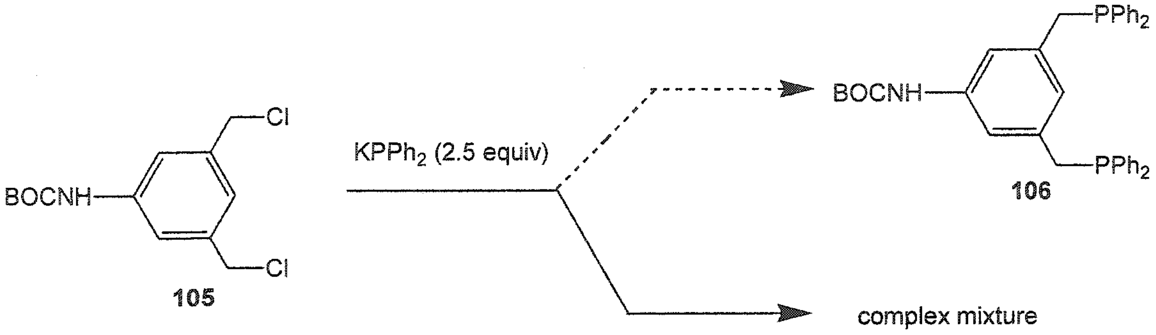
A solution of **103** (1.8 g, 5.8 mmol) in THF (50 mL) was added dropwise to a suspension of lithium aluminium hydride (0.4 g, 10.5 mmol) in THF (50 mL) at 0 °C. After the addition was complete, the mixture was warmed to room temperature. The reaction mixture was then cooled to 0 °C, and then water (0.8 mL) and 15% NaOH (3 mL) were carefully added. The precipitate formed was removed by filtration through Celite and the solvent was evaporated under reduced pressure, affording compound **104** as a white solid. Yield: 1.3 g (88%). Mp 133 °C (dec); ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ (ppm) 8.61 (s, 1H, N*H*), 7.23 (s, 2H, Ar*H*), 6.88 (s, 1H, Ar*H*), 4.84-4.69 (m, 2H, O*H*), 4.55-4.32 (m, 4H, ArCH_2O), 1.42 (s, 9H, CH_3C); ^{13}C{^{1}H} (50 MHz, $(CD_3)_2SO$) δ (ppm) 151.5 (NH*C*=O), 140.9, 137.4, 117.4, 113.8 (Ar*C*), 77.9 (CH$_3$*C*), 62.3 (*C*H$_2$O), 26.7 (*C*H$_3$C); EI MS for $C_{13}H_{19}NO_4$ 253 (M^+).

5.12 Synthesis of *N*-[3,5-Bis(chloromethyl)phenyl]-2,2-dimethylpropionamide (105)



Thionyl chloride (7.5 g, 63.0 mmol) was added dropwise to a mixture of **104** (4.0 g, 15.8 mmol) and pyridine (5.0 g, 63.2 mmol) in CH_2Cl_2 (100 mL) at 0 °C. After the addition was complete, the solution was stirred at room temperature for 18 hours. The reaction mixture was washed with water, 1 N HCl and brine, and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure affording compound **105** as a yellowish solid. Yield: 3.3 g (72%). Mp 101 °C (dec); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.37 (s, 2H, Ar*H*), 7.03 (s, 1H, Ar*H*), 6.66 (s, 1H, N*H*), 4.50 (s, 4H, $ArCH_2Cl$), 1.50 (s, 9H, CH_3C); $^{13}C\{^1H\}$ (50 MHz, $CDCl_3$) δ (ppm) 153.1 (NH*C*=O), 139.7, 139.5, 123.7, 118.9 (Ar*C*), 81.6 (CH_3C), 46.3 (CH_2Cl), 28.9 (CH_3C); EI MS for $C_{13}H_{17}NCl_2O_2$ 289 (M -H$^+$).

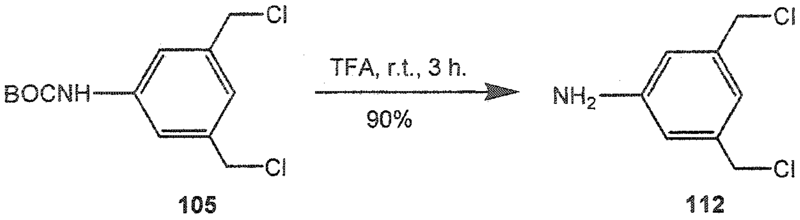
5.13 Attempted Synthesis of *N*-[3,5-Bis(diphenylphosphanylmethyl)phenyl]-2,2-dimethylpropionamide (106)



A red solution of potassium diphenylphosphide (0.2 g, 1.0 mmol) in THF (2.0 mL) was added dropwise to a solution of **105** (0.1 g, 0.4 mmol) in THF (5 mL) at -78 °C. After the addition was complete, the solution was allowed to warm up room temperature 18 hours. The solvent was removed *in vacuo*. The resulting residue was extracted with toluene. The solvent was then evaporated under reduced pressure affording a mixture (0.2 g).

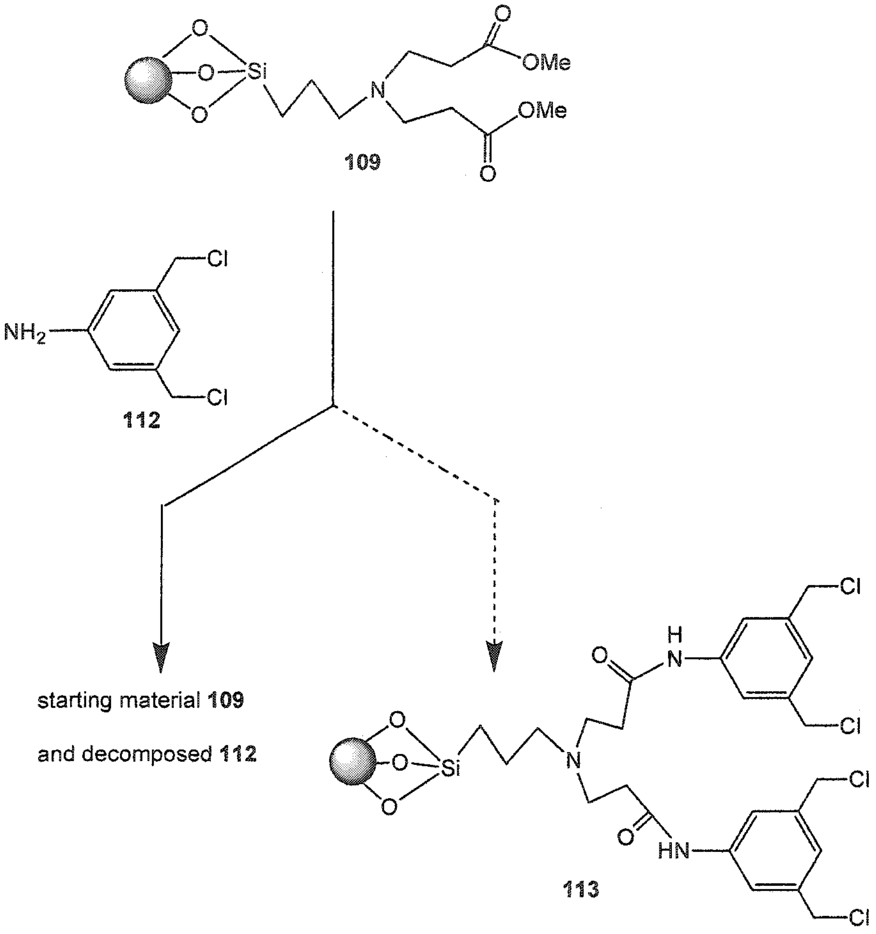
Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum.

5.14 Synthesis of 3,5-Bis(chloromethyl)phenylamine (112)



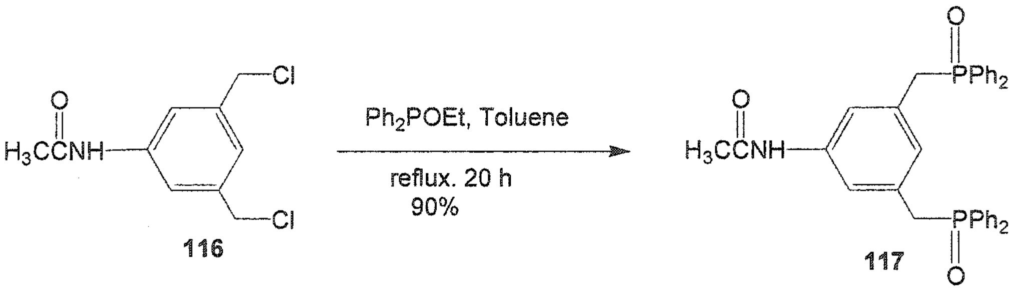
A mixture of **105** (1.7 g, 5.9 mmol) and trifluoroacetic acid (TFA) (28.6 g, 0.25 mol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 30 minutes. Then, it was evaporated to remove the excess TFA. The residue was dissolved in EtOAc, neutralized by triethylamine, washed with water, and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure affording compound **112** as a light brown solid, decomposed at r.t. Yield: 1.0 g (90%). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 6.78 (s, 1H, Ar*H*), 6.64 (s, 2H, Ar*H*), 4.48 (s, 4H, ArC*H*$_2$Cl), 3.77 (s, 2H, N*H*$_2$); $^{13}C\{^1H\}$ (50 MHz, $CDCl_3$) δ (ppm) 147.6, 139.7, 119.4, 115.7 (Ar*C*), 46.9 (*C*H$_2$Cl); EI MS for $C_8H_9NCl_2$ 189 (M^+).

5.15 Attempted Synthesis of 113



A mixture of **109** (0.9 g, 0.7 mmol) and **112** (0.9 g, 4.8 mmol) in CH_2Cl_2 (20 mL) and MeOH (50 ml) was stirred at room temperature for 5 days and at 60 °C for 3 days. The suspension was cooled and filtered through a 0.45 μm membrane filter and washed with CH_2Cl_2 several times. The residual solvent was removed under reduced pressure affording compound **109** and decomposed **112**.

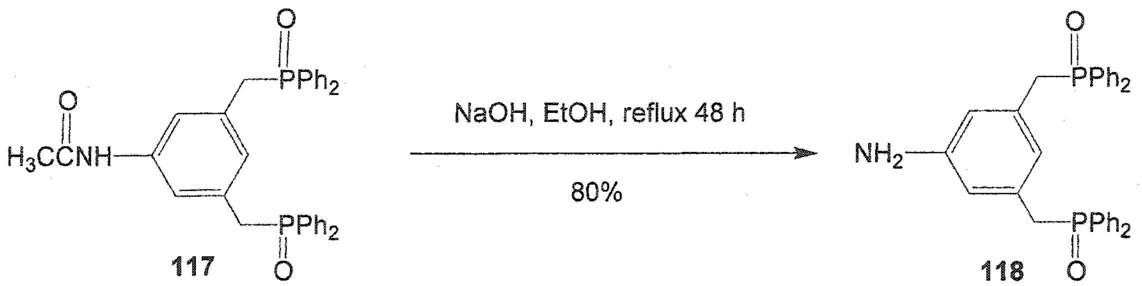
5.16 Synthesis of *N*-[3,5-Bis(diphenylphosphinoylmethyl-phenyl)]acetamide (117)



A modified literature procedure was used.(101) In a two-necked 100 mL round bottom flask, a stirred suspension of Ph_2POEt (7.4 g, 32 mmol) and compound **116** (1.8 g, 8.0 mmol) in toluene (90 mL) was refluxed for 20 h. The reaction mixture was cooled to room temperature and the white precipitated solid was filtered, washed with benzene, and dried *in vacuo* to afford compound **117** as a white solid, which was sufficiently pure for further synthesis. Yield: 4.4 g (90%). Mp 222-224 °C; ^{1}H NMR (300 MHz, CD_3OD) δ (ppm) 7.78-7.48 (m, 20H, Ar*H*), 7.21 (s, 2H, Ar*H*), 6.73 (s, 1H, Ar*H*), 3.71 (d, J = 14 Hz, 4H, PhC*H*$_2$), 2.02 (s, 3H, C*H*$_3$C=O); $^{13}C\{^1H\}$ (75 MHz, CD_3OD) δ (ppm) 170.3 (*C*=O), 138.9, 132.4, 132.1, 132.0, 131.2, 131.1, 131.0, 129.0, 128.9, 128.8, 128.1, 120.5 (Ar*C*), 37.1, 36.3 (Ph*C*H$_2$), 22.7 (*C*H$_3$C=O); ^{31}P NMR (121 MHz, CD_3OD) δ (ppm) 34.7; EI MS for $C_{34}H_{31}NO_3P_2$ 563 (M^+).

Note: In each PPh_2 unit, the two Ph groups are equivalent. Also, the two PPh_2 groups are equivalent. Total Ar carbons = 4 (Ph) + 4 (bridging/metallated group) = 4 + 4 = 8. However, each carbon atom appears as a doublet due to coupling with ^{31}P ($I = 1/2$ and natural abundance = 100%). Total Ar carbons = 8 X 2 = 16. However, the ^{13}C NMR spectrum shows only 12 peaks, which suggests that some phosphorus-carbon coupling constants are less than the resolution of the machine.

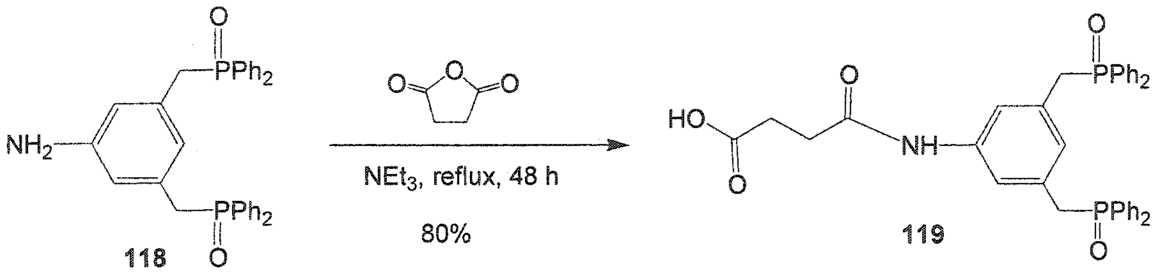
5.17 Synthesis of 3,5-Bis(diphenylphosphinoylmethyl)-phenylamine (118)



A modified literature procedure was used.(97) To a solution of **117** (4.2 g, 7.5 mmol) in 95% EtOH (100 mL) was added NaOH (1.5 g, 37.5 mmol). The mixture was refluxed for 48 hours and the solution was cooled with an ice bath, neutralized with concentrated HCl, and the majority of the solvent was removed under reduced pressure. The remaining residue was filtered, washed with water, and dissolved in methanol. The solvent was evaporated under reduced pressure affording the compound **118** as a yellow solid, which was sufficiently pure for further synthesis. Yield: 3.1 g (80%). Mp 145-146 °C; ^{1}H NMR (300.13 MHz, CD_3OD) δ (ppm) 7.74-7.47 (m, 20H, Ar*H*), 6.44 (s, 2H, Ar*H*), 6.37 (s, 1H, Ar*H*), 3.63 (d, J = 14 Hz, 4H, PhC*H*$_2$); ^{13}C{^{1}H} (50 MHz, CD_3OD) δ (ppm) 148.9, 133.9, 133.4, 132.3, 132.1, 131.9, 129.9, 129.7, 123.2, 117.0 (Ar*C*), 36.8, 35.9, (Ph*C*H$_2$); ^{31}P NMR (121 MHz, CD_3OD) δ (ppm) 34.4; Electrospray MS for $C_{32}H_{29}NO_2P_2$ 522 (M+ H$^+$).

Note: In each PPh_2 unit, the two Ph groups are equivalent. Also, the two PPh_2 groups are equivalent. Total Ar carbons = 4 (Ph) + 4 (bridging/metallated group) = 4 + 4 = 8. However, each carbon atom appears as a doublet due to coupling with ^{31}P ($I = 1/2$ and natural abundance = 100%). Total Ar carbons = 8 X 2 = 16. However, the ^{13}C NMR spectrum shows only 10 peaks, which suggests that some phosphorus-carbon coupling constants are less than the resolution of the machine.

5.18 Synthesis of *N*-[3,5-Bis(diphenylphosphinoylmethyl)phenyl]succinamic Acid (119)

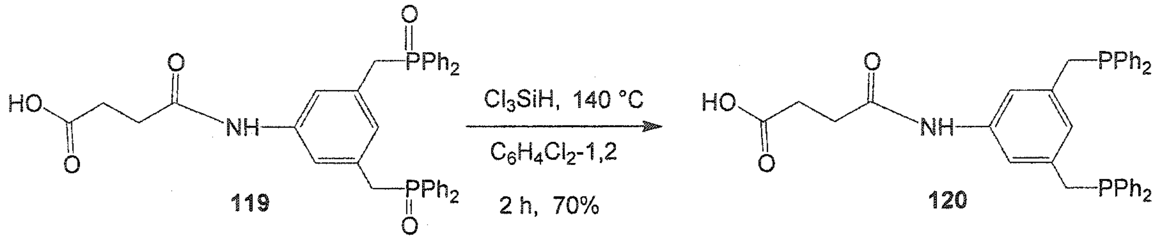


A modified literature procedure was used.(97) To a suspension of **118** (3.1 g, 6.0 mmol) and triethylamine (3.0 g, 30.0 mmol) in THF (150 mL) was added succinic anhydride (0.7 g, 7.0 mmol). The mixture was refluxed for 48 hours, cooled, and the solvent was evaporated under reduced pressure. The residue was dissolved in ethanol (120 mL) followed by addition of NaOH (8 M, 12 mL). The solvent was evaporated under reduced pressure, yielding an off-white solid material. This solid was washed with diethyl ether and then added to a 6 N HCl aqueous solution (30 mL). The residue was filtered, washed with water, and then dissolved in methanol. The solvent was evaporated under reduced pressure, affording **119** as an off-white solid, which was sufficiently pure for subsequent reactions. Yield: 3.0 g (80%). Mp 152-154 °C; ^{1}H NMR (300.13 MHz, CD_3OD) δ (ppm) 7.74-7.48 (m, 20H, Ar*H*), 7.20 (s, 2H, Ar*H*), 6.72 (s, 1H, Ar*H*), 3.71 (d, J = 13 Hz, 4H, PhC*H*$_2$), 3.46 (m, 1H, N*H*). 2.65-2.50 (m, 4H, C*H*$_2$C=O);

$^{13}C\{^1H\}$ (50 MHz, CD_3OD) δ (ppm) 176.3, 172.5 (*C*=O), 140.0, 133.7, 133.4, 133.1, 132.9, 132.3, 132.1, 131.7, 130.0, 129.8, 128.9, 121.4 (Ar*C*), 38.4, 37.1, (Ph*C*H_2), 32.3, 30.1 (*C*H_2C=O); ^{31}P NMR (121 MHz, CD_3OD) δ (ppm) 34.7; Electrospray MS for $C_{36}H_{33}NO_5P_2$ 621 (M^+).

