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Bis-Mixed-Carbene Ruthenium-Thiolate-Alkylidene Complexes: Synthesis and Olefin Metathesis Activity

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ABSTRACT: A series of *bis*-carbene Ru-hydride species, including (IMes)(Im(OMe)$_2$)(PPh$_3$)RuHCl (**1**) and (SIMes)(Me$_2$Im(OMe)$_2$)(PPh$_3$)RuHCl (**2**) were prepared and subsequently shown to react with aryl-vinyl-sulfides to give the *bis*-carbene-alkylidene complexes: Im(OMe)$_2$(SIMes)RuCl(SR)(=CHCH$_3$) (R = *p*-FC$_6$H$_4$ (**3**), *p*-(NO$_2$)C$_6$H$_4$ (**4**)), Im(OMe)$_2$(IMes)RuCl(=CHCH$_3$)(SPh) (**5**), Me$_2$Im(OMe)$_2$(SIMes)RuCl(=CHCH$_3$)(SPh) (**6**), Im(OMe)$_2$(SIMes)(F$_5$C$_6$S)RuCl(=CHR) (R = C$_4$H$_9$ (**9**), C$_5$H$_{11}$ (**10**)). The activity of these species in the standard Grubbs' tests for ring-opening metathesis polymerization, ring-closing and cross-metathesis are reported. Although these thiolate derivatives are shown to exhibit modest metathesis activities, the reactivity is enhanced in the presence of BCl$_3$.

INTRODUCTION

Olefin metathesis has become recognized as a valuable tool in synthetic chemistry where it is being used across the discipline in natural product synthesis, polymer, and pharmaceutical chemistry.[1] In the case of the Ru-based metathesis catalysts, numerous modifications to the "Grubbs' catalysts", (Cy$_3$P)$_2$Cl$_2$RuCHPh (G1)[2] and (Cy$_3$P)(SIMes)Cl$_2$RuCHPh (G2)[3] have been undertaken in attempts to improve activity and stability. For example, strategies in which phosphine donors were replaced with *N*-heterocyclic carbenes (NHCs) increased both the activity and stability of the corresponding complexes.[4] Alternatively, the incorporation of a pendant donor on the alkylidene (Grubbs-Hoveyda)[5] as well as modifications to the anionic ligands have also been reported. In the latter case, Fogg and co-workers[6] developed Ru-based systems in which the halides are replaced with either mono- or bidentate aryloxide ligands. Recently, we have described a derivative of the Grubbs catalyst in which a dithiolate ligand replaces the halides affording the species (O(CH$_2$CH$_2$S)$_2$)(SIMes)RuCHPh. While this species is inactive for metathesis, it is activated by the addition of the Lewis acid BCl$_3$.[7]

Typical methods for the formation of Ru-alkylidenes[8] involve reactions of Ru sources with cyclopropenes,[9] sulfur-ylides,[10] dihalomethanes[11] and diazomethanes.[12] Alternatively, to access Ru-based complexes incorporating allenylidene, indenylidene,[13] vinylidene[11c] or cumulenylidene[14] fragments, reactions of Ru-synthons with alkynes, propargylchlorides,[6a, 15] and propargylalcohols[16] have been used. Nonetheless, the preparation of new Ru-alkylidenes is often achieved via derivatization of Grubbs' catalysts as they serve as convenient precursors. This strategy was, for example, used by Herrmann[17] and Grubbs[18] to prepare *bis*-NHC ruthenium alkylidene complexes (**A** and **B** in Fig. 1). While these species displayed enhanced stability the activity was modest compared to the second generation Grubbs catalyst, presumably a result of the strong binding of the carbene to the metal centre. Several other reports have examined the impact of varying the nature of the carbenes on the catalytic activity. Plenio and co-workers[19] introduced electron-poor NHCs in the *bis*-NHC ruthenium systems which improved the activity in RCM reactions (**C** and **D** in Fig. 1). Nolan and coworkers[20] studied the impact of introducing one smaller NHC, (**E** in Fig. 1), in mixed carbene Ru-indenylidene complexes. Compounds with a smaller carbene showed improved activity in RCM at very low catalyst loading. In all cases, Ru-*bis*-carbene-alkylidenes metathesis catalysts are active at elevated temperatures (80 - 120 °C) and are thought to act via carbene dissociation. We have recently reported a new synthetic route for the conversion of *bis*-mixed carbene Ru-hydride complexes to *bis*-mixed carbene Ru-thiolate alkylidene species using aryl vinyl sulfides.[21] This provides a safe and cheap route to thiolate containing *bis*-carbene Ru-alkylidene complexes, Im(OMe)$_2$(SIMes)(ArS) RuCl(=CHR) Ar = Ph or C$_6$F$_5$, R = CH$_3$ or CH$_2$Ph). These species are active metathesis catalysts when activated by a Lewis acid, BCl$_3$. In this full study, we explore these systems, describing the preparation

of a family of Ru-complexes with various NHCs and altering the substituents on the thiolate and the alkylidene fragment by using a variety of aryl vinyl sulfides.

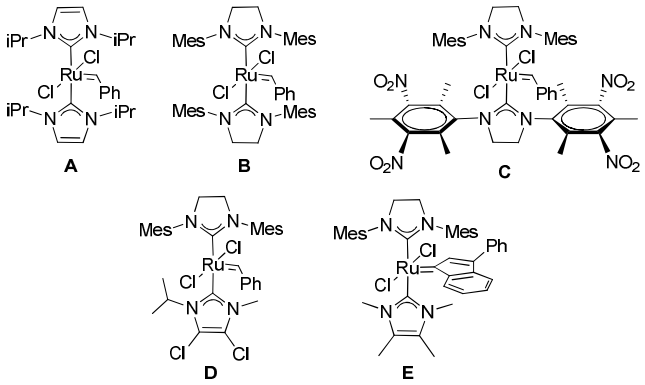


Figure 1. Examples of *bis*-carbene Ru-alkylidene complexes.

EXPERIMENTAL SECTION

General Considerations All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing a Vacuum Atmospheres glovebox and a Schlenk vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology, dispensed into thick-walled Schlenk glass flasks equipped with Teflonvalve stopcocks (pentane, hexanes, CH_2Cl_2) and stored over molecular sieves. Some solvents were dried over the appropriate agents (CaH_2, Na/benzophenone), vacuum-transferred into storage flasks with Teflon stopcocks and degassed accordingly (C_6H_6, C_6H_5Br, C_6D_5Br, C_6D_6, CD_2Cl_2). ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded at 25 °C on a Bruker 400 MHz or an Agilent 500 MHz spectrometer. Chemical shifts were given relative to $SiMe_4$ and referenced to the residual solvent signal (^1H, ^{13}C) or relative to an external standard (^{31}P: 85% H_3PO_4, ^{19}F: $CFCl_3$). In some instances, signal and/or coupling assignment was derived from two dimensional NMR experiments (HSQC). Chemical shifts are reported in ppm and coupling constants as scalary values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN analyzer. Phenyl vinyl sulfide was purchased from Sigma Aldrich and used as received. SIMes,[22] IMes,[22] 4-fluorophenyl vinyl sulfide,[23] 4-nitrophenyl vinyl sulfide,[24] and $(Im(OMe)_2)(SIMes)(PPh_3)RuHCl$[25] were prepared according to literature procedures.

