Studies of Metathesis for Materials Applications: Present and Future Possibilities

By

Joshua Marleau-Gillette

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Centre for Catalysis Research and Innovation
Department of Chemistry
Ottawa-Carleton Chemistry Institute
Faculty of Science
University of Ottawa

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Abstract

Compounds containing multiple metal-carbon bonds are now widely used as catalysts for organic and materials synthesis. Among such transformations, olefin metathesis (OM) occupies a position of pre-eminent significance. Alkyne metathesis holds great promise, but remains in a much lower state of development. The OM-directed work in this thesis sought to advance the state of the art in living, Ru-catalyzed ring-opening metathesis polymerizations (ROMP). Currently, the first- and third-generation Grubbs initiators, which exhibit the ease of handling characteristic of the late metal ruthenium, dominate ROMP applications. These initiators are characterized by extremes of reactivity, however. We describe the first ruthenium initiator capable of living ROMP at RT, irrespective of monomer bulk. Polydispersity indices as low as 1.03 are routinely attainable, and excellent control is maintained in synthesis of diblock copolymers from sterically demanding and sterically unencumbered monomers. Work on alkyne metathesis sought to expand existing understanding of the features that influence stability and reactivity in ruthenium carbynes. A classification system was developed in which Class A carbynes were defined as those that readily undergo conversion into an M=C entity (e.g. vinylidene, allenylidene, or alkylidene); Class B carbynes those that have a stable carbyne functionality. Four Ru carbyne complexes, all initially regarded as prospective Class B carbynes, were selected for study. Investigation of their reactivity resulted in categorization of several as Class A species, and development of design criteria that may open the door to assembly of stable, well-defined carbyne complexes of ruthenium.

List of Compounds

Organic Compounds

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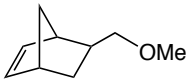
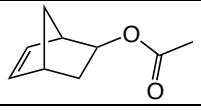
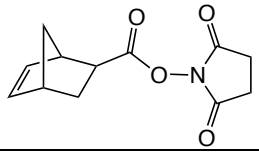
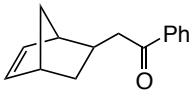
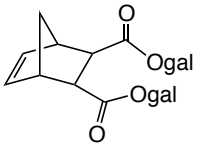
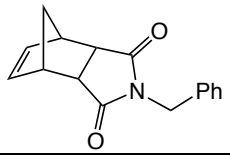
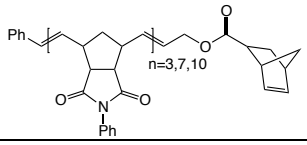
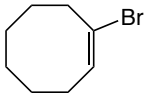
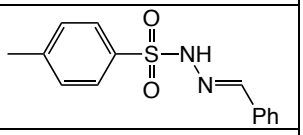
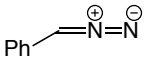
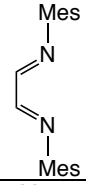
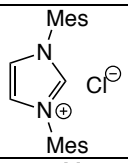
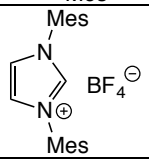
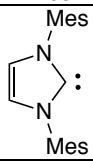
M1		**M2**	
M3		**M4**	
M5		**M6**	
M7		**1**	
2		**3**	
4		**5**	
6		**7**	
8			

Organometallic Compounds

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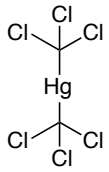
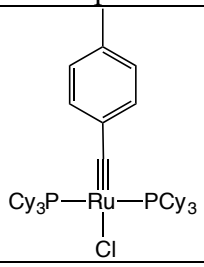
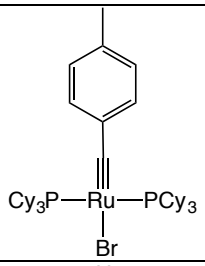
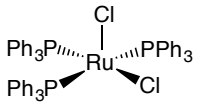
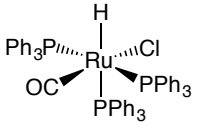
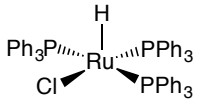
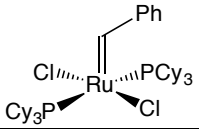
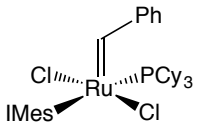
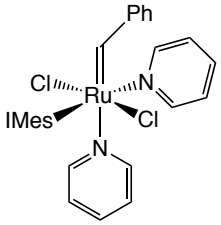
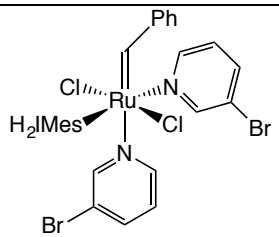
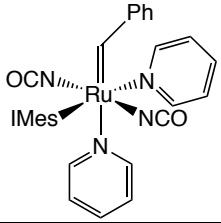
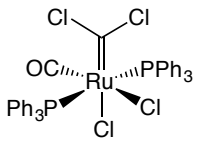
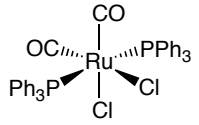
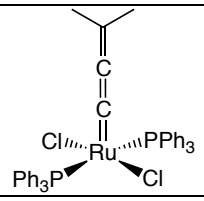
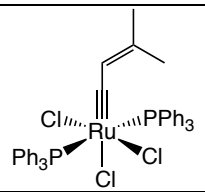
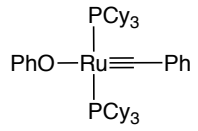
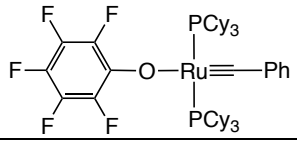
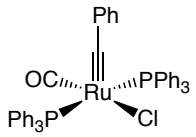
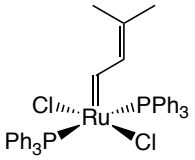
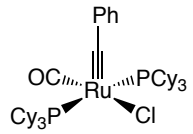
Hg-1		**Ru-Ja**	
Ru-Jb		**Ru-1**	
Ru-2		**Ru-3**	
Ru-4		**Ru-5**	
Ru-6		**Ru-7**	
Ru-8		**Ru-9**	
Ru-10		**Ru-11**	
Ru-12		**Ru-13**	

Ru-14		**Ru-15**	
Ru-16		**Ru-17**	

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List of Abbreviations

δ	Chemical shift; ppm
ACM	Alkyne cross metathesis
ADIMET	Acyclic diyne metathesis
ADMET	Acyclic diene metathesis
AM	Alkyne metathesis
ATR	Attenuated total reflectance
cat.	Catalyst
CM	Cross metathesis
COSY	Correlation spectroscopy
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
CV	Cyclic voltammetry or cyclic voltammagram
Cy	Cyclohexyl
DFT	Density functional theory
dppf	1,1'-Bis(diphenylphosphino)ferrocene
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
equiv	Equivalents
Et	Ethyl
Et_2O	Diethyl ether
EtOAc	Ethyl acetate
EVE	Ethyl vinyl ether
gal	Galactose
GPC	Gel permeation chromatography
H_2IMes	*N*,*N'*-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene
HMBC	Heteronuclear multiple bond correlation
HMQC	Heteronuclear multiple quantum coherence
HPLC	High performance liquid chromatography
Hz	Hertz (1 Hz = 1 s^{-1})

ICP-MS	Inductively coupled plasma mass spectrometry
IMes	*N*,*N'*-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene
^{i}Pr	Isopropyl
IR	Infrared
KTp	Potassium hydrotris(pyrazolyl)borate
L	Neutral donor ligand
M	Metal
Me	Methyl
MeOH	Methanol
Mes	Mesityl, 2,4,6-trimethylphenyl
M_n	Number-averaged molecular weight
MW	Molecular weight
NBE	Norbornene
^{n}Bu	Normal butyl
NHC	*N*-heterocyclic carbene
NHS	*N*-hydroxysuccinimide
NMR	Nuclear magnetic resonance
NOESY	Nuclear Overhauser effect spectroscopy
OAr	Aryloxide
OM	Olefin metathesis
OTf	Trifluoroacetate
PDI	Polydispersity index
Ph	Phenyl
ppm	Parts per million (μg/g)
py	Pyridine
py*	3-bromopyridine
RCAM	Ring closing alkyne metathesis polymerization
RCM	Ring closing metathesis
R_f	Retention factor
ROAMP	Ring-opening alkyne metathesis polymerization
ROMP	Ring-opening metathesis polymerization

RT	Room temperature
rx	Reaction
^{t}Bu	*tert*-butyl
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMB	1,3,5-Trimethoxybenzene
wt	Weight, in %
X	Anionic donor ligand
xs	Excess

Acknowledgements

First and foremost, I cannot thank you enough Deryn for this wonderful opportunity that you've provided for me. Initially, I was far too humble to think that pursuing a graduate degree in chemistry was something I was capable of, but you saw potential in me that I was completely oblivious to. Graduate school has certainly been one of the most unforgettable periods of my life and in that time I have grown such a deeper appreciation for research. If it were not for your confidence in me I would have never experienced this extraordinary adventure, and for that I am forever grateful.

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To my closest friends Colin, Evan, Jill, John, Nick, and Phil, if it were not for your ever-present striving for success and your fantastic life advice I would not be where I am today. Thank you all.

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Chapter 1: Introduction

1.1 Introduction

Compounds containing metal-carbon multiple bonds are now widely used as catalysts for organic and materials synthesis.[1-4] Among such transformations, olefin metathesis (OM) occupies a position of pre-eminent significance. Alkyne metathesis holds great promise, but is in a lower state of development. Many transition-metal complexes catalyze olefin and alkyne metathesis; however, ruthenium systems now dominate OM, and are highly desired for AM. This stems from the functional group tolerance and lower oxophilicity of the ruthenium complexes, as described below. Ru-promoted ring-opening metathesis polymerization is a particularly powerful metathesis reaction for the synthesis of functional materials. However, improvements are still needed. Of the hundreds of Ru metathesis catalysts now known, very few initiators are capable of controlled ROMP with precise specification of molecular weights, and hence polymer properties. In comparison, the state of development in Ru-promoted alkyne metathesis is many years behind. Very few ruthenium carbynes have been synthesized, and none to date are active for alkyne metathesis. The primary goals of the research in this thesis were to improve on the state of the art in terms of Ru initiators for living ROMP, and to improve the fundamental understanding of the parameters involved in designing a stable ruthenium carbyne complex.

1.2 Olefin Metathesis

1.2.1 A Brief History of Olefin Metathesis (OM)

Olefin metathesis dates back to the 1950s, to work at Du Pont involving

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norbornene polymerization with catalyst systems consisting of $TiCl_4$ and a reducing agent (EtMgBr or $LiAl(C_4H_9)_4$).[5] In later years an array of metals was found to promote such reactivity: Ti, V, Mo, Ru, Ta, W, Re, Os, and Ir.[4] Particular success was achieved with molecular Mo and Ru catalysts designed by Schrock and Grubbs, respectively. The Mo systems stand out for their high metathesis activity and truly impressive control over selectivity. The Ru catalysts are now more popular because of their higher stability to oxygen and water, which makes them easier to handle. They also show greater tolerance toward certain functional groups (e.g. aldehydes and alcohols), by which they are decomposed more slowly than the Mo systems.

In 1970, Chauvin proposed that metathesis occurs via [2+2] cycloaddition and cycloreversion between a metal alkylidene and an alkene, involving (in its simplest form) olefin cross metathesis (CM).[6] A key intermediate is the metallacyclobutane species (Scheme 1). Very recently, Piers has succeeded in observing the metallacyclobutane by low-temperature NMR analysis for Ru systems.[8] Based on the Chauvin mechanism, several related metathesis reactions may occur, depending on the olefin geometry and reaction conditions (Figure 1).[4,9,10] Ring-closing metathesis (RCM) is favoured at low concentrations, for example if given a terminal acyclic diene, while acyclic diene metathesis (ADMET) polymerization is favoured at high concentrations of the same diene substrate. Ring-opening metathesis polymerization (ROMP), one of the main focuses of this thesis work, transforms highly strained cyclic olefins into polymers with a degree of control that depends on monomer ring strain and initiator reactivity and selectivity. Initiators currently in use for this process will be discussed in Chapter 3.

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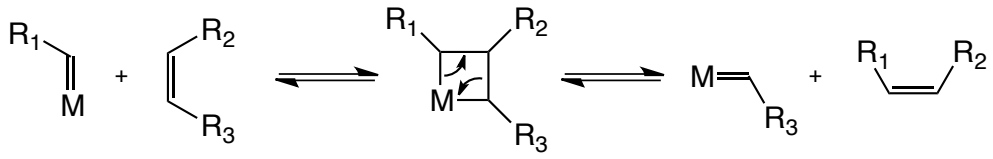

Scheme 1. Chauvin mechanism for olefin metathesis.

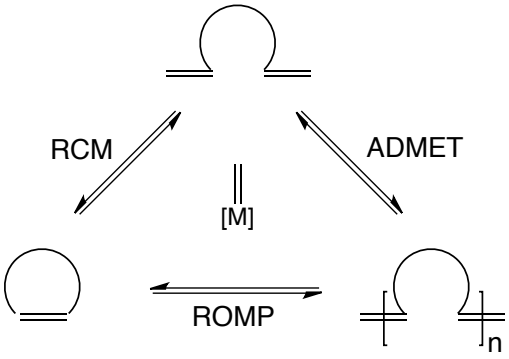

Figure 1. Key olefin metathesis reactions.

1.2.2 Ring-Opening Metathesis Polymerization (ROMP)

ROMP is a chain growth polymerization process based on ring-opening of cyclic olefins via the Chauvin mechanism (Figure 2). As noted above, ROMP dates back 60 years. With the advent of easily-handled, functional-group tolerant Ru catalysts, it has emerged as a powerful method for synthesis of "designer" materials.[11-15] Prominent applications are therapeutic uses ranging from tumor imaging to tissue engineering, drug delivery and antimicrobial action.[16-20] Other key uses include separations science and heterogeneous catalysis, microelectronics, sensor applications, and energy storage.[15,21-25]

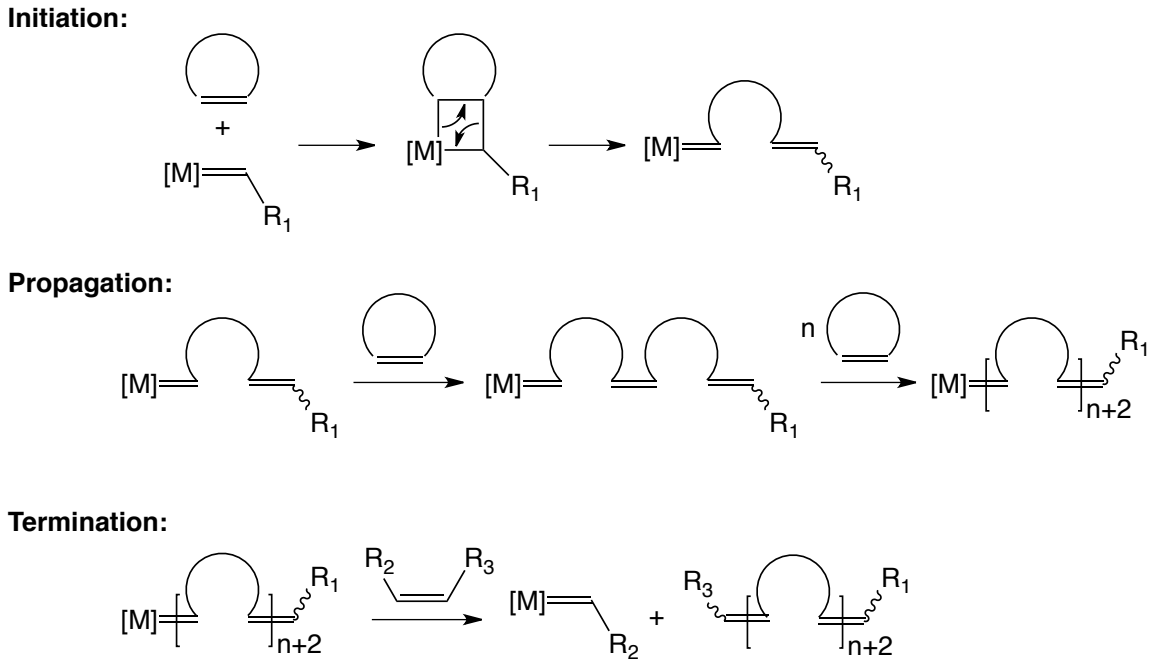

Figure 2. Reaction pathways for ROMP of a cyclic olefin.

The reversibility of olefin metathesis reactions (Figure 1) implies an equilibrium distribution of products. In cycloolefin ROMP, however, ring-opening is thermodynamically driven by release of ring strain. Ring sizes of 3, 4, 8 and higher are typically characterized by sufficient strain, while 5-7-membered rings are more problematic.[26] Secondary metathesis involving the olefin groups in the polymer backbone permit chain transfer and backbiting, the latter generating cyclic oligomers (Figure 3).[11,27]

Such ring-chain equilibria are concentration-dependent, as predicted by Jacobson-Stockmayer theory.[10,27,28] Several other factors can also affect the proportion of cyclic oligomers generated in the approach to equilibrium: the catalyst system, the reaction time, the nature of the solvent, and the cis/trans geometry of the backbone olefins, which affects ring strain. At high concentrations, ROMP is favoured; at high dilutions, cyclic

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species dominate.[10,29] Indeed, the latter conditions are essential for ring-closing metathesis (RCM), which can be recognized as the reverse of ROMP.

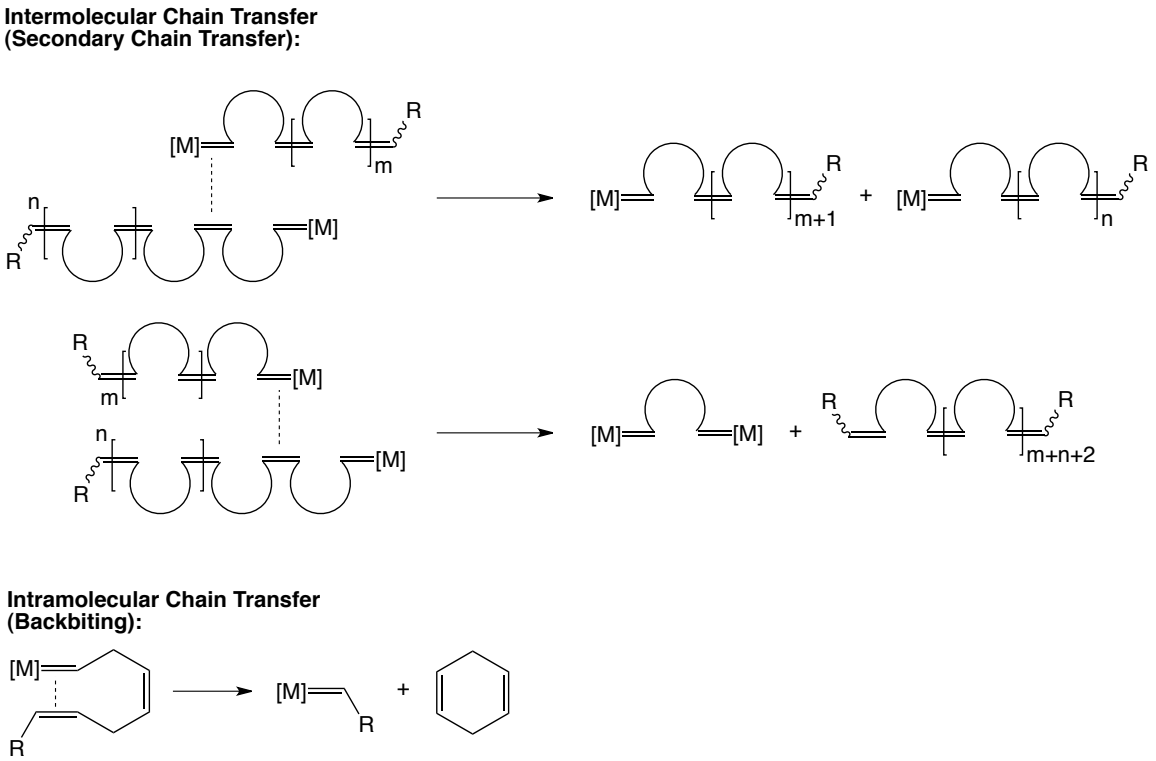

Figure 3. Secondary metathesis in ROMP. (Top) Intermolecular chain-transfer. (Bottom) Intramolecular chain-transfer (backbiting).

1.2.3 Living Ring-opening Metathesis Polymerization

A "living" polymerization was defined in 1956 by Szwarc as one that proceeds without termination *or chain transfer*[30] (italics added). The IUPAC definition stands as "chain polymerizations from which chain-transfer and chain-termination reactions are absent".[31] This definition was improved by Matyjaszweski, who pointed out that no polymerization is immortal, and instead proposed a ranking scheme with different degrees of livingness. Thus, Class I living systems are stable for ca. 1 sec in the absence of monomer, Class II for ca. 10 sec, Class III for ca. 2 min, Class IV for ca. 18 min, and

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Class V for ca. 3 h. Class VI living systems are stable for ca. 1 day with no monomer present.

The stipulation that living systems cannot undergo facile chain transfer is frequently overlooked, but in fact is key to the control over chain lengths typical in such systems. In conjunction with the long lifetime of a living catalyst, this means that chain propagation cannot dominate over initiation. This has direct implications for the relative size of the rate constants for initiation (k_i) and propagation (k_p), where for highly living polymerizations, k_i must be larger than k_p. Lower k_p/k_i ratios translate into more precise specification of polymer chain lengths.[33,34] The number-average molecular weight (M_n) then approaches the calculated molecular weight of the polymer, and the polydispersity index (PDI) is close to 1; see Equations 1 and 2.

(1) $$\frac{k_p}{k_i} = \frac{\frac{-M_0}{I_0}}{\ln\left(\frac{I_t}{I_0}\right) + (I_t)\left(\frac{I_t}{I_0} - 1\right)}$$

M_0 = Initial monomer concentration
I_0 = Initial initiator concentration
I_t = Initial concentration at time t

(2) $$PDI = \frac{M_w}{M_n}$$

M_w = Weight-averaged molecular weight
M_n = Number-averaged molecular weight

1.2.4 The Mechanism of Ru-Catalyzed Olefin Metathesis

The square pyramidal geometry characteristic of ruthenium metathesis catalysts, coupled with the high trans influence of the alkylidene ligand (which constrains this group to occupancy of the apical site), means that olefin binding requires an empty coordination site in the basal plane.[35] In the case of the Grubbs catalysts, loss of a PCy_3 ligand from the basal plane gives a 14-electron active species, which can either re-bind

PCy_3, react with olefin (Figure 4), or decompose. Olefin binding is followed by [2+2] cycloaddition to form the key metallacyclobutane intermediate. Retro-addition releases a newly formed olefin and regenerates the 14-electron species to repeat the process.

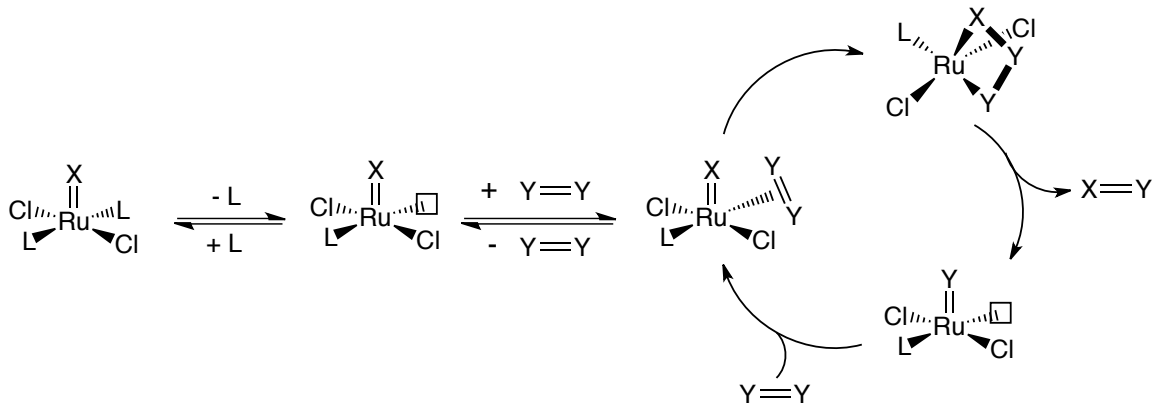


Figure 4. Mechanism for olefin metathesis via Ru catalysts.