Note: In each PPh_2 unit, the two Ph groups are equivalent. Also, the two PPh_2 groups are equivalent. Total Ar carbons = 4 (Ph) + 4 (bridging/metallated group) = 4 + 4 = 8. However, each carbon atom appears as a doublet due to coupling with ^{31}P (I = 1/2 and natural abundance = 100%). Total Ar carbons = 8 X 2 = 16. However, the ^{13}C NMR spectrum shows only 12 peaks, which suggests that some phosphorus-carbon coupling constants are less than the resolution of the machine.

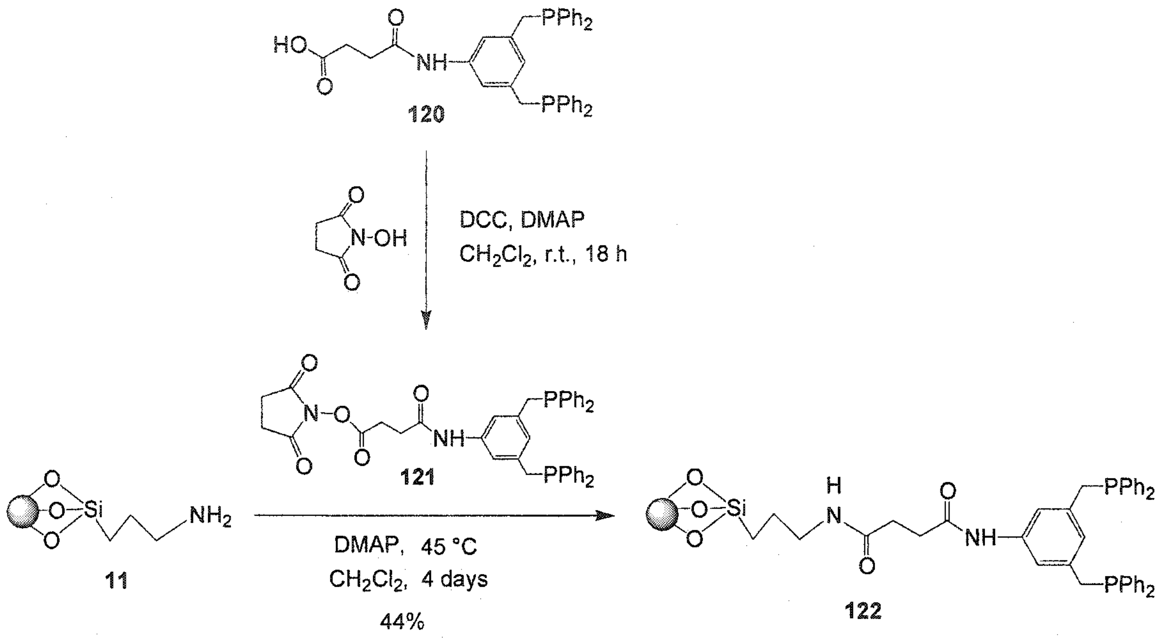
5.19 Synthesis of *N*-[3,5-Bis(diphenylphosphanylmethyl)phenyl]succinamic Acid (120)



A modified literature procedure was used.(101) In a three-necked 500-mL round bottom flask, a suspension of **119** (1.6 g, 2.6 mmol) in 1,2-dichlorobenzene (90 mL) was refluxed at 180 °C until the solution became homogeneous. The reaction solution was then cooled to 140 °C and $HSiCl_3$ (5 mL, 49 mmol) was added dropwise. The reaction mixture was then stirred at 140 °C for 2 h. This solution was cooled to 0 °C, and an aqueous NaOH (4 M, 98 mL) solution was slowly added under vigorous stirring. The aqueous solution was extracted with CH_2Cl_2, dried ($MgSO_4$) and then concentrated *in vacuo* to *ca.* 2 mL. Hexane was slowly added to precipitate an off-white solid, which was filtered and washed with hexane several times. Yield: 1.1 g (72%). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ (ppm) 7.46-7.15 (m, 20H, Ar*H*), 6.79 (s, 1H, Ar*H*), 6.74 (s, 2H, Ar*H*), 3.29 (s, 4H, PhC*H*$_2$), 2.79 (s, 4H, C*H*$_2$C=O); $^{13}C\{^1H\}$ (75.48 MHz, $CDCl_3$) δ (ppm) 175.0 (*C*=O), 139.0, 138.9, 138.8, 133.5, 133.2, 128.8, 128.7, 128.4, 128.1, 125.2 (Ar*C*), 36.3, 36.1, (PhCH$_2$), 28.1 (*C*H$_2$C=O); ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm) -9.0; Electrospray MS for $C_{36}H_{33}NO_3P_2$ 590 (M+ H$^+$).

Note: In each PPh_2 unit, the two Ph groups are equivalent. Also, the two PPh_2 groups are equivalent. Total Ar carbons = 4 (Ph) + 4 (bridging/metallated group) = 4 + 4 = 8. However, each carbon atom appears as a doublet due to coupling with ^{31}P (I = 1/2 and natural abundance = 100%). Total Ar carbons = 8 X 2 = 16. However, the ^{13}C NMR spectrum shows only 10 peaks, which suggests that some phosphorus-carbon coupling constants are less than the resolution of the machine.

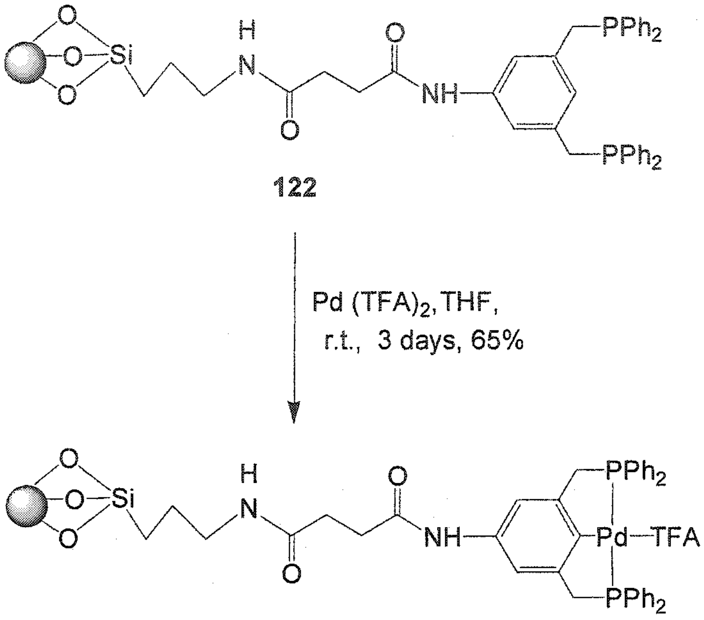
5.20 Synthesis of 122



To a solution of **120** (1.0 g, 1.7 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.21 g, 1.7 mmol) in dichloromethane (20 mL) was added 1,3-dicyclohexylcarbodiimide (DCC) (0.35 g, 1.7 mmol) in dichloromethane (1 mL) and *N*-hydroxysuccinimide (0.2 g, 1.7 mmol) at 0 °C. The mixture was stirred at room temperature for 18 h. The white solid was filtered and the solvent was evaporated under reduced pressure, affording compound **121** as a yellow solid. DMAP (0.21 g, 1.7 mmol) in dichloromethane (50 mL) and aminopropyl silica (0.5 g, 0.45 mmol) were added, the reaction was stirred at room temperature for 1 day and then heated at 45 °C for 4 days. The suspension was filtered, washed with dichloromethane several times, and dried *in* *vacuo* to afford **122** as a pale yellow solid (0.6 g). ^{31}P CP/MAS NMR δ (ppm) -10.9 and 27.1 (phosphine oxide); ^{13}C CP/MAS NMR δ (ppm) 172.1, 157.8, 140.7, 110.1, 41.5, 23.6, 10.7; ICP Analysis mass% P 1.59 (44% yield).

Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum.

5.21 Synthesis of a Generation Zero Dendrimer (G-0) (A)

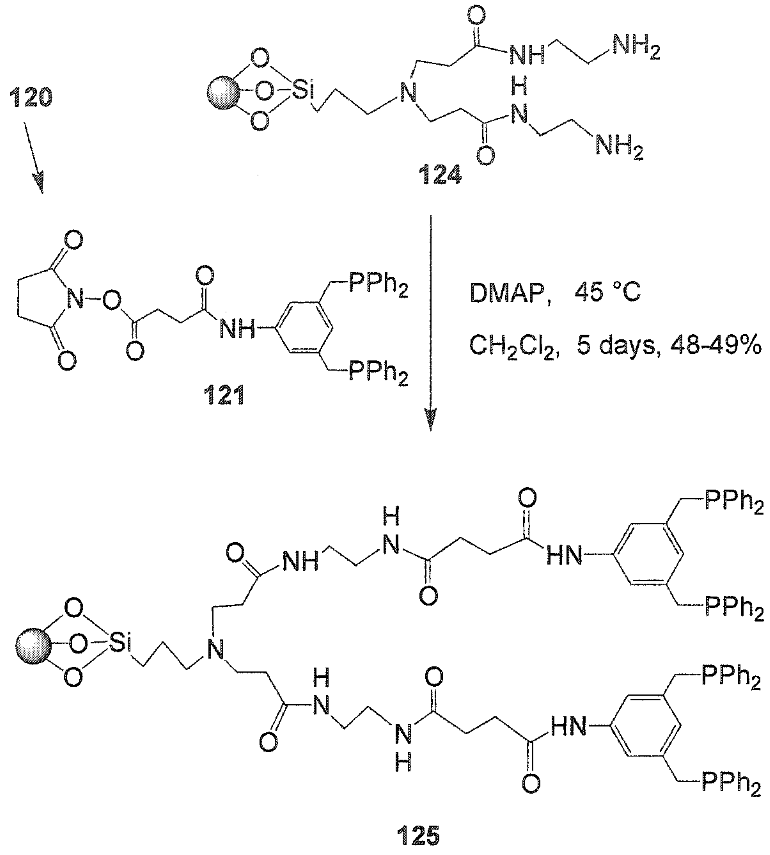


Generation zero (G-0) (A)

A suspension of compound **122** (0.5 g, 0.59 mmol), and Pd(TFA)$_2$ (0.05 g, 0.15 mmol) in THF (40 mL) was stirred at room temperature for 3 days. The suspension was filtered and washed with THF several times, dried in vacuo to afford generation zero dendrimer (**G-0**) (**A**) as a dark yellow solid (0.5g). ^{31}P CP/MAS NMR δ (ppm) 37.9 and 28.7 (phosphine oxide); ^{13}C CP/MAS NMR 173.4, 156.9, 141.9, 130.3, 108.7, 50.6, 41.9, 33.5, 26.0, 11.2; ICP Analysis mass% Pd 1.67 (65% yield).

Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum. Some of the small broad signal near the base of the ^{31}P NMR CPMAS peaks may be due to ^{31}P atoms bound to quadrupole ^{105}Pd atoms which have I = 5/2 and are 22.23% naturally abundant. In such a case one would expect broad features at the base of the ^{31}P NMR peaks.

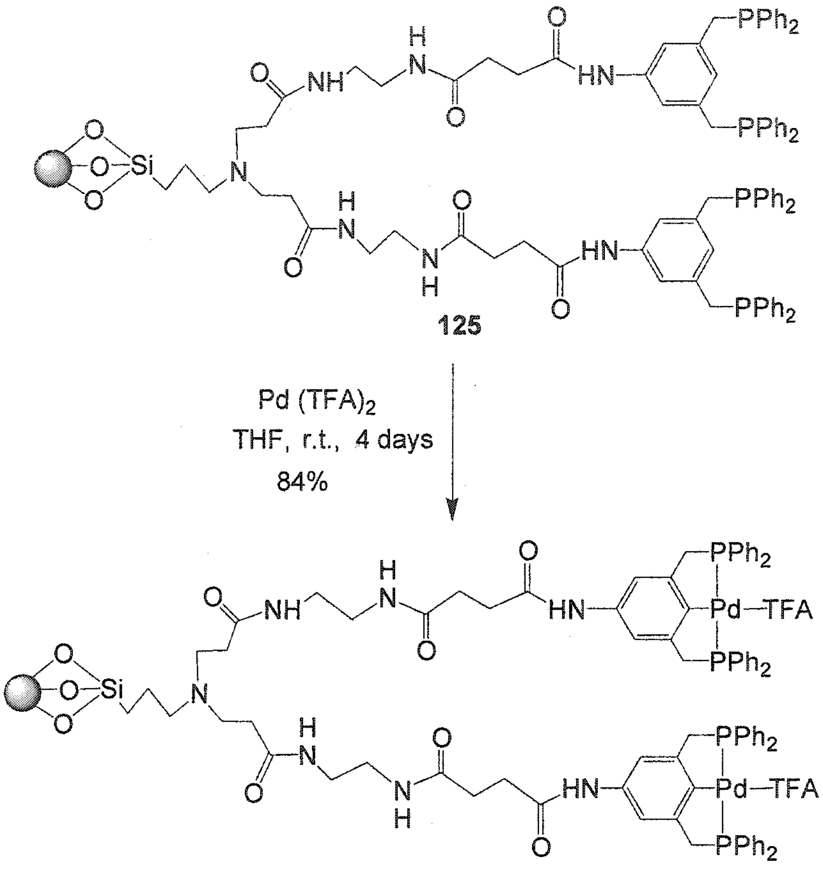
5.22 Synthesis of 125



To a solution of **120** (1.7 g, 2.9 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.35 g, 2.9 mmol) in dichloromethane (30 mL) was added 1, 3-dicyclohexylcarbodiimide (DCC) (0.59 g, 2.9 mmol) in dichloromethane (2 mL) and *N*-hydroxysuccinimide (0.33 g, 2.9 mmol) at 0 °C. The mixture was stirred at room temperature for 18 h. The white solid was filtered and the solvent was evaporated under reduced pressure, affording compound **121** as a yellow solid. DMAP (0.35 g, 2.9 mmol) in dichloromethane (80 mL) and PAMAM-SiO_2 dendrimer **124** (0.5 g, 0.75 mmol) were added, the reaction was stirred at room temperature for 1 day and then heated at 45 °C for 5 days. The suspension was filtered, washed with dichloromethane several times, and dried *in vacuo* to afford **125** as a pale yellow solid (0.7 g). ^{31}P CP/MAS NMR δ (ppm) -8.6 and 27.9 (phosphine oxide); ^{13}C CP/MAS NMR δ (ppm) 171.4, 157.3, 142.4, 107.7, 40.8, 20.3, 9.6; ICP Analysis mass% P 2.37 (48-49% yield).

Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum.

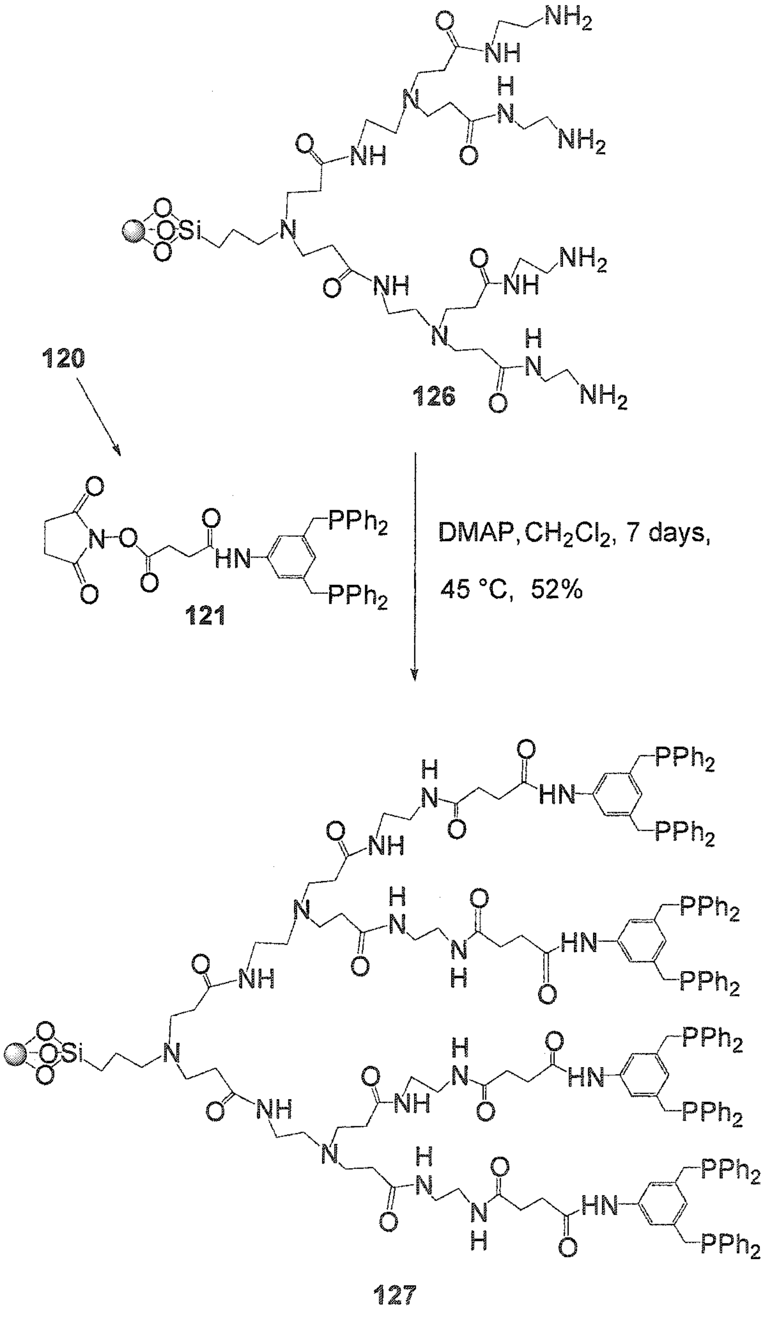
5.23 Synthesis of a Generation One Dendrimer (G-1) (B)



Generation one (G-1) (B)

A suspension of compound **125** (0.6 g, 0.97 mmol), and Pd(TFA)$_2$ (0.08 g, 0.24 mmol) in THF (50 mL) was stirred at room temperature for 4 days. The suspension was filtered and washed with THF several times, dried in vacuo to afford generation one dendrimer (**G-1**) (**B**) as a dark yellow solid (0.6 g). ^{31}P CP/MAS NMR δ (ppm) 38.7 and 29.3 (phosphine oxide); ^{13}C CP/MAS NMR 172.1, 157.5, 141.8, 130.1, 108.4, 50.4, 40.5, 31.0, 20.4, 10.0; ICP Analysis mass% Pd 3.22 (84% yield).