Synthesis of $(Im(OMe)_2)(IMes)(PPh_3)RuHCl$ (1) IMes (0.105 g, 0.354 mmol) in 5 mL THF was added to a solution of $(Im(OMe)_2)(PPh_3)_2RuHCl$ (0.150 g, 0.177 mmol) in 5 mL of THF and the mixture was heated at 60 °C for 24 h. All volatiles were removed under vacuum. The product was extracted with toluene (10 mL) and filtered through celite. The solution was concentrated to 2 mL and pentane (15 mL) was added to the red solution to precipitate the product. The red solid was collected on a frit and dried under vacuum (0.114 g, 73%). X-ray quality crystals were grown from toluene/pentane at 25 °C. ^1H NMR (400 MHz, C_6D_6): δ 7.54 (t, $^3J_{HH}$ = 8 Hz, 6H, P*Ph*$_3$), 7.39 (m, 1H, IMes-C*H*), 7.04 (m, 2H, Mes-C*H*), 6.99-6.90 (m, 13H, (9H) PPh_3 + (1H) IMes-C*H* + (2H) Mes-C*H* + (1H) $Im(OMe)_2$-C*H*), 6.66 (d, $^3J_{HH}$ = 2 Hz, 1H, $Im(OMe)_2$-C*H*), 4.68 (dd, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 3 Hz, 1H, $Im(OMe)_2$-CH_2), 3.90 (m, 1H, $Im(OMe)_2$-CH_2), 2.92-2.10 (br m, 30 H, $Im(OMe)_2$-CH_3 + $Im(OMe)_2$-CH_2 + Mes-CH_3), -28.12 (d, $^2J_{PH}$ = 26 Hz, 1H, Ru-*H*). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ 43.9 (s, PPh_3). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 141.3 (d, $^1J_{PC}$ = 30 Hz, C_{ipso}, PPh_3), 137.3 (br, C_{ipso}), 134.9 (d, $^2J_{PC}$ = 11 Hz, *o*-C, PPh_3), 134.3 (IMes-*C*H), 134.1 (IMes-*C*H), 130.3 (br, C_{ipso}) 128.9 (d, $^4J_{PC}$ = 2 Hz, *p*-C, PPh_3), 128.8 (Mes-*C*H), 128.4 (Mes-*C*H), 127.6 (d, $^3J_{PC}$ = 8 Hz, *m*-C, PPh_3), 119.9 ($Im(OMe)_2$-*C*H), 118.4 ($Im(OMe)_2$-*C*H), 72.6 ($Im(OMe)_2$-*C*H_2), 71.4 ($Im(OMe)_2$-*C*H_2), 58.2 ($Im(OMe)_2$-*C*H_3), 57.9 ($Im(OMe)_2$-*C*H_3), 48.0 ($Im(OMe)_2$-*C*H_2), 47.5 ($Im(OMe)_2$-*C*H_2), 21.3 (br s, Mes-*C*H_3), 19.7 (br s, Mes-*C*H_3). Elemental Analysis for $C_{48}H_{56}ClN_4O_2PRu$: C, 64.89; H, 6.35; N, 6.31. Found: C, 65.08; H, 6.59; N, 6.13.

Synthesis of $(Me_2Im(OMe)_2)(SIMes)(PPh_3)RuHCl$ (2) SIMes (0.070 g, 0.228 mmol) in 5 mL THF was added to a solution of $(Me_2Im(OMe)_2)(PPh_3)_2RuHCl$ (0.100 g, 0.114 mmol) in 5 mL of THF and the mixture was heated at 50 °C for 24 h. All volatiles were removed under vacuum. The product was extracted with toluene (10 mL) and filtered through celite. The solution was concentrated to 2 mL and pentane (15 mL) was added to the red solution to precipitate the product. The red solid was collected on a frit and dried under vacuum (0.076 g, 73%). ^1H NMR (400 MHz, C_6D_6): δ 7.52 (t, $^3J_{HH}$ = 8 Hz, 6H, P*Ph*$_3$), 6.94 (m, 11H, (9H) PPh_3 + (2H) Mes-C*H*), 6.82 (s, 1H, Mes-C*H*), 6.51 (s, 1H, Mes-C*H*), 4.43 (dt, $^2J_{HH}$ = 16 Hz, $^3J_{HH}$ = 4 Hz, 1H, $Me_2Im(OMe)_2$-CH_2), 3.60 (m, 1H, $Me_2Im(OMe)_2$-CH_2), 3.39-3.16 (m, 8H, (4H) $Me_2Im(OMe)_2$-CH_2 + (4H) SIMes-CH_2), 2.99 (s, 6H, $Me_2Im(OMe)_2$-CH_3 + Mes-CH_3), 2.83 (br s, 5H, Mes-CH_3 + $Me_2Im(OMe)_2$-CH_2), 2.64 (s, 6H, $Me_2Im(OMe)_2$-CH_3 + Mes-CH_3), 2.33 (s, 3H, Mes-CH_3), 2.13 (s, 3H, Mes-CH_3), 1.92 (s, 3H, $Me_2Im(OMe)_2$-4,5-CH_3), 1.83 (s, 3H, $Me_2Im(OMe)_2$-4,5-CH_3), 1.59 (s, 3H, Mes-CH_3), -27.43 (d, $^2J_{PH}$ = 27 Hz, 1H, Ru-*H*). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ 36.5 (s, PPh_3). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, partial): δ 141.2 (d, $^1J_{PC}$ = 29 Hz, C_{ipso}, PPh_3), 139.7 (C_{ipso}), 135.0 (d, $^2J_{PC}$ = 11 Hz, *o*-C, PPh_3), 129.4 (Mes-*C*H), 128.9 (d, $^4J_{PC}$ = 2 Hz, *p*-C, PPh_3), 128.8 (Mes-*C*H), 127.5 (d, $^3J_{PC}$ = 8 Hz, *m*-C, PPh_3), 125.7 (C_{ipso}), 124.5 ($Me_2Im(OMe)_2$-4,5-C_{ipso}), 122.2 ($Me_2Im(OMe)_2$-4,5-C_{ipso}), 72.9 ($Me_2Im(OMe)_2$-*C*H_2), 71.0 ($Me_2Im(OMe)_2$-*C*H_2), 58.4 ($Me_2Im(OMe)_2$-*C*H_3), 57.8 ($Me_2Im(OMe)_2$-*C*H_3), 51.5 (SIMes-*C*H_2), 50.8 (SIMes-*C*H_2), 46.5 ($Me_2Im(OMe)_2$-*C*H_2), 45.9 ($Me_2Im(OMe)_2$-*C*H_2), 21.4 (Mes-*C*H_3), 21.2 (Mes-*C*H_3), 21.0 (Mes-*C*H_3), 20.9 (Mes-*C*H_3), 19.6 (Mes-*C*H_3), 17.1 (Mes-*C*H_3), 10.3 ($Me_2Im(OMe)_2$-4,5-*C*H_3), 9.8 ($Me_2Im(OMe)_2$-4,5-*C*H_3). Elemental Analysis for $C_{50}H_{62}ClN_4O_2PRu•C_5H_{12}$: C, 66.68; H, 7.53; N, 5.66. Found: C, 66.24; H, 7.46; N, 5.85.

Synthesis of $Im(OMe)_2(SIMes)RuCl(S(p\text{-}FC_6H_4)(=CHCH_3)$ (3) 4-Fluorophenyl vinyl sulfide (0.017 g, 0.224 mmol) was added to a solution of $(Im(OMe)_2)(SIMes)(PPh_3)RuHCl$ (0.100 g,