Evidence for the catalytic cycle shown in Figure 4 has been reported by many groups. Some of the most important findings came from the Piers NMR study,[8,39] a very similar study subsequently conducted by Grubbs, and X-ray analysis from the Grubbs[36-38] and Snapper groups.[40] In particular, the ground-breaking discovery by Piers clarified the trigonal bipyramidal geometry of the metallacyclobutane intermediate. The previously-reported square pyramidal geometry found by Snapper and Grubbs was misleading, arising from perturbations created by the substrate.

1.3 Alkyne Metathesis

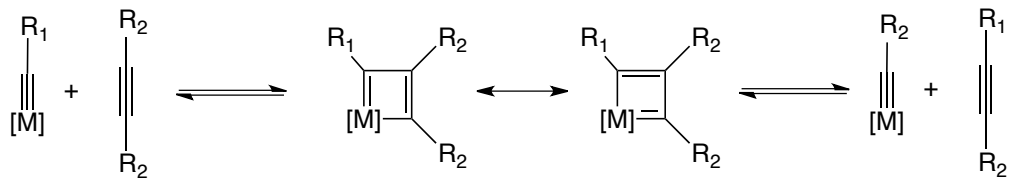
1.3.1 A Brief History of Alkyne Metathesis (AM)

Alkyne metathesis is much less investigated than olefin metathesis. Early examples of AM date back to 1968, when Pennella et al. studied systems derived from

WO_3 on silica.[41] In 1974, Blanchard and Mortreux discovered the first homogenous catalysts for AM, derived from $Mo(CO)_6$ and resorcinol.[42] A resurgence of interest in the past decade[43-46] has developed highly active group 6 AM catalysts.[43,47] Schrock carbynes stand as the benchmark for AM reactions. However, as with the group 6 OM catalysts, they are plagued by oxophilicity and lack of functional group tolerance. No AM-active ruthenium catalysts have been identified to date, in part because of the poor stability of most of the Ru carbynes. A fuller description of the established Mo/W alkyne catalysts and the structures of Ru carbynes appears in Chapter 4.

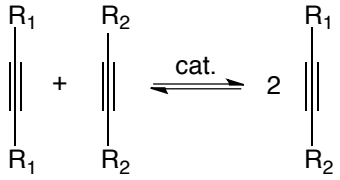
1.3.2 Mechanism for Alkyne Metathesis

The mechanism for alkyne metathesis is thought to be similar to the Chauvin mechanism for olefin metathesis. Scheme 2 shows the pathway proposed by Katz in 1975, for which experimental evidence was reported by Schrock in 1981.[48,49] Coordination of alkyne is followed by insertion via a [2+2] cycloaddition to form the metallacyclobutadiene intermediate. Through resonance the intermediate undergoes retrocycloaddition and produces a new alkyne. Reaction variants include alkyne cross metathesis (ACM), ring-closing alkyne metathesis (RCAM), ring-opening alkyne metathesis polymerization (ROAMP), and acyclic diyne metathesis (ADIMET) polymerization (Figure 5). The metallacyclobutadiene intermediate was characterized by crystallography using the complex $[W(C_3Et_3)(O\text{-}2,6\text{-}C_6H_3\text{-}^iPr_2)_3]$.[50]

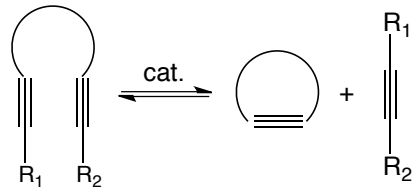


Scheme 2. Katz mechanism for alkyne metathesis.

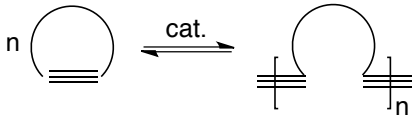
Alkyne cross-metathesis (ACM)



Ring-closing alkyne metathesis (RCAM)



Ring-opening alkyne metathesis polymerization (ROAMP)



Acyclic diyne metathesis polymerization (ADIMET)

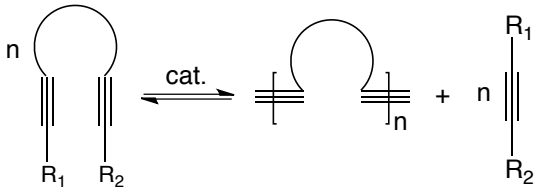
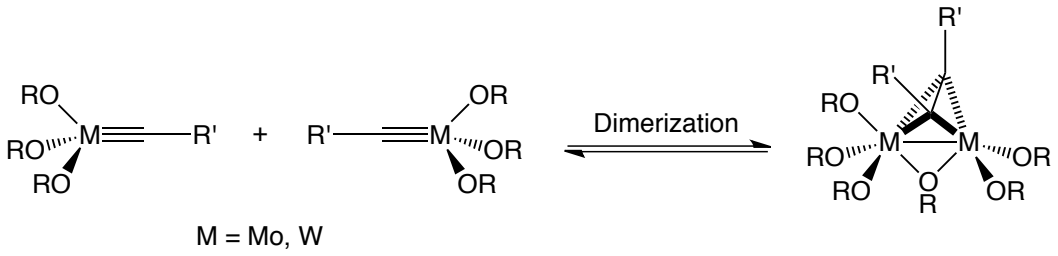


Figure 5. Examples of alkyne metathesis (AM) reaction types.

An important factor in AM, and for catalyst design, is the use of bulky ligands on the metal center. Mo and W alkylidyne catalysts are usually in equilibrium with alkyne adducts (i.e. dimerization products; Scheme 3).[51,52] This suggests that bulky R or R' groups will favor the alkylidyne side of the equilibrium. Insufficient bulk will favour dimerization products and catalyst deactivation.[52]



Scheme 3. Equilibrium between the metal alkylidyne and the dimerization product.

1.3.3 Alkyne Metathesis Applications

Alkyne metathesis enables powerful routes to natural products and conjugated polymers.[44,47] Some of the first approaches to natural product synthesis were conducted by Fürstner in RCAM to produce musk-odoured compounds.[46,53] Synthesis of *E*- or Z-macrocyclic olefins was achieved by AM followed by Lindlar or Birch reduction.[54] RCAM/reduction has also been applied to synthesis of the natural products Epothilones A and C and lactrunculin.[55]

Conjugated polymers attainable via ROAMP range from the very simple to the complex. Schrock first demonstrated the ring-opening of cyclooctyne, albeit PDIs were very high (≥4).[56] Conducting silane polymers have also been prepared,[57] and living polymerization of a complex annulyne monomer was recently described.[58] Other conducting polymers can be formed by ADIMET, such as poly(p-phenylene-ethynylene)s or poly(arylene-ethynylene)s.[59-61]

1.4 Ligands: Type and Function in Metathesis

1.4.1 Neutral and Anionic Ligands

Modification of the neutral "placeholder" ligand, which must dissociate to open a vacant site for metathesis to occur, has been shown to dramatically alter the activity of

the catalyst. Examples (Figure 6) include PCy_3 (**GI**, **GII**),[62,63] styrenyl ether (the ether moiety, **HIIa**,**b**),[64] pyridine and 3-bromopyridine (**GIIIa-d**).[65,66] The more labile the placeholder ligand, the higher the activity of the catalyst. Thus, use of PPh_3 or pyridine ligands rather than PCy_3 significantly increases initiation rates.[35,66] Grubbs has reported that the higher activity of such systems is due almost solely to enhanced initiation, not propagation.[35]

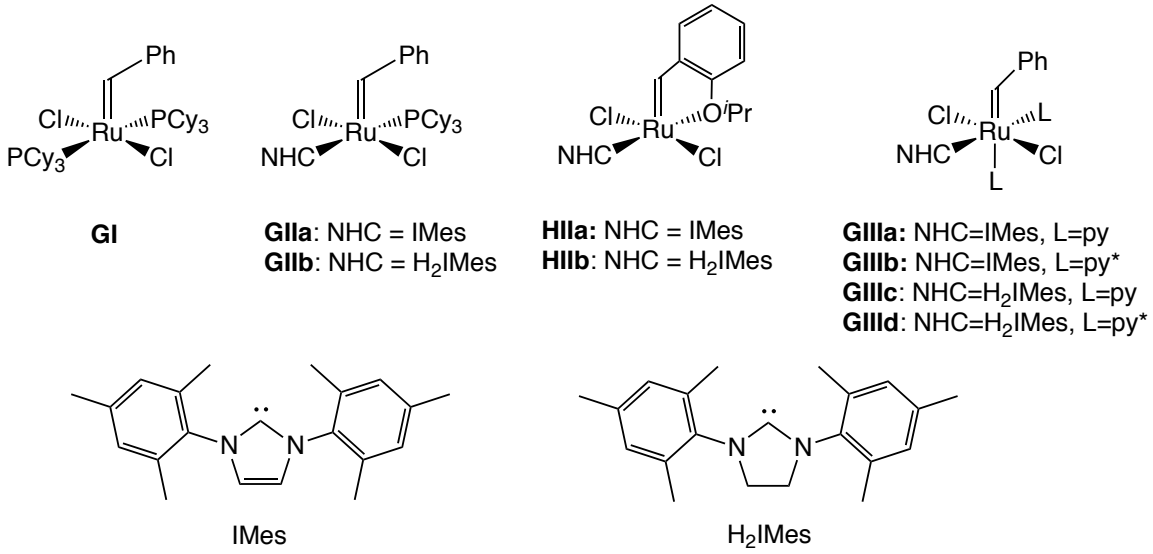


Figure 6. Key Grubbs-class metathesis catalysts.

Changing the anionic ligands was initially suggested by the Fogg group as a means of addressing decomposition pathways enabled by the chloride ligands on the Grubbs catalysts.[67-70] Aryloxide ligands showed the further advantage of high polarity in the ligand itself, which facilitated removal of Ru residues by chromatography.[73,74] The electron-deficient aryloxides required for catalyst stability[75,76] are not useful in ROMP, however, as they suffer from low initiation efficiency (see **1.4.3**).

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1.4.2 NHC Ligands

N-heterocyclic carbene (NHC) ligands have transformed olefin metathesis for applications in organic synthesis.[77] Incorporation of these donors into the Grubbs catalyst **GI** affords "second-generation" Grubbs catalysts,[63,78,79] of which most studied have been examples containing IMes and H_2IMes ligands (Figure 6). The H_2IMes derivative is most commonly employed due to its commercial availability. The NHC ligand confers higher metathesis activity, strong σ-donation, and steric protection, although steric protection is a balance between inhibiting catalyst decomposition and impeding substrate binding.[80]

1.4.3 Ligand effects in ROMP

The reactivity of complexes based on the $RuCl_2(PR_3)_2(=CHPh)$ structure can be tuned by altering the phosphine ligands,[72] the alkylidene group,[62] or the chloride ligands.[81] Even small changes to the phosphine ligand can have dramatic effects. For example, use of $PCy_2CH_2SiMe_3$ accelerates initiation but results in slower propagation compared to **GI**.[82] Installation of an *N*-heterocyclic carbene to give a second-generation Grubbs catalyst (**GII**) has the opposite effect. Polymers obtained using **GII** have very broad PDIs (>1.10) and very high molecular weights.[12] Several theoretical studies have investigated these rates and data.[74,83-86] Similar behaviour is observed for **HII** and Ru aryloxide complexes. In third-generation Grubbs complexes (**GIII**) two pyridine ligands are present. These initiate very rapidly and enable controlled ROMP of bulky norbornenes.[87] As described in Chapter 3, however, this high reactivity results in poor structural control in ROMP of unencumbered monomers.[88] Better-controlled initiators are thus desired.

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1.5 Decomposition of Grubbs Catalysts

The active species in Ru metathesis catalysts contain a common core (Figure 7). Similar catalyst deactivation pathways are thus expected. These may involve hydride formation; decomposition via attack of free phosphine on the alkylidene functionality,[35,70] or C-H bond activation with the alkylidene.[89,90,91] Decomposition can also be attributed to oxidation of the catalyst by air, or reaction with protic agents such as alcohols.[92-97] Decomposition can also occur in chlorinated solvents. Dimerization of a Ru-dcypb complex has been observed in CH_2Cl_2 or $CDCl_3$ (dcypb = bis(dicyclohexyl)-1,4-phosphinobutane) to form a mixed-valence complex,[98] while Blechert has reported decomposition of **HII** within an hour in $CDCl_3$.[99]

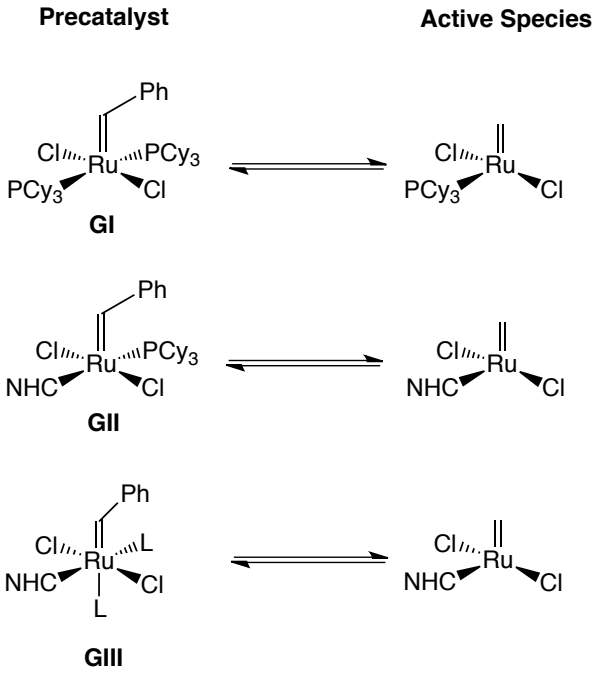

Figure 7. Key Ru Grubbs precatalysts and active species derived from these.

1.6 Scope of this Thesis

This work described in this thesis was directed at advancing the state of the art in

living, Ru-catalyzed ROMP, and investigating the parameters required to synthesize stable ruthenium carbyne complexes. Experimental methods are described in Chapter 2. Chapter 3 describes a tempered-activity Ru-isocyanate complex for living ROMP, and explores methods for removing residual ruthenium. Chapter 4 seeks to expand existing understanding of the features that influence stability and reactivity in ruthenium carbynes. It classifies the existing complexes according to their stability, and describes reactivity studies that enable further insight. Finally, Chapter 5 provides an overview of the results and some insights into future research directions.

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Chapter 2: Experimental Methods

2.1 General Procedures

Reactions were carried out under house N_2 (cryogenic boiloff, Linde) in an MBraun glovebox, or under argon (Linde industrial grade) using double-manifold Schlenk techniques, unless otherwise noted. The Ar stream was dried by passage through a column of activated (blue) Drierite. Room temperature, in air, was measured to be 24 °C, while temperature inside of the glovebox was measured to be between 26 °C and 28 °C. Glassware was oven-dried at 150 °C for at least 12 h before use, and allowed to cool under vacuum. Flash column chromatography was carried out in air by standard methods, using silica gel (60 Å, Aldrich) as the stationary phase.

2.1.1 Solvents

Dry, oxygen-free benzene, toluene, hexanes, CH_2Cl_2, THF and diethyl ether (all HPLC grade, Fisher Scientific) were obtained using a Glass Contour or Anhydrous Engineering solvent purification system, and stored over Linde 4 Å molecular sieves in the glovebox. Acetone was dried over Drierite (10 g/L) for 3 days, distilled, and stored over Linde 4 Å molecular sieves in the glovebox.[1] Methanol was dried using Mg turnings (10 g) and iodine (1 g) with 100 mL of MeOH until effervescence subsided and then 1.4 L of additional MeOH was added, distilled, and stored over Linde 3 Å molecular sieves in the glovebox.[1] Pentane was dried over $MgSO_4$ for 48 h and then with P_2O_5, distilled and stored over Linde 4 Å molecular sieves in the glovebox.[1]

Deuterated solvents were purchased from Cambridge Isotope Laboratories Ltd. or from Aldrich Chemical Co., and used as received for NMR analysis of air-stable species. For oxygen- or moisture-sensitive compounds, ampoules of C_6D_6, CD_2Cl_2, THF-d_8 were opened inside the glovebox; $CDCl_3$ was distilled from CaH_2 and stored over Linde 4 Å molecular sieves in an amber bottle inside the drybox. To prevent contamination of the NMR solvents, the glovebox atmosphere was purged to remove solvent vapors prior to opening these storage vessels.

2.1.2 Reagents

All commercial reagents were purchased from Aldrich with the exception of 3-bromopyridine, which was purchased from Acros, and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, which was purchased from Fischer Scientific. Compounds

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trans-5-norbornene-2,3-dicarbonyl chloride, Ag(NCO), TlOPh and $TlOC_6F_5$ were provided by Dr. Sebastien Monfette. Compounds $RuCl_2(CHPh)(H_2IMes)(PCy_3)$ and dry pyridine were kindly provided by Justin Lummiss.

2.1.3 Instrumental Analysis

^1H (300, 400 or 500 MHz), ^{13}C (75 or 125 MHz), and ^{31}P (121 or 202 MHz) NMR spectra were recorded on Bruker Avance-300, Avance-400 or Avance-500 spectrometers at 23 °C. Chemical shifts for ^1H and ^{13}C are reported relative to tetramethylsilane at 0 ppm, and ^{31}P NMR spectra to 85% H_3PO_4 (in a sealed NMR tube within the solvent of interest) at 0 ppm. Spectra of organometallic compounds were measured under anaerobic conditions in NMR tubes equipped with a J-Young valve, or screw-thread NMR tube fitted with PTFE/silicon septum caps.

IR spectra were measured on a Varian 640 FT-IR spectrometer, graciously provided by Professor Tom Baker, using the attenuated total reflectance (ATR) technique. Use of ATR can only be used for powdered solids that are air-stable. The technique requires ca. 10 mg of sample to be pressed on a sample plate, via the ATR arm, and then cleaned before and after with IPA. Air sensitive compounds were suspended in a Nujol mull and analyzed between KBr discs.

Polymer molecular weights and polydispersities were measured by gel-permeation chromatography (GPC) in CH_2Cl_2 (flow rate 1.0 mL min^{-1}; samples 1-2 mg mL^{-1}) using a Wyatt DAWN light-scattering instrument equipped with Optilab DSP refractometer, HPLC system with a Waters model 515 pump, Rheodyne model 7725i injector with 200 mL injection loop, and Waters Styragel HR3 and HR4 columns in series.

Inductively coupled plasma mass spectrometry (ICP-MS) analyses for Ru content were carried out by Dr. Nimal DeSilva, ICP-AES Laboratory University of Ottawa.

Electrochemical measurements were performed using a Princeton Applied Research (PAR) VersaSTAT 3 potentiostat / galvanostat / frequency response analyzer and V3-studio electrochemical software version 1.0.281 (2008) (PAR) with a 1-compartment cell, platinum wire working electrode, platinum mesh counter electrode and silver wire pseudoreference electrode, with ferrocene as an internal standard. The instrument was used under the supervision of Dr. Wendy Pell, Centre for Catalysis Research and Innovation (CCRI).

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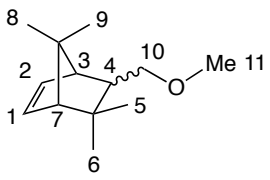
2.2 Synthesis of Substrates

2.2.1 5-(Methoxymethyl)bicyclo[2.2.1]hept-2-ene **M1**[2]



Synthesized according to a modified literature procedure.[2] In the glovebox a 25 mL Schlenk tube was loaded with 5-norbornen-1-methanol (2.51 g, 22.8 mmol) and THF (10 mL). Similarly, a 250 mL 3-neck round-bottom flask was loaded with NaH (0.58 g, 24 mmol) and THF (40 mL). The colorless NaH solution was cooled to 0 ˚C (ice bath) on the Schlenk line followed by slow cannula transfer of the norbornene solution using argon. Once bubbling of H_2 had ceased, a clear, pale-yellow solution with a beige suspension was obtained. Methyl iodide (3.42 g, 22.9 mmol) was then added against a flow of argon resulting in mild effervescence. The solution was left to stir under argon for 12 h at which point the homogeneous yellow solution was quenched with water (15 mL). The mixture was extracted with diethyl ether (4 x 25 mL), and the combined organic fractions were dried over $MgSO_4$, filtered and concentrated under reduced pressure to a yellowish oil. The crude product was purified by column chromatography (10% EtOAc in hexanes; $R_f = 0.50$) and vacuum distillation (bp. 85-90 ˚C, 70 mm Hg). Column chromatography was necessary to remove an unknown byproduct, $R_f = 0.91$, which upon removal resulted in the product being colorless as oppose to yellow. Trap-to-trap distillation was used in order to fully remove excess solvents and starting materials. Yield: 2.36 g (85%) as a 70:30 mixture of endo and exo isomers. As ^{13}C NMR signals from literature are incompletely assigned, full assignments are provided here (for numbering system, see structure). ^1H NMR ($CDCl_3$, 400 MHz): δ 6.11-6.02 (m, 1.42H, H_1 endo and H_2 exo), 6.04-6.01 (m, 0.42H, H_1 exo), 5.92-5.90 (m, 1H, H_2 endo), 3.39 (dd, $J_{8,8} = 9.2$ Hz, $J_{8,8} = 6.3$ Hz, 0.42H, H_{10} exo), 3.33 (s, 1.26H, H_{11} exo), 3.29-3.27 (m, 3.42H, H_{11} endo and H_{10} exo), 3.06 (dd, $J_{8,8} = 9.2$ Hz, $J_{8,8} = 6.7$ Hz, 1H, H_{10} endo), 2.98 (t, $J_{8,8} = 9.0$ Hz, 1H, H_{10} endo), 2.87 (br s, $w_{1/2} = 8$ Hz, 1H, H_3 endo), 2.76 (br s, $w_{1/2} = 11.5$ Hz, 1.42H, H_7 endo and H_3 exo), 2.70 (br s, $w_{1/2} = 6.5$ Hz, 0.42H, H_7 exo), 2.36-2.27 (m, 1H, H_4 endo), 1.79 (ddd, $J_{8,8} = 11.7$ Hz, $J_{8,8} = 8.5$ Hz, $J_{8,8} = 3.9$ Hz, 1H, H_6 endo), 1.69-1.62 (m, 0.42H, H_4 exo), 1.42-1.38 (m, 1H, H_8 or H_9 endo), 1.32-1.19 (m, 2.26H, H_8 or H_9 endo, H_8 exo, H_9 exo, H_5 or H_6 exo), 1.11-1.06 (m, 0.42H, H_5 or H_6 exo), 0.42 (ddd, $J_{8,8} = 11.6$ Hz, $J_{8,8} = 4.5$ Hz, $J_{8,8} = 2.7$ HZ, 1H, H_5 endo). $^{13}C\{^1H\}$ ($CDCl_3$, 101 MHz): δ 137.0 (C_1 endo), 136.53 (C_1 or C_2 exo), 136.51 (C_1 or C_2 exo), 132.4 (C_2 endo), 77.5 (C_{10} exo), 76.6 (C_{10} endo), 58.7 (C_{11} exo), 58.6 (C_{11} endo), 49.4

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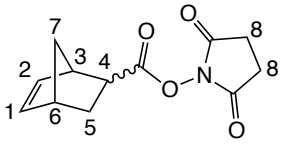
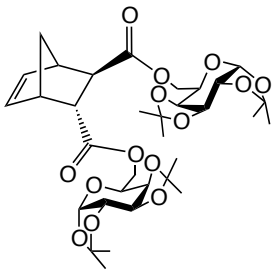
($C_{8/9}$ endo), 45.0 ($C_{8/9}$ exo), 43.9 (C_3 endo), 43.6 (C_7 exo), 42.1 (C_7 endo), 41.5 (C_3 exo), 38.8 (C_4 exo), 38.7 (C_4 endo), 29.6 ($C_{5/6}$ exo), 29.1 ($C_{5/6}$ endo).