5.24 Synthesis of 127

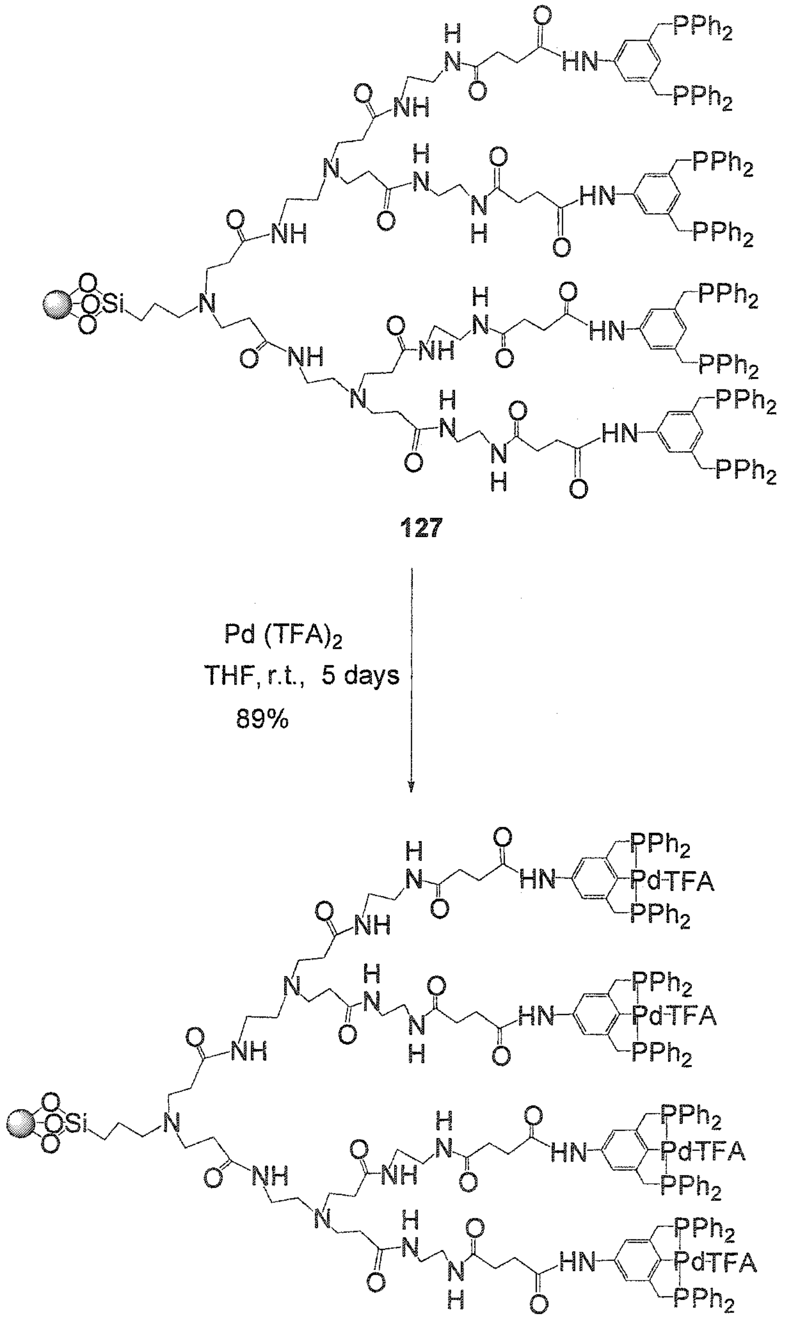


DMAP, CH_2Cl_2, 7 days, 45 °C, 52%

To a solution of **120** (2.9 g, 4.9 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.6 g, 4.9 mmol) in dichloromethane (70 mL) was added 1, 3-dicyclohexylcarbodiimide (DCC) (1.01 g, 4.9 mmol) in dichloromethane (5 mL) and *N*-hydroxysuccinimide (0.6 g, 4.9 mmol) at 0 °C. The mixture was stirred at room temperature for 18 h. The white solid was filtered and the solvent was evaporated under reduced pressure, affording compound **121** as a yellow solid. DMAP (0.6 g, 4.9 mmol) in dichloromethane (50 mL) and PAMAM-SiO_2 dendrimer compound **126** (0.5 g, 1.12 mmol) were added, the reaction was stirred at room temperature for 1 day and then heated at 45 °C for 7 days. The suspension was filtered, washed with dichloromethane several times, and dried *in vacuo* to afford **127** as a pale yellow solid. (0.8 g). ^{31}P CP/MAS NMR δ (ppm) -11.3 and 27.1 (phosphine oxide); ^{13}C CP/MAS NMR δ (ppm) 172.7, 157.7, 143.3, 108.5, 40.2, 26.0, 10.6; ICP Analysis mass% P 3.0 (50-52% yield).

Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum.

5.25 Synthesis of a Generation Two Dendrimer (G-2) (C)



127

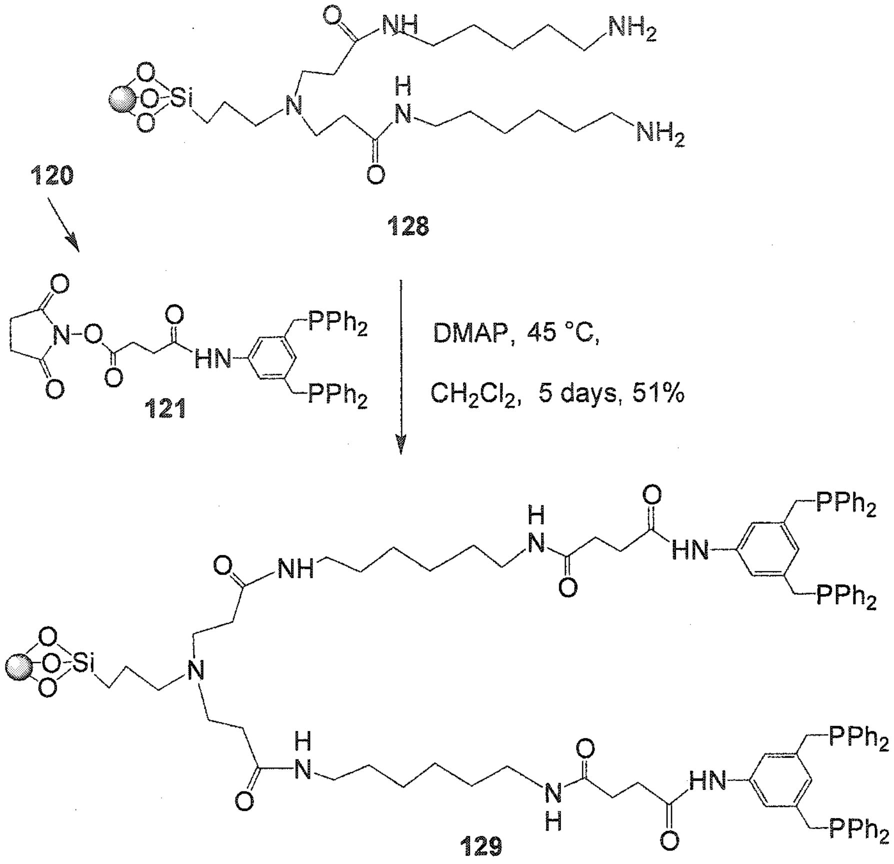
Pd (TFA)$_2$
THF, r.t., 5 days
89%

Generation two (G-2) (C)

A suspension of **127** (0.7 g, 1.35 mmol), and Pd(TFA)$_2$ (0.11 g, 0.34 mmol) in THF (50 mL) was stirred at room temperature for 5 days. The suspension was filtered and washed with THF several times, dried in vacuo to afford generation two dendrimer **(G-2)** (**C**) as a dark yellow solid (0.7 g). ^{31}P CP/MAS NMR δ (ppm) 36.3 and 28.7 (phosphine oxide); ^{13}C CP/MAS NMR 172.5, 156.3, 142.3, 131.4, 108.4, 48.1, 40.9, 31.0, 26.0, 10.3: ICP Analysis mass% Pd 4.29 (89% yield)

Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum. Some of the small broad signal near the base of the ^{31}P NMR CPMAS peaks may be due to ^{31}P atoms bound to quadrupole ^{105}Pd atoms which have I = 5/2 and are 22.23% naturally abundant. In such a case one would expect broad features at the base of the ^{31}P NMR peaks.

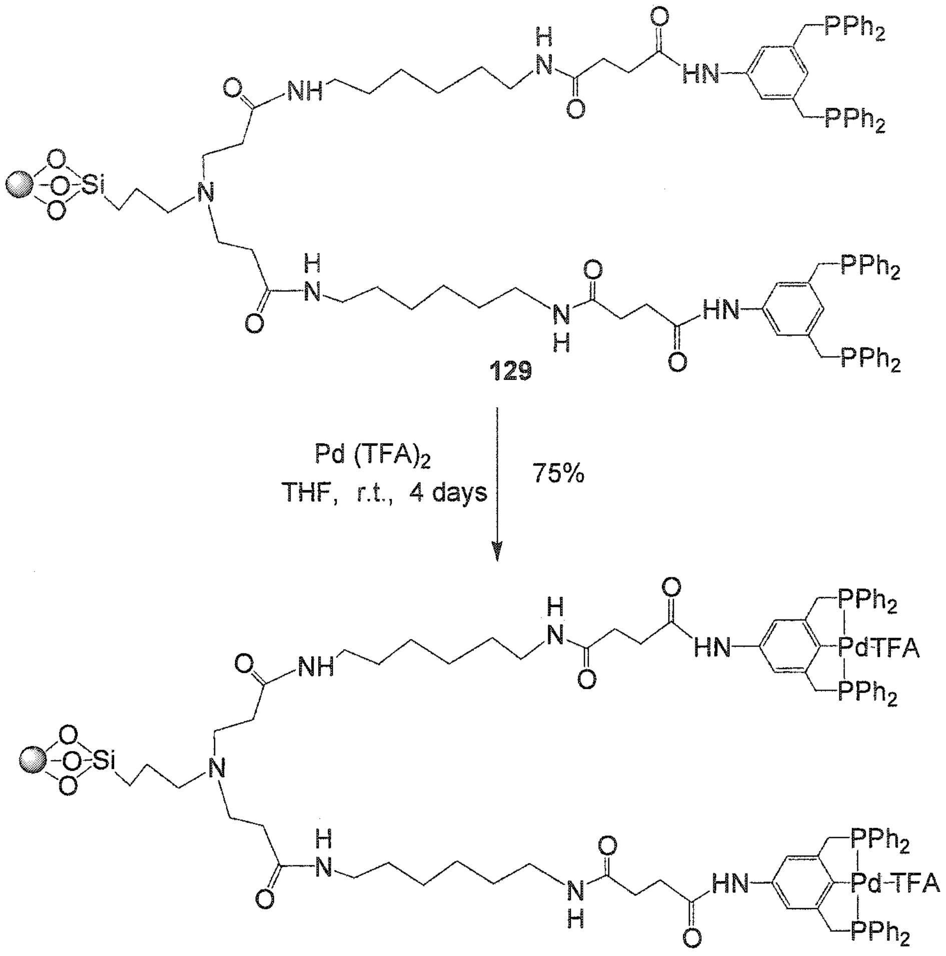
5.26 Synthesis of 129



To a solution of **120** (1.7 g, 2.9 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.35 g, 2.9 mmol) in dichloromethane (30 mL) was added 1, 3-dicyclohexylcarbodiimide (DCC) (0.59 g, 2.9 mmol) in dichloromethane (2 mL) and *N*-hydroxysuccinimide (0.33 g, 2.9 mmol) at 0 °C. The mixture was stirred at room temperature for 18 h. The white solid was filtered and the solvent was evaporated under reduced pressure, affording compound **121** as a yellow solid. DMAP (0.35 g, 2.9 mmol) in dichloromethane (80 mL) and PAMAM-SiO_2 dendrimers, **128** (0.5 g, 0.69 mmol) were added, the reaction was stirred at room temperature for 1 day and then heated at 45 °C for 5 days. The suspension was filtered, washed with dichloromethane several times, and dried *in vacuo* to afford **129** as a pale yellow solid (0.7 g). ^{31}P CP/MAS NMR δ (ppm) -11.2; ^{13}C CP/MAS NMR δ (ppm) 172.9, 158.9, 129.1, 107.8, 39.9, 27.9, 10.6; ICP Analysis mass% P 2.33% (49-51% yield).

Note: The reaction was carried out under Argon. The solvent was degassing 3 times with liquid nitrogen under vacuum.

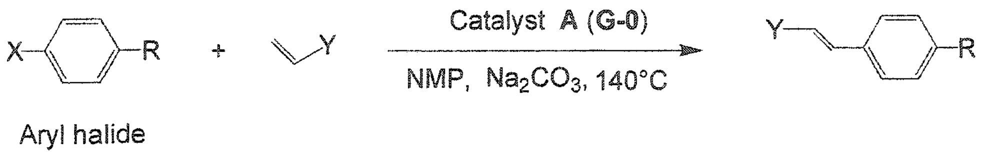
5.27 Synthesis of a Generation One Dendrimer (G-1) (D)



Generation one (G-1) (D)

A suspension of **129** (0.6 g, 0.91 mmol), and Pd(TFA)$_2$ (0.07 g, 0.22 mmol) in THF (50 mL) was stirred at room temperature for 4 days. The suspension was filtered and washed with THF several times, dried in vacuo to afford generation one dendrimer (**G-1**) (**D**) as a dark yellow solid (0.6 g). ^{31}P CP/MAS NMR δ (ppm) 35.6; ^{13}C CP/MAS NMR 172.8, 157.5, 143.3, 131.3, 106.8, 51.9, 40.5, 28.6, 22.7, 10.6; ICP Analysis mass% Pd 2.84 (75% yield).

5.28 General Procedure for the Heck Reactions

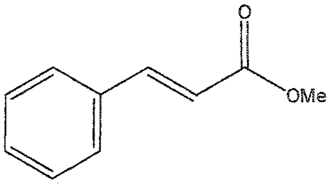


A solution of bromoarene (2 mmol) or iodoarene (12 mmol), olefin (2.4 mmol for bromoarene or 14.4 mmol for iodoarene), sodium carbonate (5 mmol for bromoarene or 30 mmol for iodoarene), and catalyst **A** (100 mg, 0.8 mol% for bromoarene or 25 mg, 0.03 mol% for iodoarene) in 10 mL of NMP for bromoarene, or 50 mL of NMP for iodoarene, was heated at 140 °C for 24 hours (bromoarene) or 6 hours (iodoarene) under nitrogen. After the reaction, the mixture was allowed to cool, and filtered to separate the catalyst from the liquid phase. The catalyst was washed several times with water and diethyl ether. NMP was in the aqueous phase. The aqueous phase was extracted with diethyl ether several times and the combined organic phase was washed with saturated aqueous NaCl solution and water, and then dried ($MgSO_4$). The catalyst was dried under reduced pressure before being recycled.

Similar procedures were used for catalysts **B**, **C**, and **D** except for different amounts of catalysts and the amount of bromobenzene.

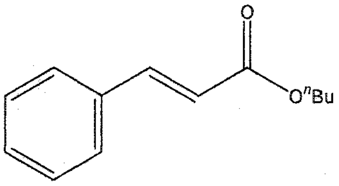
The products were analyzed by gas chromatography and (or) ^{1}H NMR spectroscopy, and identified by comparison with literature data.(102-105)

Trans-cinnamic acid methyl ester.



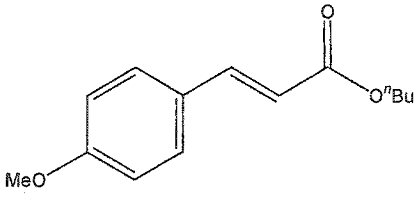
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.68 (d, J = 16.2 Hz, 1H, C*H*=CHCOOMe), 7.56-7.46 (m, 2H, Ar*H*), 7.44-7.29 (m, 3H, Ar*H*), 6.42 (d, J = 16.2 Hz, 1H, CH=C*H*COOMe), 3.78 (s, 3H, C*H*$_3$O); EI MS for $C_{10}H_{10}O_2$ 162 (M^+).

Trans-cinnamic acid *n*-butyl ester.



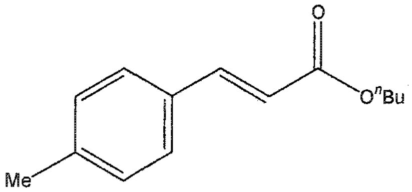
^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.66 (d, J = 16 Hz, 1H, C*H*=CHCOOBu) 7.61-7.19 (m, 5H, Ar*H*), 6.42 (d, J = 16 Hz, 1H, CH=C*H*COOBu), 4.19 (t, J = 6.6 Hz, 2H, CH=COOC*H*$_2$CH$_2$), 1.81-1.53 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 1.53-1.28 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 0.94 (t, J = 7.3 Hz, 3H, CH$_2$C*H*$_3$); EI MS for $C_{13}H_{16}O_2$ 204 (M^+).

4-Methoxy- *trans*-cinnamic acid *n*-butyl ester.



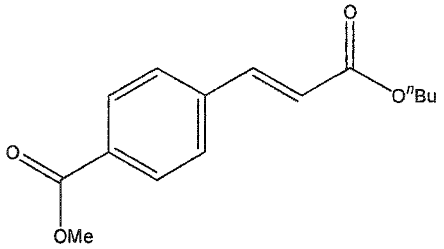
^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.61 (d, J = 16 Hz, 1H, C*H*=CHCOOBu), 7.45 (d, J = 8.8 Hz, 2H, Ar*H*), 6.87 (d, J = 8.8 Hz, 2H, Ar*H*), 6.28 (d, J = 16 Hz, 1H, CH=C*H*COOBu), 4.16 (t, J = 6.6 Hz, 2H, CH=COOCH_2CH$_2$), 3.81 (s, 3H, CH_3O), 1.73-1.51 (m, 2H, CH$_2$CH_2CH$_2$), 1.51-1.22 (m, 2H, CH$_2$CH_2CH$_3$), 0.95 (t, J = 7.4 Hz, 3H, CH$_2$CH_3); EI MS for $C_{14}H_{18}O_3$ 234 (M^+).

4-Methyl- *trans*-cinnamic acid *n*-butyl ester



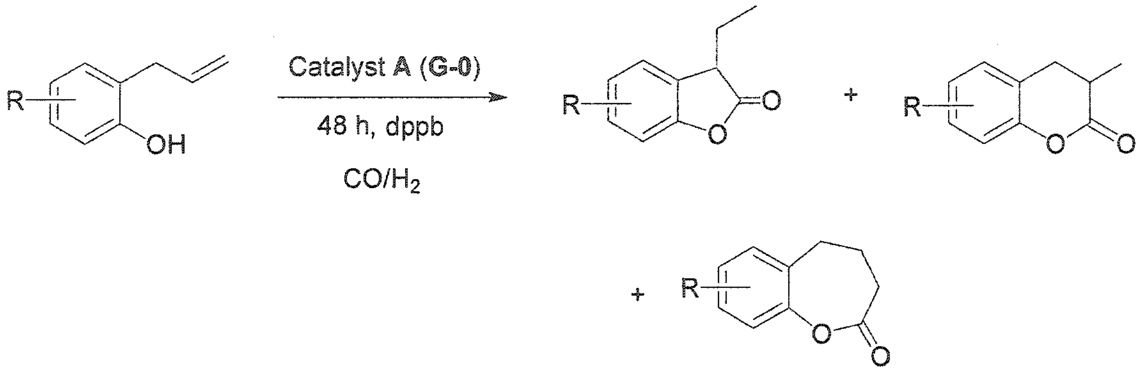
^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.64 (d, J = 16 Hz, 1H, C*H*=CHCOOBu), 7.38 (d, J = 8 Hz, 2H, Ar*H*), 7.15 (d, J = 8 Hz, 2H, Ar*H*), 6.37 (d, J = 16 Hz, 1H, CH=C*H*COOBu), 4.18 (t, J = 6.5 Hz, 2H, CH=COOCH_2CH$_2$), 2.33 (s, 3H, C*H*$_3$Ar), 1.82-1.54 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 1.54-1.31 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 0.94 (t, J = 7.3 Hz, 3H, CH$_2$C*H*$_3$); EI MS for $C_{14}H_{18}O_2$ 218 (M$^+$).