0.112 mmol) in 5 mL CH_2Cl_2 at room temperature. The solution was then stirred for 4 h before the solvent was concentrated to 0.5 mL and 15 mL of pentane was added and the resulting mixture was filtered over a pad of celite. The pentane was then removed *in vacuo* and the resulting residue was layered with 10 mL of pentane and left standing overnight. The free triphenylphosphine is taken up into the pentane layer yielding a red solid (0.070 g, 80%). X-ray quality crystals were grown from benzene/pentane at 25 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 18.34 (br s, 1H, Ru=C*H*), 7.01(s, 2H, Mes-C*H*), 6.96 (s, 1H, Mes-C*H*), 6.93 (s, 1H, Mes-C*H*), 6.86 (d, $^3J_{HH}$ = 2 Hz, 1H, Im(OMe)$_2$-C*H*), 6.68 (br s, 1H, Im(OMe)$_2$-C*H*), 6.51 (m, 2H, *p*-F-C$_6H_5$), 6.34 (app t, $^3J_{HH}$ = 9 Hz, 2H, *p*-F-C$_6H_5$), 3.92 (m, 4H, SIMes-CH_2), 3.44-3.26 (br s, 4H, Im(OMe)$_2$-CH_2), 3.23 (br s, 3H, Im(OMe)$_2$-CH_3), 3.16 (s, 3H, Im(OMe)$_2$-CH_3), 3.13-3.00 (br s, 4H, Im(OMe)$_2$-CH_2), 2.74 (s, 3H, Mes-CH_3), 2.61 (s, 3H, Mes-CH_3), 2.48 (s, 3H, Mes-CH_3), 2.40 (s, 3H, Mes-CH_3), 2.36 (s, 3H, Mes-CH_3), 2.31 (s, 3H, Mes-CH_3), 1.63 (d, $^3J_{HH}$ = 5 Hz, Ru=CHCH_3). ^{19}F{^{1}H} NMR (178 MHz, CD_2Cl_2): δ -124.49 (br s). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 313.5 (Ru=*C*HCH$_3$), 223.9 (N*C*N), 188.8 (N*C*N), 159.7 (d, $^1J_{FF}$ = 239 Hz, S(*C*$_6$H$_4$F)), 147.0 (d, $^4J_{FC}$ = 3 Hz, S(*C*$_6$H$_4$F)), 140.5 (C$_{ipso}$), 139.9 (C$_{ipso}$), 138.6 (C$_{ipso}$), 138.5 (C$_{ipso}$), 138.1 (C$_{ipso}$), 137.9 (C$_{ipso}$), 137.8 (C$_{ipso}$), 135.6 (C$_{ipso}$), 133.9 (br d, $^3J_{FC}$ = 7 Hz, S(*C*$_6$H$_4$F)), 129.8 (Mes-*C*H), 129.6 (Mes-*C*H), 121.7 (Im(OMe)$_2$-*C*H), 121.1 (Im(OMe)$_2$-*C*H), 113.7 (d, $^2J_{FC}$ = 21 Hz, S(*C*$_6$H$_4$F)), 73.6 (Im(OMe)$_2$-*C*H$_2$), 72.2 (Im(OMe)$_2$-*C*H$_2$), 58.4 (Im(OMe)$_2$-*C*H$_3$), 58.2 (Im(OMe)$_2$-*C*H$_3$), 51.3 (SIMes-*C*H$_2$), 51.1 (SIMes-*C*H$_2$), 49.7 (Im(OMe)$_2$-*C*H$_2$), 48.9 (Im(OMe)$_2$-*C*H$_2$), 46.8 (Ru=CH*C*H$_3$), 21.1 (Mes-*C*H$_3$), 21.0 (Mes-*C*H$_3$), 20.7 (Mes-*C*H$_3$), 20.5 (Mes-*C*H$_3$), 19.3 (Mes-*C*H$_3$), 19.2 (Mes-*C*H$_3$). Elemental Anal.: $C_{38}H_{50}ClFN_4O_2RuS$: C, 58.33; H, 6.44; N, 7.16. Found: C, 58.27; H, 6.87; N, 7.13.

Synthesis of Im(OMe)$_2$(SIMes)RuCl(S(*p*-(NO$_2$)C$_6$H$_4$)(=CHCH$_3$) (4) 4-Nitrophenyl vinyl sulfide (0.041 g, 0.224 mmol) was added to a solution of (Im(OMe)$_2$)(SIMes)(PPh$_3$)RuHCl (0.100 g, 0.112 mmol) in 5 mL CH_2Cl_2 at room temperature. The solution was then stirred for 4 h before the solvent was concentrated to 0.5 mL and 15 mL of pentane was added and the resulting mixture was filtered over a pad of celite. The pentane was then removed *in vacuo* and the resulting residue was layered with 10 mL of pentane and left standing overnight. The free triphenylphosphine is taken up into the pentane layer yielding a purple solid (0.068 g, 75%). ^{1}H NMR (400 MHz, C_6D_6): δ 18.42 (q, $^3J_{HH}$ = 6 Hz, 1H, Ru=C*H*), 7.71 (d, $^3J_{HH}$ = 9 Hz, 2H, *p*-NO$_2$(C$_6H_4$)), 6.75 (m, 7H, *p*-NO$_2$(C$_6H_4$), Mes-C*H*, Im(OMe)$_2$-C*H*), 6.49 (s, 1H, Im(OMe)$_2$C*H*), 3.44 (m, 3H, Im(OMe)$_2$-CH_2), 3.32-3.21 (m, 4H, SIMesCH_2), 3.13-2.94 (m, 3H, Im(OMe)$_2$CH_2), 2.86 (s, 3H, Im(OMe)$_2$CH_3), 2.76 (s, 5H, Im(OMe)$_2$CH_2, Mes-CH_3), 2.73 (s, 3H, Im(OMe)$_2$-CH_3), 2.64 (s, 6H, Mes-CH_3), 2.49 (s, 3H, Mes-CH_3), 2.12 (s, 3H, Mes-CH_3), 2.09 (s, 3H, Mes-CH_3), 1.87 (d, $^3J_{HH}$ = 6 Hz, Ru=CHCH_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 314.2, (Ru=*C*H), 222.0 (N*C*N), 186.9 (N*C*N), 141.6 (C$_{ipso}$), 139.8 (C$_{ipso}$), 139.0 (C$_{ipso}$), 138.6 (C$_{ipso}$), 138.1 (C$_{ipso}$), 137.7 (C$_{ipso}$), 137.3 (C$_{ipso}$), 137.2 (C$_{ipso}$), 133.9 (C$_{ipso}$), 133.7 (C$_{ipso}$), 130.7 (*p*-NO$_2$-*C*$_6$H$_4$) 129.7 (Mes-*C*H), 129.5 (Mes-*C*H), 129.2 (Mes-*C*H), 128.8 (Mes-*C*H), 121.5 (Im(OMe)$_2$-*C*H), 121.3 (Im(OMe)$_2$-*C*H), 121.1 (*p*-NO$_2$-*C*$_6$H$_4$), 72.7 (Im(OMe)$_2$-*C*H$_2$), 71.5 (Im(OMe)$_2$-*C*H$_2$), 58.0 (Im(OMe)$_2$-*C*H$_3$), 57.9 (Im(OMe)$_2$-*C*H$_3$), 50.8 (SIMes-*C*H$_2$), 50.7 (SIMes-*C*H$_2$), 49.5 (Im(OMe)$_2$-*C*H$_2$), 46.3 (Ru=CH*C*H$_3$), 20.6 (Mes-*C*H$_3$), 20.5 (Mes-*C*H$_3$), 20.1 (Mes-*C*H$_3$), 19.5 (Mes-*C*H$_3$), 18.7 (Mes-*C*H$_3$), 18.6 (Mes-*C*H$_3$). Elemental Analysis for $C_{38}H_{50}ClN_5O_4RuS•C_5H_{12}$: C, 58.58; H, 7.09; N, 7.94. Found: C, 58.21; H, 6.76; N, 7.72.

Synthesis of Im(OMe)$_2$(IMes)RuCl(=CHCH$_3$)(SPh) (5) Phenyl vinyl sulfide (16.7 µL, 0.128 mmol) was added to a solution of **1** (0.100 g, 0.112 mmol) in 5 mL CH_2Cl_2 at room temperature. The solution was then stirred for 5 hours before the solvent was concentrated to 0.5 mL and 15 mL of pentane was added and the resulting mixture was filtered over a pad of celite. The pentane was then removed *in vacuo* and the resulting residue was layered with 10 mL of pentane and left standing overnight. The free triphenylphosphine is taken up into the pentane layer yielding a red solid (0.050 g, 59%). X-ray quality crystals were grown from benzene/pentane at 25 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 19.09 (q, $^3J_{HH}$ = 6 Hz, 1H, Ru=C*H*), 7.03(br m, 1H, S(C$_6H_5$)), 7.01 (br m, 1H, S(C$_6H_5$)), 6.94 (d, $^3J_{HH}$ = 2 Hz, 1H, Im(OMe)$_2$-C*H*), 6.85-6.73 (br m, 7H, (3H) S(C$_6H_5$), (4H) Mes-C*H*), 6.65 (s, 1H, d, $^3J_{HH}$ = 2 Hz, 1H, Im(OMe)$_2$-C*H*), 6.24 (d, $^3J_{HH}$ = 2 Hz, 1H, Mes-C*H*), 6.23 (d, $^3J_{HH}$ = 2 Hz, 1H, Mes-C*H*), 3.84 (br s, 2H, Im(OMe)$_2$-CH_2), 3.56 (m, 1H, Im(OMe)$_2$-CH_2), 3.46 (m, 1H, Im(OMe)$_2$-CH_2), 3.21 (m, 2H, Im(OMe)$_2$-CH_2), 3.08 (m, 1H, Im(OMe)$_2$-CH_2), 2.96 (s, 3H, Im(OMe)$_2$-CH_3), 2.85 (m, 1H, Im(OMe)$_2$-CH_2), 2.77 (s, 3H, Im(OMe)$_2$-CH_3), 2.73 (s, 3H, Mes-CH_3), 2.67 (s, 3H, Mes-CH_3), 2.48 (s, 6H, Mes-CH_3), 2.16 (s, 3H, Mes-CH_3), 2.15 (s, 3H, Mes-CH_3), 2.08 (d, $^3J_{HH}$ = 5Hz, 3H, Ru=CHCH_3). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 313.6 (Ru=*C*HCH$_3$), 193.9 (N*C*N), 189.8 (N*C*N), 139.4 (C$_{ipso}$), 139.2 (C$_{ipso}$), 138.7 (C$_{ipso}$), 137.8 (C$_{ipso}$), 137.2 (C$_{ipso}$), 135.9 (S(*C*$_6$H$_5$)), 133.0 (S(*C*$_6$H$_5$)), 129.6 (Mes-C*H*), 129.4 (Mes-C*H*), 129.3 (Mes-C*H*), 129.2 (Mes-*C*H), 127.0 (S(*C*$_6$H$_5$)), 124.0 (IMes-*C*H), 123.6 (IMes-*C*H), 121.8 (Im(OMe)$_2$-*C*H), 121.2 (Im(OMe)$_2$-*C*H), 73.5 (Im(OMe)$_2$-*C*H$_2$), 72.4 (Im(OMe)$_2$-*C*H$_2$), 58.3 (Im(OMe)$_2$-*C*H$_3$), 58.2 (Im(OMe)$_2$-*C*H$_3$), 49.8 (Im(OMe)$_2$-*C*H$_2$), 49.0 (Im(OMe)$_2$-*C*H$_2$), 47.5 (Ru=CH*C*H$_3$), 21.1 (Mes-*C*H$_3$), 21.0 (Mes-*C*H$_3$), 20.4 (Mes-*C*H$_3$), 20.3 (Mes-*C*H$_3$), 19.1 (Mes-*C*H$_3$), 19.0 (Mes-*C*H$_3$). Elemental Anal.: $C_{38}H_{49}ClN_4O_2RuS$: C, 59.86; H, 6.48; N, 7.35. Found: C, 60.02; H, 6.20; N, 7.22.