2.2.2 Bicyclo[2.2.1]hept-5-ene-*exo*-2-carboxylic acid *N*-hydroxysuccinimide ester **M3**[3]



Reaction carried out in air. In a modification of a literature procedure, where use of recrystallization in EtOAc isolates more of the *exo* isomer, [3] a 100 mL round-bottom flask was loaded with norbornene acid (3.07 g, 22.2 mmol), *N*-hydroxysuccinimide (3.38 g, 29.4 mmol) and CH_2Cl_2 (20 mL). To this was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (5.50 g, 28.7 mmol) and the resulting solution turned pale yellow in color. The reaction mixture was concentrated under reduced pressure to afford pale yellow oil. The crude product was purified by column chromatography (CH_2Cl_2; R_f = 0.13). Initial yield: 5.03 g (96%) consisting of a 70:30 ratio of *exo* and *endo* isomers. The product was dissolved in hot EtOAc (5 mL) and hexanes (15 mL) were added to recrystallize the *exo* compound. Norbornene **M3** was then filtered and dried (under vacuum) providing a final product ratio of 95:5 exo and endo isomers. Yield: 3.18 g (61%). ^{1}H NMR ($CDCl_3$, 400MHz): δ 6.22 (dd, *J*=5.4, 1H, H_2), 6.12 (dd, *J*=5.9, 1H, H_1), 3.38 (br s, 1H, H_4), 3.25 (m, 2H, H_7), 2.96 (br s, 1H, H_3), 2.80 (d, *J*=10.5, 4H, H_8), 2.00 (ddd, *J*=10.1, 3.0, 1H, H_6), 1.32 (m, 2H, H_5).

2.2.3 Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-*O*-yl) 5-norbornene-*trans*-2,3-dicarboxylate **M5**[4]



In a modification of a literature procedure, where the galactopyranose solution is chilled to 0 °C and not –50 °C,[4] the contents of a 100 mL Schlenk tube containing a solution of *trans*-5-norbornene-2,3-dicarbonyl chloride (6.0 g, 27 mmol) in ether (50 mL) was added dropwise (via cannula) over 30 min to a 250 mL 3-neck round-bottom flask containing a solution of 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (14.3g, 54.9 mmol) in ether (150 mL) and triethylamine (5.7 g, 56 mmol) at 0 °C under Ar. The solution was then allowed to stir at RT for 12 h upon which a white precipitate had formed. The solution was washed with 10% Na_2CO_3 (3 x 50 mL), brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a yellow oil. The crude product was purified by column chromatography to

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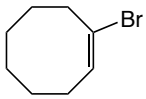
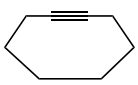
obtain a colorless oil. Removal of the residual solvent on a Schlenk line resulted in a white crystalline powder. Yield: 10.6 g (58%). Spectroscopic values match those for the published compound;[4] key spectroscopic values are provided for convenience. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.24 (m, 1H) and 6.11 (dd, 1H) (olefinic protons); 5.51 (t, 2H), 4.59 (d, 2H), 4.22-3.90 (m, 8H) (sugar group protons); 1.47 (d, 6H), 1.43 (s, 6H), 1.30 (s, 12H) (cyclic acetal protons).

2.2.4 1-Bromocyclooctene **1** [5]



In a modification of a literature procedure, where bromine addition is performed at 0 °C (not –20 °C) and excess bromine is removed by a rapid stream of air, [5] a 100 mL round-bottom flask was loaded with *cis*-cyclooctene (4.7 g, 43 mmol) and CH_2Cl_2 (15 mL). The solution was cooled to 0 °C (ice bath) and bromine (2.2 mL, 43 mmol) was added dropwise by syringe. After addition of Br_2, the reddish-brown solution was left to stir for 15 min. Excess bromine was evaporated via a rapid stream of air. The crude product, consisting principally of 1,2-dibromocyclooctane, was isolated by stripping off the solvent on the Schlenk line (N.B. the pump oil was changed after this procedure was complete). In the glovebox, two 50 mL Schlenk tubes were loaded with ether (15 mL) and KO^{t}Bu (7.5 g, 67 mmol) in THF (20 mL) respectively. On the Schlenk line the crude product solution was cooled to 0 °C (ice bath) and the ether was transferred via cannula to the crude mixture under argon. The KO^{t}Bu solution was then added dropwise via cannula addition under argon. The resulting light brown solution was allowed to stir for 1 h at ambient temperature. Distilled H_2O (20 mL) was added to quench any remaining KO^{t}Bu forming an orange solution. The crude mixture was extracted with ether (3 x 20 mL) and the combined organic fractions were dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford an orange oil. The crude product was purified by column chromatography (10% EtOAc in hexanes; R_f = 0.80) to obtain a clear oil. Yield: 5.09 g (63%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.05 (t, *J*=8.5, 1H), 2.65-2.60 (m, 2H), 2.15-2.09 (m, 2H), 1.68-1.62 (m, 2H), 1.60-1.49 (m, 6H).

2.2.5 Cyclooctyne **2** [5]

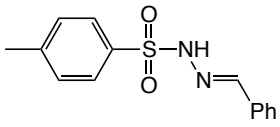


In a modification of a literature procedure, where addition of lithium diisopropylamide is added at –20 °C (not –78 °C) and lithium diisopropylamide was purchased from Aldrich (not made *in situ*),[5] a 100 mL round-bottom flask was loaded with 1-

bromocyclooctene **1** (2.75 g, 14 mmol) and THF (5 mL) via cannula transfer under argon. The mixture was cooled to –20 °C (dry ice and ethylene glycol) and a 2.0 M solution of lithium diisopropylamide (11 mL, 22 mmol) was added dropwise via syringe. The clear solution was left to stir for 3 h, while being warmed to ambient temperature, where a color change from colorless to brown was observed. Afterwards, 3 M HCl was added to neutralize the amine until a neutral pH was obtained (checked by pH paper). The solution was extracted with pentane (3 x 20 mL), and the combined organic layers were washed with distilled H_2O (3 x 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford a clear oil. The crude product was purified by vacuum distillation (bp. 55 ˚C, 70 mm Hg) to obtain a colorless oil. Yield: 0.93 g (59%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.20-2.13 (m, 4H), 1.90-1.82 (m, 4H), 1.65-1.57 (m, 4H).

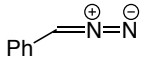
2.3 Synthesis of Ligands

2.3.1 *N*-Tosylhydrazone **3**[6]



Reaction carried out in air. A 500 mL round-bottom flask was loaded with MeOH (175 mL) and 4-toluenesulfonehydrazine (30 g, 16 mmol). The suspension was stirred until a clear, pale yellow solution was obtained. The solution was then cooled to 0 ˚C, and benzaldehyde (17.1 g, 16.0 mmol) was added. The solution was allowed to warm to room temperature resulting in the formation of a white precipitate. The solid was collected by filtration, and the filtrate then concentrated (rotovap) to afford a second crop of the desired **3**. The yellow coloration could be removed by recrystallization from 1:1 CH_2Cl_2:hexanes. Yield: 40.5 g (92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 (br s, 1H, N*H*), 7.89 (d, *J*=9.0, 2H, Ar*H*), 7.80 (s, 1H, C*H*), 7.52-7.61 (m, 2H, Ar*H*), 7.26-7.37 (m, 5H, Ar*H*), 2.37 (s, 3H, CH_3).[6]

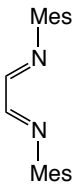
2.3.2 Phenyl diazomethane **4**[6]



Reaction carried out in air. The product was kept for a maximum of 3 h before use. In a modification of a literature procedure, where KOH is used instead of sodium methoxide and an extraction is performed rather than a distillation,[6] a 250 mL round-bottom flask was loaded with *N*-tosylhydrazone **3** (5.82 g, 20.8 mmol) and triethylene glycol (55 mL). The suspension was warmed to 70 ˚C to and dissolution of **3** afforded a pale yellow solid. Following addition of a solution of KOH (2.39 g, 42.6 mmol) in water (10 mL), an immediate

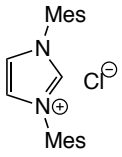
color change to red was observed. The solution was stirred at 70 ˚C for 10 min and distilled water (20 mL) was then added to give a white precipitate in an orange solution. The product was extracted with hexanes (3 x 40 mL) and the combined organic fractions were washed with brine (1 x 40 mL), dried over $MgSO_4$, filtered and concentrated (rotovap) to afford a dark red oil. *Note: exposure to vacuum should be minimized to avoid loss of volatile **4***. Yield: 0.959 g (39%). Compound **4** was used as is, without analysis for purity.

2.3.3 Glyoxal-bis-(2,4,6-trimethylphenyl)imine **5**[7]



Reaction carried out in air. In a modification of a literature procedure,[7] a 250 mL round-bottom flask was loaded with 2,4,6-trimethylaniline (23.2 g, 172 mmol), methanol (50 mL), glyoxal (9.9 mL, 40% solution in water, 86 mmol) and formic acid (0.1 mL) as a catalyst. A yellow precipitate formed within a few minutes. The reaction was left to stir for 24 h at room temperature and the yellow product was then collected by filtration and was washed with methanol (100 mL) until the washings were colorless. The yellow solid was dried under vacuum over night. Yield: 22.5 g (89%). Spectroscopic values match those for the published compound;[7] key spectroscopic values are provided for convenience. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13 (s, 2H, C*H*), 6.93 [s, 4H, *m*-C*H*], 2.32 [s, 6H, *p*-CH_3], 2.19 [s, 12H, *o*-CH_3].

2.3.4 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride **6**[8]



Reaction carried out in air. In a modification of a literature procedure,[8] a 250 mL round-bottom flask was loaded with glyoxal-bis-(2,4,6-trimethylphenyl)imine **5** (15.3 g, 52.3 mmol), paraformaldehyde (2.06 g, 68.6 mmol), and THF (75 mL). A solution of HCl in dioxane (4 M, 14 mL, 56 mmol) was added dropwise to the solution ensuring the temperature of the reaction stayed below 30 ˚C. After complete addition of the HCl, the brown solution was stirred for 24 h at ambient temperature. The off-white precipitate was collected by filtration, and washed with THF (75 mL) until colorless washings were obtained. The solid was vacuum dried overnight. Yield: 12.1 g (68%). Spectroscopic values match those for the published compound;[8] key spectroscopic values are provided for convenience. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.02 (s, 1H, IMes NC*H*N), 7.58 (s, 2H, IMes =C*H*), 7.04 (s, 4H, Mes =C*H*), 2.32 (s, 6H, Mes *p*-CH_3), 2.20 (s, 12H, Mes *o*-CH_3).

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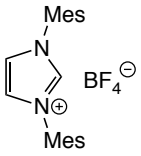
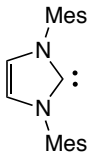
2.3.5 1,3-Bis(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate **7**



Reaction carried out in air. A 100 mL round-bottom flask was loaded with 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride **6** (12.1 g, 35.5 mmol) and a minimum of distilled H_2O to completely dissolve the salt (ca. 30 mL). HBF_4 (6.49 g, 48% in water, 35.5 mmol) was added to the yellow solution resulting in the formation of a white precipitate. Stirring was continued for 20 min at RT and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over $MgSO_4$, stripped of solvent (rotovap) and dried under vacuum. Yield: 10.0 g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.88 (t, $^4J_{HH}$ = 1.6 Hz, 1H, IMes NC*H*N), 7.56 (d, $^4J_{HH}$ = 1.6 Hz, 2H, IMes =C*H*), 7.03 (s, 4H, Mes =C*H*), 2.35 (s, 6H, Mes *p*-CH_3), 2.11 (s, 12H, Mes *o*-CH_3). ^{13}C{^{1}H} ($CDCl_3$, 75 MHz): d 141.3 (IMes N*C*HN), 137.1 (Mes *p*-*C*), 134.0 (Mes *i*-*C*), 130.4 (Mes *o*-*C*), 129.8 (Mes =*C*H), 125.1 (IMes =*C*H), 21.1 (Mes *p*-*C*H_3), 17.1 (Mes *o*-*C*H_3).

2.3.6 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene **8** [8]



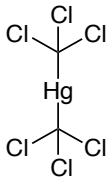
Inside the glovebox, a 250 mL round-bottom flask was loaded with 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride **7** (5.09 g, 12.9 mmol), THF (100 mL), NaH (619 mg, 25.8 mmol) and KO^{t}Bu (72 mg, 0.64 mmol, 5 mol%). The solution was stirred at ambient temperature for 3 h and then stripped of to yield a yellow solid. The crude product was dissolved in toluene (35 mL), filtered through Celite, and reduced to a minimum (ca. 10 mL). The solution was cooled to –35 °C and precipitated by adding hexanes (75 mL). The white crystalline product was filtered and dried under vacuum. Yield: 3.10 g (79%). Spectroscopic values match those for the published compound; [8] key spectroscopic values are provided for convenience. ^{1}H NMR (THF-d_8, 300 MHz) δ 7.04 (s, 2H, NC*H*), 6.94 (s, 4H, Mes =C*H*), 2.30 (s, 6H, Mes *p*-CH_3), 2.02 (s, 12H, Mes *o*-CH_3).

2.4 Mercury Compounds

2.4.1 Bis(trichloromethyl)mercury **Hg-1** [9]

Note: The toxicity of mercury, organomercury compounds in particular, is well established.[10] *Care must be taken to prevent introduction into the body by inhalation, ingestion via contaminated hands or gloves, or through the skin. All mercury reagents and waste, including*

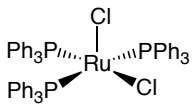
contaminated solvents, were handled using double-glove and secondary containment procedures, with separate disposal of solid and liquid wastes in accordance with government regulations. Glassware contaminated with mercury was washed first with the minimum volume of concentrated nitric acid and left to sit in boiling water for at least 1 h.



Reaction carried out in air. In a modification of a literature procedure, where a slightly longer reaction time (1 h versus 45 min) is used to ensure completion of the reaction rather than monitoring by water effervescence,[9] a 100 mL round-bottom flask was loaded with mercuric chloride (3.98 g, 14.6 mmol), sodium trichloroacetate (5.40 g, 29.4 mmol) and 1,2-dimethoxyethane (35 mL). The mixture was heated at reflux and left to stir for 1 h, where the color changed from colorless to a cloudy pale yellow within 15 min. Distilled H_2O (50 mL) was added and the mixture was extracted with ether (3 x 50 mL). The combined organic fractions were washed again with distilled H_2O (50 mL), dried over $MgSO_4$, filtered and stripped of solvent (Schlenk line) to a give a white solid. Recrystallization from chloroform afforded a white solid. Yield: 3.59 g (60%). IR values agree with literature.[11] IR (ATR, cm^{-1}): 802 (w, υ_s(CCl)), 689 (s, υ_{as} (CCl)).

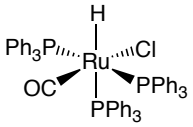
2.5 Ruthenium Complexes

2.5.1 $RuCl_2(PPh_3)_3$ **Ru-1**[12]



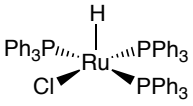
In accordance with a literature procedure,[12] a three-neck 500 mL round-bottom flask was loaded with $RuCl_3 \cdot 3H_2O$ (2.02 g, 40-43% Ru, ca. 7.72 mmol), PPh_3 (12.1 g, 46.1 mmol) and methanol (200 mL). The mixture was refluxed under argon for 2 h forming a brown solution. The solution was then filtered and washed with ether (5 x 100 mL) in the glovebox to remove excess PPh_3 resulting in a brown solid. Yield: 6.27 g (85%). Spectroscopic values match those reported;[12] key spectroscopic values are provided for convenience. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 44.5 (s), -2.03 (s, 5% free PPh_3)

2.5.2 $RuHCl(CO)(PPh_3)_3$ **Ru-2**[13]



Reaction carried out in air. In accordance with a literature procedure,[13] a 1 L round-bottom flask was loaded with PPh_3 (6.26 g, 23.8 mmol) and 2-methoxyethanol (240 mL). The solution was heated to boiling reflux upon which a solution of $RuCl_3(H_2O)_x$ in 80 mL of 2-methoxyethanol (1.04 g, 40-43% Ru, ca. 3.98 mmol) and a formaldehyde solution (80 mL, 37% w/v) were quickly added one after the other. The solution turned from orange to yellow with a beige precipitate after 10 min. The crude product was filtered and then washed with ethanol (80 mL), distilled H_2O (80 mL), ethanol (80 mL) and then hexanes (80 mL). The product was dried under vacuum to afford a beige powder. Yield: 2.79 g (74%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 42.3 (d, $^2J_{PP}$ = 15.7 Hz, 2P), 14.6 (t, $^2J_{PP}$ = 15.7 Hz, 1P). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.2-6.5 (m, 45H, PPh_3); -7.2 (dt, $^2J_{HP}$ = 23, 105 Hz, 1H, Ru*H*).

2.5.3 $RuHCl(PPh_3)_3$ **Ru-3**[14]



In a modification of a literature procedure, where NaH is used instead of KOPh,[14] a 50 mL Schlenk tube, in the glovebox, was loaded with NaH (77 mg, 3.21 mmol) and dry isopropanol (15 mL) to give a clear solution. In a 250 mL three-neck round-bottom flask was loaded $RuCl_2(PPh_3)_3$ **Ru-1** (2.68 g, 2.80 mmol) and dry benzene (125 mL) to give a brown solution. The NaH solution was slowly transferred by cannula to the brown mixture to give a yellowish-brown color. The solution was refluxed, outside of the glovebox, for 1.5 h to obtain a purple suspension and then the solvent stripped to dryness (Schlenk line). In the glovebox, the purple powder was washed with dry methanol (20 mL) and hexanes (3 x 5 mL), filtered and dried (Schlenk line) to afford clean **Ru-3**. Yield: 2.25 g (87%). Spectroscopic values match those reported;[14] key spectroscopic values are provided for convenience. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 56.5 (br s). ^1H NMR ($CDCl_3$, 300 MHz): δ -17.7 (q, $^2J_{HP}$ = 25.9 Hz, 1H).

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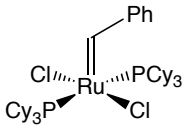
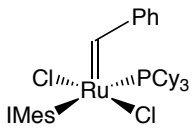
2.5.4 $RuCl_2(CHPh)(PCy_3)_2$ **Ru-4**[15]



In a modification of a literature procedure, where addition of PCy_3 is added at 0 °C and not –50 °C,[15] a 250 mL three-neck round-bottom flask was loaded with $RuCl_2(PPh_3)_3$ **Ru-1** (3.01 g, 3.14 mmol) and CH_2Cl_2 (90 mL). The brown solution was cooled to –78 ˚C (dry ice and acetone) at which point a solution of phenyl diazomethane **4** (0.74 g, 6.26 mmol) in hexanes (10 mL) was slowly added by cannula, causing a color change to yellow-brown. The solution was stirred at –78 ˚C for an additional 20 min, and then warmed to 0 ˚C (ice bath), and stirred for a further 20 minutes. A colorless solution of PCy_3 (1.96 g, 6.99 mmol) in hexanes (25 mL) was added by cannula causing a color change to dark red-purple. The reaction was left to stir for 1.5 h while being warmed to RT. The volatiles were then removed under vacuum (Schlenk line) to afford a red-purple solid. In the glovebox, the crude product was washed with dry methanol (150 mL), filtered, washed with dry acetone (50 mL) and dried under vacuum. Yield: 1.96 g (76%). Spectroscopic values match those reported;[15] key spectroscopic values are provided for convenience. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 36.9 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 19.95 (s, 1H, RuC*H*).

2.5.5 $RuCl_2(CHPh)(IMes)(PCy_3)$ **Ru-5**[8]



In accordance with a literature procedure,[8] in the glovebox a 100 mL round-bottom flask was loaded with $RuCl_2(CHPh)(PCy_3)_2$ **Ru-4** (1.52 g, 1.85 mmol) and dry toluene (25 mL) to afford a purple solution. To the mixture was added 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene **8** (0.618 g, 2.03 mmol) as a solution in dry toluene (10 mL) producing a red color. The solution was stirred at room temperature for 2 h at which point all volatiles were removed under vacuum (Schelnk line). The red crude product was washed with hexanes (2 x 15 mL) at –78 ˚C (dry ice and acetone) to afford a pink solid. Yield: 1.19 g (76%). Spectroscopic values match those reported;[8] key spectroscopic values are provided for convenience. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 300 MHz): δ 32.4 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 19.40 (s, 1H, RuC*H*).

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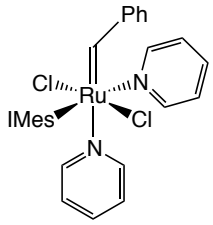
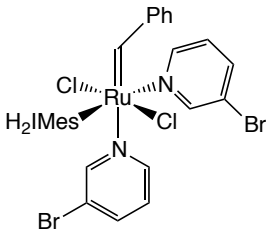
2.5.6 $RuCl_2(CHPh)(IMes)(py)_2$ **Ru-6**[16]



In accordance with a literature procedure,[16] a 25 mL round-bottom flask was loaded with $RuCl_2(CHPh)(IMes)(PCy_3)$ **Ru-5** (1.04 g, 1.23 mmol) and dry pyridine (1 mL) affording an immediate color change from pink to green. Addition of small amounts of pyridine (0.5 mL) was sometimes needed in order to fully dissolve the starting material. The suspension was stirred for 15 min to ensure complete reaction. Hexanes (50 mL) were added to precipitate a green solid, which was collected by filtration, washed with hexanes (3 × 10 mL) and dried under vacuum (Schlenk line). Yield: 879 mg (>99%). Spectroscopic values match those reported;[16] key spectroscopic values are provided for convenience. ^{1}H NMR (C_6D_6, 300 MHz): δ 20.02 (s, 1H, RuC*H*), 9.33 (d, $^3J_{HH}$ = 4.3, 2H, py), 8.55 (d, $^3J_{HH}$ = 4.7, 2H, py).

2.5.7 $RuCl_2(CHPh)(H_2IMes)(3\text{-bromopyridine})_2$ **Ru-7**[17]



In accordance with a literature procedure,[17] a 25 mL round-bottom flask was loaded with $RuCl_2(CHPh)(H_2IMes)(PCy_3)$ (280 mg, 0.330 mmol) and 3-bromopyridine (500 μL) affording an immediate color change from pink to green. Addition of small amounts of pyridine (0.5 mL) was sometimes needed in order to fully dissolve the starting material. The suspension was stirred for 15 min to ensure complete reaction. Hexanes (10 mL) were added to precipitate a green solid, which was collected by filtration, washed with hexanes (3 × 5 mL) and dried under vacuum (Schlenk line). Yield: 291 mg (>99%). Spectroscopic values match those reported;[17] key spectroscopic values are provided for convenience. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 19.10 (s, 1H, Ru=C*H*Ph), 8.72 (s, 1H, py), 8.57 (s, 1H, py), 7.97 (s, 1H, py), 7.79 (s, 1H, py), 7.73 (s, 1H, py).

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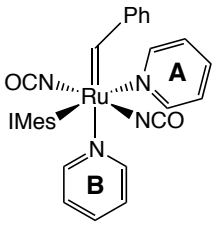
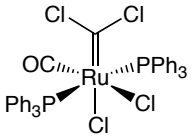
2.5.8 Ru(NCO-κ*N*)$_2$(CHPh)(IMes)(py)$_2$ **Ru-8**



A 100 mL round-bottom flask was loaded with $RuCl_2(CHPh)(IMes)(py)_2$ (500 mg, 0.690 mmol), dry benzene (20 mL) and Ag(NCO) (228 mg, 1.52 mmol). The solution underwent an immediate color change to emerald green forming a light brown precipitate. The suspension was stirred for 1 h, filtered through Celite, and solvent removed under vacuum (Schlenk line) to obtain a green solid. Recrystallization from a minimum of THF by slow addition of hexanes yielded a green solid. Yield: 427 mg (84%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 18.72 (s, 1H, Ru=C*H*), 8.58 (br s, 2H, py$_B$. *o*-C*H*), 7.82 (br s, 2H, py$_A$. *o*-C*H*), 7.65 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ph *o*-C*H*), 7.48 (m, 1H, py$_B$. *p*-C*H*), 7.42 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ph *p*-C*H*), 7.29 (t, $^3J_{HH}$ = 7.8 Hz, 1H, py$_A$. *p*-C*H*), 7.07 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ph *m*-C*H*), 7.03 (s, 2H, IMes =C*H*), 7.00 (m, 2H, py$_B$. *m*-C*H*), 6.78 (m, 2H, py$_A$. *m*-C*H*), 6.70 (s, 4H, Mes C*H*), 2.17 (s, 6H, Mes *p*-CC*H*$_3$), 2.17 (s, 12H, Mes *o*-CC*H*$_3$). ^{13}C{^{1}H} (CD_2Cl_2, 125 MHz): δ 318.6 (Ru=*C*H), 183.7 (IMes N*C*N), 156.4 (Mes *i*-*C*), 152.3 (Ph *i*-*C*), 151.5 (py$_A$. *o*-*C*H), 150.2 (py$_B$. *o*-*C*H), 139.4 (Mes *p*-*C*CH$_3$), 137.0 (Mes *o*-*C*CH$_3$), 136.6 (2 overlapping signals, py$_A$. *p*-*C*H and N*C*O), 135.3 (py$_B$. *p*-*C*H), 130.1 (2 overlapping signals, Ph *o*-*C*H and *p*-*C*H), 129.3 (Mes *C*H), 128.4 (Ph *m*-*C*H), 124.9 (IMes =*C*H), 123.85 (2 overlapping signals, py$_B$. *m*-*C*H and py$_A$. *m*-*C*H), 21.1 (Mes *p*-*C*H$_3$), 18.0 (Mes *o*-*C*H$_3$). IR (Nujol, cm^{-1}): 2230 (m, NCO).