4-(2-Butoxycarbonyl)vinylbenzoic acid methyl ester



^{1}H NMR (200 MHz, CDCl$_3$) δ (ppm) 7.94 (d, J = 8.2 Hz, 2H, Ar*H*), 7.60 (d, J = 16 Hz, 1H, C*H*=CHCOOBu), 7.48 (d, J = 8.2 Hz, 2H, Ar*H*), 6.43 (d, J = 16 Hz, 1H, CH=C*H*COOBu), 4.13 (t, J = 6.6 Hz, 2H, CH=COOC*H*$_2$CH$_2$), 3.83 (s, 3H, C*H*$_3$O), 1.73-1.52 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 1.48-1.23 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 0.88 (t, J = 7.3 Hz, 3H, CH$_2$C*H*$_3$); EI MS for $C_{15}H_{18}O_4$ 262 (M$^+$).

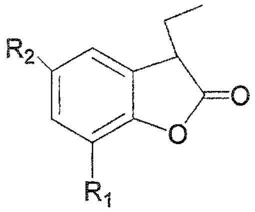
5.29 General Procedure for the Cyclocarbonylation Reactions



A mixture of 2-allylphenols (1 mmol), catalyst **A** (50 mg) and dppb (0.04 mmol in dry solvent (5 mL) was placed in a 45 mL autoclave equipped with a magnetic stirring bar. The autoclave was flushed three times with CO and then was pressured using a predetermined ratio of carbon monoxide and hydrogen gases. The autoclave was placed in an oil bath preheated to the appropriate temperature. The reaction mixture was magnetically stirred for 48 h and then cooled to room temperature and the unreacted carbon monoxide was slowly released. The mixture was filtered to separate the catalyst from the liquid phase. The catalyst was washed several times with CH_2Cl_2 and dried under reduced pressure before being recycled. The organic layer was concentrated by rotary evaporation affording oil.

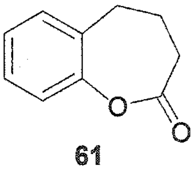
Analogous procedures were used for catalysts **B**, **C**, and **D** except for different amounts of catalysts and the amount of the 2-allylphenol.

The products were separated by thin-layer chromatography (TLC) plates, using 1:9 ethyl acetate-hexane as the optimum mobile phase. The identity of the products was confirmed by comparing to the literature data.(106-109) However, trace amount of 133, R_1 = Me, R_2 = H, which was detected in the mixture of products, was too small amount to be characterized.



133, R_1 = Me, R_2 = H

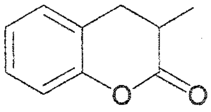
4,5-Dihydrobenzooxepine-2-one



61

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.32-7.01 (m, 4H, Ar*H*), 2.81 (t, J = 7.2 Hz, 2H, $ArCH_2CH_2$), 2.46 (t, J = 7.2 Hz, 2H, $OCCH_2CH_2$), 2.17 (tt, J = 7.2, 7.2 Hz, 2H, $H_2CCH_2CH_2$).

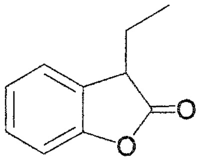
3-Methylchroman-2-one



62

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.23-6.98 (m, 4H, Ar*H*), 3.02-2.87 (m, 1H, CH_2CHCH_3), 2.87-2.68 (m, 2H, $ArCH_2CH$), 1.35 (d, J = 6.3 Hz, 3H, $HCCH_3$).

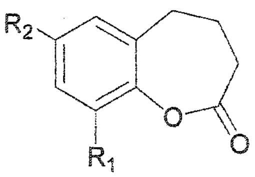
3-Ethylbenzofuran-2-one



63

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.19-6.91 (m, 4H, Ar*H*), 3.65 (t, J = 5.9 Hz, 1H, $ArCHCH_2$), 2.09-1.98 (m, 2H, $CHCH_2CH_3$), 0.91 (t, J = 7.5 Hz, 3H, CH_2CH_3).

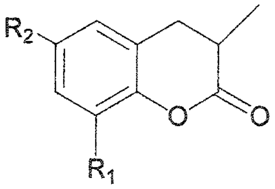
9-Methyl-4,5-dihydrobenzooxepin-2-one



131, R_1 = Me, R_2 = H

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.19-6.95 (m, 3H, Ar*H*), 2.79 (t, J = 7.2 Hz, 2H, $ArCH_2CH_2$), 2.44 (t, J = 7.2 Hz, 2H, $OCCH_2CH_2$), 2.27 (s, 3H, $ArCH_3$), 2.15 (tt, J = 7.2, 7.2 Hz, 2H, $H_2CCH_2CH_2$).

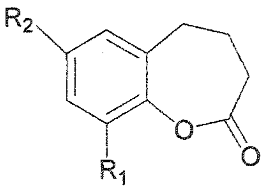
3,8-Dimethylchroman-2-one



132, R_1 = Me, R_2 = H

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.12-6.89 (m, 3H, Ar*H*), 2.98-2.83 (m, 1H, CH_2CHCH_3), 2.83-2.64 (m, 2H, $ArCH_2CH$), 2.28 (s, 3H, $ArCH_3$), 1.35 (d, J = 6 Hz, 3H, $HCCH_3$).

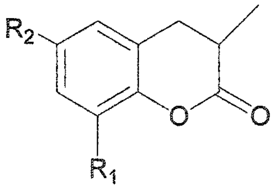
7-Chloro-4,5-dihydrobenzooxepin-2-one



131, R_1 = H, R_2 = Cl

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.29-7.04 (m, 3H, Ar*H*), 2.81 (t, J = 7.2 Hz, 2H, ArC*H*$_2$CH$_2$), 2.46 (t, J = 7.2 Hz, 2H, OCC*H*$_2$CH$_2$), 2.17 (tt, J = 7.2, 7.2 Hz, 2H, H$_2$CC*H*$_2$CH$_2$).

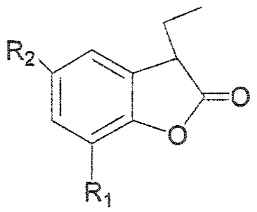
6-Chloro-3-methylchroman-2-one



132, R_1 = H, R_2 = Cl

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.23-6.92 (m, 3H, Ar*H*), 3.05-2.83 (m, 1H, CH$_2$C*H*CH$_3$), 2.83-2.63 (m, 2H, ArC*H*$_2$CH), 1.35 (d, J = 6.3 Hz, 3H, HCC*H*$_3$).

5-Chloro-3-ethylbenzofuran-2-one



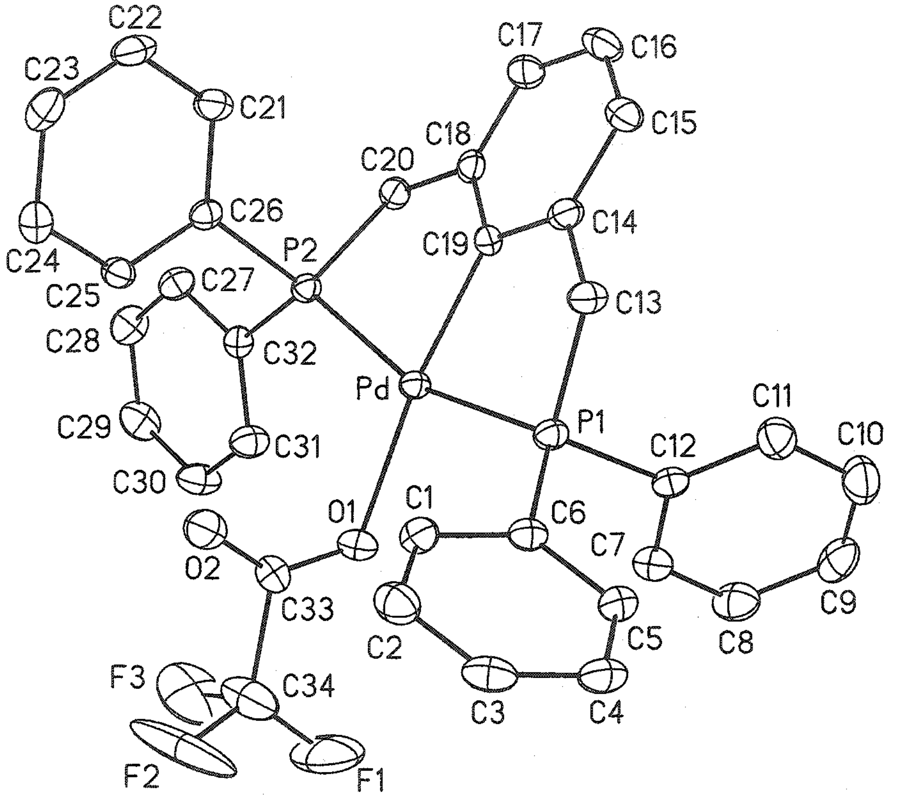
133, R_1 = H, R_2 = Cl

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.25-6.89 (m, 3H, Ar*H*), 3.68 (t, J = 5.8 Hz, 1H, ArC*H*CH_2), 2.03-1.92 (m, 2H, CHC*H*$_2$$CH_3$), 0.92 (t, J = 7.5 Hz, 3H, CH_2C*H*$_3$).

6

Appendix

6.1 Data for Crystal Structure of 34, R = Ph



ORTEP Diagram of Complex 1 (hydrogen atoms omitted for clarity)

Table 1. Crystal data and structure refinement for ha2006.

Identification code	ha2006
Empirical formula	C34 H27 F3 O2 P2 Pd
Formula weight	692.90
Temperature	203(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 17.312(3) A alpha = 90 deg.
	b = 15.632(3) A beta = 90 deg.
	c = 22.256(3) A gamma = 90 deg.
Volume	6023.0(17) A^3
Z, Calculated density	8, 1.528 Mg/m^3
Absorption coefficient	0.771 mm^-1
F(000)	2800
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	1.83 to 28.78 deg.
Limiting indices	-22<=h<=13, -20<=k<=19, -30<=l<=29
Reflections collected / unique	26770 / 7181 [R(int) = 0.0522]
Completeness to theta = 28.78	91.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8610 and 0.8610
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7181 / 30 / 407
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.0843
R indices (all data)	R1 = 0.0812, wR2 = 0.0971
Largest diff. peak and hole	1.293 and -0.720 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ha2006. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd	1029(1)	5817(1)	3882(1)	25(1)
P(1)	541(1)	7168(1)	3763(1)	28(1)
P(2)	1569(1)	4616(1)	4301(1)	25(1)
O(1)	919(2)	5505(2)	2950(1)	36(1)
O(2)	2175(2)	5634(2)	2734(1)	50(1)
F(1)	617(5)	5489(9)	1788(7)	111(5)
F(2)	1790(7)	5612(10)	1578(5)	155(8)
F(3)	1346(6)	4446(4)	1883(3)	107(2)
F(1')	685(7)	5035(11)	1804(8)	92(7)
F(2')	1869(7)	5186(12)	1605(8)	110(7)
F(3')	1162(10)	6230(6)	1727(4)	123(5)
C(1)	1622(2)	7779(3)	2960(2)	35(1)
C(2)	1930(3)	8371(3)	2567(2)	42(1)
C(3)	1491(3)	9046(3)	2364(2)	41(1)
C(4)	724(3)	9116(3)	2537(2)	39(1)
C(5)	415(2)	8523(2)	2936(2)	33(1)
C(6)	864(2)	7862(2)	3158(2)	28(1)
C(7)	-886(2)	6681(3)	3352(2)	38(1)
C(8)	-1686(3)	6683(3)	3320(2)	49(1)
C(9)	-2106(3)	7201(3)	3706(2)	51(1)
C(10)	-1739(3)	7711(3)	4114(2)	54(1)
C(11)	-937(3)	7711(3)	4149(2)	43(1)
C(12)	-503(2)	7205(2)	3762(2)	30(1)
C(13)	876(2)	7682(2)	4453(2)	32(1)
C(14)	873(2)	6998(2)	4932(2)	31(1)
C(15)	778(3)	7215(3)	5534(2)	40(1)
C(16)	783(3)	6585(3)	5972(2)	47(1)
C(17)	893(2)	5740(3)	5815(2)	40(1)
C(18)	984(2)	5508(2)	5212(2)	29(1)
C(19)	970(2)	6138(2)	4759(2)	25(1)
C(20)	1092(2)	4580(2)	5032(2)	30(1)
C(21)	2885(2)	4958(3)	5016(2)	38(1)
C(22)	3666(3)	5156(3)	5082(2)	46(1)
C(23)	4143(2)	5184(3)	4590(2)	43(1)
C(24)	3865(2)	4978(3)	4027(2)	35(1)
C(25)	3092(2)	4777(2)	3956(2)	29(1)
C(26)	2593(2)	4772(2)	4448(2)	26(1)
C(27)	1880(2)	2862(2)	4234(2)	35(1)
C(28)	1840(3)	2068(3)	3966(2)	44(1)
C(29)	1440(3)	1961(3)	3435(2)	48(1)
C(30)	1069(3)	2643(3)	3174(2)	47(1)
C(31)	1104(3)	3447(3)	3440(2)	40(1)
C(32)	1513(2)	3562(2)	3969(2)	27(1)
C(33)	1507(2)	5516(2)	2634(2)	30(1)
C(34)	1306(3)	5373(4)	1949(2)	68(2)

Table 3. Bond lengths [A] and angles [deg] for ha2006.

Pd-C(19)	2.019(3)
Pd-O(1)	2.139(2)
Pd-P(1)	2.2899(11)
Pd-P(2)	2.2958(10)
P(1)-C(12)	1.808(4)
P(1)-C(6)	1.818(4)
P(1)-C(13)	1.828(4)
P(2)-C(32)	1.808(4)
P(2)-C(26)	1.819(4)
P(2)-C(20)	1.826(4)
O(1)-C(33)	1.236(4)
O(2)-C(33)	1.193(5)
F(1)-C(34)	1.258(10)
F(2)-C(34)	1.235(9)
F(3)-C(34)	1.459(8)
F(1')-C(34)	1.239(11)
F(2')-C(34)	1.275(10)
F(3')-C(34)	1.449(9)
C(1)-C(2)	1.378(6)
C(1)-C(6)	1.391(5)
C(2)-C(3)	1.377(6)
C(3)-C(4)	1.385(6)
C(4)-C(5)	1.392(5)
C(5)-C(6)	1.384(5)
C(7)-C(8)	1.387(6)
C(7)-C(12)	1.393(5)
C(8)-C(9)	1.386(6)
C(9)-C(10)	1.367(7)
C(10)-C(11)	1.390(6)
C(11)-C(12)	1.390(5)
C(13)-C(14)	1.509(5)
C(14)-C(15)	1.392(5)
C(14)-C(19)	1.409(5)
C(15)-C(16)	1.386(6)
C(16)-C(17)	1.380(6)
C(17)-C(18)	1.397(5)
C(18)-C(19)	1.409(5)
C(18)-C(20)	1.518(5)
C(21)-C(26)	1.391(5)
C(21)-C(22)	1.395(6)
C(22)-C(23)	1.372(6)
C(23)-C(24)	1.380(6)
C(24)-C(25)	1.383(5)
C(25)-C(26)	1.397(5)
C(27)-C(28)	1.380(6)
C(27)-C(32)	1.397(5)
C(28)-C(29)	1.379(6)
C(29)-C(30)	1.373(6)
C(30)-C(31)	1.391(6)
C(31)-C(32)	1.385(5)
C(33)-C(34)	1.579(6)
C(19)-Pd-O(1)	171.95(13)

C(19)-Pd-P(1)	82.19(10)
O(1)-Pd-P(1)	93.79(8)
C(19)-Pd-P(2)	80.26(10)
O(1)-Pd-P(2)	104.06(8)
P(1)-Pd-P(2)	162.09(3)
C(12)-P(1)-C(6)	106.69(17)
C(12)-P(1)-C(13)	107.74(18)
C(6)-P(1)-C(13)	105.22(17)
C(12)-P(1)-Pd	113.47(13)
C(6)-P(1)-Pd	121.51(13)
C(13)-P(1)-Pd	101.03(13)
C(32)-P(2)-C(26)	104.41(17)
C(32)-P(2)-C(20)	108.16(17)
C(26)-P(2)-C(20)	106.49(17)
C(32)-P(2)-Pd	123.88(12)
C(26)-P(2)-Pd	111.12(11)
C(20)-P(2)-Pd	101.71(13)
C(33)-O(1)-Pd	118.4(2)
C(2)-C(1)-C(6)	120.2(4)
C(3)-C(2)-C(1)	120.6(4)
C(2)-C(3)-C(4)	119.9(4)
C(3)-C(4)-C(5)	119.6(4)
C(6)-C(5)-C(4)	120.5(4)
C(5)-C(6)-C(1)	119.2(3)
C(5)-C(6)-P(1)	122.4(3)
C(1)-C(6)-P(1)	118.0(3)
C(8)-C(7)-C(12)	120.5(4)
C(9)-C(8)-C(7)	119.5(4)
C(10)-C(9)-C(8)	120.6(4)
C(9)-C(10)-C(11)	120.1(4)
C(10)-C(11)-C(12)	120.3(4)
C(11)-C(12)-C(7)	118.9(4)
C(11)-C(12)-P(1)	123.9(3)
C(7)-C(12)-P(1)	117.3(3)
C(14)-C(13)-P(1)	106.3(3)
C(15)-C(14)-C(19)	120.6(3)
C(15)-C(14)-C(13)	120.5(4)
C(19)-C(14)-C(13)	118.9(3)
C(16)-C(15)-C(14)	120.2(4)
C(17)-C(16)-C(15)	120.1(4)
C(16)-C(17)-C(18)	120.5(4)
C(17)-C(18)-C(19)	120.2(3)
C(17)-C(18)-C(20)	121.1(3)
C(19)-C(18)-C(20)	118.7(3)
C(18)-C(19)-C(14)	118.3(3)
C(18)-C(19)-Pd	121.2(3)
C(14)-C(19)-Pd	120.5(3)
C(18)-C(20)-P(2)	105.2(2)
C(26)-C(21)-C(22)	119.7(4)
C(23)-C(22)-C(21)	120.4(4)
C(22)-C(23)-C(24)	120.5(4)
C(23)-C(24)-C(25)	119.6(4)
C(24)-C(25)-C(26)	120.6(3)
C(21)-C(26)-C(25)	119.1(4)
C(21)-C(26)-P(2)	123.1(3)
C(25)-C(26)-P(2)	117.5(3)
C(28)-C(27)-C(32)	120.0(4)