Synthesis of Me$_2$Im(OMe)$_2$(SIMes)RuCl(=CHCH$_3$)(SPh) (6) Phenyl vinyl sulfide (17.0 µL, 0.131 mmol) was added to a solution of **2** (0.100 g, 0.109 mmol) in 5 mL CH_2Cl_2 at room temperature. The solution was then stirred for 1 h before the solvent was concentrated to 0.5 mL and 15 mL of pentane was added and the resulting mixture was filtered over a pad of celite. The pentane was then removed *in vacuo* and the resulting residue was layered with 10 mL of pentane and left standing overnight. The free triphenylphosphine is taken up into the pentane layer

yielding a red solid (0.069 g, 80%). X-ray quality crystals were grown from benzene/pentane at 25 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 19.05 (br s, 1H, Ru=C*H*), 7.05(m, 2H, S(C_6H_5)), 6.97 (s, 1H, Mes-C*H*), 6.94 (s, 1H, Mes-C*H*), 6.82 (s, 2H, Mes-C*H*), 6.67 (m, 3H, S(C_6H_5)), 3.73-3.03 (br m, 12H, SIMes-CH_2 + $Me_2Im(OMe)_2$-CH_2), 2.99 (s, 3H, $Me_2Im(OMe)_2$-CH_3), 2.94 (s, 3H, Mes-CH_3), 2.91 (s, 3H, Mes-CH_3), 2.78 (s, 3H, $Me_2Im(OMe)_2$-CH_3), 2.68 (s, 3H, Mes-CH_3), 2.66 (s, 3H, Mes-CH_3), 2.25 (s, 3H, Mes-CH_3), 2.13 (s, 3H, Mes-CH_3), 2.07 (d, $^3J_{HH}$ = 6Hz, 3H, Ru=CHCH_3). 1.70 (s, 3H, $Me_2Im(OMe)_2$-4,5-CH_3), 1.44 (s, 3H, $Me_2Im(OMe)_2$-4,5-CH_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 312.0 (Ru=*C*HCH$_3$), 223.7 (N*C*N), 186.3 (N*C*N), 152.1 (C_{ipso}), 140.1 (C_{ipso}), 139.7 (C_{ipso}), 138.6 (C_{ipso}), 138.5 (C_{ipso}), 138.2 (C_{ipso}), 137.9 (C_{ipso}), 137.7 (C_{ipso}), 136.0, 133.4 (S(*C*$_6$H$_5$)) 130.3 (Mes-*C*H), 129.9 (Mes-*C*H), 129.7 (Mes-*C*H), 129.6 (Mes-*C*H), 126.3 (S(*C*$_6$H$_5$)), 126.1 ($Me_2Im(OMe)_2$-C_{ipso}), 125.5 ($Me_2Im(OMe)_2$-C_{ipso}), 121.1 (S(*C*$_6$H$_5$)), 74.5 ($Me_2Im(OMe)_2$-*C*H$_2$), 72.7 ($Me_2Im(OMe)_2$-*C*H$_2$), 58.3 ($Me_2Im(OMe)_2$-*C*H$_3$), 58.2 ($Me_2Im(OMe)_2$-*C*H$_3$), 51.3 (SIMes-*C*H$_2$), 51.1 (SIMes-*C*H$_2$), 47.7 ($Me_2Im(OMe)_2$-*C*H$_2$) 46.5 (Ru=CH*C*H$_3$), 46.0 ($Me_2Im(OMe)_2$-*C*H$_2$), 20.9 (Mes-*C*H$_3$), 20.6 (Mes-*C*H$_3$), 20.5 (Mes-*C*H$_3$), 19.2 (Mes-*C*H$_3$), 19.1 (Mes-*C*H$_3$), 9.3 ($Me_2Im(OMe)_2$-4,5-*C*H$_3$), 8.9 ($Me_2Im(OMe)_2$-4,5-*C*H$_3$). Elemental Analysis for $C_{40}H_{55}ClN_4O_2RuS$: C, 60.62; H, 7.00; N, 7.07. Found: C, 60.86; H, 7.11; N, 6.78.

Synthesis of $(C_6F_5)SCHCH(C_3H_7)$ (7) and $(C_6F_5)SCHCH(C_4H_9)$ (8) These compounds were prepared in a similar fashion and thus only one preparation is detailed. A mixture of 1-pentyne (0.74 mL, 7.50 mmol) and pentafluorothiophenol (1.00 mL, 7.50 mmol) was stirred in 6 mL of H_2O at room temperature for 4 hours. The reaction mixture was extracted with Et_2O (3 x 20 mL) and the ether extract was dried over $MgSO_4$. Solvent removal *in vacuuo* gave a mixture of the (*E*)- and (*Z*)- isomers as a clear colorless liquid (1.61 g, 80%).

7: ^{1}H NMR (400 MHz, C_6D_6): Isomer 1: δ 5.91-5.84 (m, 2H, (C_6F_5)SC*H*C*H*(C_3H_7)), 2.00 (m, 2H, (C_6F_5)SCHCH(C_3H_7)), 1.34 (m, 2H, (C_6F_5)SCHCH(C_3H_7)), 0.82 (m, 3H, (C_6F_5)SCHCH(C_3H_7)). Isomer 2: δ 5.84 (d, $^3J_{HH}$ = 9 Hz, 1H, (C_6F_5)SC*H*C*H*(C_3H_7)), 5.76 (m, 1H, (C_6F_5)SC*H*C*H*(C_3H_7)), 2.21 (m, 2H, (C_6F_5)SCHCH(C_3H_7)), 1.41 (m, 2H, (C_6F_5)SCHCH(C_3H_7)), 0.89 (m, 3H, (C_6F_5)SCHCH(C_3H_7)). ^{19}F{^{1}H} NMR (178 MHz, C_6D_6): δ -132.99 (m, 2F, *o*-F), -153.05 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-F), -161.00 (m, 2F, *m*-F). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 147.2 (dm, $^1J_{CF}$ = 247 Hz, *C*$_6$F$_5$), 141.2 (dm, $^1J_{CF}$ = 252 Hz, *C*$_6$F$_5$), 137.7 (dm, $^1J_{CF}$ = 252 Hz, *C*$_6$F$_5$). Isomer 1: 134.2 ((C_6F_5)S*C*HCH(C_3H_7)), 120.8 ((C_6F_5)SC*H*C*H*(C_3H_7)), 34.7 ((C_6F_5)SCHCH(*C*$_3$H$_7$)), 22.1 ((C_6F_5)SCHCH(*C*$_3$H$_7$)), 13.4 ((C_6F_5)SCHCH(C_3H_7)). Isomer 2: 137.7 ((C_6F_5)S*C*HCH(C_3H_7)), 118.7 ((C_6F_5)SC*H*C*H*(C_3H_7)), 35.0 ((C_6F_5)SCHCH(*C*$_3$H$_7$)), 21.9 ((C_6F_5)SCHCH(C_3H_7)), 13.3 ((C_6F_5)SCHCH(*C*$_3$H$_7$)). HRMS-ESI$^+$ m/z [M+H]$^+$ calc for $C_{11}H_{10}F_5S$: 269.04191, found: 269.04179.