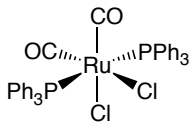
2.5.9 $RuCl_2(CCl_2)(CO)(PPh_3)_2$ **Ru-9**[18]



In a modification of a literature procedure, where the reaction is carried out under Ar and not air due to carbonylation of the product,[18] a 500 mL round-bottom flask was loaded with bis(trichloromethyl)mercury **Hg-1** (1.18 g, 2.70 mmol), $RuHCl(CO)(PPh_3)_3$ **Ru-2** (1.17g, 1.23 mmol) and dry toluene (170 mL) and purged with Ar. The solution was refluxed for 30 min with rapid stirring, where a color change from white to clear orange had occurred. A dark brown residue remained on the bottom of the flask, which is attributed to the deposition of elemental mercury. The solution was filtered through Celite and the solvent was removed under vacuum (Schlenk line). The orange solid was recrystallized in 1:1 CH_2Cl_2:MeOH to obtain pure **Ru-9** as an orange powder. Yield: 879 mg (88%). As ^{1}H and ^{31}P NMR values are not reported they are provided here. IR and ^{13}C NMR values match those reported;[18] characteristic values are reported here for convenience. ^{31}P{^{1}H}

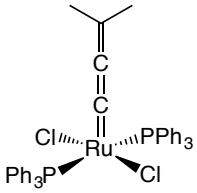
($CDCl_3$, 202 MHz): δ 16.8 (s, *P*Ph_3). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.0-6.7 (m, 30H, Ph*H*). $^{13}C\{^1H\}$ ($CDCl_3$, 125 MHz): δ 223.5 (*C*Cl_2), 192.5 (*C*O), 135.1-127.3 (Ph *C*). IR (ATR, cm^{-1}): 2030 (s, υ(CO)), 860 (s, υ(CCl)), 790 (m, υ(CCl)).

2.5.10 Reaction of **Ru-9** with H_2O; $RuCl_2(CO)_2(PPh_3)_2$ **Ru-10**



A 20 mL vial was loaded with $RuCl_2(CCl_2)(CO)(PPh_3)_2$ **Ru-9** (100 mg, 0.124 mmol) and distilled H_2O (10 mL). The reaction was left to stir at RT for 3 days, where a change in color from orange to off-white occurred. The crude solid was filtered, washed with hexanes (10 mL) and dried under vacuum. Yield: 90 mg (96%). $^{31}P\{^1H\}$ ($CDCl_3$, 202 MHz): δ 34.9 (s, *P*Ph_3). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.0-6.7 (m, 30H, Ph*H*). $^{13}C\{^1H\}$ ($CDCl_3$, 125 MHz): δ 192.5 (*C*O), 135.1-127.3 (Ph *C*). IR (ATR, cm^{-1}): 2062 (s, υ_s(CO)), 1998 (s, υ_{as}(CO)).

2.5.11 Reaction of **Ru-12** with NEt_3; RuCl2(C=C=CMe_2)(PPh_3)$_2$ **Ru-11**[19]



In accordance with a literature procedure,[19] in the glovebox a 20 mL vial was loaded with $RuCl_3(\equiv CCHCMe_2)(PPh_3)_2$ **Ru-12** (100 mg, 0.125 mmol) and CH_2Cl_2 (7.5 mL) and triethylamine (35 uL, 0.250 mmol). Within minutes of adding the triethylamine, the solution turned from orange to dark green. Sample was left to stir for 30 min and then washed with MeOH (3 x 10 mL) and hexanes (3 x 10 mL). The crude product was filtered and dried under vacuum to yield a dark green solid. Yield: 95 mg (95%). $^{31}P\{^1H\}$ (C_6D_6, 121 MHz): δ 30.1 (s, *P*Ph_3). ^{1}H NMR (C_6D_6, 300 MHz): δ 8.10-6.85 (m, 30H, Ph*H*), 1.15 (s, 6H, CH_3). $^{13}C\{^1H\}$ (C_6D_6, 125 MHz): δ 303.5 (t, Ru=*C*, *J*(PC) = 13.1 Hz), 228.5 (s, Ru=C=*C*), 146.5 (s, *C*$(CH_3)_2$), 137.0-129.5 (Ph *C*), 28.5 (s, *C*H_3), 28.0 (s, *C*H_3).

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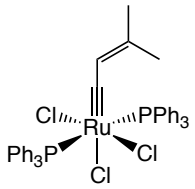
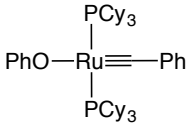
2.6 Ruthenium Carbynes

2.6.1 $RuCl_3(\equiv CCHCMe_2)(PPh_3)_2$ **Ru-12**[20]



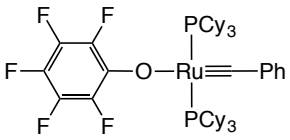
In accordance with a literature procedure,[20] in the glovebox a 20 mL vial was loaded with $RuHCl(PPh_3)_3$ **Ru-3** (500 mg, 0.541 mmol) and THF (10 mL) to afford a purple solution. To this was added 3-chloro-3-methylbut-1-yne (243 µL, 2.16 mmol) and the solution turned dark brown within minutes. The mixture was stirred for 72 h. Afterwards an orange precipitate had formed and the solution was diluted with hexanes (5 mL). Product was filtered, washed with hexanes (3 x 10 mL) and dried under vacuum affording a light orange powder. Yield: 415 mg (96%). Spectroscopic values match those reported;[20] key spectroscopic values are provided for convenience. $^{31}P\{^1H\}$ ($CDCl_3$, 121 MHz): δ 8.9 (s, *P*Ph_3). ^1H NMR ($CDCl_3$, 300 MHz): δ 4.36 (s, 1H, C*H*).

2.6.2 $Ru(\equiv CPh)(OPh)(PCy_3)_2$ **Ru-13**[21]



In a modification of a literature procedure, where TlOPh is used instead of NaOPh,[21] in the glovebox a 50 mL round-bottom flask was loaded with $RuCl_2(CHPh)(PCy_3)_2$ **Ru-4** (198.1 mg, 0.241 mmol), TlOPh (146.0 mg, 0.491 mmol) and THF (10 mL). The solution was stirred for 12 h where the color changed from purple to dark green. The solution was filtered through Celite, solvent stripped (glovebox vacuum) and dried under vacuum. The green crude product was suspended in –35 °C dry pentane, filtered and washed with dry pentane (3 x 5 mL) to obtain a clean dark green product. Yield: 118 mg (58%). Spectroscopic values match those reported;[21] key spectroscopic values are provided for convenience. $^{31}P\{^1H\}$ (C_6D_6, 121 MHz): δ 43.8 (s, *P*Cy_3).

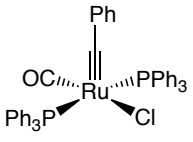
2.6.3 $Ru(\equiv CPh)(OC_6F_5)(PCy_3)_2$ **Ru-14**[22]



In accordance with a literature procedure,[22] in the glovebox a 50 mL round-bottom flask was loaded with a solution of $RuCl_2(CHPh)(PCy_3)_2$ **Ru-4** (196.7 mg, 0.239 mmol) in dry benzene (7.5 mL) and a solution of $TlOC_6F_5$ (185.2 mg, 0.478 mmol) in dry toluene (7.5 mL). The purple solution was stirred for 3.5 h resulting in a color change of dark green. The suspension was filtered and concentrated to dryness under vacuum (glovebox vacuum). The green crude product

was suspended in –35 °C ether, filtered and washed with ether (3 x 5 mL) to obtain the clean dark green product. Yield: 113.9 g (51%). Spectroscopic values match those reported;[22] key spectroscopic values are provided for convenience. $^{31}P\{^{1}H\}$ (C_6D_6, 121 MHz): δ 42.6 (s, *P*Cy_3).

2.6.4 $RuCl(\equiv CPh)(CO)(PPh_3)_2$ **Ru-15**[23]



In a modification of a literature procedure, where H_2O is not used in the washing process to prevent possible decomposition of the carbyne,[23] in the glovebox a 50 mL Schlenk tube was loaded with $RuCl_2(CCl_2)(CO)(PPh_3)_2$ **Ru-9** (618 mg, 0.764 mmol) and THF (20 mL) forming an orange solution. The Schlenk tube was cooled to –78 °C (dry ice and acetone) and phenyllithium (1 mL, 1.8 mmol, 1.8 M) was transferred by cannula to the solution. The reaction was left to stir for 10 min at –78 °C and then stirred for 10 min at 0 °C (ice bath) affording a brown solution. The solvent was removed under vacuum (Schlenk line) and the crude product was suspended in ether (25 mL). The suspension was filtered and the collected brown solid was washed with dry methanol (15 mL) and hexanes (15 mL). The product was dried under vacuum (Schlenk line) resulting in a dark green powder. Yield: 481 mg (81%). As ^{1}H and ^{31}P NMR values are not reported they are provided here. IR and ^{13}C NMR values match those reported;[23] characteristic values are reported here for convenience. $^{31}P\{^{1}H\}$ ($CDCl_3$, 202 MHz): δ 38.8 (s, *P*Ph_3). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.5-7.0 (m, 35H, Ph*H*). $^{13}C\{^{1}H\}$ ($CDCl_3$, 125 MHz): δ 196.8 (*C*O), 135.0-129.5 (Ph *C*). IR (ATR, cm^{-1}): 1873 (s, υ(CO)), 1582, 1326 (w, υ(Ru≡C)).

2.6.5 Attempted synthesis of $RuCl_3(\equiv CCHCMe_2)(IMes)(PPh_3)$

To **Ru-12** (21.4 mg, 0.027 mmol) in 5 mL C_6D_6 was added 1.1 equivalents of **11** (9 mg, 0.029 mmol). The reaction was left to stir for ca. 3 hours and produced the expected $^{31}P\{^{1}H\}$ NMR signal for free PPh_3 (–5.5 ppm); however, several unidentified phosphorus peaks were also observed, indicating product decomposition.

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2.7 Monitoring ROMP Reactions

2.7.1 Representative Procedure for ROMP Kinetics

A solution of monomer **M3** (101 mg, 0.429 mmol) in THF (4.3 mL) was added to a rapidly stirred solution of **Ru-8** (31.7 mg, 0.043 mmol) in THF (4.3 mL). Aliquots (1 mL) were removed periodically, quenched by addition of potassium hydrotris(pyrazolyl)borate (KTp) in THF (100 mL, 30 mg/mL, 119 mM, ca. 277 equiv), and stripped to dryness. Conversions were determined by ^{1}H NMR analysis in $CDCl_3$ by integrating the olefinic signals of **M3** relative to those of the polymer.

2.7.2 Representative Procedure for RT ROMP

In the glovebox, a 20 mL vial was loaded with M3 (104 mg, 0.442 mmol) and THF (3 mL). The solution was rapidly added to a green solution of Ru-8 (32.5 mg, 0.044 mmol, 10 mol%) in THF (3 mL). The solution was stirred vigorously until ROMP was complete, as indicated by ^{1}H NMR analysis. The metal end-group was cleaved by addition of 0.5 mL ethyl vinyl ether and the resulting solution was stripped of solvent (rotovap) to yield a gummy residue. The residue was dissolved in a minimum of CH_2Cl_2 (ca. 1 mL) and precipitated in methanol. The grey polymer powder was dried under vacuum, weighed, and analyzed by light-scattering GPC.

2.7.3 Representative Procedure for Cryogenic ROMP

In the glovebox, a 10 mL Schlenk tube was loaded with M3 (103 mg, 0.438 mmol) and THF (3 mL). The solution was cooled to –78 °C (dry ice and acetone) followed by addition of Ru-7 (38.4 mg, 0.043 mmol, 10 mol%) in THF (3 mL) via cannula. The Schlenk was then transferred to a –20 °C bath (dry ice and ethylene glycol) and gradually warmed to ambient temperature over a period of 1 h. The solution was stirred vigorously until ROMP was complete, as indicated by ^{1}H NMR analysis. The metal end-group was cleaved by addition of 0.5 mL ethyl vinyl ether and the resulting solution was stripped of solvent (rotovap) to yield a gummy residue. The residue was dissolved in a minimum of CH_2Cl_2 (ca. 1 mL) and precipitated in methanol. The grey polymer powder was dried under vacuum, weighed, and analyzed by light-scattering GPC.

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2.7.4 Representative Procedure for Coblock Polymer ROMP

In the glovebox, a 20 mL vial was loaded with M3 (25 mg, 0.106 mmol) and THF (3 mL). The solution was rapidly added to a green solution of Ru-8 (3.14 mg, 4.25×10^{-3} mmol, 4 mol%) in THF (3 mL). The solution was stirred vigorously until ROMP was complete (1 h), as indicated by ^{1}H NMR analysis. To this solution was then added M5 (71 mg, 0.106 mmol) in THF (3 mL). The solution was stirred vigorously until ROMP was complete (4 h), as indicated by ^{1}H NMR analysis. The metal end-group was cleaved by addition of 1 mL ethyl vinyl ether and the resulting solution was stripped of solvent (rotovap) to yield a gummy residue. The residue was dissolved in a minimum of CH_2Cl_2 (ca. 1 mL) and precipitated in ice-cold methanol. The grey polymer powder was dried under vacuum, weighed, and analyzed by light-scattering GPC. Yield: 85.2 mg (89%).

2.8 Removal of Residual Ruthenium from ROMP Polymers

2.8.1 Representative Procedure for the Quantification of Residual Ru in ROMP Polymers after Column Chromatography

In the glovebox a 20 mL vial was loaded with **M5** (202 mg, 0.303 mmol) and THF (6 mL). To this was added a solution of **Ru-8** (15.7 mg, 0.021 mmol, 6.6 mol%) in THF (6 mL). The mixture was left to stir for 30 min and then quenched with ethyl vinyl ether (1 mL) followed by opening the reaction to air. The solvents were removed (rotovap) and the resulting gummy residue was dissolved in a minimum of CH_2Cl_2 (ca. 1 mL) and precipitated in methanol. The grey polymer powder was dissolved in a minimum of CH_2Cl_2. The dark yellowish-brown oil was loaded on to a silica column (1 cm diameter packed with 14 cm of silica) and eluted with CH_2Cl_2 in to 1 mL glass test tubes (R_f 0.15). The fractions that contained product were combined and concentrated under vacuum (rotovap) to give a white powder. Yield: 185 mg (92%). Samples were analyzed by Dr. Nimal Desilva, University of Ottawa, for Ru analysis using ICP-MS: 691 ppm.

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2.8.2 Representative Procedure for the Quantification of Residual Ru in ROMP Polymers after Activated Charcoal, Silica Slurry or Silica-based Spherical Scavengers

In the glovebox a 20 mL vial was loaded with **M5** (105 mg, 0.157 mmol) and THF (3 mL). To this was added a solution of **Ru-8** (2.3 mg, 3.2 μmol, 2 mol%) in THF (3 mL). The mixture was left to stir for 30 min and then quenched with ethyl vinyl ether (0.5 mL) followed by opening the reaction to air. The solvents were removed (rotovap) and the resulting gummy residue was dissolved in a minimum of CH_2Cl_2 (ca. 1 mL) and precipitated in methanol. The product was dissolved in CH_2Cl_2 (20 mL) and to this was added activated carbon (50% w/w to catalyst, 3.7 g) forming a black slurry. Solution was stirred for 12 h and filtered, concentrated (rotovap) and dried under vacuum. Yield: 50 mg (48%). Samples were analyzed by Dr. Nimal Desilva, University of Ottawa, for Ru analysis using ICP-MS: 90 ppm.

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Chapter 3. A Tempered-Activity Ruthenium Initiator for Living Ring-Opening Metathesis Polymerization

3.1 Introduction

Ring-opening metathesis polymerization (ROMP) is an important methodology for synthesis of new materials. While ROMP dates back to the 1950s,[1] opportunities in the area expanded greatly with the advent of well-defined ruthenium initiators in 1995. The popularity of the Ru systems relative to the longer-established, high-performing group 6 initiators (e.g. the Schrock catalyst **Mo-1**; Figure 1a) is due to their lower oxophilicity and relative robustness, which translate into greater ease of handling.[2] In catalysis in general, resistance to deactivation or termination pathways is valuable in reducing catalyst loadings and associated process costs. In polymerization, the stakes are higher. Here unintended termination is catastrophic, because it skews control over chain lengths, the distribution of chain lengths, and polymer microstructure, all of which affect polymer properties.[3] Thus, while the Schrock initiators permit precise specification of polymer structure under pristine conditions, control is harder to achieve in practice. Traces of oxygen, water, and aldehydic or protic functionalities cause premature chain termination and/or chain coupling, both of which undermine control over chain lengths and block architectures.[4]

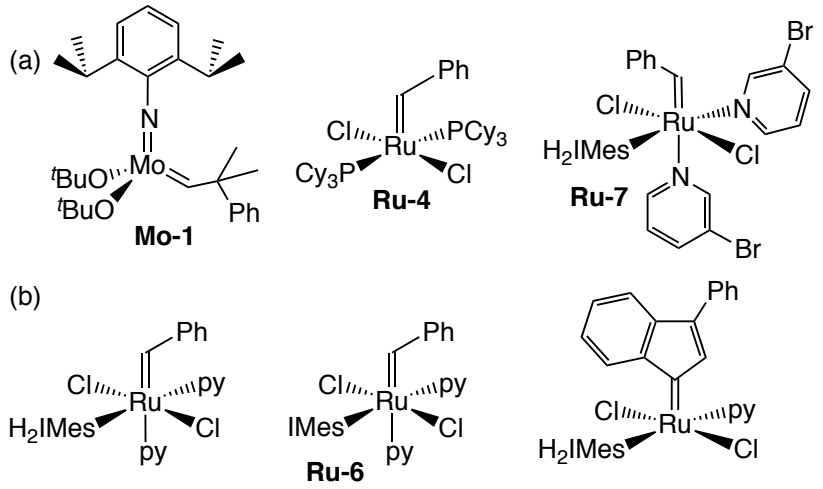

Figure 1. Initiators capable of living ROMP. (a) Initiators in dominant use. (b) Analogues of **Ru-7** catalyst, which vary in the nature of the pyridine, alkylidene, or NHC ligand.

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Of the many ruthenium metathesis catalysts now known, strikingly few are capable of living ROMP. Most important are the first-generation Grubbs complex **Ru-4** and the third-generation H_2IMes complex **Ru-7** (Figure 1a**)**. Pyridine, IMes, and indenylidene analogues of **Ru-7** catalyst are also known (Figure 1b**)**: while these are considerably less studied, the available data indicate behavior similar to **Ru-7**. It should also be noted that the catalysts that dominate ring-closing and cross-metathesis reactions (that is, the second-generation Grubbs and Hoveyda catalysts **GII** and **HII**, Figure 2) do not permit controlled ROMP.[5,6] These complexes initiate very slowly, and propagate rapidly. In consequence, polymer polydispersities are invariably high (one report cites a PDI of 2.51 for ROMP of glucose-functionalized **M5** by **GII**),[7] and chain lengths range from ca. 2-5 times the theoretical values.

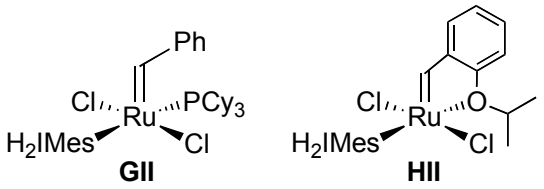
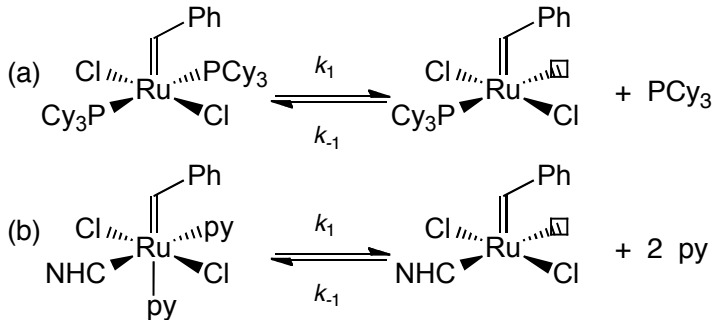


Figure 2. Important Ru metathesis catalysts that are not capable of controlled ROMP.

The key Ru initiators for living ROMP are thus **Ru-4** and **Ru-7**. These complexes exhibit opposite extremes of reactivity and stability, reflecting the lower lability of PCy_3, relative to pyridine. Thus, the phosphine ligand in **Ru-4** is lost much less rapidly than the pyridine ligands in **Ru-7**: it is also more aggressive in re-binding the initiating and propagating species (Scheme 1).[8] This stabilizes the propagating species against deactivation, at the expense of overall activity. Because rates of phosphine dissociation from the initiating and propagating species are comparable, living ROMP is possible for **Ru-4**, but reaction rates are much lower than those found for **Ru-7**.[5,7,9]



Scheme 1: Ligand lability and recoordination for **Ru-4** and **Ru-7**.

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Nevertheless, **Ru-4** rapidly polymerizes norbornenes bearing a single, sterically undemanding substituent, with 50 equiv monomer often being consumed within an hour at RT (see below). Sterically congested monomers are much more problematic. Three days were required for the corresponding reaction of *endo,exo*-disubstituted **M5** (Figure 3), in which the substituents are bulky acetyl-protected galactose units,[10] while ROMP of the *endo,endo*-dicarboximide norbornene **M6** was only 70% complete after a week.[10] Even monosubstituted norbornenes may react very slowly with **Ru-4**, if the substituents are particularly bulky. Thus, ROMP of "macromonomers" (norbornenes bearing a pendant oligonorbornene chain) such as **M7** was incomplete even after 48 hours in CH_2Cl_2, at which point only 5-8 repeat units were achieved.[11]

In contrast, the lability of the pyridine ligand in **Ru-7** and its analogues enables relatively rapid polymerization of bulky monomers. Thus, ROMP of galactose-functionalized **M5** (50 equiv) by **Ru-6** (or **Ru-7**; see below) is complete within 3 h at room temperature in CH_2Cl_2.[10] Likewise, ROMP of **M6** by **Ru-6** is complete within 6 h.[10]

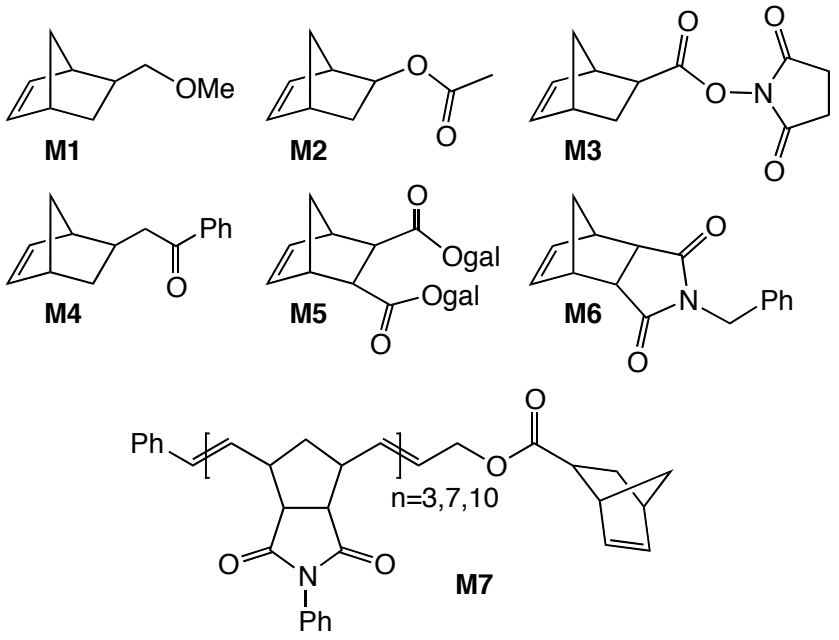

Figure 3. Representative norbornene monomers discussed in text.