C(29)-C(28)-C(27)	120.3(4)
C(30)-C(29)-C(28)	120.2(4)
C(29)-C(30)-C(31)	120.1(4)
C(32)-C(31)-C(30)	120.1(4)
C(31)-C(32)-C(27)	119.3(3)
C(31)-C(32)-P(2)	119.6(3)
C(27)-C(32)-P(2)	121.1(3)
O(2)-C(33)-O(1)	133.9(4)
O(2)-C(33)-C(34)	114.6(4)
O(1)-C(33)-C(34)	111.5(4)
F(2)-C(34)-F(1')	122.9(12)
F(2)-C(34)-F(1)	114.2(9)
F(1')-C(34)-F(1)	33.5(10)
F(2)-C(34)-F(2')	31.5(11)
F(1')-C(34)-F(2')	114.1(10)
F(1)-C(34)-F(2')	126.0(13)
F(2)-C(34)-F(3')	67.0(9)
F(1')-C(34)-F(3')	99.0(9)
F(1)-C(34)-F(3')	66.9(8)
F(2')-C(34)-F(3')	98.0(9)
F(2)-C(34)-F(3)	101.5(8)
F(1')-C(34)-F(3)	65.9(9)
F(1)-C(34)-F(3)	99.2(7)
F(2')-C(34)-F(3)	71.0(9)
F(3')-C(34)-F(3)	153.1(6)
F(2)-C(34)-C(33)	116.9(7)
F(1')-C(34)-C(33)	120.2(9)
F(1)-C(34)-C(33)	117.6(8)
F(2')-C(34)-C(33)	116.4(10)
F(3')-C(34)-C(33)	103.7(5)
F(3)-C(34)-C(33)	103.1(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for ha2006.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd	27(1)	26(1)	21(1)	2(1)	-2(1)	0(1)
P(1)	33(1)	25(1)	25(1)	2(1)	-4(1)	1(1)
P(2)	25(1)	26(1)	24(1)	3(1)	-1(1)	1(1)
O(1)	42(2)	40(2)	26(1)	-2(1)	-4(1)	-4(1)
O(2)	42(2)	70(2)	39(2)	-2(2)	0(1)	-1(2)
F(1)	89(7)	191(15)	54(5)	10(9)	-38(5)	-26(7)
F(2)	183(14)	253(17)	29(4)	-28(8)	32(7)	-179(13)
F(3)	125(7)	108(6)	89(5)	-61(4)	-5(5)	-33(6)
F(1')	86(10)	155(15)	35(5)	-5(9)	-4(6)	-89(10)
F(2')	69(9)	204(18)	57(8)	-63(10)	12(6)	3(11)
F(3')	230(15)	96(7)	42(5)	36(5)	-41(7)	-26(9)
C(1)	37(2)	36(2)	32(2)	1(2)	-4(2)	5(2)
C(2)	37(2)	54(3)	34(2)	-2(2)	4(2)	-8(2)
C(3)	54(3)	44(3)	25(2)	7(2)	-3(2)	-14(2)
C(4)	52(3)	38(2)	28(2)	7(2)	-8(2)	0(2)
C(5)	35(2)	36(2)	29(2)	3(2)	-3(2)	2(2)
C(6)	35(2)	24(2)	25(2)	0(1)	-4(2)	-4(2)
C(7)	41(3)	42(2)	32(2)	0(2)	-2(2)	-3(2)
C(8)	41(3)	62(3)	45(3)	2(2)	-7(2)	-11(2)
C(9)	25(2)	66(3)	62(3)	17(2)	2(2)	1(2)
C(10)	45(3)	59(3)	59(3)	-4(2)	10(2)	10(2)
C(11)	42(3)	42(3)	45(2)	-6(2)	-1(2)	2(2)

C(12)	34(2)	30(2)	26(2)	6(2)	-3(2)	0(2)
C(13)	39(2)	29(2)	28(2)	0(2)	-7(2)	0(2)
C(14)	31(2)	34(2)	27(2)	3(2)	-5(2)	2(2)
C(15)	51(3)	38(2)	31(2)	-9(2)	-5(2)	9(2)
C(16)	64(3)	53(3)	23(2)	-3(2)	2(2)	12(2)
C(17)	49(3)	46(3)	25(2)	9(2)	3(2)	9(2)
C(18)	22(2)	35(2)	29(2)	4(2)	3(2)	4(2)
C(19)	23(2)	29(2)	24(2)	-3(1)	1(2)	2(2)
C(20)	28(2)	34(2)	29(2)	6(2)	3(2)	2(2)
C(21)	36(2)	52(3)	26(2)	1(2)	-1(2)	-2(2)
C(22)	41(3)	65(3)	33(2)	-1(2)	-15(2)	-2(2)
C(23)	25(2)	50(3)	52(3)	6(2)	-4(2)	1(2)
C(24)	31(2)	32(2)	41(2)	2(2)	6(2)	3(2)
C(25)	33(2)	30(2)	24(2)	-3(2)	-1(2)	1(2)
C(26)	29(2)	22(2)	27(2)	3(1)	-3(2)	2(2)
C(27)	35(2)	33(2)	38(2)	4(2)	-5(2)	-2(2)
C(28)	50(3)	27(2)	55(3)	6(2)	-3(2)	2(2)
C(29)	66(3)	31(2)	47(3)	-9(2)	4(2)	-6(2)
C(30)	70(3)	39(2)	33(2)	-3(2)	-9(2)	-2(2)
C(31)	50(3)	34(2)	36(2)	1(2)	-8(2)	1(2)
C(32)	27(2)	25(2)	29(2)	2(1)	3(2)	0(2)
C(33)	32(2)	26(2)	33(2)	-4(2)	4(2)	-6(2)
C(34)	63(4)	106(5)	37(3)	-11(3)	7(3)	-34(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ha2006.

	x	y	z	U(eq)
H(1A)	1926	7319	3093	42
H(2A)	2443	8312	2437	50
H(3A)	1711	9459	2110	49
H(4A)	416	9561	2384	47
H(5A)	-104	8572	3057	40
H(7A)	-600	6323	3096	46
H(8A)	-1942	6336	3038	59
H(9A)	-2648	7201	3686	61
H(10A)	-2029	8062	4372	65
H(11A)	-687	8055	4435	52
H(13A)	1398	7912	4399	38
H(13B)	530	8152	4565	38
H(15A)	709	7791	5644	48
H(16A)	711	6734	6378	56
H(17A)	908	5317	6115	48
H(20A)	592	4288	5002	36
H(20B)	1413	4278	5326	36
H(21A)	2558	4949	5353	46
H(22A)	3867	5272	5466	55
H(23A)	4663	5345	4637	51
H(24A)	4199	4975	3694	42
H(25A)	2902	4641	3572	35
H(27A)	2154	2932	4596	42
H(28A)	2087	1597	4145	53
H(29A)	1422	1420	3251	57
H(30A)	791	2565	2815	57
H(31A)	851	3913	3260	48

Table 6. Torsion angles [deg] for ha2006.

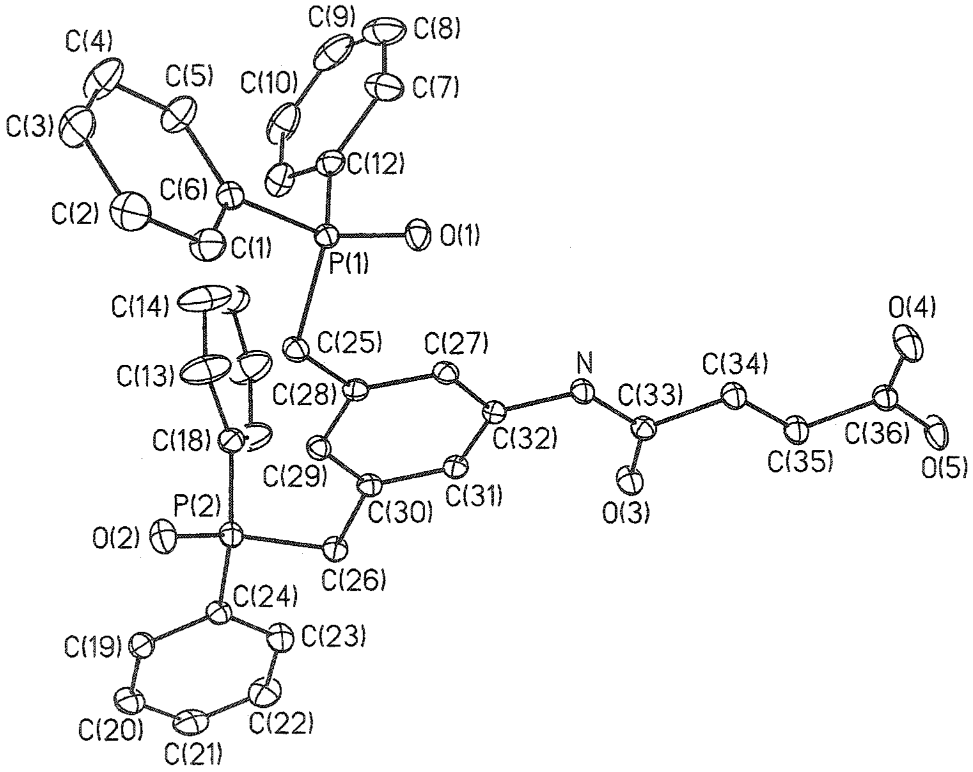
C(19)-Pd-P(1)-C(12)	-89.85(17)
O(1)-Pd-P(1)-C(12)	83.14(15)
P(2)-Pd-P(1)-C(12)	-101.31(17)
C(19)-Pd-P(1)-C(6)	140.86(18)
O(1)-Pd-P(1)-C(6)	-46.15(16)
P(2)-Pd-P(1)-C(6)	129.40(17)
C(19)-Pd-P(1)-C(13)	25.18(17)
O(1)-Pd-P(1)-C(13)	-161.83(15)
P(2)-Pd-P(1)-C(13)	13.72(19)
C(19)-Pd-P(2)-C(32)	150.62(18)
O(1)-Pd-P(2)-C(32)	-22.44(17)
P(1)-Pd-P(2)-C(32)	162.13(17)
C(19)-Pd-P(2)-C(26)	-83.88(16)
O(1)-Pd-P(2)-C(26)	103.06(14)
P(1)-Pd-P(2)-C(26)	-72.36(18)
C(19)-Pd-P(2)-C(20)	29.12(17)
O(1)-Pd-P(2)-C(20)	-143.93(15)
P(1)-Pd-P(2)-C(20)	40.64(19)
C(19)-Pd-O(1)-C(33)	162.4(8)
P(1)-Pd-O(1)-C(33)	102.7(3)
P(2)-Pd-O(1)-C(33)	-75.9(3)
C(6)-C(1)-C(2)-C(3)	-0.4(6)
C(1)-C(2)-C(3)-C(4)	-2.5(6)
C(2)-C(3)-C(4)-C(5)	3.0(6)
C(3)-C(4)-C(5)-C(6)	-0.6(6)
C(4)-C(5)-C(6)-C(1)	-2.3(6)
C(4)-C(5)-C(6)-P(1)	170.5(3)
C(2)-C(1)-C(6)-C(5)	2.8(6)
C(2)-C(1)-C(6)-P(1)	-170.3(3)
C(12)-P(1)-C(6)-C(5)	23.6(4)
C(13)-P(1)-C(6)-C(5)	-90.6(3)
Pd-P(1)-C(6)-C(5)	155.8(3)
C(12)-P(1)-C(6)-C(1)	-163.5(3)
C(13)-P(1)-C(6)-C(1)	82.2(3)
Pd-P(1)-C(6)-C(1)	-31.3(3)

C(12)-C(7)-C(8)-C(9)	-1.2(6)
C(7)-C(8)-C(9)-C(10)	0.4(7)
C(8)-C(9)-C(10)-C(11)	-0.4(7)
C(9)-C(10)-C(11)-C(12)	1.2(7)
C(10)-C(11)-C(12)-C(7)	-1.9(6)
C(10)-C(11)-C(12)-P(1)	179.3(3)
C(8)-C(7)-C(12)-C(11)	1.9(6)
C(8)-C(7)-C(12)-P(1)	-179.2(3)
C(6)-P(1)-C(12)-C(11)	-99.1(4)
C(13)-P(1)-C(12)-C(11)	13.4(4)
Pd-P(1)-C(12)-C(11)	124.4(3)
C(6)-P(1)-C(12)-C(7)	82.0(3)
C(13)-P(1)-C(12)-C(7)	-165.4(3)
Pd-P(1)-C(12)-C(7)	-54.4(3)
C(12)-P(1)-C(13)-C(14)	85.9(3)
C(6)-P(1)-C(13)-C(14)	-160.5(3)
Pd-P(1)-C(13)-C(14)	-33.3(3)
P(1)-C(13)-C(14)-C(15)	-152.8(3)
P(1)-C(13)-C(14)-C(19)	27.3(4)
C(19)-C(14)-C(15)-C(16)	0.5(6)
C(13)-C(14)-C(15)-C(16)	-179.4(4)
C(14)-C(15)-C(16)-C(17)	0.9(7)
C(15)-C(16)-C(17)-C(18)	-1.4(7)
C(16)-C(17)-C(18)-C(19)	0.5(6)
C(16)-C(17)-C(18)-C(20)	-178.9(4)
C(17)-C(18)-C(19)-C(14)	0.9(6)
C(20)-C(18)-C(19)-C(14)	-179.7(4)
C(17)-C(18)-C(19)-Pd	-175.9(3)
C(20)-C(18)-C(19)-Pd	3.5(5)
C(15)-C(14)-C(19)-C(18)	-1.4(6)
C(13)-C(14)-C(19)-C(18)	178.5(3)
C(15)-C(14)-C(19)-Pd	175.4(3)
C(13)-C(14)-C(19)-Pd	-4.7(5)
O(1)-Pd-C(19)-C(18)	101.0(9)
P(1)-Pd-C(19)-C(18)	161.5(3)
P(2)-Pd-C(19)-C(18)	-22.1(3)
O(1)-Pd-C(19)-C(14)	-75.7(10)
P(1)-Pd-C(19)-C(14)	-15.2(3)
P(2)-Pd-C(19)-C(14)	161.2(3)
C(17)-C(18)-C(20)-P(2)	-157.3(3)
C(19)-C(18)-C(20)-P(2)	23.3(4)
C(32)-P(2)-C(20)-C(18)	-166.4(3)
C(26)-P(2)-C(20)-C(18)	81.9(3)
Pd-P(2)-C(20)-C(18)	-34.6(3)
C(26)-C(21)-C(22)-C(23)	1.1(7)
C(21)-C(22)-C(23)-C(24)	-3.0(7)
C(22)-C(23)-C(24)-C(25)	2.7(6)
C(23)-C(24)-C(25)-C(26)	-0.6(6)
C(22)-C(21)-C(26)-C(25)	0.9(6)
C(22)-C(21)-C(26)-P(2)	-173.4(3)
C(24)-C(25)-C(26)-C(21)	-1.2(5)
C(24)-C(25)-C(26)-P(2)	173.4(3)
C(32)-P(2)-C(26)-C(21)	-123.2(3)
C(20)-P(2)-C(26)-C(21)	-8.9(4)
Pd-P(2)-C(26)-C(21)	101.0(3)
C(32)-P(2)-C(26)-C(25)	62.4(3)
C(20)-P(2)-C(26)-C(25)	176.7(3)

Pd-P(2)-C(26)-C(25)	-73.4(3)
C(32)-C(27)-C(28)-C(29)	0.1(7)
C(27)-C(28)-C(29)-C(30)	-1.0(7)
C(28)-C(29)-C(30)-C(31)	1.0(7)
C(29)-C(30)-C(31)-C(32)	-0.2(7)
C(30)-C(31)-C(32)-C(27)	-0.7(6)
C(30)-C(31)-C(32)-P(2)	178.8(3)
C(28)-C(27)-C(32)-C(31)	0.7(6)
C(28)-C(27)-C(32)-P(2)	-178.8(3)
C(26)-P(2)-C(32)-C(31)	-130.3(3)
C(20)-P(2)-C(32)-C(31)	116.5(3)
Pd-P(2)-C(32)-C(31)	-2.0(4)
C(26)-P(2)-C(32)-C(27)	49.1(3)
C(20)-P(2)-C(32)-C(27)	-64.0(4)
Pd-P(2)-C(32)-C(27)	177.5(3)
Pd-O(1)-C(33)-O(2)	3.9(6)
Pd-O(1)-C(33)-C(34)	-173.5(3)
O(2)-C(33)-C(34)-F(2)	-18.4(12)
O(1)-C(33)-C(34)-F(2)	159.6(10)
O(2)-C(33)-C(34)-F(1')	161.6(11)
O(1)-C(33)-C(34)-F(1')	-20.5(12)
O(2)-C(33)-C(34)-F(1)	-160.1(8)
O(1)-C(33)-C(34)-F(1)	17.9(9)
O(2)-C(33)-C(34)-F(2')	17.0(11)
O(1)-C(33)-C(34)-F(2')	-165.0(10)
O(2)-C(33)-C(34)-F(3')	-89.3(8)
O(1)-C(33)-C(34)-F(3')	88.7(8)
O(2)-C(33)-C(34)-F(3)	92.0(6)
O(1)-C(33)-C(34)-F(3)	-90.0(6)

Symmetry transformations used to generate equivalent atoms:

6.2 Data for Crystal Structure of *N*-[3,5-Bis(diphenylphosphinoylmethyl)phenyl]succinamic Acid (119)



ORTEP diagram of *N*-[3,5-Bis(diphenylphosphinoylmethyl)phenyl]succinamic acid (119) (hydrogen atoms omitted for clarity)

Table 1. Crystal data and structure refinement for ha2004.