8: Starting with 1-hexyne (0.86 mL, 7.48 mmol) and pentafluorothiophenol (1.00 mL, 7.5 mmol) the product was isolated as a clear colourless liquid in 91% yield. ^{1}H NMR (400 MHz, C_6D_6): Isomer 1: δ 5.80-5.74 (m, 2H, (C_6F_5)SC*H*C*H*(C_4H_9)), 1.81 (m, 2H, (C_6F_5)SCHCH(C_4H_9)), 1.13 (m, 4H, (C_6F_5)SCHCH(C_4H_9)), 0.79 (m, 3H, (C_6F_5)SCHCH(C_4H_9)). Isomer 2: δ 5.69 (d, $^3J_{HH}$ = 9 Hz, 1H, (C_6F_5)SC*H*CH(C_4H_9)), 5.55 (dt, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 1H, (C_6F_5)SCHC*H*(C_4H_9)), 2.19 (m, 2H, (C_6F_5)SCHCH(C_4H_9)), 1.26 (m, 4H, (C_6F_5)SCHCH(C_4H_9)), 0.84 (m, 3H, (C_6F_5)SCHCH(C_4H_9)). ^{19}F{^{1}H} NMR (178 MHz, C_6D_6): δ -133.94 (m, 2F, *o*-F), -154.03 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-F), -161.80 (m, 2F, *m*-F). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 146.9 (dm, $^1J_{CF}$ = 247 Hz, *C*$_6$F$_5$), 141.2 (dm, $^1J_{CF}$ = 252 Hz, *C*$_6$F$_5$), 137.6 (dm, $^1J_{CF}$ = 252 Hz, *C*$_6$F$_5$). Isomer 1: 134.1 ((C_6F_5)SCH*C*H(C_4H_9)), 120.5 ((C_6F_5)S*C*HCH(C_4H_9)), 31.0 ((C_6F_5)SCHCH(*C*$_4$H$_9$)), 28.6 ((C_6F_5)SCHCH(C_4H_9)), 22.3 ((C_6F_5)SCHCH(*C*$_4$H$_9$)), 13.7 ((C_6F_5)SCHCH(C_4H_9)). Isomer 2: 138.0 ((C_6F_5)SCH*C*H(C_4H_9)), 118.0 ((C_6F_5)S*C*HCH(C_4H_9)), 32.5 ((C_6F_5)SCHCH(*C*$_4$H$_9$)), 30.9 ((C_6F_5)SCHCH(C_4H_9)), 22.2 ((C_6F_5)SCHCH(*C*$_4$H$_9$)), 13.7 ((C_6F_5)SCHCH(C_4H_9)). HRMS-ESI$^+$ m/z [M+H]$^+$ calc for $C_{12}H_{12}F_5S$: 283.05847, found: 283.05744.

Synthesis of $Im(OMe)_2(SIMes)(F_5C_6S)RuCl(=CHC_4H_9)$ (9) and $Im(OMe)_2(SIMes)(F_5C_6S)RuCl(=CHC_5H_{11})$ (10) These compounds were prepared in a similar fashion and thus only one preparation is detailed. **7** (0.060 g, 0.224 mmol) was added to a solution of ($Im(OMe)_2$)(SIMes)(PPh_3)RuHCl (0.100 g, 0.112 mmol) in 2 mL C_6H_5Br at room temperature. The solution was then stirred for 24 hours before the solution was added dropwise to 15 mL of cold pentane to precipitate the product. The orange/brown solid was collected on a frit and dried under vacuum (0.073 g, 73%).

9: X-ray quality crystals were grown from bromobenzene/pentane at 25 °C. ^{1}H NMR (400 MHz, C_6D_5Br): δ 16.37 (t, $^3J_{HH}$ = 5 Hz, 1H, Ru=C*H*), 7.04 (d, $^3J_{HH}$ = 2 Hz, 1H, Im(OMe)$_2$-C*H*), 6.85 (s, 2H, Mes-C*H*), 6.83 (d, $^3J_{HH}$ = 2 Hz, 1H, Im(OMe)$_2$-C*H*), 6.71 (s, 2H, Mes-C*H*), 4.16 (m, 1H, Im(OMe)$_2$-CH_2), 3.69 (m, 3H, Im(OMe)$_2$-CH_2), 3.59 (m, 1H, Im(OMe)$_2$-CH_2), 3.55 (m, 4H, SIMes-CH_2), 3.37 (m, 1H, Im(OMe)$_2$-CH_2), 3.15 (m, 2H, Im(OMe)$_2$-CH_2), 2.92 (s, 3H, Im(OMe)$_2$-CH_3), 2.90 (s, 3H, Im(OMe)$_2$-CH_3), 2.66 (s, 6H, 2 x Mes-CH_3), 2.23 (s, 6H, 2 x Mes-CH_3), 2.16 (s, 6H, 2 x Mes-CH_3), 1.31 (m, 2H, pentylidene-CH_2), 1.13 (m, 2H, pentylidene-CH_2), 1.05 (m, 2H, pentylidene-CH_2), 0.83 (t, $^3J_{HH}$ = 7 Hz, 3H, pentylidene-CH_3) . ^{19}F{^{1}H} NMR (376 MHz, C_6D_5Br): δ -131.87 (br s, 1F, *o*-S(C_6F_5)), -132.41 (br s, 1F, *o*-S(C_6F_5)), -162.70 (t, $^3J_{FF}$ = 22 Hz, 1F, *p*-S(C_6F_5)), -166.45 (br s, 1F, *m*-S(C_6F_5)), -166.98 (br s, 1F, *m*-S(C_6F_5)). ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br, partial): δ 315.2 (Ru=*C*H), 212.6 (N*C*N), 181.8 (N*C*N), 137.9 (C_{ipso}), 137.4 (C_{ipso}), 129.9 (Mes-*C*H), 129.6 (Mes-*C*H), 122.6 (Im(OMe)$_2$-*C*H), 121.3 (Im(OMe)$_2$-*C*H), 73.0 (Im(OMe)$_2$-*C*H$_2$), 71.4 (Im(OMe)$_2$-*C*H$_2$), 58.5 (Im(OMe)$_2$-*C*H$_3$), 58.0 (Im(OMe)$_2$-*C*H$_3$), 52.2 (SIMes-*C*H$_2$), 49.4 (Im(OMe)$_2$-*C*H$_2$), 48.3 (Im(OMe)$_2$-*C*H$_2$), 29.3 (pentylidene-

CH_2), 22.9 (pentylidene-CH_2), 21.0 (Mes-CH_3), 19.6 (Mes-CH_3), 18.7 (Mes-CH_3), 14.3 (pentylidene-CH_3). Elemental Analysis for $C_{41}H_{52}ClF_5N_4O_2RuS\bullet(C_6H_5Cl)$: C, 55.47; H, 5.77; N, 5.88. Found: C, 55.78; H, 5.87; N, 6.06.