For sterically accessible monomers, however, this high reactivity exacts a price in terms of chain-length control. In a representative reaction, room-temperature ROMP of NBE-CH_2Ph

M1 by **Ru-7** yielded a 140-mer rather than the 100-mer predicted from the reaction stoichiometry.[12] Low temperatures are essential to limit secondary metathesis and chain transfer. ROMP of monosubstituted norbornenes via **Ru-7** at –20 ˚C results in molecular weights very close to theoretical values.

These reactions are slow, however, and they are therefore sometimes permitted to warm to room temperature to accelerate polymerization. Kiessling and co-workers described such a procedure for ROMP of **M3** (10 equiv) by **Ru-7**.[13] The reaction was begun at –30 ˚C in CH_2Cl_2, and allowed to warm to RT at a reportedly slow (unspecified) rate. ROMP was found to be complete at 0.5 h. While molecular weights in good agreement with theoretical values were inferred from NMR endgroup analysis, this conclusion should be regarded with caution. This analysis is predicated on the absence of branching for ROMP polymers, which means that average chain lengths can be assessed according to Equations 1 and 2.

$$(1) \qquad n = \frac{\left(\dfrac{\text{Sum of olefin backbone proton integrals}}{\text{\# of olefin backbone protons}}\right)}{\left(\dfrac{\text{Sum of end group proton integrals}}{\text{\# of end group protons}}\right)}$$

$$(2) \qquad M_n = (\text{MW of endgroups}) + (\text{MW of repeating unit})(n)$$

However, accurate integration of NMR signals due to the endgroups is complicated by the typically poor resolution of polymer signals (see Figure 4). As well, a more fundamental problem lies in the fact that integration will inevitably report an average chain length that corresponds to the stoichiometric ratio, as long as ROMP is complete. Analysis of molecular weights by gel permeation chromatography (GPC) is a much more reliable way of assessing actual chain lengths. Unfortunately, molecular weight data were not provided, although GPC experiments were evidently carried out, as the polydispersity (PDI) of the oligomeric product was reported. This value was rather high (PDI 1.2), indicating a rather broad distribution of chain lengths. Broadening of the distribution could potentially indicate chain-transfer processes during warming.

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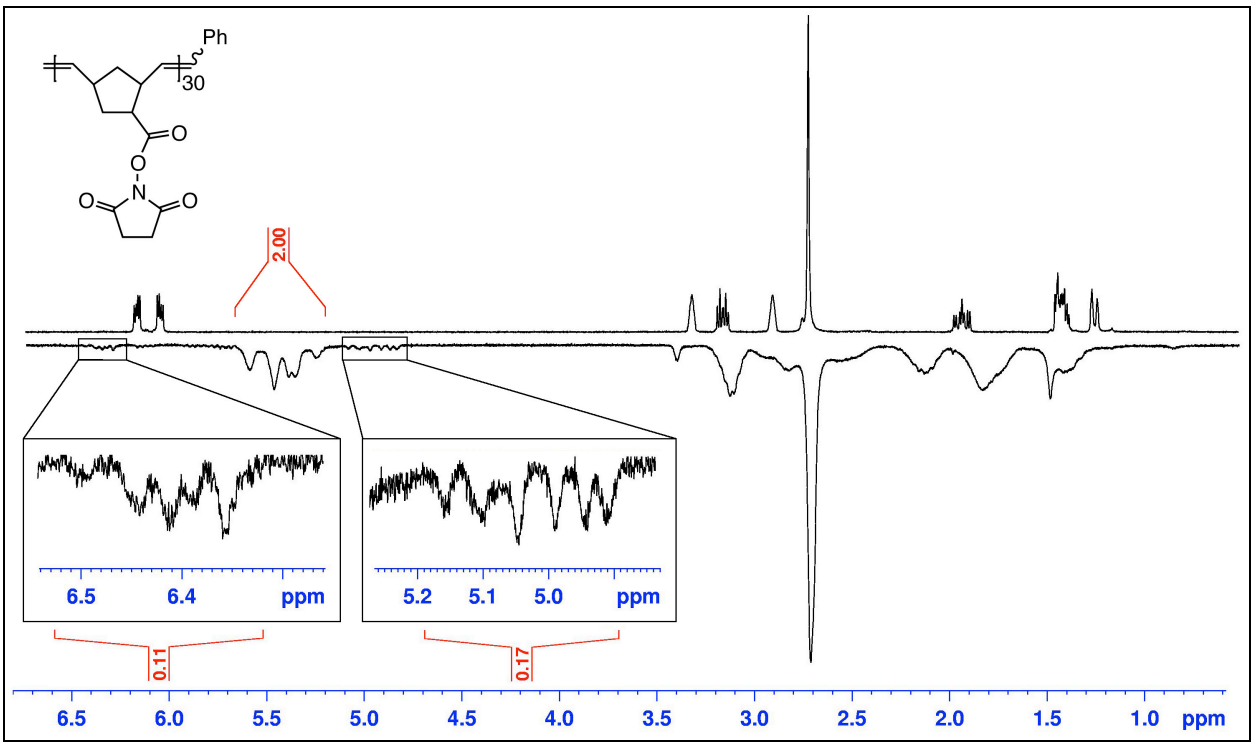

Figure 4. ^{1}H NMR spectrum (500 MHz) for 30 equivalents of **M3**. Top: monomer; inverted: spectrum after ROMP is complete; insets: methylene and phenyl endgroups in the latter.

To test the impact of uncontrolled warming in ROMP via these reactive pyridine initiators, a preliminary experiment was carried out in which 10 equiv **M3** was added to **Ru-7** at –20 ˚C, and the cold bath was removed after 5 min, with continued stirring. ^{1}H NMR analysis of a reaction aliquot confirmed complete reaction after 0.5 h, and GPC analysis indicated a PDI of 1.17. When the temperature was raised in increments of 5 °C every 5 min, the PDI declined to 1.09. Much improved control was found on halving the temperature ramp (i.e. raising the temperature by 5 ˚C every 10 min): this caused PDIs to drop to 1.03. In short, control can be achieved on use of **Ru-7** to polymerize very reactive norbornene derivatives such as **M3**, but protocols are cumbersome. (It should be noted that establishing accurate timescales in low-temperature ROMP reactions of these reactive initiators is itself non-trivial. Warming of samples in the short time required to syringe reaction aliquots out of the -20 ˚C solution means that these samples over-report the progress of ROMP, even when they are quenched immediately on removal. Better temperature control is achieved via in situ NMR experiments, but these under-report reaction rates, as polymerization is then diffusion-limited).

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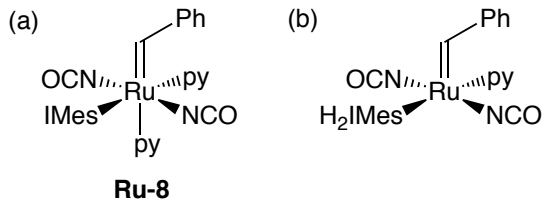
A need thus exists for Ru initiators that are both highly active *and* highly selective for ring-opening at RT. A new initiator developed by Sebastien Monfette of this research group (**Ru-8**, Figure 5a)[14] was a promising candidate identified at the outset of this study, with the potential for fast, controlled ROMP at ambient temperatures. In preliminary work by Sebastien Monfette, ROMP of benzyl-functionalized monomer **M1** (100 equiv) was found to be complete in 10 min, with a PDI of ca. 1.1. This result stood in striking contrast with the behaviour of related aryloxide catalysts (e.g. $RuCl(OC_6Br_5)(IMes)(py)(=CHPh)$, Ru(*o*-cat)(IMes)(py)(=CHPh), etc.), for which rates of propagation significantly exceed rates of initiation.[15,16]

A key objective of this thesis work was therefore a detailed assessment of the reactivity of **Ru-8**, and examination of its capacity for living ROMP. Specifically, we wished to establish whether **Ru-8** was capable of living ROMP of norbornene monomers of widely varying bulk, without need for a cryogenic brake-pedal to suppress backbiting and inter-chain metathesis. Noteworthy in this context is the limited control achieved in RT ROMP of norbornene by the H_2IMes analogue of NCO (Figure 5b), reported by the Buchmeiser group while this work was in progress.[17]

An additional question arises from the potential to remove these catalysts once metathesis is complete. We earlier demonstrated that the aryloxide catalysts show a high affinity for silica gel, facilitating their removal post-RCM.[18] We thus wished to assess whether the isocyanate ligands on **Ru-8** would likewise be sufficiently polar to aid chromatographic separation. This is important given the potential of ROMP polymers in biomedical and therapeutic applications, as FDA regulations limit platinoid residues in biological environments to 0.5 ppm for parenteral dosage, and 5 ppm in oral dosage.[19] It may be noted that even more stringent requirements may apply in device and microelectronics manufacturing,[20] another key application of ROMP materials.



Ru-8

Figure 5. Ru-isocyanate initiators. (a) **Ru-8**, IMes derivative synthesized by Sebastien Monfette of this research group.[14] (b) H_2IMes derivative reported by Buchmeiser and co-workers.[17]

3.2 Assessing ROMP Activity

Our first experiments focused on activity, rather than selectivity. Thus, we sought to benchmark the activity of **Ru-8** between the extremes established for **Ru-4** and the pyridine initiators such as **Ru-7**, by undertaking ROMP of the bulky galactose monomer **M5** (Figure 6). Earlier work demonstrated that the Grubbs initiator **Ru-4** requires 3 days to polymerize 50 equivalents of the bulky digalactose monomer **M5** at RT, a reaction that is complete in 2.5 h with **M3** (Table 1, entry 1 and Figure 6).[10] We find that **Ru-8** effects this transformation in 4 h (entry 3), indicating a level of activity only slightly tempered relative to **Ru-6**, and significantly higher than that of **Ru-4**. Experimentally measured chain lengths are very close to that predicted from the stoichiometric ratio, and PDIs are very low (≤1.03). It should be noted that similar control is achieved with **Ru-7** even at ambient temperatures, owing to the inhibiting effect on secondary metathesis exerted by the bulky carbohydrate substituents.

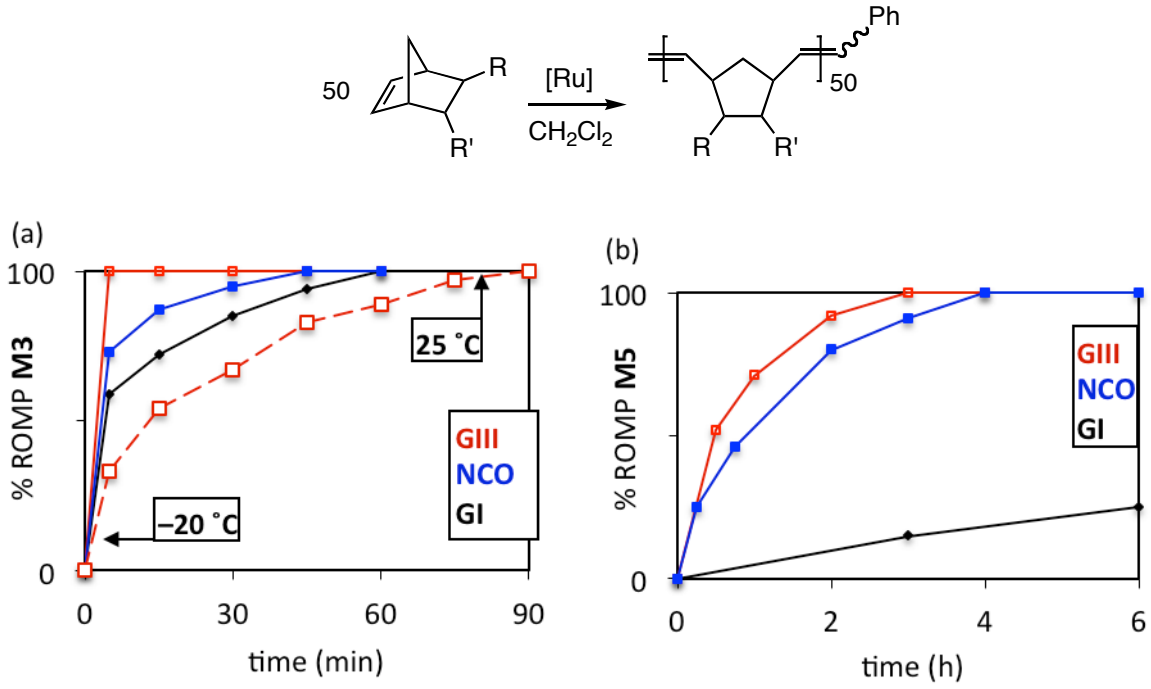


Figure 6. Relative reactivity of **Ru-8**, **Ru-4** and **Ru-7** in ROMP of 50 equiv of norbornene monomers that exhibit widely differing bulk. (a) Mono-succinimide monomer **M3**. (b) Digalactose monomer **M5**. For conditions, see Table 1; reactions at RT except where indicated.

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Table 1. ROMP performance of **Ru-8** vs. benchmark initiators.[a]

	Initiator	Monomer	M:I	Reaction time	M_n exptl (calc); kDa	PDI	Yield; %
1	Ru-4	**M5**	50	3 d	40.2 (33.4)	1.02	90
2	Ru-6	**M5**	50	2.5 h	32.8 (33.4)	1.02	90
3	Ru-8	**M5**	50	4 h	34.7 (33.4)	1.03	93
4	Ru-7	**M3**	50	≤5 min	12.5 (11.9)	1.2	90
5	Ru-7	**M3**	10	≤5 min	2.76 (2.35)	1.3	88
6	Ru-7	**M3**	10	0.5 h[b]	N.R.[c]	1.2	41
7	Ru-8	**M3**	50	0.75 h	12.3 (11.9)	1.02	92
8	Ru-8	**M3**	100	1.5 h	24.9 (23.5)	1.03	92
9	Ru-8	**M3**	10	0.5 h (THF)	2.75 (2.35)	1.03	90
10	Ru-8	**M3**	10	0.5 h	3.18 (2.35)	1.03	89
11	Ru-8	**M3** + **M5**	25 + 25	4 h (THF)	23.8 (22.7)	1.04	94

[a] 100 mg scale, RT, CH_2Cl_2, except where indicated. Time to completion judged by ^{1}H NMR analysis at 15 min intervals for the first hour, except for **Ru-7**/RT (5 min). Yields refer to isolated polymer. [b] Initiated at –30 ˚C, then allowed to warm to RT[13]. N.R. = not reported.

Our second question centered on the extent to which **Ru-8** could permit controlled ROMP at RT for monomers that are not sterically protected. Given its high reactivity toward bulky **M5**, we were surprised to find that **Ru-8** is able to effect chain-length precise ROMP of the much more reactive succinimide monomer **M3** *without* the cryogenic brake-pedal required for **Ru-7**. Illustrative of the latter is the very rapid but uncontrolled ROMP of **M3** by **Ru-7** at RT, which yields polymers with PDIs of 1.2 for a 50-mer (Table 1, entry 4), and 1.3 for a 10-mer (entry 5). Even for reactions of **Ru-7** initiated at –30 ˚C, Kiessling and coworkers reported a PDI of 1.2 for an [**M3**]$_{10}$ target (entry 6).[13] ROMP via **Ru-8**, in contrast, proceeds with very high precision at room temperature: with 50 or 100 **M3**, a PDI of 1.02-1.03 is obtained, again with chain lengths in excellent agreement with the reaction stoichiometry (entries 7, 8). Comparable control is maintained down to the demanding ten repeat-unit level, albeit with slightly better performance in THF, vs. CH_2Cl_2 (entries 9, 10).[9]

The capacity of **Ru-8** to support living ROMP of both bulky and sterically undemanding norbornenes is shown more explicitly in Figure 7. For ROMP of both **M1** and **M2**, a direct, linear correlation is found between the experimental chain lengths (i.e. the degree of polymerization) and the monomer-to-initiator ratio, a key marker of living polymerizations.[3,5,6,21,22]

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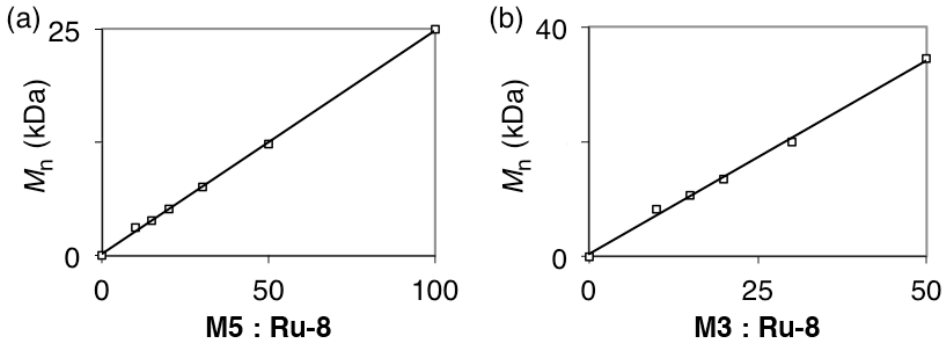

Figure 7. Dependence of polymer chain length on reaction stoichiometry in **Ru-8**-mediated ROMP of (a) **M5** and (b) **M3** (CH_2Cl_2, RT).

The high but controlled activity of **Ru-8** is of keen interest as a potential means of accessing well-defined block copolymers from monomers of widely different steric demand. To date, such materials cannot be efficiently prepared at RT. As expected from the behaviour of Fig. 7, diblock copolymers $[\mathbf{M5}]_{25}[\mathbf{M3}]_{25}$ (Table 1, entry 11) were readily obtained by sequential addition of **M5** and **M3** to **Ru-8** in THF at RT. Molecular weights are in excellent agreement with predicted values, and isolated yields exceed 90%. Current work focuses on the potential of such copolymers as a platform for assembly of neoglycopolymers tagged with a "tail-block" of diverse recognition epitopes, via nucleophilic functionalization at the succinimide sites.[23,24]

3.4 Removing Residual Ruthenium from Norbornene Polymers

The importance of minimizing ruthenium residues in ROMP materials was discussed above: levels below 5 ppm are mandated by FDA regulations, and lower concentrations may be essential for microelectronics applications. In earlier work on RCM with **Ru-4**, Fogg and co-workers reported ruthenium levels of ca. 2450 ppm after silica-gel chromatography. A series of experiments was therefore undertaken in which ROMP was carried out using 15 equiv of **M3** for 45 min, the reactions were then terminated with EVE (100 equiv), and the polymer was isolated by precipitation in ice-cold methanol, prior to column chromatography on silica gel (60 Å).

Visual inspection indicated that removal of **Ru-4** was best achieved using 9:1 hexanes:ethyl acetate as eluent. This effected good separation **M3** (R_f = 0.15) and minimized streaking of the Ru residues (Figure 8a). Use of more polar solvents such as CH_2Cl_2 results in considerable streaking, as seen in Figure 8b. Interestingly, the pseudohalide initiator **Ru-8** does not streak and appears to provide excellent separation (Figure 8c). However, analysis by ICP-MS

revealed that ca. 600 ppm of residual ruthenium was still present for the **M3** 15-mer. This suggests that the polarity of the isocyanate ligands is considerably less than that of (e.g.) the perfluoroaryloxide ligand.

A **B** **C**

Figure 8. Silica flash chromatography of A) **Ru-4** in 9:1 hexanes:ethyl acetate; B) **Ru-4** in CH_2Cl_2; C) **Ru-8** in CH_2Cl_2.

Ten-mers of **M3** and **M5** resisted elution by flash chromatography in CH_2Cl_2. TLC indicated an R_f value of 0 irrespective of solvent (Table 2). An increase in R_f values was found on increasing poly(**M3**) lengths from 15, 20, 30 to 50 (Table 2). We speculate that the comparative rigidity of these semi-rigid rod polynorbornenes maximizes interaction between the polar substituents on the 10-mers and the silica gel (Figure 9). Even a slight increase in chain length, to 15-mers, appears sufficient to enable a more protected structure, which can thus elute faster. As chain lengths increase, 20 units, 30 units, etc., the polymer has more degrees of freedom for folding, allowing even faster elution.

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Table 2. Retention factors (R_f values) for poly(**M3**) in silica gel chromatography.[a]

Entry	Theor. M_n[b] (theor. *n*)	Exptl. M_n[b] (found *n*)	R_f Value in CH_2Cl_2[d]	PDI	Isolated Yield (%)
1	0.235 (1)	0.235 (1)	0.13	-	88
2	2.35 (10)	-[c]	0[d]	-	-
3	3.52 (15)	3.36 (14)	0.15	1.05	85
4	4.70 (20)	4.99 (21)	0.25	1.03	89
5	7.05 (30)	6.95 (30)	0.35	1.04	90
6	11.7 (50)	12.4 (52)	0.78	1.02	92

[a] Typical ROMP conditions: THF, 55 mM, 25 °C. Purification conditions: precipitation with MeOH followed by flash chromatography with 1 cm diameter column and 14 cm of packed 60 Å silica. [b] Values are in Da (x10^3). [c] Polymer did not elute from column. [d] Other solvent systems attempted were 9:1 Hexanes:EtOAc, toluene, EtOAc and MeOH.

Chain length = 10 **Chain length = 50**

Figure 9. Cartoon illustrating potential for greater interaction between polar substituents (red) of 10-mers relative to longer chains.

Additional literature methods were employed to remove spent **Ru-8** from **M5** and **M3** (Table 5). In each case the proportion of residual ruthenium analyses was assessed by ICP-MS. Least successful was the use of silica-based spherical scavengers (QuadraSil MP),[25] which resulted in only a 50% decrease in residual ruthenium, to ca. 850 ppm. Stirring with a silica slurry[26] was minimally better (ca. 820 ppm Ru), while treatment with activated carbon for 24 h[27] was most effective, giving a final Ru content of ca. 130. In comparison, flash chromatography with CH_2Cl_2 was ineffective (ca. 700 ppm). However, ca. 50% of the polymer is lost in purification by adhesion to the activated carbon, as compared to only 10% using flash chromatography. The effect of increasing amounts of activated carbon were explored using the 50-mer. Higher proportions of activated charcoal were found to severely decrease yields (entries 6, 8 and 9) although improving ruthenium removal. Best results were found by combining this treatment with chromatography, but yields were then only 40%.

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Table 3. Comparison of residual % Ru present after various purification methods used after the initial precipitation with methanol.[a]

Entry	Mono-mer	M/I	Method (solvent system)	Yield (%)	% Ru (ppm)
1[10]	**M3**	15:1	–	95	1923
2[10]	**M3**	15:1	stirred with QuadraSil MP (10% w/w; CH_2Cl_2)	61	848
3	**M3**	15:1	stirred with SiO2 (10% w/w; CH_2Cl_2)	48	816
4	**M3**	15:1	flash chromatography (CH_2Cl_2)	88	691
5	**M3**	15:1	stirred with activated carbon (50% w/w; CH_2Cl_2)	45	127
6[13]	**M5**	50:1	stirred with activated carbon (0.5% w/w; CH_2Cl_2)	84	493
7	**M5**	50:1	flash chromatography (9:1 hexanes: ethyl acetate)	84	358
8	**M5**	50:1	stirred with activated carbon (20% w/w; CH_2Cl_2)	55	176
9	**M5**	50:1	stirred with activated carbon (50% w/w; CH_2Cl_2)	48	90
10	**M5**	50:1	stirred with activated carbon (50% w/w; CH_2Cl_2) then flash chromatography (9:1 hexanes: ethyl acetate)	32	41

[a] Standard ROMP conditions: 2.0-6.6 mol% catalyst, [**M5**] or [**M3**] = 55 mM, THF, 25 °C, 30 min.

Good results have been reported on use of 15% H_2O_2 to oxidize first and second generation Grubbs as well as Hoveyda Grubbs catalysts immediately after RCM has been performed.[28] While no polymer oxidation was evident from ^{1}H NMR integration against trimethoxybenzene as an internal standard, and GPC analysis indicated a PDI of 1.04 before and after treatment, [**M3**]$_{15}$ and [**M5**]$_{15}$ polymers remained discoloured, suggesting that Ru removal was unsuccessful. Quantification was not undertaken, however, and this treatment may thus be worth closer examination.