Identification code	ha2004
Empirical formula	C37 H37 N O6 P2
Formula weight	653.62
Temperature	203(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.3465(13) A alpha = 96.027(2) deg. b = 12.6981(15) A beta = 115.308(2) deg. c = 13.0406(15) A gamma = 97.546(2) deg.
Volume	1656.4(3) A^3
Z, Calculated density	2, 1.311 Mg/m^3
Absorption coefficient	0.179 mm^-1
F(000)	688
Crystal size	0.20 x 0.20 x 0.10 mm
Theta range for data collection	1.64 to 28.84 deg.
Limiting indices	-15<=h<=13, -16<=k<=16, 0<=l<=16
Reflections collected / unique	12268 / 7209 [R(int) = 0.0191]
Completeness to theta = 28.84	83.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.926861
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7209 / 0 / 416
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.1015
R indices (all data)	R1 = 0.0499, wR2 = 0.1081
Largest diff. peak and hole	0.478 and -0.366 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ha2004.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
P(1)	4829(1)	7753(1)	2286(1)	22(1)
P(2)	333(1)	3287(1)	2248(1)	27(1)
N	6760(1)	4439(1)	4149(1)	26(1)
O(1)	6274(1)	8057(1)	3170(1)	30(1)
O(2)	-143(1)	4327(1)	2282(1)	39(1)
O(3)	6620(1)	2805(1)	4741(1)	34(1)
O(4)	11486(1)	3656(1)	5842(2)	51(1)
O(5)	11248(1)	2069(1)	6377(1)	47(1)
O(6)	6969(2)	9080(1)	5419(1)	56(1)
C(1)	4211(2)	9727(1)	2754(2)	37(1)
C(2)	3791(2)	10688(2)	2498(2)	46(1)
C(3)	3329(2)	10883(2)	1383(2)	50(1)
C(4)	3301(3)	10135(2)	524(2)	55(1)
C(5)	3719(2)	9166(2)	770(2)	42(1)
C(6)	4173(2)	8952(1)	1888(1)	25(1)
C(7)	5659(2)	7091(2)	667(2)	46(1)
C(8)	5504(3)	6506(2)	-365(2)	62(1)
C(9)	4330(3)	5774(2)	-1065(2)	60(1)
C(10)	3312(3)	5621(2)	-760(2)	54(1)
C(11)	3444(2)	6201(2)	263(2)	39(1)
C(12)	4622(2)	6937(1)	984(1)	29(1)
C(13)	447(3)	3620(2)	232(2)	68(1)
C(14)	409(3)	3325(3)	-843(2)	83(1)
C(15)	220(3)	2234(2)	-1298(2)	66(1)
C(16)	-18(4)	1462(2)	-715(2)	77(1)
C(17)	11(3)	1760(2)	357(2)	60(1)
C(18)	275(2)	2834(2)	851(2)	34(1)
C(19)	-1959(2)	2293(2)	2274(2)	35(1)
C(20)	-2796(2)	1461(2)	2406(2)	44(1)
C(21)	-2347(2)	541(2)	2753(2)	45(1)
C(22)	-1067(2)	438(2)	2983(2)	45(1)
C(23)	-217(2)	1261(1)	2858(2)	38(1)
C(24)	-664(2)	2190(1)	2491(1)	28(1)
C(25)	3789(2)	7052(1)	2842(1)	26(1)
C(26)	2022(2)	3349(1)	3336(1)	28(1)
C(27)	5264(2)	5662(1)	3486(1)	24(1)
C(28)	4013(2)	5933(1)	3107(1)	22(1)
C(29)	2942(2)	5176(1)	3025(1)	24(1)
C(30)	3123(1)	4160(1)	3312(1)	23(1)
C(31)	4378(2)	3881(1)	3671(1)	24(1)
C(32)	5451(1)	4638(1)	3767(1)	22(1)
C(33)	7277(2)	3604(1)	4643(1)	25(1)
C(34)	8783(2)	3775(1)	5090(2)	28(1)
C(35)	9311(2)	2791(1)	5518(2)	33(1)
C(36)	10787(2)	2906(1)	5929(1)	29(1)
C(37)	7574(2)	10166(2)	5527(2)	55(1)

Table 3. Bond lengths [A] and angles [deg] for ha2004.

P(1)-O(1)	1.5135(11)
P(1)-C(12)	1.7996(17)
P(1)-C(6)	1.8093(16)
P(1)-C(25)	1.8171(15)
P(2)-O(2)	1.4955(13)
P(2)-C(26)	1.8176(16)
P(2)-C(24)	1.8183(16)
P(2)-C(18)	1.8222(19)
N-C(33)	1.367(2)
N-C(32)	1.4175(19)
O(3)-C(33)	1.2288(19)
O(4)-C(36)	1.2042(19)
O(5)-C(36)	1.326(2)
O(6)-C(37)	1.422(3)
C(1)-C(2)	1.389(3)
C(1)-C(6)	1.400(2)
C(2)-C(3)	1.382(3)
C(3)-C(4)	1.377(3)
C(4)-C(5)	1.396(3)
C(5)-C(6)	1.394(2)
C(7)-C(8)	1.396(3)
C(7)-C(12)	1.401(2)
C(8)-C(9)	1.389(4)
C(9)-C(10)	1.371(4)
C(10)-C(11)	1.392(3)
C(11)-C(12)	1.399(3)
C(13)-C(14)	1.394(4)
C(13)-C(18)	1.392(3)
C(14)-C(15)	1.400(4)
C(15)-C(16)	1.368(4)
C(16)-C(17)	1.394(3)
C(17)-C(18)	1.381(3)
C(19)-C(24)	1.399(2)
C(19)-C(20)	1.400(2)
C(20)-C(21)	1.378(3)
C(21)-C(22)	1.379(3)
C(22)-C(23)	1.398(2)
C(23)-C(24)	1.396(2)
C(25)-C(28)	1.525(2)
C(26)-C(30)	1.5245(19)
C(27)-C(28)	1.393(2)
C(27)-C(32)	1.405(2)
C(28)-C(29)	1.406(2)
C(29)-C(30)	1.397(2)
C(30)-C(31)	1.403(2)
C(31)-C(32)	1.400(2)
C(33)-C(34)	1.527(2)
C(34)-C(35)	1.513(2)
C(35)-C(36)	1.506(2)
O(1)-P(1)-C(12)	111.68(7)

O(1)-P(1)-C(6)	110.36(7)
C(12)-P(1)-C(6)	107.01(8)
O(1)-P(1)-C(25)	112.22(7)
C(12)-P(1)-C(25)	109.38(8)
C(6)-P(1)-C(25)	105.89(7)
O(2)-P(2)-C(26)	113.93(8)
O(2)-P(2)-C(24)	112.91(8)
C(26)-P(2)-C(24)	104.66(7)
O(2)-P(2)-C(18)	111.49(8)
C(26)-P(2)-C(18)	107.17(8)
C(24)-P(2)-C(18)	106.10(8)
C(33)-N-C(32)	129.20(12)
C(2)-C(1)-C(6)	120.45(18)
C(3)-C(2)-C(1)	120.04(19)
C(4)-C(3)-C(2)	120.25(19)
C(3)-C(4)-C(5)	120.2(2)
C(6)-C(5)-C(4)	120.16(18)
C(5)-C(6)-C(1)	118.84(16)
C(5)-C(6)-P(1)	122.44(13)
C(1)-C(6)-P(1)	118.56(13)
C(8)-C(7)-C(12)	119.6(2)
C(7)-C(8)-C(9)	119.8(2)
C(10)-C(9)-C(8)	120.9(2)
C(9)-C(10)-C(11)	120.2(2)
C(10)-C(11)-C(12)	119.8(2)
C(7)-C(12)-C(11)	119.76(17)
C(7)-C(12)-P(1)	118.20(14)
C(11)-C(12)-P(1)	121.96(13)
C(14)-C(13)-C(18)	120.4(2)
C(13)-C(14)-C(15)	119.9(2)
C(16)-C(15)-C(14)	119.4(2)
C(15)-C(16)-C(17)	120.3(3)
C(18)-C(17)-C(16)	121.0(2)
C(17)-C(18)-C(13)	118.64(19)
C(17)-C(18)-P(2)	123.58(14)
C(13)-C(18)-P(2)	117.71(16)
C(24)-C(19)-C(20)	120.04(18)
C(21)-C(20)-C(19)	120.15(18)
C(20)-C(21)-C(22)	120.30(16)
C(21)-C(22)-C(23)	120.29(19)
C(24)-C(23)-C(22)	120.08(17)
C(23)-C(24)-C(19)	119.12(15)
C(23)-C(24)-P(2)	123.76(13)
C(19)-C(24)-P(2)	117.11(13)
C(28)-C(25)-P(1)	117.05(10)
C(30)-C(26)-P(2)	117.35(11)
C(28)-C(27)-C(32)	120.57(13)
C(27)-C(28)-C(29)	119.18(14)
C(27)-C(28)-C(25)	121.84(13)
C(29)-C(28)-C(25)	118.88(13)
C(30)-C(29)-C(28)	120.51(14)
C(29)-C(30)-C(31)	120.18(13)
C(29)-C(30)-C(26)	122.35(13)
C(31)-C(30)-C(26)	117.32(14)
C(32)-C(31)-C(30)	119.42(14)
C(31)-C(32)-C(27)	120.11(13)
C(31)-C(32)-N	123.46(14)

C(27)-C(32)-N	116.42(12)
O(3)-C(33)-N	124.50(14)
O(3)-C(33)-C(34)	122.88(14)
N-C(33)-C(34)	112.61(12)
C(35)-C(34)-C(33)	111.55(12)
C(36)-C(35)-C(34)	113.50(13)
O(4)-C(36)-O(5)	122.72(15)
O(4)-C(36)-C(35)	124.60(15)
O(5)-C(36)-C(35)	112.65(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for ha2004. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

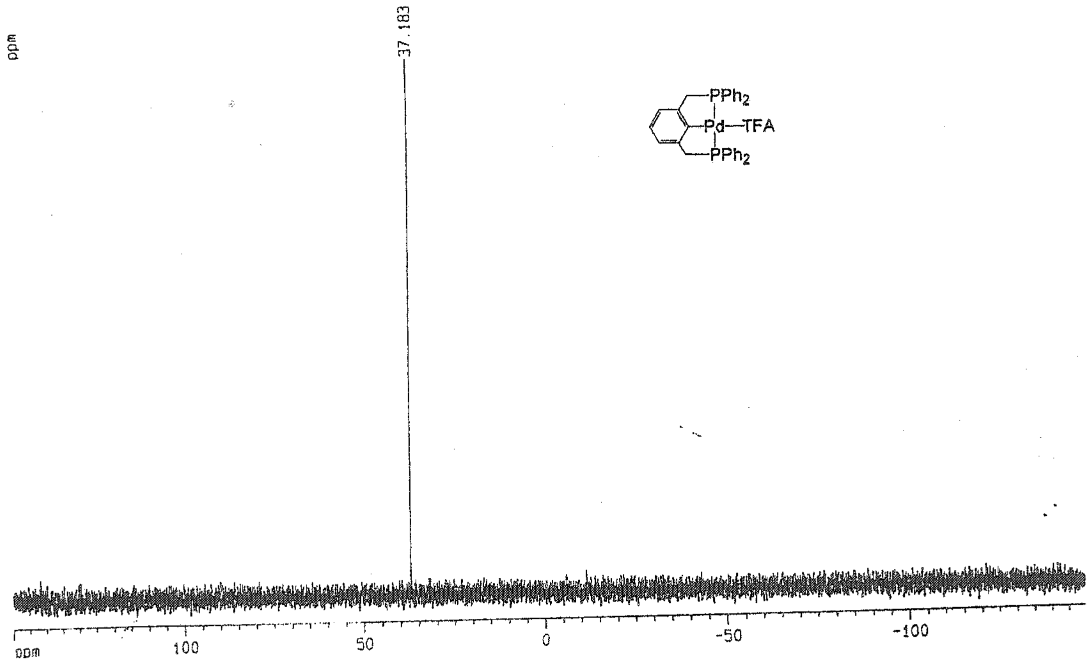
	U11	U22	U33	U23	U13	U12
P(1)	22(1)	19(1)	27(1)	6(1)	12(1)	4(1)
P(2)	23(1)	22(1)	36(1)	9(1)	13(1)	1(1)
N	22(1)	23(1)	35(1)	11(1)	14(1)	3(1)
O(1)	22(1)	27(1)	38(1)	9(1)	11(1)	4(1)
O(2)	32(1)	26(1)	60(1)	14(1)	20(1)	6(1)
O(3)	29(1)	26(1)	52(1)	16(1)	20(1)	5(1)
O(4)	31(1)	39(1)	93(1)	36(1)	30(1)	8(1)
O(5)	27(1)	43(1)	79(1)	38(1)	24(1)	14(1)
O(6)	70(1)	49(1)	44(1)	4(1)	28(1)	-6(1)
C(1)	48(1)	29(1)	40(1)	9(1)	24(1)	12(1)
C(2)	63(1)	28(1)	61(1)	10(1)	38(1)	16(1)
C(3)	58(1)	32(1)	72(2)	24(1)	32(1)	21(1)
C(4)	74(2)	45(1)	47(1)	23(1)	20(1)	26(1)
C(5)	55(1)	33(1)	35(1)	10(1)	15(1)	16(1)
C(6)	24(1)	20(1)	33(1)	7(1)	13(1)	3(1)
C(7)	62(1)	40(1)	57(1)	16(1)	44(1)	16(1)
C(8)	102(2)	60(2)	67(2)	32(1)	68(2)	43(2)
C(9)	110(2)	55(1)	33(1)	18(1)	36(1)	51(2)
C(10)	70(2)	49(1)	30(1)	2(1)	7(1)	28(1)
C(11)	43(1)	37(1)	32(1)	3(1)	11(1)	14(1)
C(12)	40(1)	24(1)	31(1)	10(1)	20(1)	13(1)
C(13)	94(2)	51(1)	46(1)	9(1)	29(1)	-25(1)

C(14)	99(2)	88(2)	46(1)	16(1)	33(1)	-32(2)
C(15)	66(2)	94(2)	37(1)	11(1)	25(1)	7(1)
C(16)	131(3)	61(2)	54(2)	16(1)	50(2)	39(2)
C(17)	106(2)	39(1)	51(1)	17(1)	46(1)	21(1)
C(18)	26(1)	38(1)	34(1)	11(1)	12(1)	0(1)
C(19)	26(1)	41(1)	34(1)	10(1)	12(1)	2(1)
C(20)	27(1)	61(1)	41(1)	10(1)	16(1)	-6(1)
C(21)	41(1)	47(1)	41(1)	9(1)	19(1)	-16(1)
C(22)	50(1)	31(1)	54(1)	17(1)	23(1)	-3(1)
C(23)	33(1)	30(1)	54(1)	14(1)	21(1)	2(1)
C(24)	25(1)	26(1)	30(1)	6(1)	12(1)	-1(1)
C(25)	27(1)	22(1)	33(1)	8(1)	18(1)	6(1)
C(26)	25(1)	23(1)	34(1)	9(1)	13(1)	0(1)
C(27)	24(1)	21(1)	28(1)	6(1)	14(1)	1(1)
C(28)	26(1)	20(1)	24(1)	5(1)	14(1)	3(1)
C(29)	23(1)	24(1)	27(1)	5(1)	12(1)	4(1)
C(30)	23(1)	21(1)	25(1)	3(1)	11(1)	0(1)
C(31)	26(1)	20(1)	26(1)	5(1)	13(1)	3(1)
C(32)	23(1)	22(1)	23(1)	4(1)	11(1)	4(1)
C(33)	26(1)	22(1)	28(1)	5(1)	14(1)	4(1)
C(34)	25(1)	24(1)	37(1)	9(1)	14(1)	4(1)
C(35)	25(1)	30(1)	46(1)	18(1)	15(1)	5(1)
C(36)	26(1)	26(1)	36(1)	12(1)	14(1)	5(1)
C(37)	59(1)	49(1)	50(1)	8(1)	20(1)	-1(1)

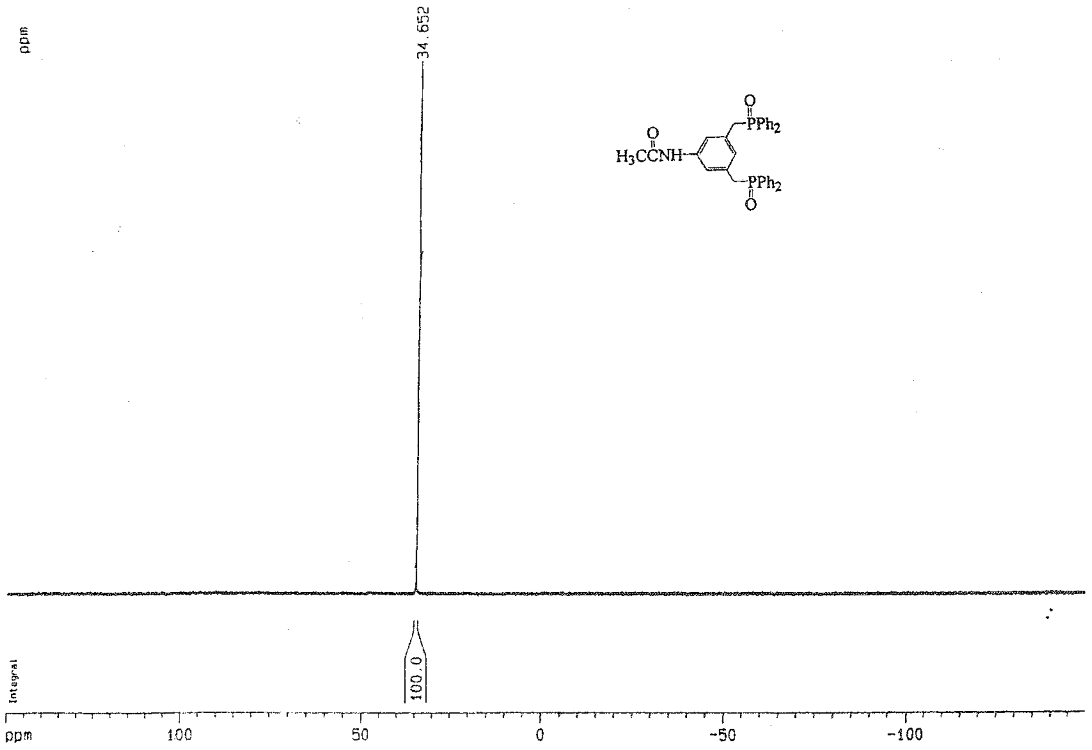
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ha2004.

	x	y	z	U(eq)
H(0A)	7312	4916	4055	31
H(5B)	12031	2114	6488	71
H(6A)	6837	8728	4793	84
H(1A)	4524	9597	3513	44
H(2A)	3820	11205	3084	56
H(3A)	3033	11529	1210	60
H(4A)	2999	10277	-230	66
H(5A)	3695	8656	180	50
H(7A)	6453	7584	1147	55
H(8A)	6192	6608	-587	74
H(9A)	4232	5378	-1757	72
H(10A)	2523	5124	-1243	65
H(11A)	2744	6098	469	46
H(13A)	589	4354	541	82
H(14A)	511	3859	-1263	99
H(15A)	256	2032	-1997	79
H(16A)	-202	727	-1039	92
H(17A)	-153	1222	749	72
H(19A)	-2268	2920	2039	41
H(20A)	-3666	1531	2259	53
H(21A)	-2915	-18	2832	54
H(22A)	-764	-189	3226	55
H(23A)	656	1188	3021	46
H(25A)	3919	7507	3551	31
H(25B)	2858	6983	2281	31
H(26A)	2043	3512	4096	33
H(26B)	2233	2629	3264	33
H(27A)	5989	6168	3555	28
H(29A)	2096	5354	2776	29
H(31A)	4497	3191	3846	28
H(34A)	9011	3931	4469	34
H(34B)	9207	4399	5720	34
H(35A)	9102	2651	6152	39
H(35B)	8854	2164	4893	39
H(37A)	7932	10528	6322	83
H(37B)	6916	10537	5032	83
H(37C)	8287	10174	5303	83