10: Starting with **8** (0.063 g, 0.224 mmol) and $(Im(OMe)_2)(SIMes)(PPh_3)RuHCl$ (0.100 g, 0.112 mmol) the product was isolated as an orange/brown solid in 71% yield. X-ray quality crystals were grown from bromobenzene/pentane at 25 °C. ^{1}H NMR (400 MHz, C_6D_5Br): δ 16.44 (t, $^3J_{HH}$ = 5 Hz, 1H, Ru=C*H*), 7.00 (s, 1H, Im(OMe)$_2$-C*H*), 6.85 (s, 2H, Mes-C*H*), 6.82 (d, $^3J_{HH}$ = 2 Hz, 1H, Im(OMe)$_2$-C*H*), 6.71 (s, 2H, Mes-C*H*), 4.15 (dd, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 4 Hz, 1H, Im(OMe)$_2$-CH_2), 3.67 (m, 2H, Im(OMe)$_2$-CH_2), 3.59 (m, 1H, Im(OMe)$_2$-CH_2), 3.50 (m, 4H, SIMes-CH_2), 3.33 (m, 1H, Im(OMe)$_2$-CH_2), 3.12 (m, 1H, Im(OMe)$_2$-CH_2), 2.92 (s, 4H, Im(OMe)$_2$-CH_2 + Im(OMe)$_2$-CH_3), 2.89 (s, 4H, Im(OMe)$_2$-CH_2 + Im(OMe)$_2$-CH_3), 2.66 (s, 7H, hexylidene-CH_2 + 2 x Mes-CH_3), 2.22 (s, 6H, 2 x Mes-CH_3), 2.15 (s, 7H, hexylidene-CH_2 + 2 x Mes-CH_3), 1.21 (m, 3H, hexylidene-CH_2), 1.07 (m, 3H, hexylidene-CH_2), 0.85 (t, $^3J_{HH}$ = 7 Hz, 3H, hexylidene-CH_3). ^{19}F{^{1}H} NMR (376 MHz, C_6D_5Br): δ -131.83 (br s, 1F, *o*-S(C_6F_5)), -132.44 (br s, 1F, *o*-S(C_6F_5)), -162.69 (t, $^3J_{FF}$ = 22 Hz, 1F, *p*-S(C_6F_5)), -166.42 (br s, 1F, *m*-S(C_6F_5)), -166.96 (br s, 1F, *m*-S(C_6F_5)). ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br, partial): δ 315.3 (Ru=*C*H), 212.3 (N*C*N), 181.8 (N*C*N), 137.7 (C_{ipso}), 137.2 (C_{ipso}), 129.3 (Mes-*C*H), 129.0 (Mes-*C*H), 122.0 (Im(OMe)$_2$-*C*H), 120.7 (Im(OMe)$_2$-*C*H), 72.9 (Im(OMe)$_2$-*C*H_2), 71.4 (Im(OMe)$_2$-*C*H_2), 58.5 (Im(OMe)$_2$-*C*H_3), 58.0 (Im(OMe)$_2$-*C*H_3), 52.3 (SIMes-*C*H_2), 49.4 (Im(OMe)$_2$-*C*H_2), 48.3 (Im(OMe)$_2$-*C*H_2), 32.0 (hexylidene-*C*H_2), 26.7 (hexylidene-*C*H_2), 22.8 (hexylidene-*C*H_2), 21.05 (hexylidene-*C*H_2), 21.0 (Mes-*C*H_3), 19.5 (Mes-*C*H_3), 18.7 (Mes-*C*H_3), 14.2 (hexylidene-*C*H_3). Elemental Analysis for $C_{42}H_{54}ClF_5N_4O_2RuS\bullet(C_6H_5Cl)$: C, 55.91; H, 5.89; N, 5.80. Found: C, 56.27; H, 5.83; N, 6.19.

Ring-Opening Metathesis Polymerization (ROMP) The required amount of the catalyst (1 mol%), was weighed out and dissolved in 0.5 mL CD_2Cl_2. For the tests that involved the use of an additive (i.e. BCl_3, 1M in hexane) the required volume was added and the mixture was allowed to stand for 5 min. The solutions were placed in an NMR tube, 1,5-cyclooctadiene (60 µL, 0.50 mmol) was added, the NMR tube was capped and the solution was mixed at the desired temperature. Reaction progress was monitored by ^{1}H NMR every 2 hours (unless otherwise noted). Reaction progress was determined by comparing the ratio of the integrals of the peaks corresponding to the methylene protons in the starting material versus the product.

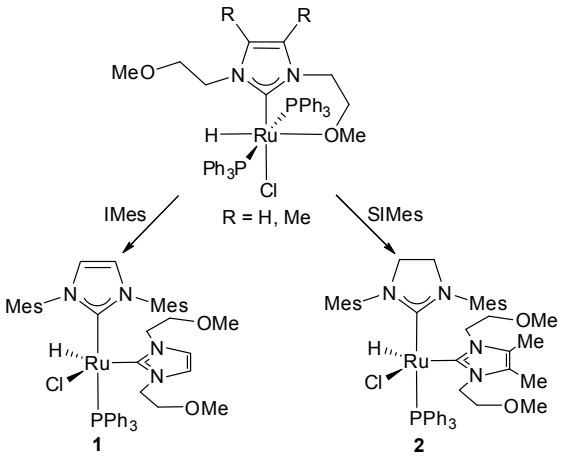
Ring-Closing Metathesis (RCM) of diethyl diallylmalonate. The required amount of catalyst (5 mol%) was weighed out and dissolved in 0.5 mL CD_2Cl_2. For the tests that involved the use of an additive (i.e. BCl_3, 1M in hexane) the required volume was added and the mixture was allowed to stand for 5 min. The solution was placed in an NMR tube, diethyl diallylmalonate (20 µL, 0.50 mmol) was added, the NMR tube was capped and the solution was mixed at the desired temperature. Reaction progress was monitored by ^{1}H NMR every 2 hours (unless otherwise noted). Reaction progress was determined by integration of the olefinic peaks of the starting material versus the product.

Cross-Metathesis (CM) of 5-hexenyl acetate and methyl acrylate. The required amount of catalyst (2 mol%) was weighed out and dissolved in 0.5 mL CD_2Cl_2. For the tests that involved the use of an additive (i.e. BCl_3, 1M in hexane) the required volume was added and the mixture was allowed to stand for 5 min. The solution was placed in an NMR tube and a mixture of 5-hexenyl acetate (20 µL, 0.12 mmol) and methyl acrylate (10 µL, 0.11 mmol) was added and the solution was mixed at the desired temperature. Reaction progress was monitored by ^{1}H NMR every 2 hours (unless otherwise noted). Reaction progress was determined by integration of the olefinic peaks of the starting material versus the product.[26]

X-ray Data Collection, Reduction, Solution and Refinement Single crystals were coated in Paratone-N oil in the glove-box, mounted on a MiTegen Micromount and placed under an N_2 stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K for all crystals. Data reduction was performed using the SAINT software package, and an absorption correction was applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least squares on F^2 using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

DISCUSSION

In recent communications[25] we described a synthetic strategy to the species of the general formula $(Im(OMe)_2)(SIMes)(PPh_3)RuHCl$ ($Im(OMe)_2$ = $(C_3H_2(NCH_2CH_2OMe)_2)$. In a similar fashion a series of related species were synthesized. Thus, the reaction of $(Im(OMe)_2)(PPh_3)_2RuHCl$[25b] with IMes in THF at 60 °C overnight produced a color change from yellow to red. After workup, **1** was isolated as a red solid in 73% yield (Scheme 1). The ^{1}H NMR spectrum of **1** revealed a doublet at -28.12 ppm, with a coupling constant of 26 Hz, indicative of a hydride coupled to a single phosphorus center. The ^{31}P{^{1}H} NMR spectrum showed a singlet at 43.9 ppm. Single-crystal X-ray analysis of **1** confirmed the formulation as $(IMes)(Im(OMe)_2)(PPh_3)RuHCl$ (Fig. 2) with a five-coordinate square-pyramidal ruthenium where the two NHCs, chloride, and phosphine form the base of the pyramid and the hydride occupies the apex. The Ru-C distances for IMes and $Im(OMe)_2$ are 2.077(2) and 1.969(2) Å. The *trans* influence of these carbene ligands is reflected in the elongated Ru-P and Ru-Cl distances of 2.2880(6) and 2.4509(6) Å, respectively. The Ru-H distance is 1.50(3) Å and the *cis* disposition of the carbene ligands in **1** results in a C-Ru-C angle of 91.27(9)°.