3.4 Conclusions

The foregoing describes a new Ru-isocyanate catalyst that exhibits superb versatility in terms of its capacity to effect efficient, controlled, ambient-temperature ROMP of norbornene monomers that are characterized by extremes of steric bulk. Precise specification of molecular weights is maintained down to the oligomeric level, even for a highly reactive monosubstituted norbornene, without recourse to low temperatures to curb runaway reaction. This rare balance of properties enables straightforward, efficient access to well defined diblock copolymers from monomers of widely differing reactivity.

Control over run lengths, and hence the number of binding or signaling sites, is central to many of the leading applications of ROMP polymers. The high performance of **Ru-8**, its

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excellent selectivity for ring-opening at ambient temperatures, and its consequent compatibility with robust, convenient glovebox operations, are likely to significantly expand opportunities in the rapidly developing applications of ROMP-based designer materials.

Less satisfactory, however, is its affinity for silica gel. Our initial hope that this affinity would be sufficiently high to facilitate removal of Ru-residues post-metathesis was not met. A combination of stirring with activated carbon and flash chromatography reduces residual ruthenium levels to ca. 41 ppm, but yields are then low (32%). This suggests that the isocyanate groups do not confer sufficient polarity for Si-gel affinity. An alternative possibility that should be reexamined is that retention of Ru is associated with incomplete cleavage of the Ru endgroups from the polymer by treatment with ethyl vinyl ether.

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(20) Solid-supported catalysts (more generally explored for RCM and CM) would of course obviate this problem, if leaching is minimal. (Recent reviews: (a) Halbach, T. S.; Mix, S.; Fischer, D.; Maechling, S.; Krause, J. O.; Sievers, C.; Blechert, S.; Nuyken, O.; Buchmeiser, M. R., *J. Org. Chem.* **2005**, *70*, 4687-4694. (b) Buchmeiser, M. R., *Chem. Rev.* **2009**, *109*, 303-321). The growing ROMP polymer may occlude Ru sites, limiting control over polymer chain length and polydispersities (it must also be cleaved to release the free polymer chain). Nervertheless, recent reports describe Ru levels ranging from 16-22 ppm to as low as <7 ppb in polynorbornene and polycyclooctene prepared using supported ROMP initiators. See: (c) **Bek Topic Catl 2010 200;** (d) Van Berlo, B.; Houthoofd, K.; Sels, B. F.; Jacobs, P. A. *Adv. Synth. Catal.* **2008**, *350*, 1949-1953.
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Chapter 4: Synthesis and Reactivity of Ruthenium Carbynes

4.1 Introduction

Metal carbyne chemistry began with Fischer's unexpected discovery of $[W(\equiv CPh)(CO)_4Cl]$ in 1973.[1] This species resulted from attempts to replace the ethoxy group of a classic Fischer carbene with chlorine, by reaction with BCl_3.[1] Many carbyne complexes have since been prepared.[2] The opportunities for alkyne metathesis, by analogy to the olefin metathesis processes enabled by the corresponding M=CRR' species, were recognized at an early date. Many prominent catalysts for alkyne metathesis are now known. Almost all examples come from the group 6 metals tungsten and molybdenum: in one instance, a rhenium complex has been reported (Figure 1).[3-6] Ruthenium-catalyzed alkyne metathesis has the potential to expand uptake of this methodology in synthesis, just as Grubbs' discovery of Ru catalysts transformed uptake of olefin metathesis. The anticipated advantages, as compared to the group 6 metals, lie in improved ease of handling (important for uptake by synthetic organic chemists) and greater functional group tolerance.

Synthesis and study of ruthenium carbynes has fallen off following Roper's pioneering work of the 1980's and early 1990's.[7,8] Several dozen ruthenium carbyne complexes are now known, but in most cases their reaction chemistry is dominated by transformation of the Ru-carbyne functionality into a Ru=C group. Most Ru carbyne complexes are prepared by protonating allenylidene or vinylidene functionalities (Figure 2). Particularly important contributions to this area have been made by the groups of Dixneuf[9-11] and Werner,[12-15] as well as Spivak,[16-18] Gimeno,[19] and Valerga.[20] These carbynes are highly base-sensitive, readily undergoing deprotonation and reversion to the parent cumulenylidene complex in the presence of (e.g.) NEt_3 (Figure 2b). Ru(IV) carbynes are in fact generally susceptible to this behaviour, as are cationic M(II) carbynes; M = Ru, Os (Figure 3).[12,14,21] It should be noted that for neutral Ru(II) carbynes, no such behavior has been uncovered to date. The reduced electrophilicity of such systems may be important in stabilizing the carbyne structure.

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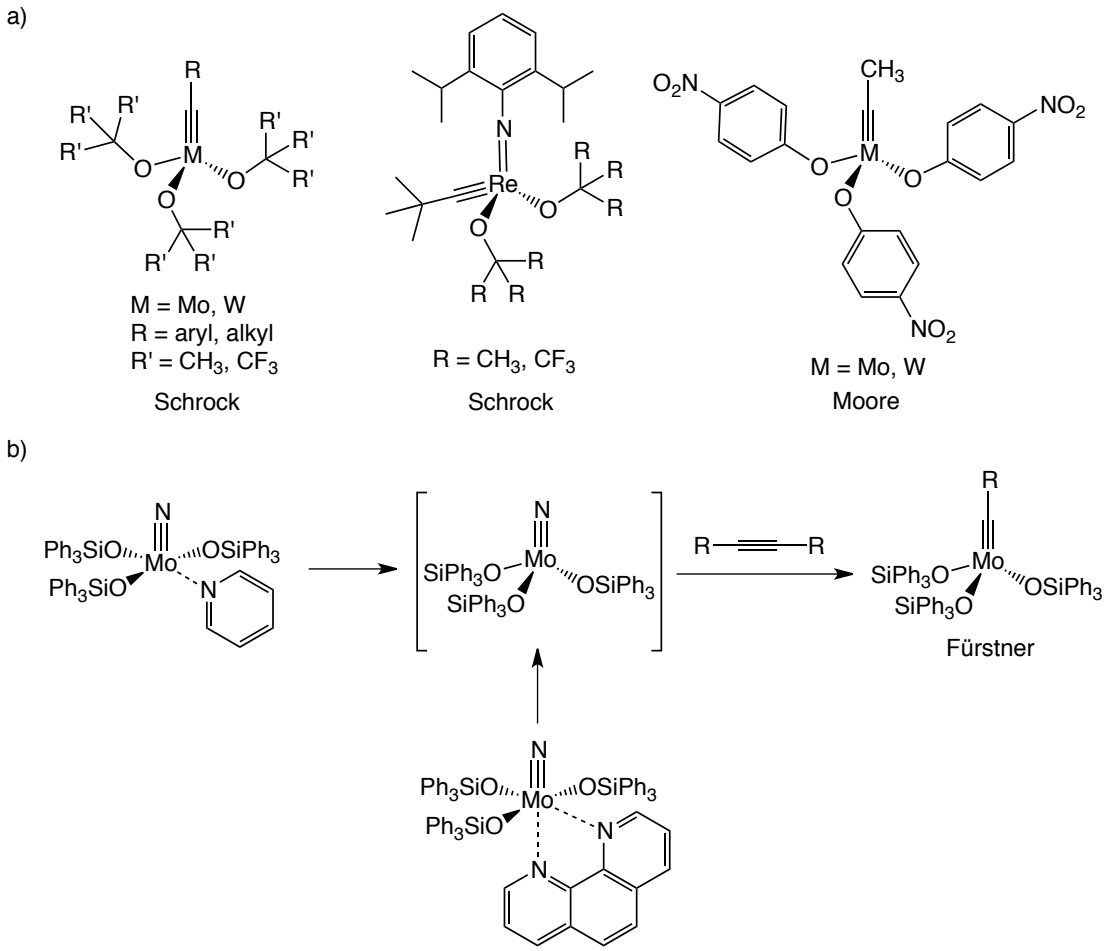

Figure 1. Alkyne metathesis catalysts in dominate use: a) catalysts not requiring alkyne activation and b) precatalysts requiring alkyne activation.

We will term as "Class A" carbynes those carbyne complexes that are similarly susceptible to reformation of an M=C entity (whether a cumulenylidene or – as discussed later – an alkylidene moiety). That is, Class A carbynes can be viewed as latent M=C complexes. We will use the term "Class B" carbynes to describe complexes in which the carbyne functionality is not mutable. The complexes of Figure 1 would fall in this category: this enables reactivity with alkynes but immunity to olefins. Such orthogonal reactivity is central to selectivity.

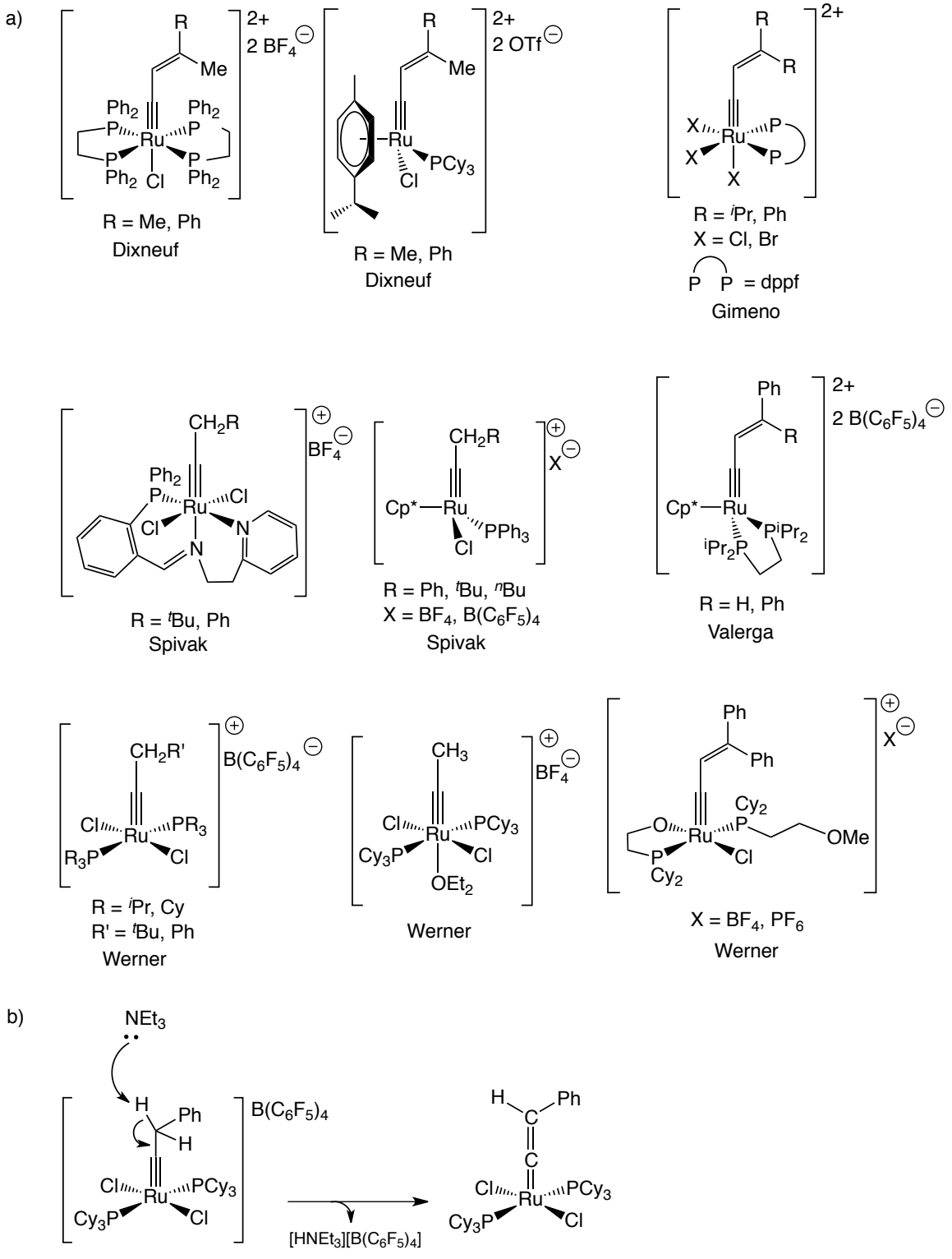

Figure 2. a) Ruthenium carbyne complexes formed by protonation of cumulenylidenes. b) Representative reaction with base.

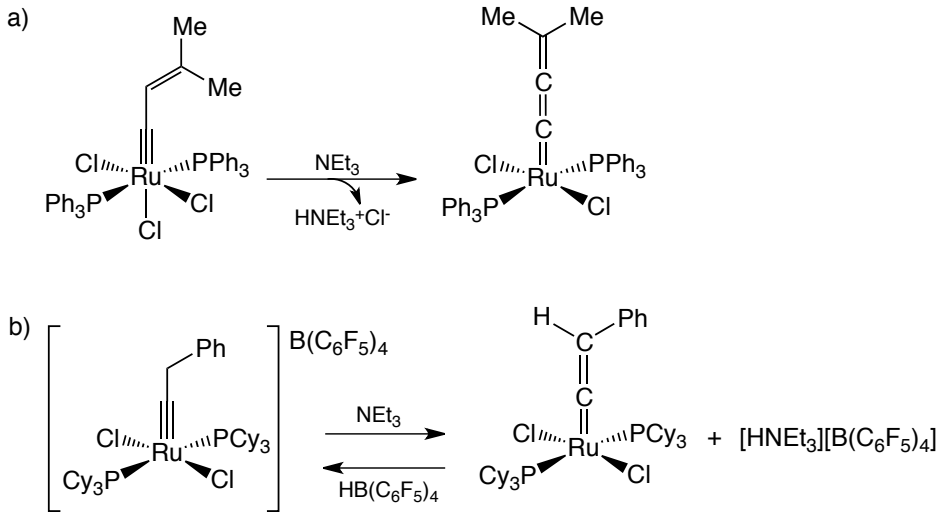

Figure 3. Representative base sensitive reactions for a) Ru(IV) carbynes and b) cationic Ru(II) carbynes.

A smaller number of ruthenium carbyne complexes are accessed by routes other than protonation of a cumulenylidene complex (Figure 4). Many of these complexes were uncovered in pioneering work by Roper and co-workers.[7,8,22-25] Otherwise most extensive studies have been carried out by the Johnson group, which reported a series of five-coordinate Ru(IV) carbynes of the type $RuX_3(\equiv CAr)(L)$ (X = halide, triflate; L = PCy_3, H_2IMe).[26-28] These are designed to mimic the $MX_3(\equiv CR)$ structure of the prominent group 6 alkyne metathesis catalysts shown in Figure 4 (M = Mo, W; X = OAr, etc.)[27] To date, the $RuX_3(\equiv CAr)(L)$ complexes have not shown alkyne metathesis activity. Given the presence of a proton at the β-position of the carbyne, and the high formal oxidation state of these complexes, it seems likely that they may also undergo facile deactivation into vinylidenes through rapid, base-induced loss of HCl. They are therefore provisionally classified as masked Class A carbynes.

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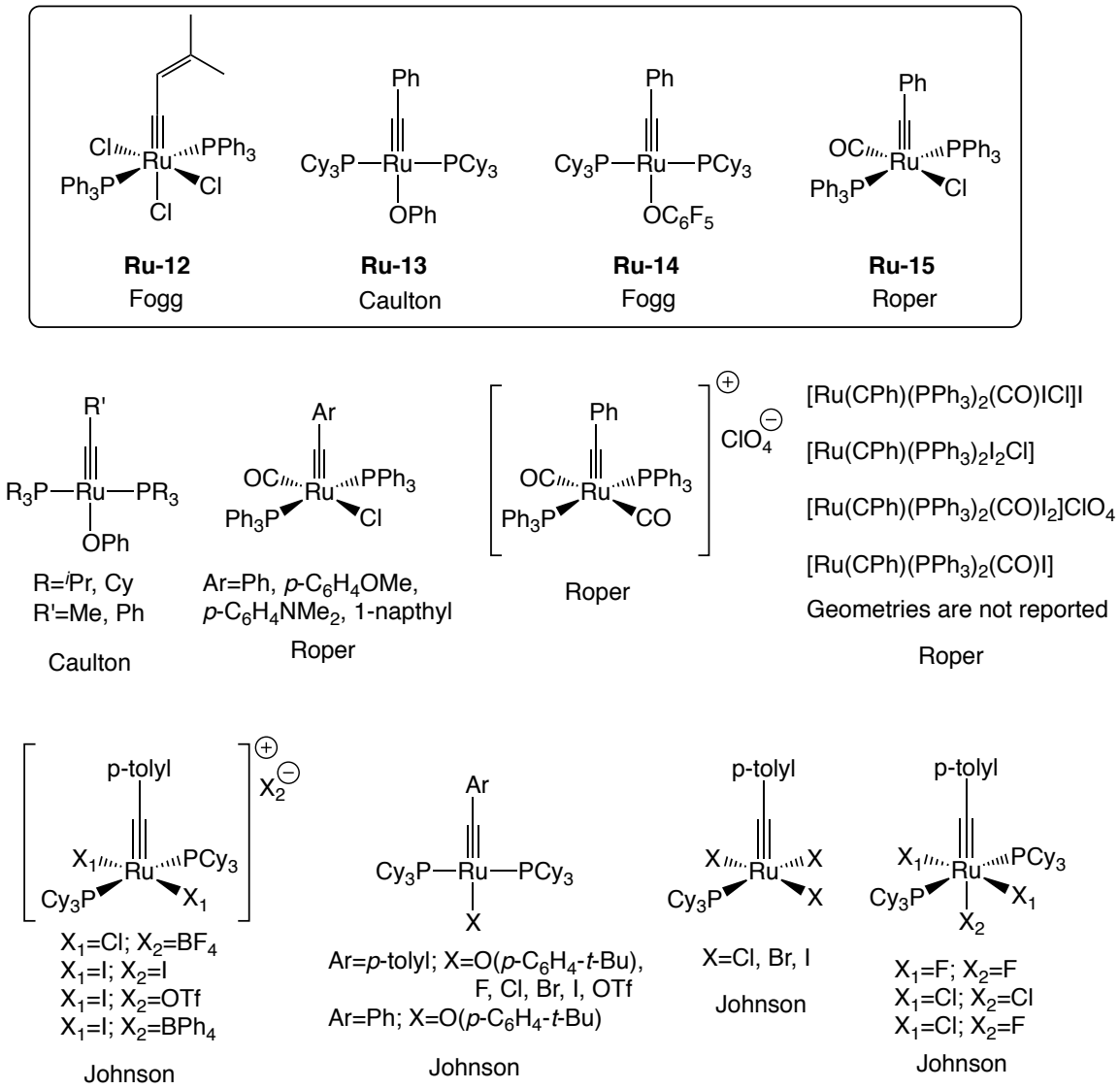
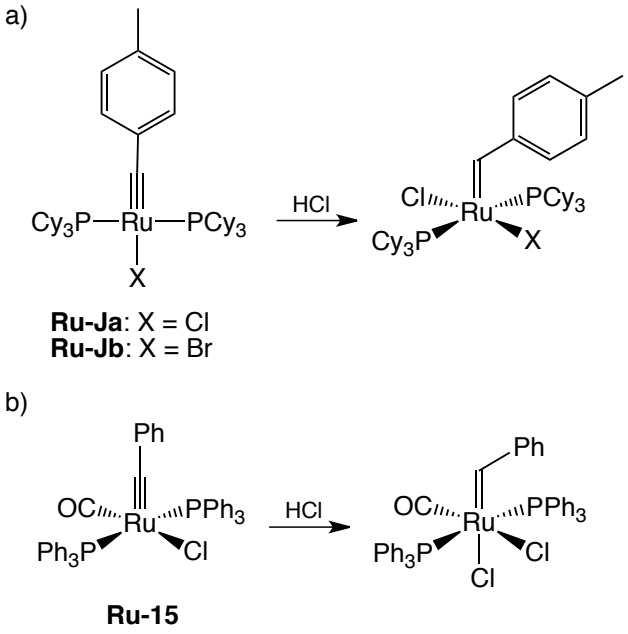


Figure 4. Ruthenium carbyne complexes formed by routes other than protonation. Inset shows ruthenium carbynes studied in this chapter.

Figure 4 also includes the known examples of four-coordinate carbynes, developed by the groups of Caulton, Fogg, and Johnson.[29-31] One of these (**Ru-J**, Scheme 1), as well as the Roper carbyne **Ru-15**, has been shown to exhibit sensitivity to acid, rather than base. Thus, **Ru-J** and **Ru-15** react with HCl to generate alkylidene derivatives (Scheme 1). Again, we classify these as Class A carbynes, as these species likewise regenerate Ru=C species (in this instance, Ru-alkylidene) in the presence of acid. However, it is unclear how general this behavior is: that is, whether it is also triggered by

weaker acids, and whether changes to the ligands (**Ru-Ja** and **Ru-Jb)** could shut down this behavior. In short, the organometallic chemistry of ruthenium carbynes beyond those of Figure 2 is little explored and poorly understood.



Scheme 1. Neutral carbynes that react with acid. a) Johnson's **Ru-J** complexes and b) Roper's **Ru-15** complex.

Development of routes to sterically and electronically tunable Ru carbyne complexes requires a clearer picture of the fundamental factors controlling their stability. This chapter aims to add to our understanding through studies of the synthesis, bonding, and reactivity of four potentially Class B ruthenium carbynes, ranging in coordinate number from four to six, and differing significantly in the electron density at the Ru center. These are six-coordinate vinylcarbyne **Ru-12**, reported by Amoroso and Fogg; the five-coordinate Roper carbyne **Ru-15**; and the four-coordinate complexes **Ru-13** and **Ru-14**. Reactivity studies focus on ligand exchange reactions, the susceptibility of the carbyne functionality to nucleophilic attack, and the tolerance of these species for air and water.

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4.2 A Six-coordinate Vinylcarbyne Complex of Ruthenium

4.2.1 Analysis of Ru-12 by Cyclic Voltammetry

Cyclic voltammetry (CV) can provide direct insight into the redox potentials required to induce reduction or oxidation of molecular complexes. CV analysis of Ru(IV) vinylcarbyne complex **Ru-12** was used to determine how readily reduction could be induced. The spectrum was measured for a CH_2Cl_2 solution of **Ru-12** with $[^nBu_4N][PF_6]$ as the supporting electrolyte. Two reduction and oxidation peaks were observed, at E_{pc} = –1.55 V, –1.77 V and E_{pa} = 0.18 V, 0.37 V respectively (E_{pc} = cathodic potential; E_{pa} = anodic potential), as shown in Figure 5, with identical voltammetric profiles irrespective of the scan direction. No corresponding oxidation or reduction peaks are seen for the peaks reported above, indicating irreversible behavior, whether transformation of Ru(IV) into Ru(II), or reduction at a ligand site. The nature of this transformation emerged more clearly in preparative-scale chemistry described in the next section.

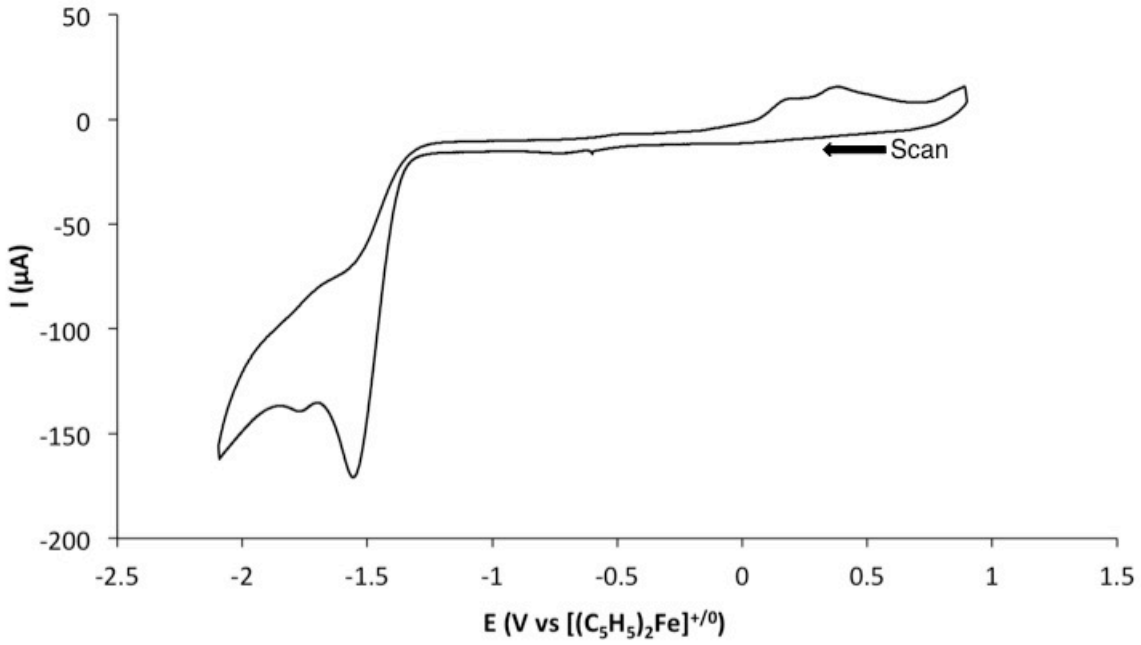

Figure 5. Cyclic voltammagram of $RuCl_3(\equiv CCHCMe_2)(PPh_3)_2$, **Ru-12** (3 mM in CH_2Cl_2) with $[(^nBu)_4N][PF_6]/CH_2Cl_2$ (0.05 M). Scan rate of 1.5 V/sec using a platinum wire working electrode, platinum mesh counter electrode and silver wire pseudoreference electrode, with ferrocene as an internal standard.