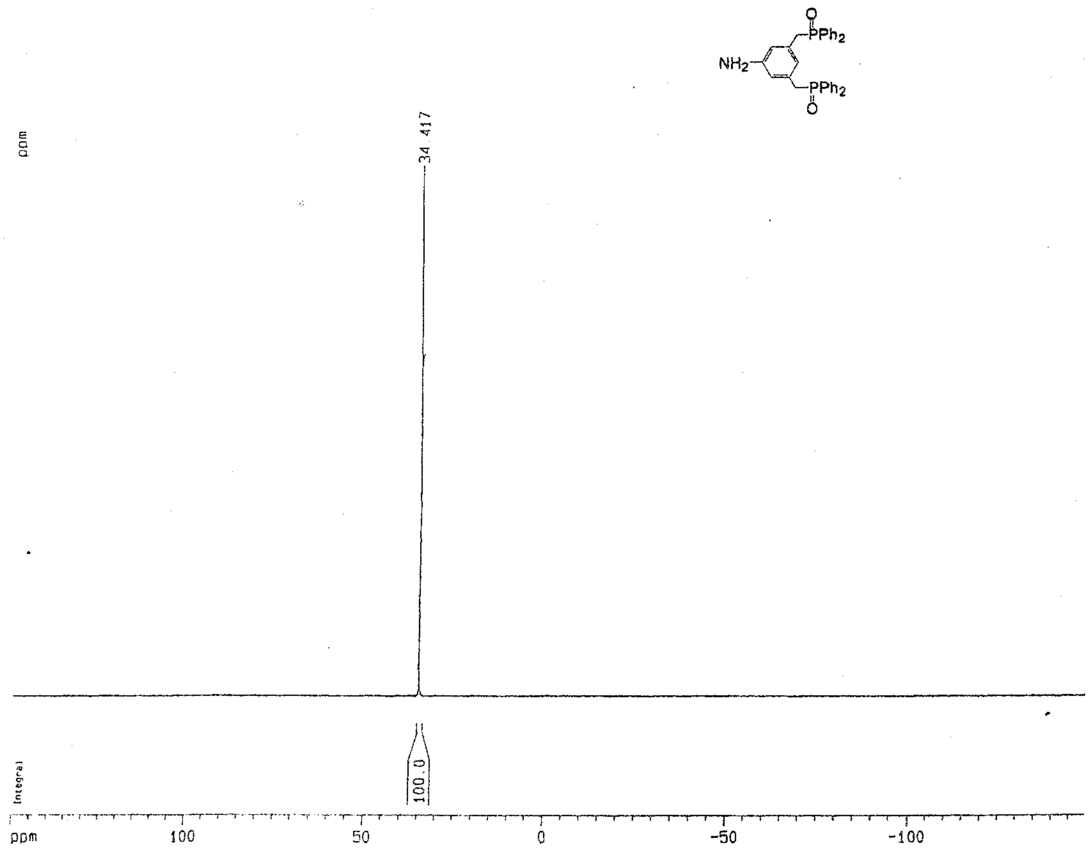
6.3 ^{31}P NMR of Complex 34, R = Ph



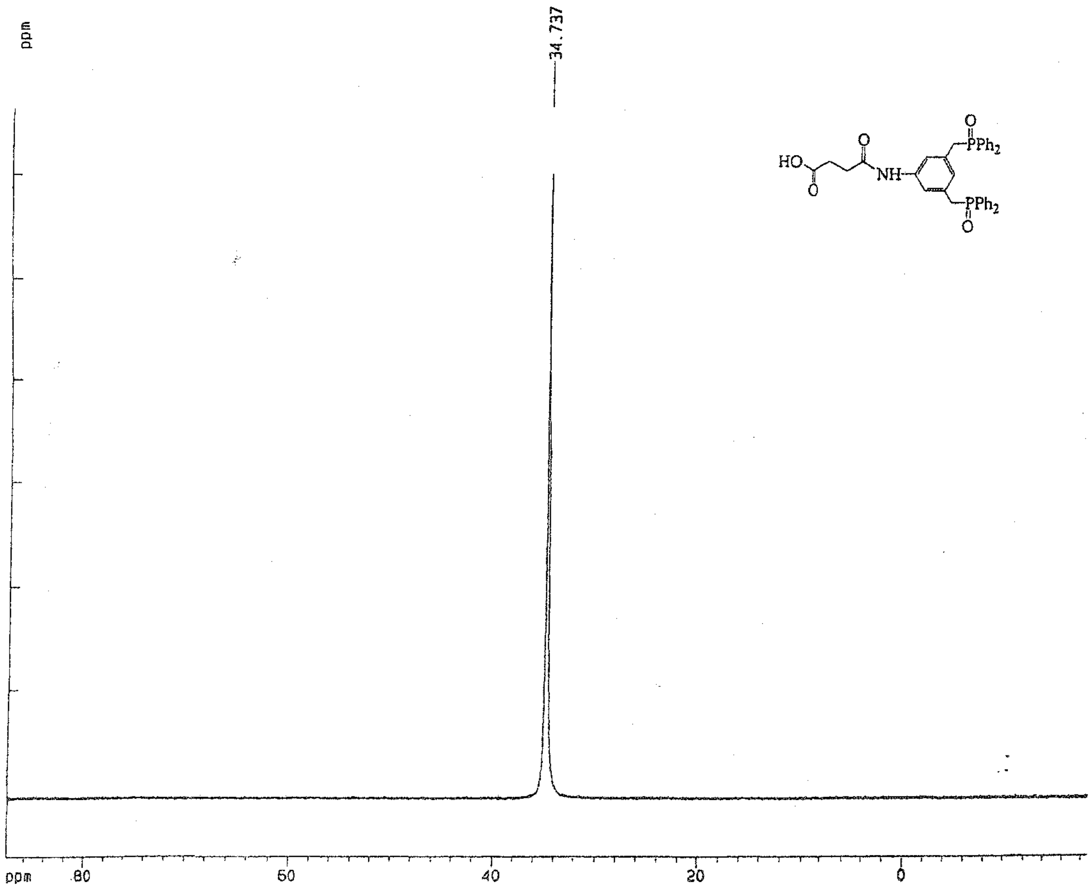
6.4 ^{31}P NMR of *N*-[3,5-Bis(diphenylphosphinoylmethyl-phenyl)]acetamide (117)



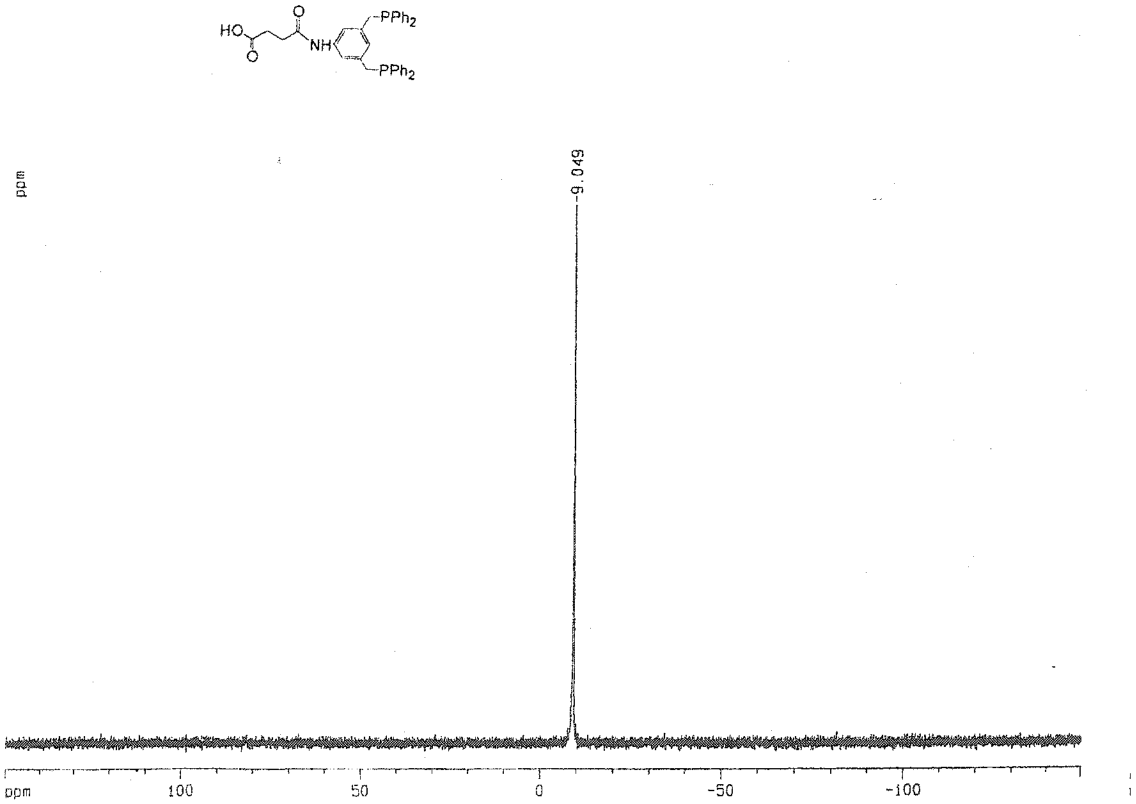
6.5 ^{31}P NMR of 3,5-Bis(diphenylphosphinoylmethyl)-phenylamine (118)



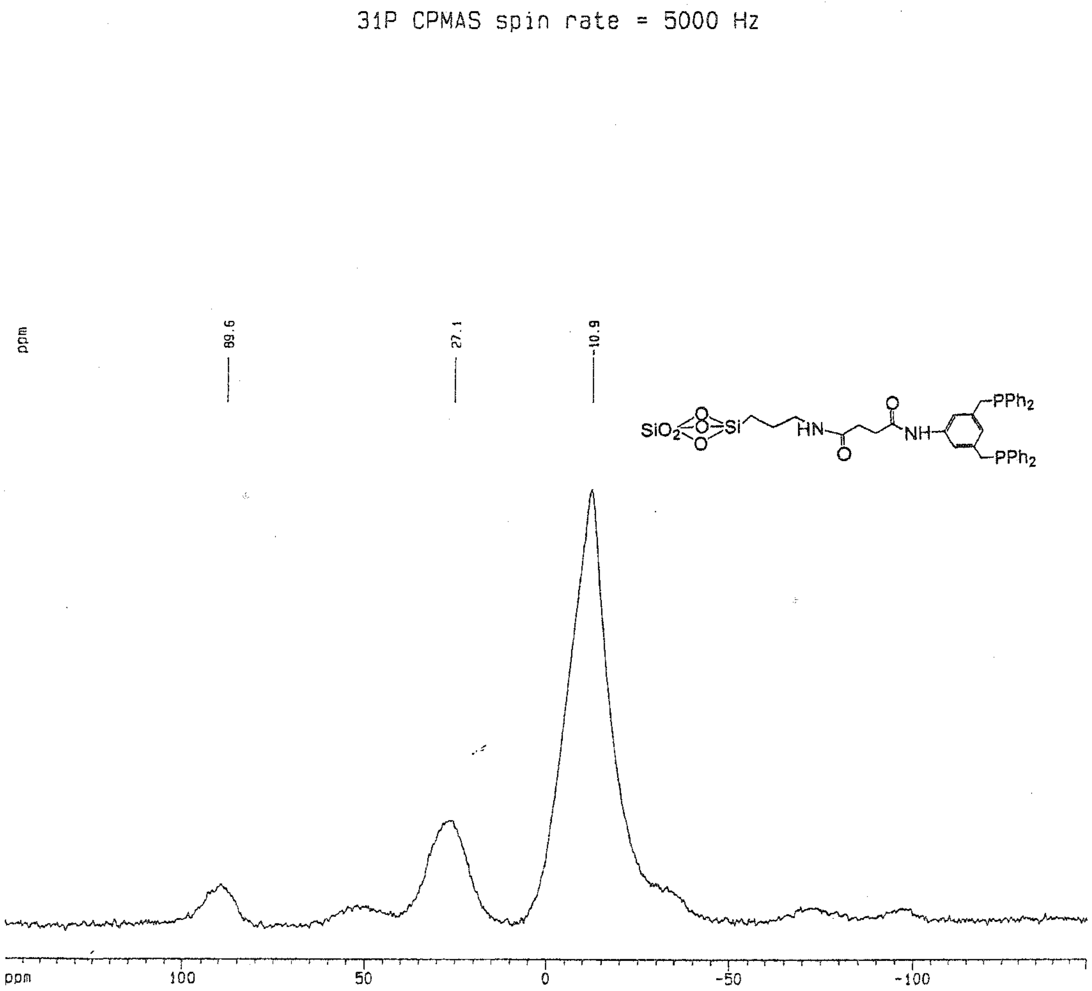
6.6 ^{31}P NMR of *N*-[3,5-Bis(diphenylphosphinoylmethyl)-phenyl]succinamic Acid (119)



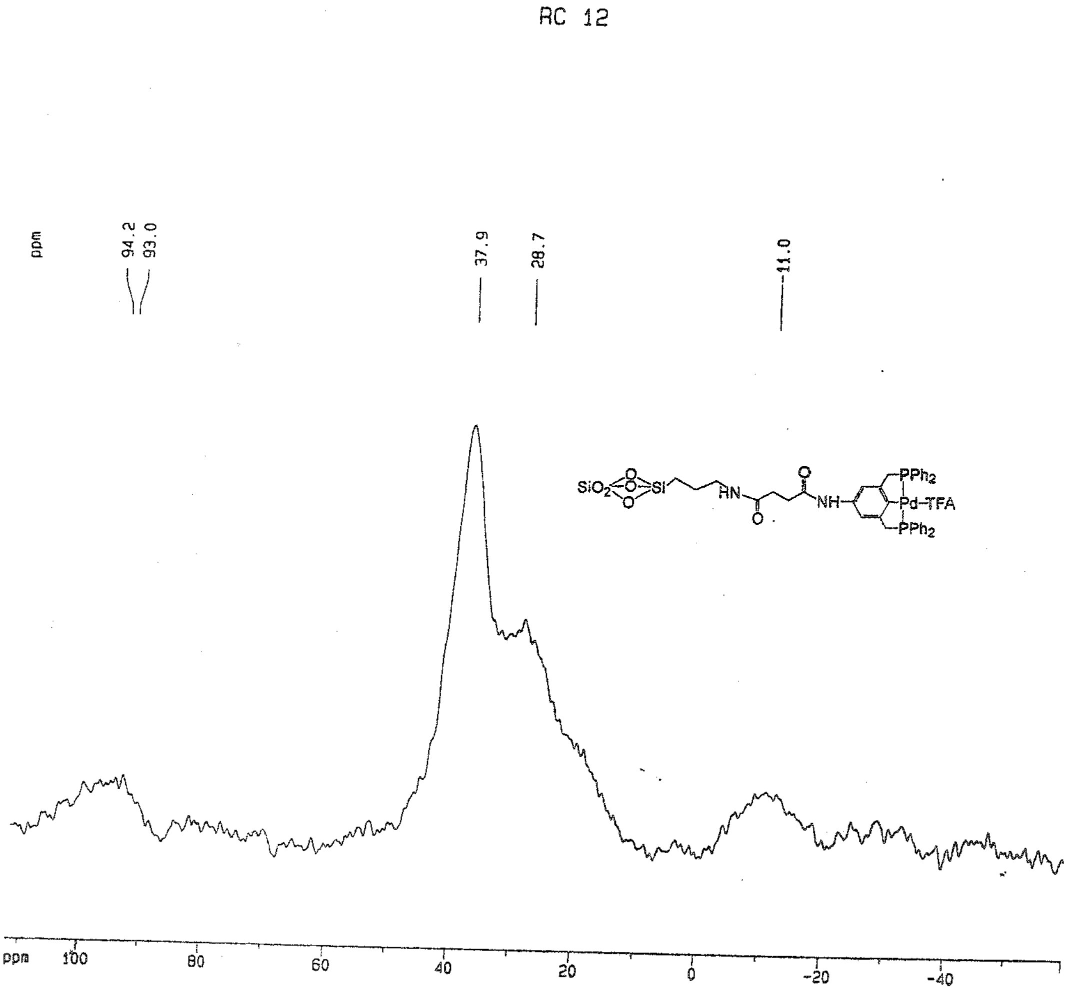
6.7 ^{31}P NMR of *N*-[3,5-Bis(diphenylphosphanylmethyl)-phenyl]succinamic Acid (120)