Scheme 1. Synthesis of compounds **1-2.**

In a similar fashion, $(Me_2Im(OMe)_2)(PPh_3)_2RuHCl$[25a] reacts with SIMes in THF at 50 °Cfor 24 hours to give **2** in 73% yield. The hydride and phosphorus signals in the ^1H and $^{31}P\{^1H\}$ NMR spectra for **2** were observed at -27.43 ppm and 36.5 ppm, respectively. An X-ray analysis of **2** confirmed it as $(SIMes)(Me_2Im(OMe)_2)(PPh_3)RuHCl$ (Fig. 3). The Ru-C distances for SIMes and $Me_2Im(OMe)_2$ were found to be 2.077(3) and 1.985(3) Å, respectively, similar to those in **1**. The Ru-P and Ru-Cl distances are 2.3384(8) and 2.4583(9) Å, respectively, while the Ru-H distance is 1.50(3) Å. The *cis* disposition of the carbene ligands in **2** results in a C-Ru-C angle of 92.1(1)°.

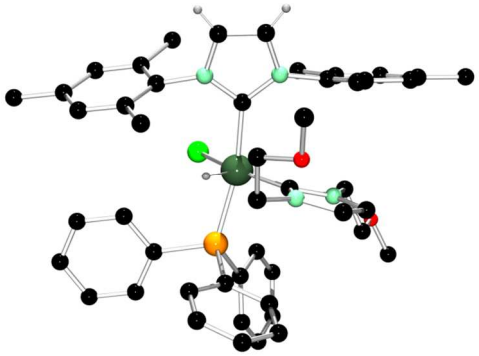


Figure 2. POV-ray depiction of the molecular structure of **1**. Ru: dark green, O: red; Cl: green; N: aquamarine, P: orange, C: black, H: gray. H-atoms except for Ru-H and IMes-CH omitted for clarity.

With a series of *bis*-carbene Ru-hydride species in hand, reactions with vinyl-sulfides were explored. For example, 4-fluorophenyl vinyl sulfide was added to a solution of $Im(OMe)_2(SIMes)(PPh_3)RuHCl$[25b] in CH_2Cl_2 and stirred for four hours at room temperature. Subsequent workup afforded the isolation of compound **3** as a red solid in 80% yield (Scheme 2). The ^1H NMR spectrum of **3** revealed a broad singlet at 18.34 ppm which integrated to one proton and was assigned to the Ru=CH fragment. The corresponding carbon signal was derived from two dimensional NMR experiments (HSQC) and was found at 313.5 ppm. The $^{19}F\{^1H\}$ NMR spectrum showed a broad singlet at -124.49 ppm which corresponds to the *p*-fluorophenyl thiolate moiety. A single crystal X-ray analysis of **3** confirmed the formulation as $Im(OMe)_2(SIMes)RuCl(S(p\text{-}FC_6H_4)(=CHCH_3)$. The geometry around the metal center is best described as distorted square pyramid (Fig. 4) and is similar to that seen in earlier examples of *bis*-carbene Ru-alkylidene compounds[21a] in which the two carbenes are *trans* disposed with a C-Ru-C angle of 158.6(1)°. The two anionic groups in **3** are also mutually *trans* while the alkylidene fragment occupies the pseudo-apical position. The Ru-C distances for the carbenes are found to be 2.089(3) Å and 2.101(3) Å for SIMes and $Im(OMe)_2$, respectively, while the Ru-C distance for the alkylidene is 1.807(4) Å. The corresponding Ru-Cl distance is 2.5009(9) Å while the Ru-S distance is 2.3494(9) Å.

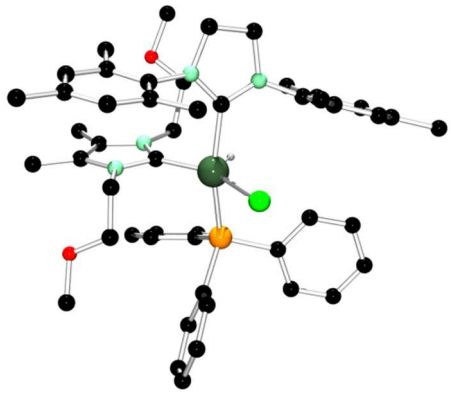


Figure 3. POV-ray depiction of the molecular structure of **2.** Ru: dark green, O: red; Cl: green; N: aquamarine, P: orange, C: black, H: gray. H-atoms except for Ru-H omitted for clarity.

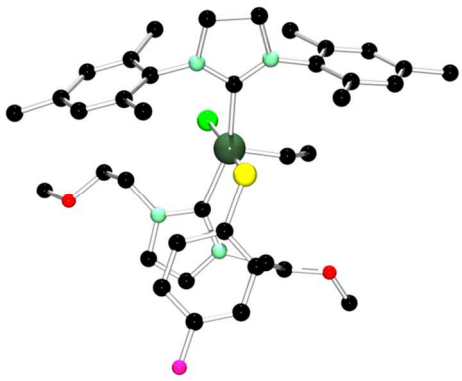
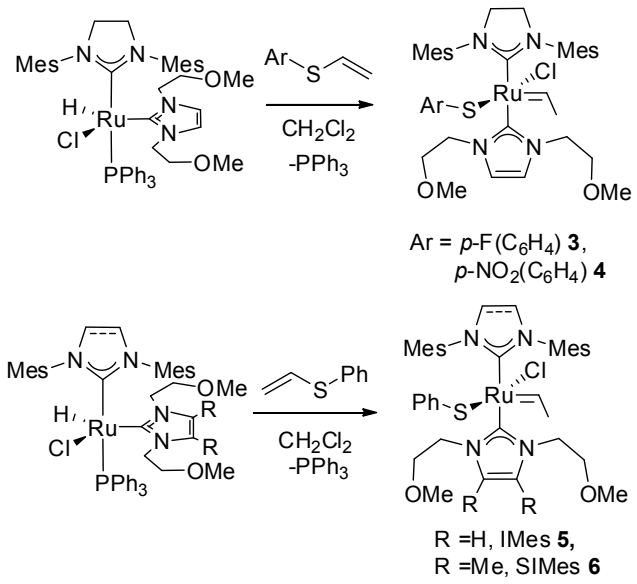


Figure 4. POV-ray depiction of the molecular structure of **3**. Ru: dark green, S: yellow, O: red; Cl: green; N: aquamarine, F: deep pink, C: black. H-atoms omitted for clarity.

In a similar fashion, addition of 4-nitrophenyl vinyl sulfide to a solution of $Im(OMe)_2(SIMes)(PPh_3)RuHCl$ in CH_2Cl_2 results in a deep purple solution. Stirring for four hours at room temperature, followed by workup afforded **4** as a purple solid in 75% yield (Scheme 2). The ^1H NMR data for **4** revealed signals arising from carbene and thiolate ligands as well as a quartet at

18.42 ppm, with a $^3J_{HH}$ of 6 Hz, which integrated to one proton and could be assigned to the Ru=CH fragment. The corresponding carbon signal for this fragment was seen at 314.2 ppm. The NMR data are consistent with the formulation of **4** as Im(OMe)$_2$(SIMes)RuCl(S(*p*-(NO$_2$)C$_6$H$_4$)(=CHCH$_3$).



Scheme 2. Synthesis of compounds **3-6.**

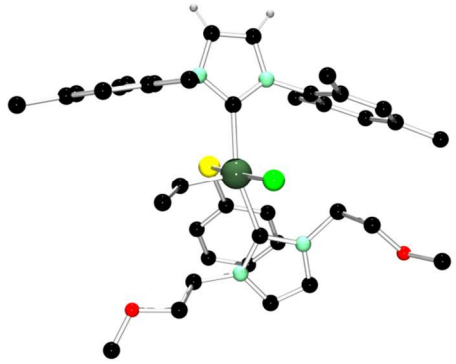


Figure 5. POV-ray depiction of the molecular structure of **5.** Ru: dark green, S: yellow, O: red, Cl: green, N: aquamarine, C: black, H: gray. H-atoms except for IMes-CH omitted for clarity.