4.2.2 Reactivity of Vinylcarbyne Ru-12 Toward Base

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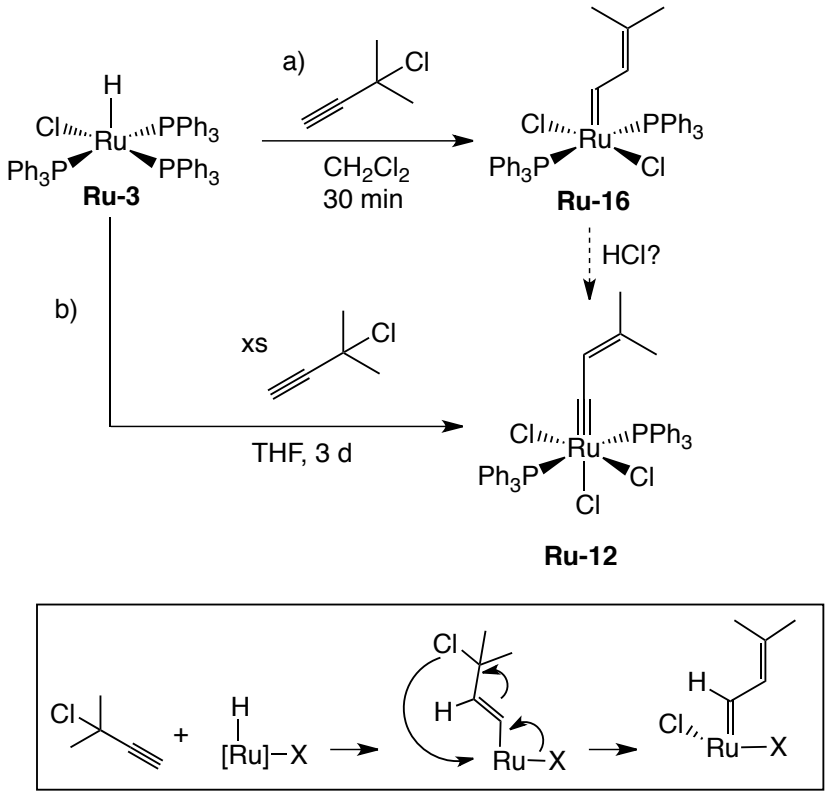
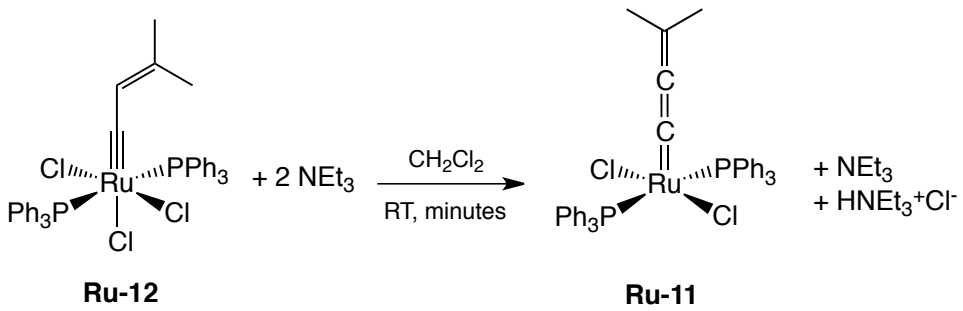
Vinylcarbyne **Ru-12** was originally observed by Dino Amoroso of the Fogg group as a minor byproduct in the synthesis of vinylcarbene **Ru-16** by reaction of $RuHCl(PPh_3)_3$ with excess propargyl chloride (Scheme 2a).[30] It was subsequently prepared in 75% yield by using an excess of propargyl chloride, although a contaminant in the reagent (perhaps HCl; Scheme 2b) was suggested as the origin of the side-reaction.



Scheme 2. Syntheses of a) vinylcarbene **Ru-16** and b) vinylcarbyne **Ru-12**.[30] Inset shows the proposed mechanism for formation of **Ru-16**, according to Diver.[32] Propargyl chloride = 3-chloro-3-methyl-1-butyne.

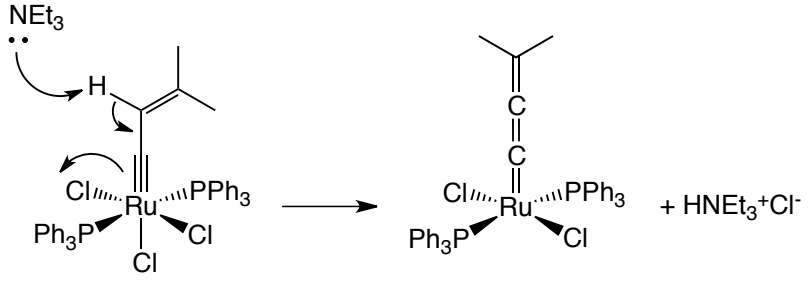
In the present work, vinylcarbyne **Ru-12** was viewed as a potential entry point to diverse Ru carbynes, offset by the possibility that it is formed by protonation of an allenylidene intermediate, and is hence a Class A carbyne. Experiments were therefore undertaken in which **Ru-12** was treated with a twofold excess of triethylamine in CH_2Cl_2 (Scheme 3). Within minutes of adding base, the solution turned from orange to dark green. A dark green solid was isolated in 95% yield.



Ru-12 **Ru-11**

Scheme 3. Conversion of vinylcarbyne **Ru-12** to allenylidene **Ru-11** by treatment with base.

NMR analysis of the isolated green powder indicated complete loss of the vinyl proton observed at 4.36 ppm for **Ru-12**. Consistent with identification of the product as an allenylidene, only aromatic and methyl signals are evident in the ^{1}H NMR spectrum, while the $^{13}C\{^{1}H\}$ NMR spectrum shows a diagnostic triplet for the Ru=*C* carbon at 303.5 ppm (^{2}J(PC) = 13.1 Hz), and the expected singlets for Cβ and Cα at 228.5 and 146.5 ppm, respectively. These NMR values are very similar to those reported for the diphenyl analogue: $^{13}C\{^{1}H\}$ triplet for Ru=*C* carbon at 301.2 ppm (^{2}J(PC) = 12.9 Hz), and singlets for Cβ and Cα at 225.4 and 145.0 ppm, respectively.[33,34] This rapid base-induced elimination of HCl confirms that **Ru-12** should be reassigned as a Class A carbyne. A possible mechanism for its formation is given in Scheme 4.



Ru-12 **Ru-11**

Scheme 4. Proposed mechanism for base-induced transformation of vinylcarbyne **Ru-12** into allenylidene **Ru-11**.

4.2.3 Reactivity of $RuCl_3(\equiv CCHCMe_2)(PPh_3)_2$ Ru-12 in Ligand Exchange with IMes

Electron-rich ligands may be important to stabilize the carbyne against nucleophilic attack.[7] Examples of such behavior include the base-sensitivity described above, but literature reports also highlight 1,2-migration of phosphine,[35] chloride,[26] and

hydride[36] ligands. Attempts to replace the triphenylphosphine ligand in **Ru-12** with the NHC ligand IMes, however, led to unexpected decomposition. Thus, treating **Ru-12** with IMes (1 equiv) on NMR scale in C_6D_6 showed after 3 h a singlet for free PPh_3 (–5.5 ppm) by $^{31}P\{^1H\}$ NMR analysis, accompanied by a multitude of phosphorus peaks (Figure 6). Treatment with a fourfold excess of free IMes resulted in complete decomposition within 30 min, with no signals being apparent for either starting **Ru-12** or allenylidene **Ru-11**. The reason for this behavior is unclear, but it is maintained irrespective of the batch of IMes, **Ru-12**, or solvent. To preclude the possibility of contamination by air and/or water, one such experiment was carried out in an NMR tube equipped with a J. Young valve, and charged in an N_2-filled glovebox.

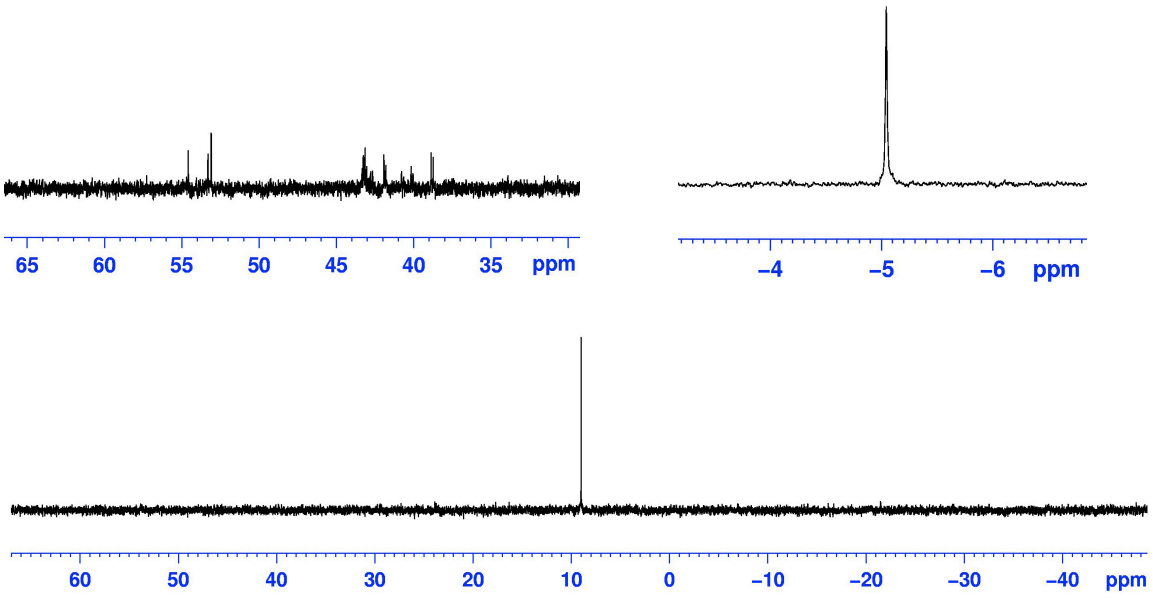


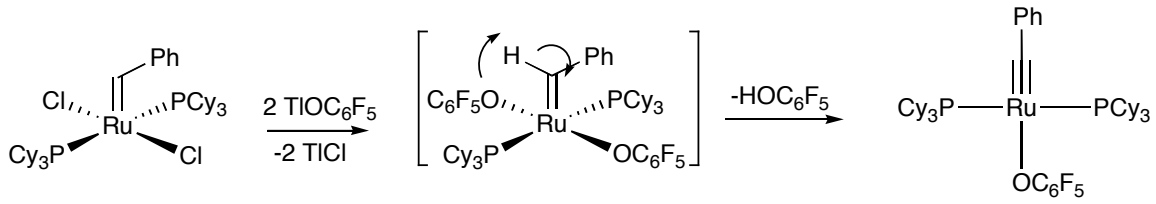
Figure 6. $^{31}P\{^1H\}$ NMR spectra (300 MHz, C_6D_6) indicating decomposition of $RuCl_3(\equiv CCHCMe_2)(PPh_3)_2$ **Ru-12** on attempted reaction with IMes. Top: reaction mixture after 3 h. Bottom: starting **Ru-12**.

4.2.4 Reactivity of $RuCl_3(\equiv CCHCMe_2)(PPh_3)_2$ Ru-12 Toward Air and Water

A qualitative assay of the stability of **Ru-12** was undertaken by exposing an NMR tube of **Ru-12** (ca. 20 mg) in $CDCl_3$ (ca. 0.5 mL) to atmospheric conditions. Over a period of 2-3 minutes the orange compound had changed to a dark greenish-brown color.

4.3 Four-coordinate Ru Benzylidyne Complexes

To date, very few four-coordinate ruthenium carbyne complexes are known. The first example, square planar Ru(≡CPh)(PCy_3)$_2$(OPh) (**Ru-13**), was unexpectedly obtained by Caulton following treatment of the first-generation Grubbs catalyst with two equivalents of sodium phenoxide.[37] The Fogg group showed that identical behavior occurs with perfluorophenoxide despite co-formation of highly acidic pentafluorophenol (Scheme 5), convincing evidence that the reaction proceeds via sterically-driven α-elimination.[31] Most recently, Johnson and co-workers prepared the halide analogues **Ru-Ja** and **Ru-Jb** (respectively) by use of an alkyl germylene in place of the aryloxide ligand.[27]



Scheme 5. Sterically-driven α-elimination as a route to carbyne complexes from alkylidene parents.[31]

Classification of **Ru-J** as a Class A carbyne, on the basis of its instability toward formation of a Ru-alkylidene in the presence of acid, was discussed in section 4.1 above. This instability can be understood in terms of electrophilic attack at the carbyne carbon, implying a high electron density at this site. Here we wished to establish whether this vulnerability could be limited by replacing the chloride ligand with phenoxide, with its more electronegative oxygen donor, or (in the extreme) perfluorophenoxide. These phenoxide and perfluorophenoxide complexes were synthesized as described in the literature reports.[31,37]

4.3.1 Sensitivity of Four-coordinate Ru Benzylidynes Toward Air and Water

Qualitative assessment of aryloxides **Ru-13** and **Ru-14** demonstrated higher sensitivity to moisture and air than the six-coordinate **Ru-12**, with decomposition within seconds of exposing to air. This higher reactivity is hardly surprising given the low coordination number. Surprisingly, however, a preliminary DFT analysis of **Ru-13** indicated that the highly covalent Ru-C bond greatly diminishes the strength of the trans-

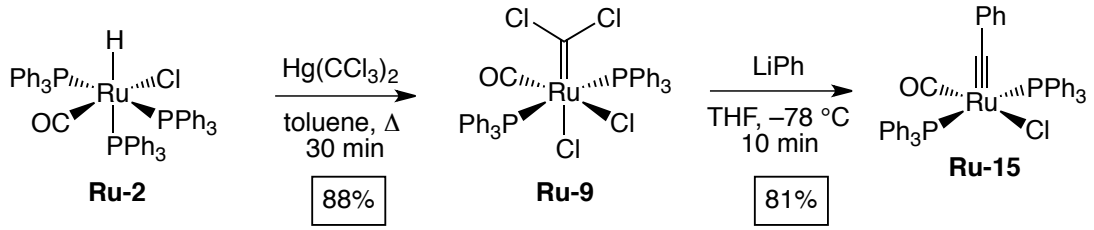
disposed Ru-OAr bond (bond orders >2.2 vs. 0.2, respectively). The ionic character of the latter presumably contributes to its vulnerability towards Bronsted acids such as water. On a practical level, the high sensitivity of these species means that even if they were metathesis-active, they would be no easier to handle than their group 6 predecessors. It should be noted that a stable trichloride, $RuCl_3(PCy_3)(\equiv CH)$, is readily accessible from these four-coordinate complexes,[27] which may be a promising precursor for future synthetic studies.

4.4 A Five-Coordinate Benzylidyne Complex: Studies of the Roper Carbyne $RuCl(\equiv CPh)(CO)(PPh_3)_2$

4.4.1 Synthesis

Ru-15 is reported to show excellent stability toward air and water. This tolerance to water makes **Ru-15** a compelling lead compound: the high sensitivity of **Ru-14** and **Ru-13** (all of which are decomposed by air within seconds) means that even if these species were metathesis-active, they would be no easier to handle than their group 6 predecessors. The original synthesis of **Ru-15** was serendipitous: attempts to functionalize the dichlorocarbene ligand in by reaction with phenyllithium instead led to benzylidyne **Ru-15**.[23] The complex was subsequently prepared by the method depicted in Scheme 6. This two-step procedure is rapid (complete in <1 h) and straightforward, but relies on use of the carbene transfer agent $Hg(CCl_3)_2$ to install the dichlorocarbene ligand. Organomercury compounds, while known for their excellent alkyl-transfer capabilities,[25,38] are also notorious for their high toxicity (LD_{50}: 50 μg/kg for dimethylmercury; figures for the trichloromethyl derivative are not reported).[39] The $Hg(CCl_3)_2$ reagent was handled with the utmost care using double-glove techniques and rigorous secondary containment, as described in the Experimental section (Chapter 2). The reaction of **Ru-2** with $Hg(CCl_3)_2$ at reflux works in part because the Hg(II) is ultimately deposited as elemental mercury, which is removed by filtering through Celite. This reaction was found to proceed readily and in high yield. The subsequent reaction to prepare **Ru-15**, however, presented complications. These were traced to an unexpectedly high sensitivity of **Ru-9** to water, as discussed in the following section. Ultimately, however, synthesis of **Ru-15** by the method of Scheme 6 below,[23] but using standard

Schlenk and glovebox techniques to protect against unwanted hydrolysis, afforded clean **Ru-15** in 81% isolated yield.



Scheme 6. Synthesis of RuCl(≡CPh)(CO)(PPh_3)$_2$, **Ru-15**.

4.4.2 Synthesis of Dichlorocarbene Ru-9, a Potentially Versatile Carbyne Precursor

Access to **Ru-15** necessitates clean synthesis of **Ru-9**, as illustrated in Scheme 6. As well, however, the latter complex is of broader interest. While in the present work our chief focus was on the product **Ru-15**, dichlorocarbene **Ru-9** is of keen interest for its potential to give access to a range of carbyne complexes. Roper has described the transformation of the dichlorocarbene ligand in **Ru-9** by reactions with H_2X (X = O, S) to give carbyne derivatives RuCl2(≡CX)(CO)(PPh_3)$_2$ (e.g. **Ru-15**, where X = O).[22] In contrast, however, reactions with RXH give carbene complexes (Figure 7). A qualitative ranking of reactivities appears in Table 1.[40] Dichlorocarbene **Ru-9** was shown to be less reactive than its difluoro analogue in transformation into the carbyne, but also less susceptible to formation of the undesired Fischer carbene on reaction with methanol, although methanethiol yields a carbene product.

Table 1. Qualitative comparison of the reactivity of dihalocarbenes $MCl_2(=CX_2)(CO)(PPh_3)_2$.

	$L_nRu(=CF_2)$		$L_nRu(=CCl_2)$		$L_nOs(=CFCl)$	
Nu^-	Rate	Product	Rate	Product	Rate	Product
H_2O	Fast	CO	Slow	CO	Slow	CO
MeOH	Fast	=C(F)OMe	No rx	No rx	No rx	No rx
MeSH	No rx	No rx	Fast	$=C(SMe)_2$	Fast	=C(F)SMe

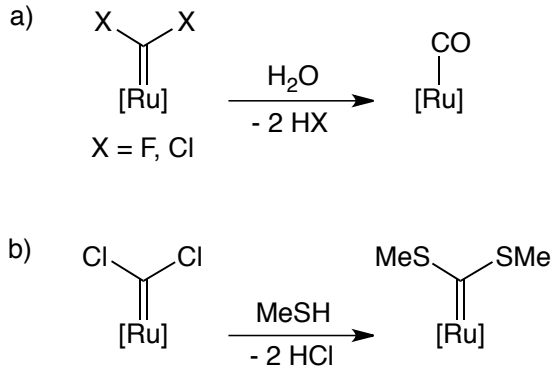
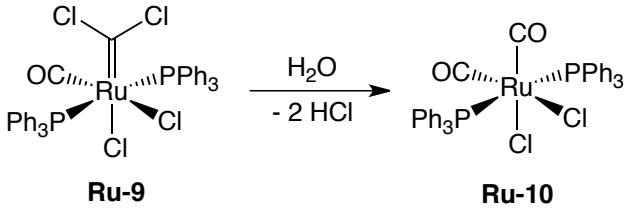


Figure 7. Representative reactions of dihalocarbenes from Table 1 with a) H_2O and b) MeSH.

The data of Table 1 indicate that **Ru-9** is less susceptible to nucleophilic attack by H_2O than the fluorinated carbene. Indeed, Roper's original synthesis of **Ru-9** was carried out at reflux in air. In repeating this preparation, the 30 min reflux period was carried out under argon, but using non-dried solvents and with workup in air, according to the original procedure.[25] The yield was low, however, and significant amounts (35%) of a side-product were evident by $^{31}P\{^{1}H\}$ NMR analysis (Figure 9). This species was identified as dicarbonyl **Ru-10**, formed by hydrolysis of the chloroalkylidene. The dicarbonyl product is formed via de-insertion of the chlorine groups and addition of oxygen to the alkylidene, as shown in Figure 8. Assignment of the observed product as **Ru-10** was confirmed by the excellent agreement with the literature $^{31}P\{1H\}$ NMR chemical shift (a singlet at 34.9 ppm). Infrared analysis was also consistent with this product. Stretching bands for the symmetrical and asymmetrical stretches of the cis-disposed CO ligands were seen at 2062 and 1998 cm^{-1}, respectively, again in agreement with literature values.[41]



Ru-9 **Ru-10**

Figure 8. Hydrolysis of dichlorocarbene **Ru-9** to yield dicarbonyl complex **Ru-10**.

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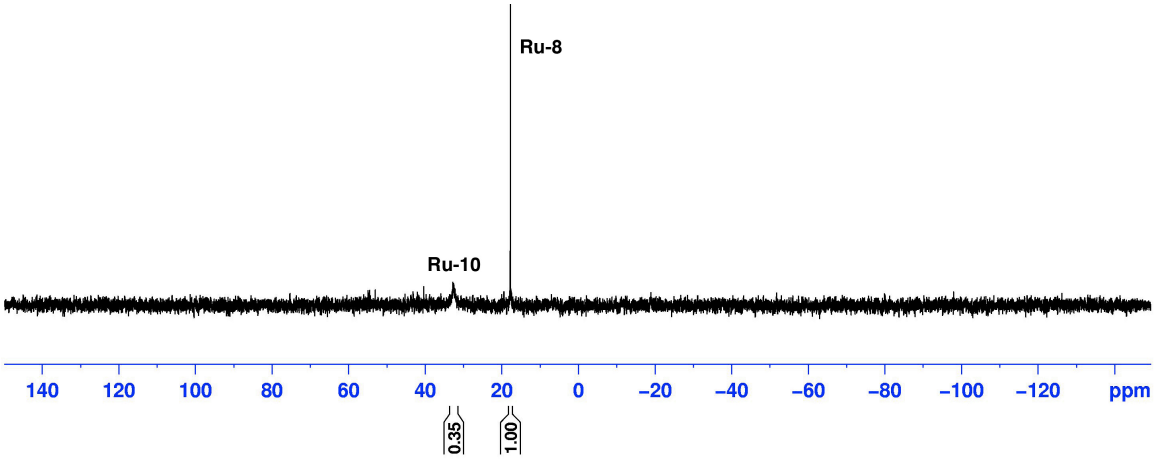

Figure 9. $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture formed on heating $RuHCl(CO)(PPh_3)_3$ **Ru-2** with $Hg(CCl_3)_2$ in toluene (Fischer, unpurified) under argon, with workup in air. Peaks at 16.8 and 34.9 ppm represent **Ru-9** and **Ru-10** respectively; 74% yield **Ru-9**.