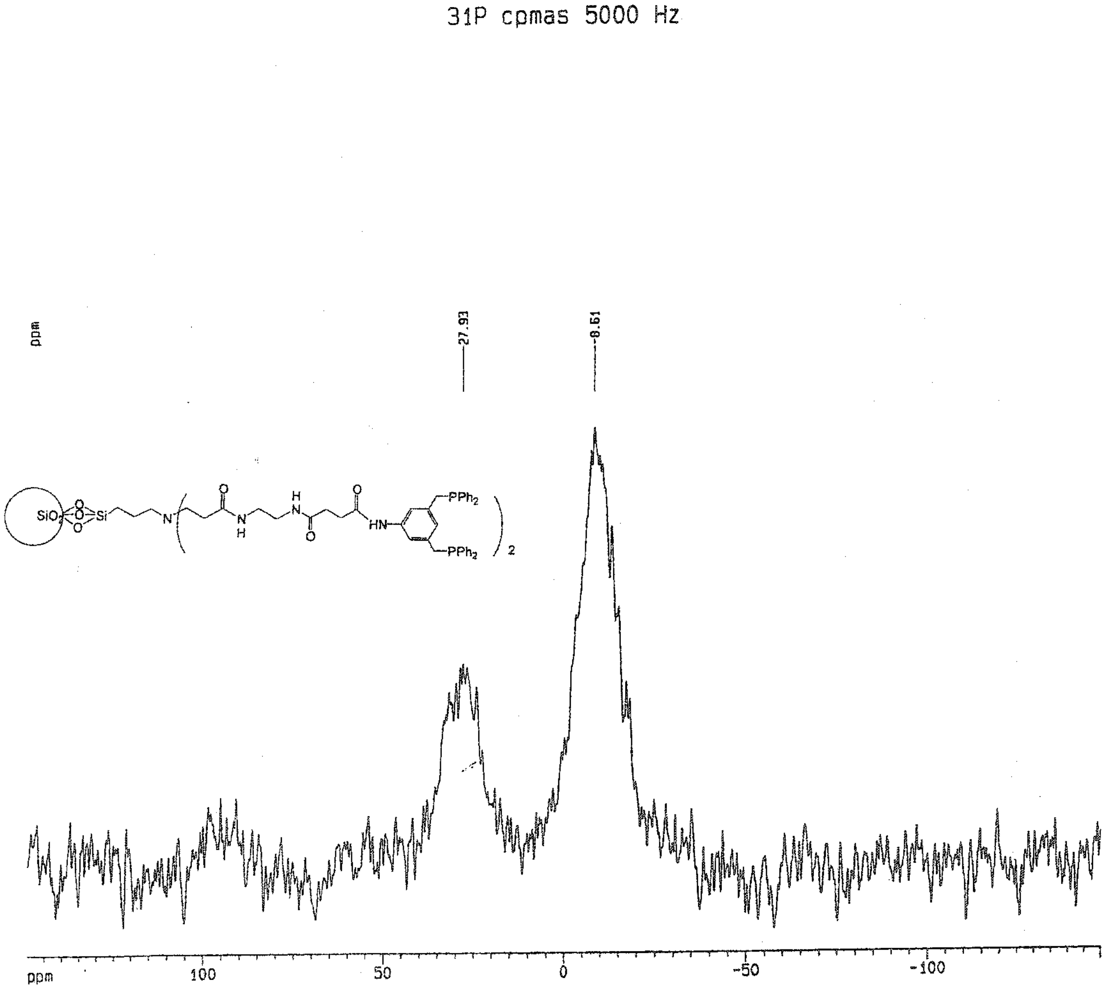
6.8 ^{31}P CP/MAS NMR of 122



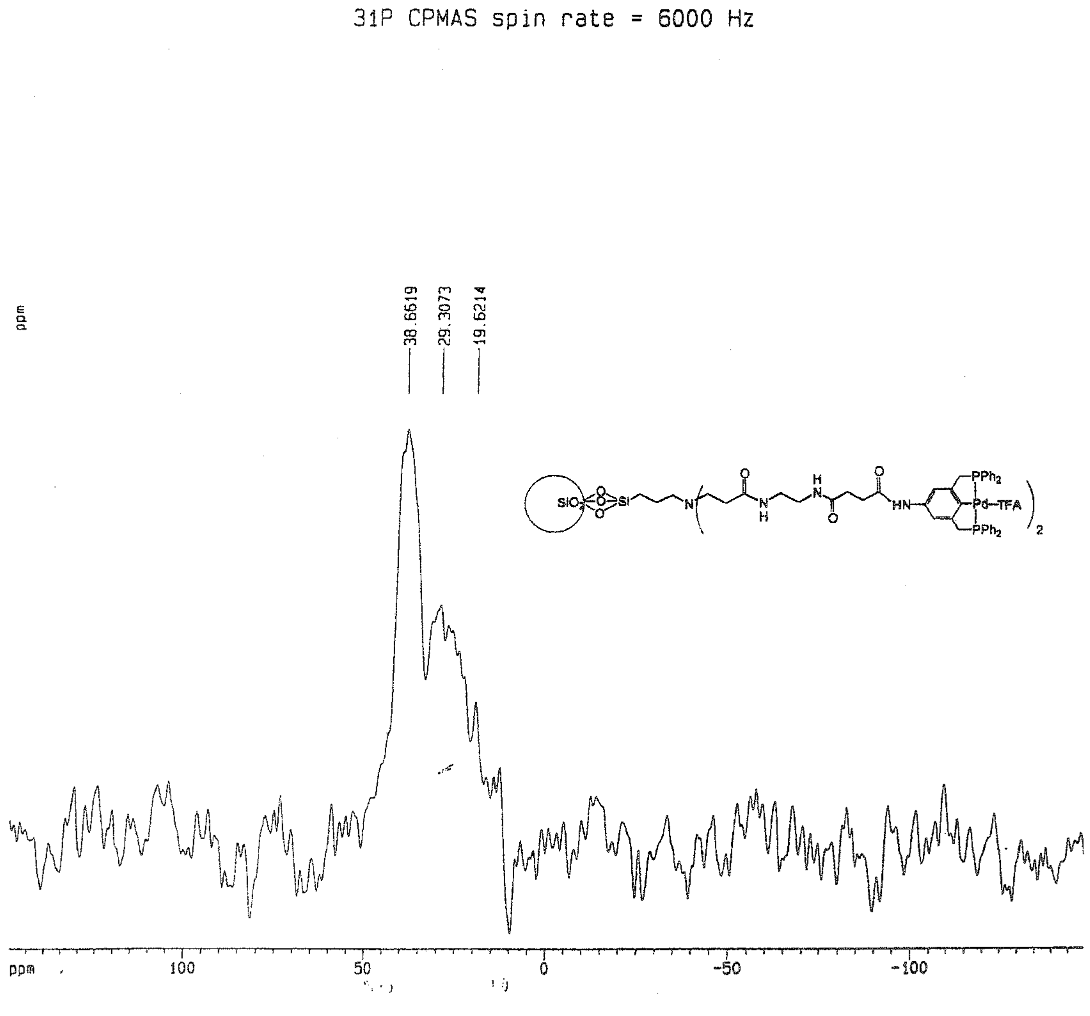
6.9 ^{31}P CP/MAS NMR of Generation Zero Dendrimer (G-0) (A)



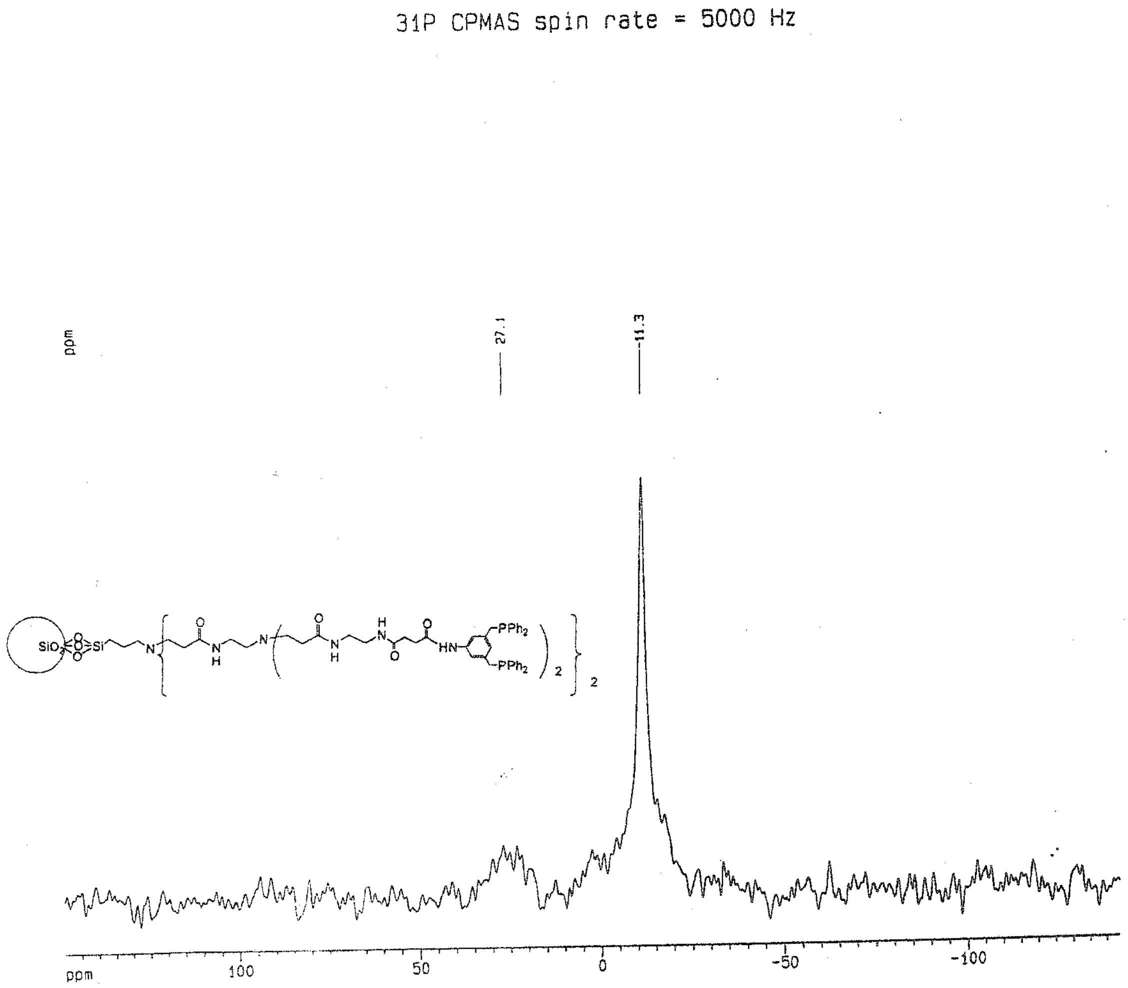
6.10 ^{31}P CP/MAS NMR of 125



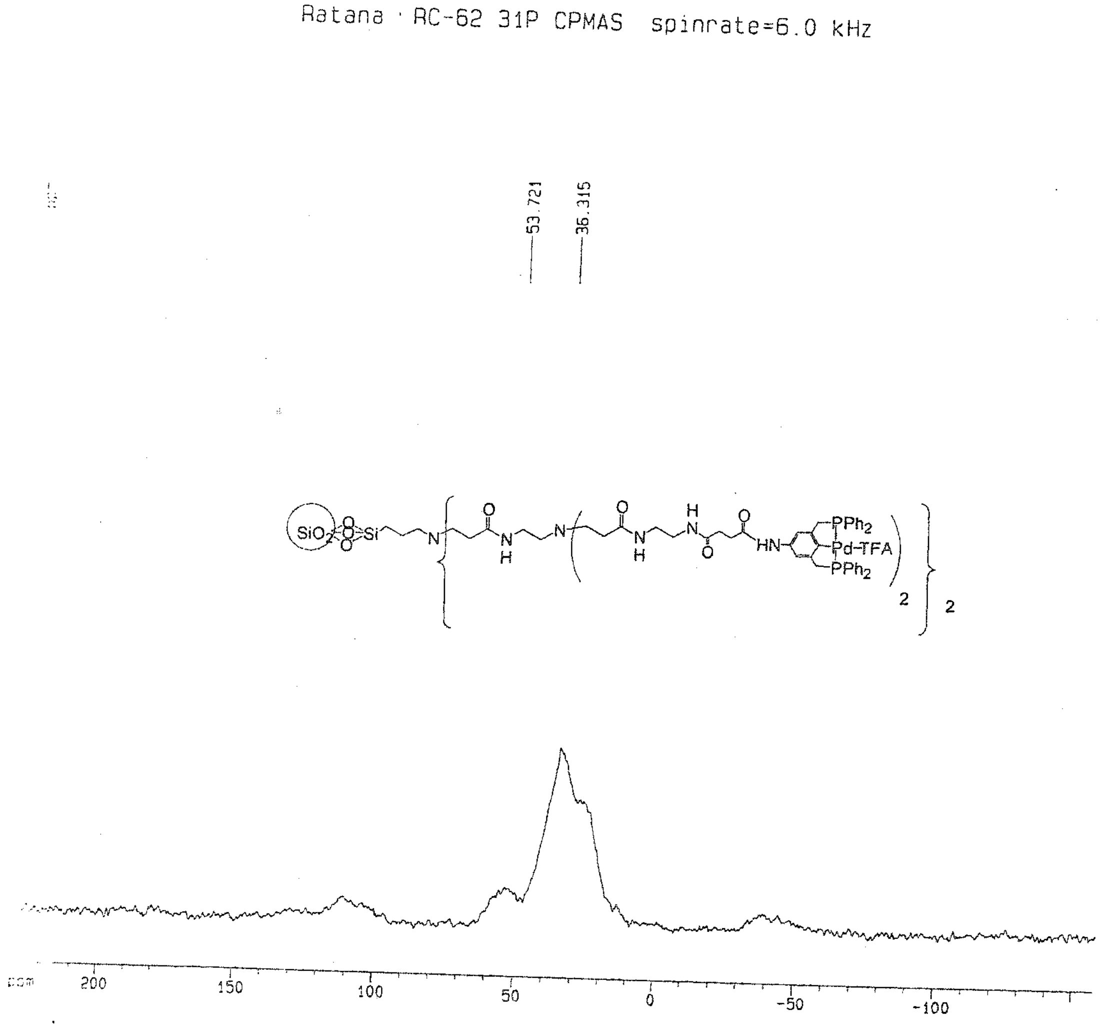
6.11 ^{31}P CP/MAS NMR of Generation One Dendrimer (G-1) (B)



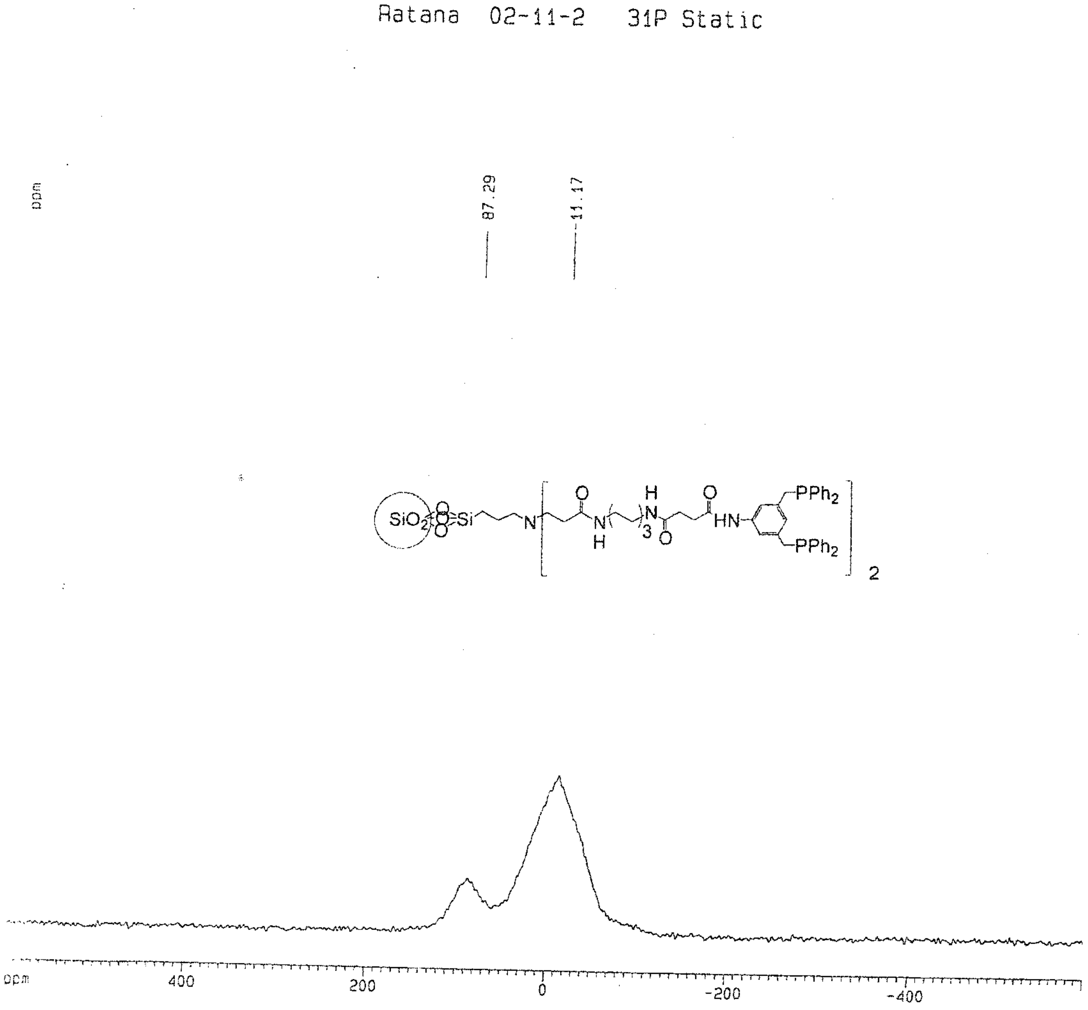
6.12 ^{31}P CP/MAS NMR of 127



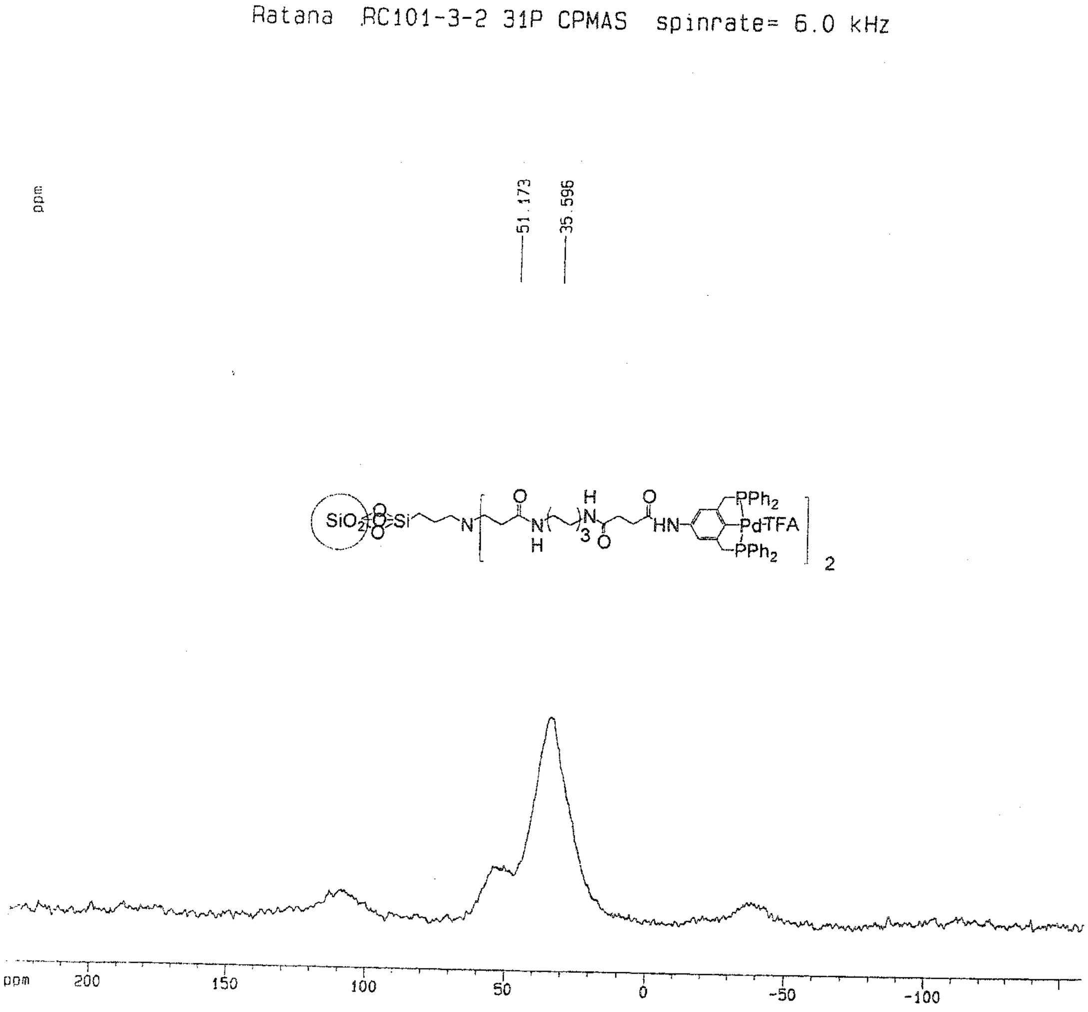
6.13 ^{31}P CP/MAS NMR of Generation Two Dendrimer (G-2) (C)



6.14 ^{31}P CP/MAS NMR of 129



6.15 ^{31}P CP/MAS NMR of Generation One Dendrimer (G-1) (D)


Ratana RC101-3-2 31P CPMAS spinrate= 6.0 kHz

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Claims to Original Research

1. The successful immobilization of a PCP-type palladium(II) complex onto silica and silica supported dendrimers combine the advantages of heterogeneous and homogeneous catalysts under mild conditions. These complexes are stable towards oxygen and moisture.

2. These complexes show high catalytic activity in the Heck reaction and they can be recycled by simple filtration in air and reused with little or moderate loss of activity.

3. These complexes are also effective recyclable catalysts for the synthesis of five- or seven-membered ring lactones in good selectivity and in high yields.

Publications

- ☐ Chanthateyanonth, R.; Alper, H., The First Synthesis of Stable Palladium(II) PCP-Type Catalysts Supported on Silica–Application to the Heck Reaction, *J. Mol. Catal. A,* **2003**, *201*, 23.

- ☐ Chanthateyanonth, R.; Alper, H., Recyclable Tridentate Stable Palladium(II) PCP-type Catalysts Supported on Silica for the Selective Synthesis of Lactones, *Adv. Synth. Cat.,* **2004**, *346*, 1375.