When synthesis of **Ru-9** is carried out using dry solvents under argon using standard Schlenk techniques, followed by workup in a glovebox, no contaminating **Ru-10** can be seen, and isolated yields of **Ru-9** reach 88%. With clean **Ru-9** in hand, the rate of the hydrolysis reaction was re-examined under controlled conditions. Thus, hydrolysis was carried out on a suspension of 100 mg **Ru-9** in water (non-degassed) at RT. Aliquots were removed periodically and dissolved in $CDCl_3$ for $^{31}P\{^{1}H\}$ NMR analysis, monitoring for the disappearance of the singlet at 16.8 ppm due to **Ru-9**, and emergence of the singlet at 34.9 ppm due to **Ru-10**. The rate curve for hydrolysis is shown in Figure 10. Complete conversion of **Ru-9** to **Ru-10** requires 3 days at RT. Under thermolytic conditions, however, decomposition is fast, as noted above (25% after 0.5 h in refluxing toluene). This sensitivity, and the need for rigorous water-exclusion, should be borne in mind not only for the transformation of dichlorocarbene **Ru-9** into the phenylcarbyne **Ru-15**, but for any future reactions in which **Ru-9** is used as a precursor to additional carbynes.

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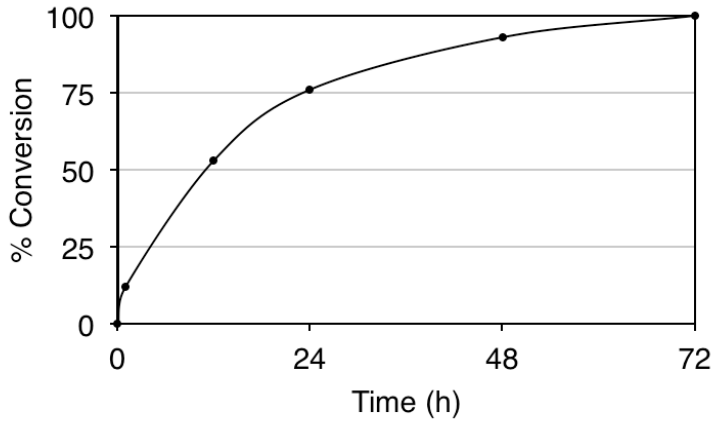

Figure 10. Rate curve for hydrolysis of **Ru-9** in H_2O at RT. Assessed by $^{31}P\{^1H\}$ NMR analysis of aliquots dissolved in $CDCl_3$.

4.4.3 Ligand Exchange of RuCl(≡CPh)(CO)(PPh_3)$_2$, Ru-15

Ligand exchange (and salt metathesis) reactions of **Ru-15** are of interest for their potential to give access to an array of carbyne products. Preliminary investigations of the reactivity of carbyne **Ru-15** focused on ligand exchange with PCy_3 at room temperature in THF-d_8. $^{31}P\{^1H\}$ NMR analysis after 1 h indicated a new singlet at 40.5 ppm, accompanied by a singlet of equal integrated intensity for free PPh_3. The product is thus provisionally assigned as PCy_3 derivative **Ru-17**. Exchange is very slow, however, with the proportion of **Ru-17** being just 5% at this point, and reaching only 20% after a week (Figure 11). The high pi-acidity of the carbyne, added to that of the carbonyl ligand, clearly has a drastically inhibiting effect on the lability of the PPh_3 ligand, even in THF (a solvent known to favor ligand exchange in closely related benzylidene complexes).[42]

While ligand exchange would undoubtedly be accelerated by use of higher temperatures, our interest in these five- and six-coordinate carbyne complexes lies in identifying ligand parameters that will support reaction under mild conditions: in this case, ambient-temperature exchange. An important implication of this study thus lies in the implication that the cumulative effect of the carbyne and carbonyl ligands will prevent achieving this goal, and that refinements of this ligand design should focus on pi-donor, rather than pi-acid sites.

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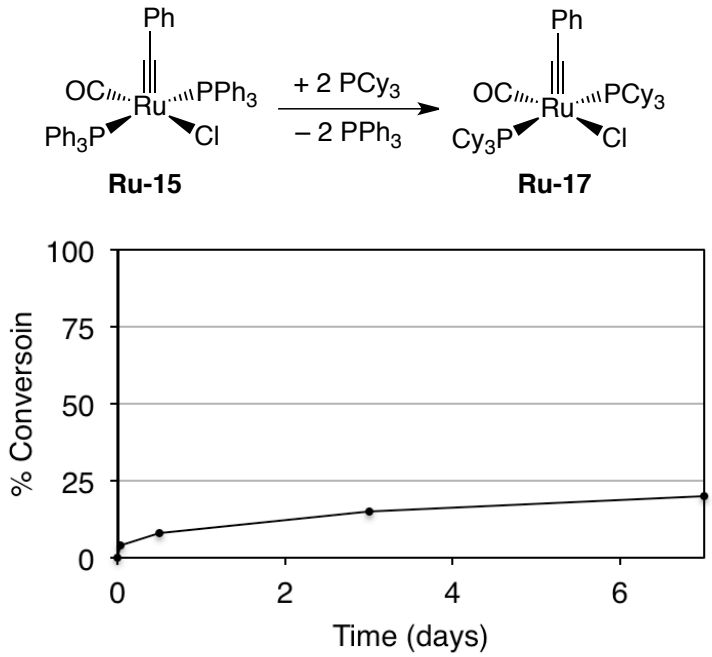

Figure 11. Rate curve for the ligand exchange between **Ru-15** and PCy_3 over 7 days at RT in THF.

4.5 ROAMP Studies

The studies above were designed to advance our understanding of parameters that govern the stability and reactivity of late-metal carbynes by examining four (potential) Class B complexes, rather than to design a catalyst for alkyne metathesis. Such activity is unlikely for different reasons, ranging from non-lability (**Ru-12**) to the absence of a suitably oriented acceptor d-orbital to interact with incoming alkyne (**Ru-13**, **Ru-14**). Despite these expectations, they were tested for their activity using the "spring-loaded" substrate cyclooctyne, for which release of ring strain via ring-opening alkyne metathesis (ROAMP) could help drive reaction.

Complex **Ru-12** (5 mol%) demonstrated no polymerization activity in ROAMP of cyclooctyne in $CDCl_3$, with no change in the ^1H NMR spectrum over 6 h at RT. The Roper carbyne, **Ru-15** (1 mol%), also proved unreactive in ROAMP of cyclooctyne in $CDCl_3$, with no change in the ^1H NMR spectrum over 6 h at RT. Complexes **Ru-14** and **Ru-13** (5 mol%) likewise showed no polymerization in C_6D_6 by ^1H NMR analysis, while catalyst decomposition was evident from $^{31}P\{^1H\}$ NMR analysis. The choice of solvent in these systems was dependent upon the solubility of the catalyst and catalyst loadings

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were decided based on amount of material present at that time.

4.6 Conclusions

This chapter was aimed at increasing our understanding of the stability and reactivity of selected Ru carbyne complexes. These were the six-coordinate vinylcarbyne **Ru-12**, reported by Amoroso and Fogg; the five-coordinate Roper carbyne **Ru-15**; and the four-coordinate complexes **Ru-13** and **Ru-14**. These and prior reported Ru(IV) and cationic Ru(II) complexes were classified according to the stability of the metal-carbyne functionality. We defined as Class A carbynes those that are susceptible to reformation of an M=C entity (e.g. vinylidene, allenylidene, or alkylidene), and defined as Class B carbynes those that have a stable carbyne functionality. The four carbyne complexes selected for study were all initially regarded as prospective Class B carbynes. Investigation of their reactivity resulted in categorization of **Ru-12** and **Ru-15** as Class A species.

The four-coordinate complexes **Ru-13** and **Ru-14** have yet to be studied under acidic or basic conditions and thus classification is still pending. A related complex, a chloride derivative, has been shown by Johnson to undergo conversion into an alkylidene complex on treatment with HCl. It is unclear whether this sensitivity (which implies a buildup of negative charge at the carbyne carbon) can be reduced by replacing the anionic ligand with a more electron-withdrawing donor such as phenoxide, with its more electronegative oxygen donor, or (in the extreme) perfluorophenoxide. If either did confer greater stability on the carbyne, this could open the door to the design of Class B carbyne complexes.

Finally, the five-coordinate Ru carbyne **Ru-15** is of interest as a potential entry point to new carbyne complexes. Roper reported that this complex was likewise acid-sensitive, leading to our Class A classification noted above. The very slow rate of ligand exchange of **Ru-15** with PCy_3 (20% after 1 week at RT) indicates that the combined pi-acidity of the carbonyl and carbyne ligands severely depresses ligand lability. Replacing the carbonyl with alternative donor ligands should be undertaken. Alternatively, Hieber-type base reactions, involving treatment of **Ru-15** with KOH, might enable elimination of the carbonyl as CO_2 and installation of a hydride in place of the CO ligand. These

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reactions could offer promising access to a broader range of carbyne complexes, and aid in refining our ideas of the parameters that govern the stability of the Ru≡C functionality.

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Chapter 5: Conclusions and Future Directions

5.1 Conclusions

The work described in this thesis was focused on two different applications of Ru-promoted metathesis to materials synthesis, involving olefin or alkyne metathesis, respectively. These two topics are at very different stages in their scientific development. Thus, many catalysts are now known for ring-opening metathesis polymerization (ROMP) of olefins, although very few ruthenium initiators are capable of living ROMP. This project was aimed at evaluating the capacity of a ruthenium isocyanide catalyst for living ROMP of norbornene monomers of widely differing steric bulk, without the present need for cryogenic down-regulation of activity. This could enable straightforward access to bi- or multi-block copolymers relevant to a broad range of contexts, ranging from biomedical and tissue engineering applications to microelectronics.

The Ru-NCO initiator **Ru-8** was shown to effect controlled living ROMP at RT for both bulky and sterically accessible norbornenes, and this was extended to synthesis of a diblock copolymerization. Polydispersities were impressively low (PDI $\leq$1.03), and superb control over chain lengths was indicated by the excellent agreement between theoretical molecular weights and experimental M_n values determined by light-scattering GPC. Less success was found in attempts to exploit the polarity of the isocyanate group to facilitation removal of Ru residues by column chromatography on silica gel. Analysis by ICP-MS indicated that Ru levels could be decreased to as low as 41 ppm using a combination of column chromatography and activated carbon, but yields are compromised in these methods to 32%.

The second project focused on an examination of the parameters involved in synthesis of stable ruthenium carbyne complexes. Such species are ultimately of interest for alkyne metathesis, a potentially general, important route to conjugated materials. This field is in its infancy, however: successful development of Ru-catalyzed alkyne metathesis requires a much better understanding of the factors that govern reactivity and stability in this under-explored family of complexes. This work was thus aimed at much more fundamental studies. Selected ruthenium carbyne complexes from the literature, from our group and others, were examined to establish the stability of the carbyne moiety,

and the capacity of the complexes to participate in ligand exchange. A six-coordinate vinylcarbyne complex, **Ru-12**, was shown to revert to an allenylidene on exposure to base. Two four-coordinate benzylidyne complexes, **Ru-13** and **Ru-14**, were found to be highly air-sensitive, perhaps because of facile protonation. Their susceptibility to decomposition makes these complexes impractical for use. Finally, the five-coordinate carbonyl-containing carbyne, **Ru-15**, was shown to react very slowly in ligand exchange with PCy_3 (20% after 1 week at RT), indicating that the combined effect of the pi-acid carbyne and carbonyl functionalities effectively suppresses ligand dissociation. Synthetic routes to the dichlorocarbene precursor were refined; prior reports have shown that this is a versatile entry point to alternative carbyne complexes.

5.2 Future Directions

5.2.1 Ruthenium NCO Linear Pseudohalide Catalyst

The impressive performance of the NCO initiator in living ROMP at RT, regardless of monomer steric bulk, improves upon the state of the art. This more regulated activity may indicate increased robustness of this initiator, relative to the "third-generation" Grubbs pyridine initiator. This initiator may offer considerable potential in tandem catalysis. A key question is the stability of the anionic chloride ligand, vs. the isocyanate ligand, under conditions such as hydrogenolysis, aimed at transforming the alkylidene moiety into (e.g.) hydride.

Also worth further exploration is the failure of the NCO endgroup to stick to silica gel. Control experiments should be carried out to ensure that the endgroup was in fact cleaved from the polymers by reaction with ethyl vinyl ether. Finally, the affinity of the short oligomers for silica is striking. Of interest is the possibility that hydrogenation of the polymer backbone (which increases the degrees of freedom within the polymer, enabling greater folding of the polymer), would shield the polar substituents and enable elution. These experiments could be complicated, however, by the lower solubility characteristic of hydrogenation ROMP polymers, relative to their unsaturated precursors.

5.2.2 Ruthenium Carbyne Complexes

Promising future work in this area builds on the Roper complex **Ru-15**. Bulky anionic or neutral ligands cis to the alkyne could improve ligand lability. The ligand exchange experiments should thus be expanded. Alternatively, the four-coordinate carbyne complexes of the type **Ru-14** may improve from the introduction of greater steric bulk, as well as ligands designed to reduce their nucleophilicity. Their reactivity toward acids should be examined to shed light on whether they indeed decompose via protonation of the carbyne carbon, as suggested, and whether the product is the suspected Ru-alkylidene derivative. Use of acids with a range of pKas would provide an experimental metric for the vulnerability of this site to attack. Further modifications to the neutral donor ligands would be advantageous in establishing optimal steric protection.

A. NMR Spectra

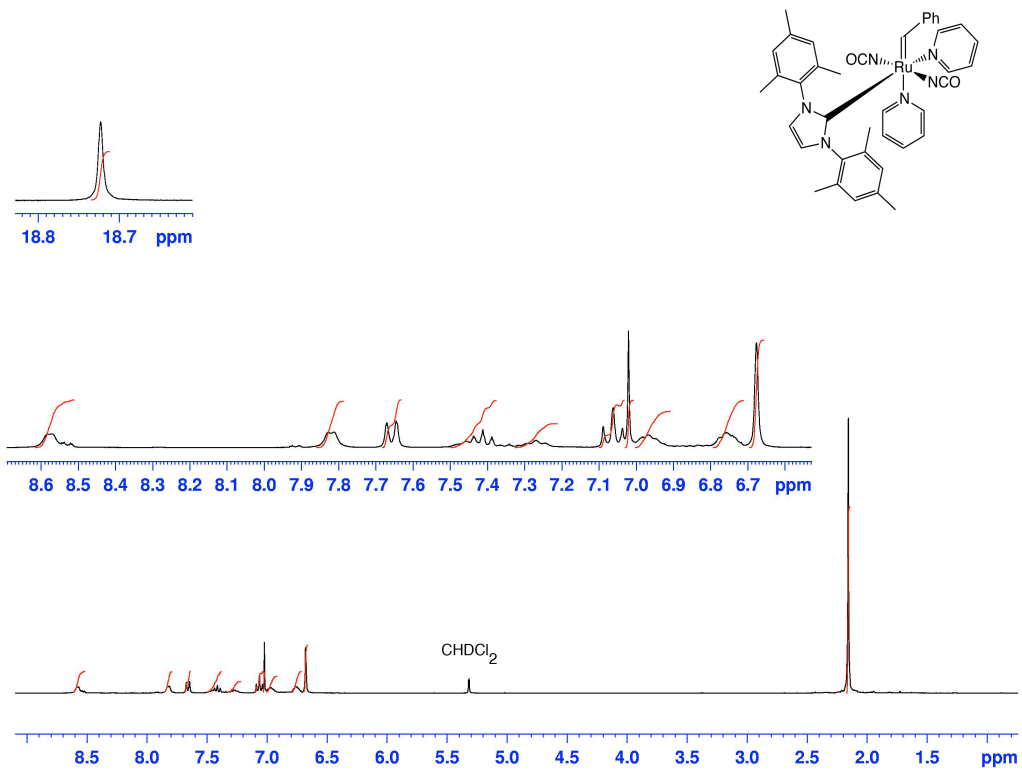

Figure A1. ^{1}H NMR spectra of Ru(NCO-κ*N*)$_2$(CHPh)(IMes)(py)$_2$, **Ru-8** (CD_2Cl_2, 500 MHz, 298 K).

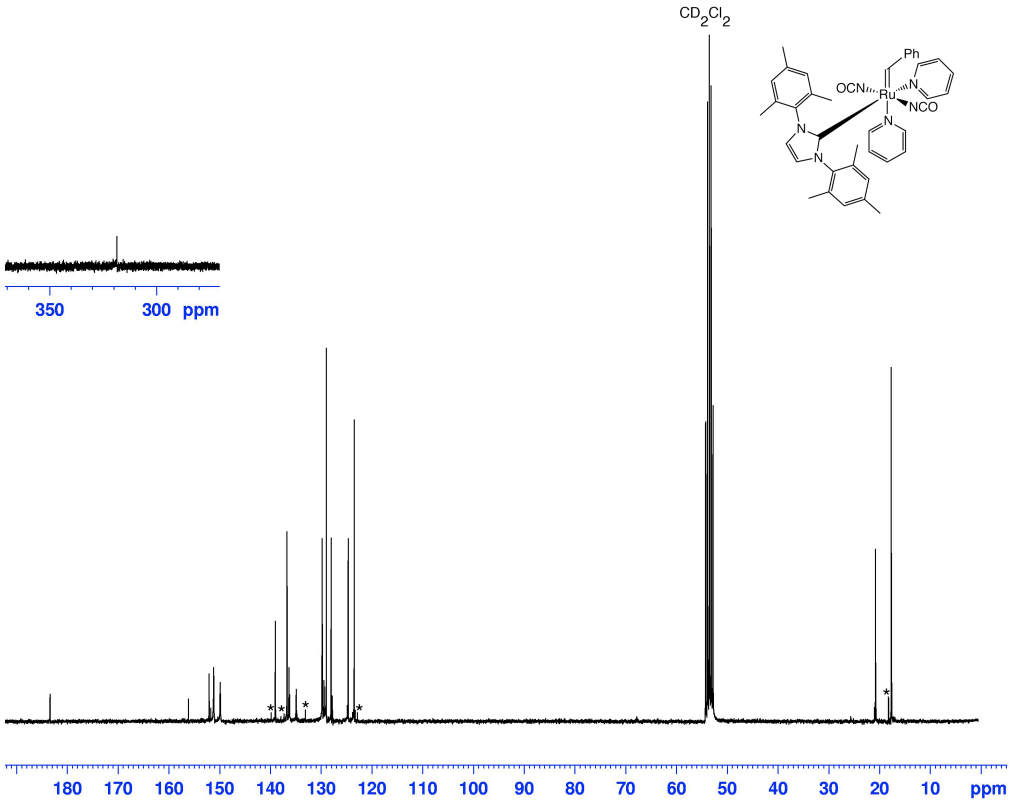

Figure A2. ^{13}C NMR spectra of Ru(NCO-κ*N*)$_2$(CHPh)(IMes)(py)$_2$, **Ru-8** (CD_2Cl_2, 500 MHz, 298 K). * = 4% impurity of residual [Ag(IMes)$_2$][NCO].

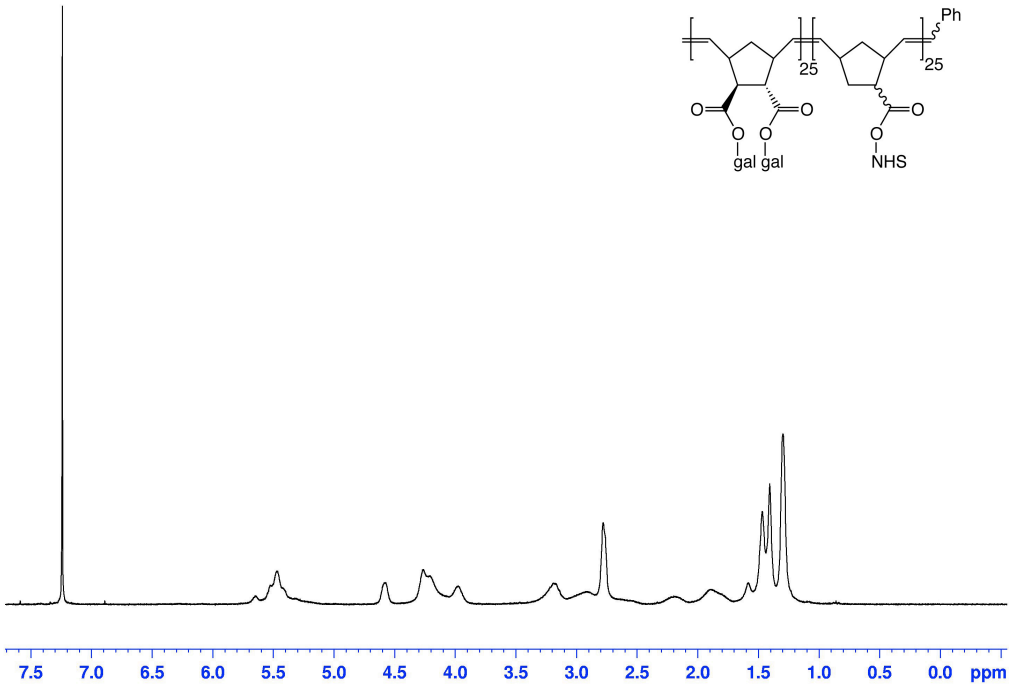

Figure A3. ^{1}H NMR spectra of co-block polymer **M5** and **M3**, [**M5**]$_{25}$[**M3**]$_{25}$ ($CDCl_3$, 300 MHz, 298 K).

B. IR Spectra

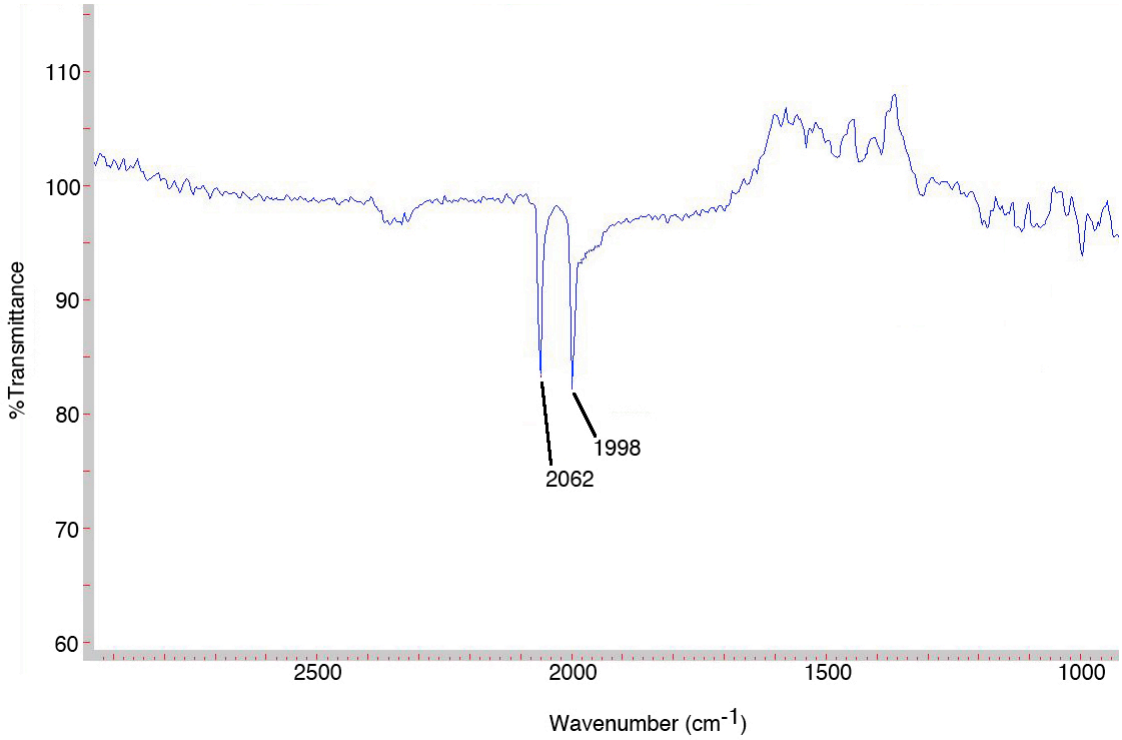

Figure B1. IR spectra of $RuCl_2(CO)_2(PPh_3)_2$, **Ru-10**, using attenuated total reflectance.

C. List of Contributions

Manuscripts Published:

1- "A Ru-Isocyanate Initiator for Fast, Living Ring-Opening Metathesis Polymerization at Ambient Temperatures." S. Monfette, J. Marleau-Gillette, J.C. Conrad, R. McDonald, D.E. Fogg, *Dalton Trans*. **2012**, 41, 14476-14479.

Poster Presentations:

1- 'A Powerful New Ruthenium Initiator for Living Ring-opening Metathesis Polymerization: Precise, Ambient-temperature Control and Facile Removal' Marleau-Gillette, J., Monfette, S., Fogg, D.E. 94th Canadian Society for Chemistry Conference and Exibition , Montreal, QC, June 5-June 9, 2011.