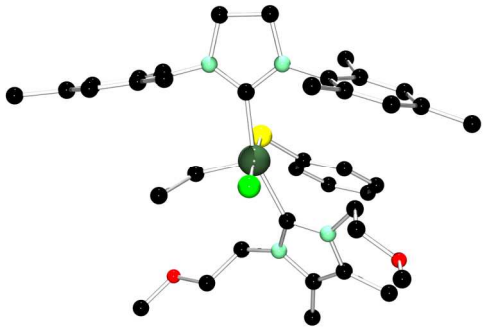
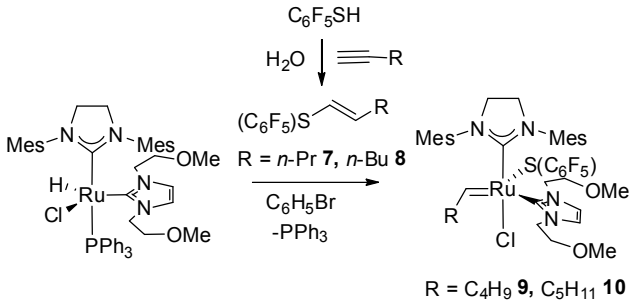


Figure 6. POV-ray depiction of the molecular structure of **6.** Ru: dark green, S: yellow, O: red, Cl: green, N: aquamarine, C: black. H-atoms omitted for clarity.

Using an analogous procedure, compounds **5** and **6** were prepared by the addition of phenyl vinyl sulfide to a solution of **1** and **2** affording red solids in 59% and 80% yields, respectively (Scheme 3). The ^{1}H NMR data for **5** and **6** showed a quartet at 19.09 ppm, with a coupling constant of 6 Hz, and a broad singlet at 19.05 ppm, respectively, attributable to the Ru=CH fragments. The corresponding carbon signals for these fragments were derived from two dimensional NMR experiments (HSQC) at 313.6 and 312.0 ppm, respectively. X-ray analyses confirmed the formulations of **5** and **6** as distorted square pyramidal species Im(OMe)$_2$(IMes)RuCl (=CHCH$_3$)(SPh) (Fig. 5) and Me$_2$Im(OMe)$_2$(SIMes)RuCl(=CHCH$_3$)(SPh) (Fig. 6), respectively. Similar to **3**, the Ru-C distances for the NHCs in **5** are 2.102(3) Å and 2.086(3) Å and 2.070(5) Å and 2.114(5) Å for **6** with *trans* carbene C-Ru-C angle of 158.2(1)^o in both cases. The Ru-alkylidene Ru-C distances in **5** and **6** are 1.818(4) Å and 1.811(5) Å, respectively, while the Ru-Cl and Ru-S distances are found to be 2.4783(9) Å and 2.3592(9) Å in **5** and 2.469(1) Å and 2.366(1) Å in **6**.

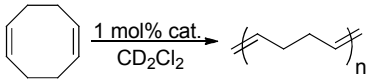
Analogues incorporating pentafluorophenylthiolate groups are accessible as the *E* and *Z* isomers of pentafluorophenyl alkenyl sulfides are readily prepared employing a modification of the literature procedure described by Ranu and coworkers.[27] In this fashion, (C$_6$F$_5$)SCH=CHR (R = *n*-Pr **7**, *n*-Bu **8**) were prepared. The subsequent reactions of **7** and **8** with Im(OMe)$_2$(SIMes)(PPh$_3$)RuHCl afforded orange/brown solids Im(OMe)$_2$(SIMes)(F$_5$C$_6$S)RuCl(=CHC$_4$H$_9$) **9** and Im(OMe)$_2$(SIMes)(F$_5$C$_6$S)RuCl(=CHC$_5$H$_{11}$) **10** in 73% and 71% yield, respectively (Scheme 3). The ^{1}H NMR spectra revealed a triplet at 16.37 ppm with a coupling constant of 5 Hz for **9** and a triplet at 16.44 ppm with a coupling constant of 5 Hz for **10** which correspond to the Ru=CH fragments. The corresponding carbon signals for these fragments were derived from two dimensional NMR experiments (HSQC) at 315.2 and 315.3 ppm, for **9** and **10**, respectively. The ^{19}F NMR spectra of **9** and **10** showed five signals indicating a dissymmetric environment for the (C$_6$F$_5$)S$^-$ moiety. Repeated crystallization attempts of **9** and **10** yielded crystals of poor quality, nonetheless preliminary X-ray studies (see Figure S1 and S2 in supporting information) confirmed the formulations. In contrast to **3-6** the two carbenes in **9** and **10** adopt a *cis* orientation similar to that seen previously for Im(OMe)$_2$(SIMes)(F$_5$C$_6$S)RuCl(=CHCH$_2$Ph).[21a]



Scheme 3. Synthesis of compounds **7-10**.

The utility of compounds **3-6** and **9-10** as metathesis catalysts was assessed using standard metathesis tests[26] established by Grubbs and coworkers. These included ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene, ring-closing metathesis (RCM) of diethyl diallylmalonate, and cross metathesis (CM) of 5-hexenyl acetate with methyl acrylate. Pentafluorophenyl thiolate-containing compounds are shown to be more active for ROMP (Table 1) than phenyl thiolate analogues. At room temperature conversions of 95 and 93% are observed after 24 hours for **9** and **10** (entries 5 and 6), respectively, while no catalysis was seen with compounds **3-6**. It is also observed that, at 45 °C compounds with more electron donating carbenes (i.e. $Me_2Im(OMe)_2$ vs. $Im(OMe)_2$ and SIMes vs. IMes) show better activity with **6** being the most active (quantitative conversion after 4 hours, entry 4). It has been demonstrated that Ru-alkylidene complexes with more electron donating NHCs tend to be more active for olefin metathesis. This is presumably because they are expected to enhance the rate of oxidative addition needed to metallacyclobutane formation during catalysis.[4c] The addition of BCl_3 as a co-catalyst enhances the activity of all the pre-catalysts tested both at room temperature and at 45 °C. Again the catalyst generated from **6** and BCl_3 was the fastest affording complete polymerization after 30 minutes at 45 °C (entry 13). To compare the activity of the reported catalysts, **3-6**, **9** and **10**, catalytic runs employing the Grubbs' catalysts (G1 and G2) were undertaken. Using 1 mol% of G1at 25 °C results in 91% conversion to the polymer after 7 hours (entry 16) while, under the same conditions, G2 give 100% conversion after 3 hours (entry 17).

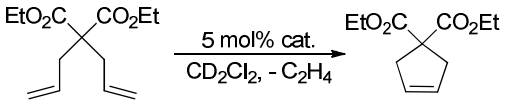
Table 1: Ring-Opening Metathesis Polymerization of 1,5-Cyclooctadiene



Entry	Catalyst (1 mol%)	BCl_3 (mol%)	T (°C)	Time (h)	Conversion[a] (%)
1	**3**	0	45	24	100
2	**4**	0	45	24	58
3	**5**	0	45	24	69
4	**6**	0	45	4	100
5	**9**	0	25	24	95
6	**10**	0	25	24	93
7	**3**	1	25	8	100
8	**3**	1	45	2	100
9	**4**	1	25	2	100
10	**5**	1	25	24	92
11	**5**	1	45	8	100
12	**6**	1	25	6	100
13	**6**	1	45	0.5	100
14	**9**	1	25	2	100
15	**10**	1	25	2	100
16	**G1**	0	25	7	91
17	**G2**	0	25	3	100

[a] Conversions determined by ^{1}H NMR spectroscopy.

Table 2: Ring-Closing Metathesis of Diethyl Diallylmalonate



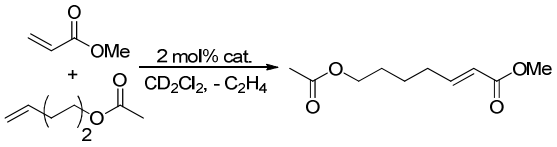
Entry	Catalyst (5 mol%)	BCl_3 (mol%)	T (°C)	Time (h)	Conversion[a] (%)
1	**3**	0	45	8	16
2	**4**	0	45	24	0
3	**5**	0	45	24	0
4	**6**	0	45	4	12
5	**9**	0	25	24	7
6	**9**	0	45	24	60
7	**10**	0	25	24	15
8	**10**	0	45	24	56
9	**3**	5	25	24	33
10	**3**	5	45	6	100
11	**4**	5	25	24	10
12	**4**	5	45	24	52
13	**5**	5	45	24	100
14	**6**	5	25	24	79
15	**6**	5	45	2	100
16	**9**	5	25	24	88
17	**9**	5	45	2	100
18	**10**	5	25	24	93
19	**10**	5	45	2	100
20	**G1**	0	25	0.5	83
21	**G2**	0	25	0.5	100

[a] Conversions determined by ^{1}H NMR spectroscopy.

Fogg and coworkers have reported substituting the chlorides with catecholate[6d] or phenoxide[6b, 28] based anionic ligands mainly to avoid catalyst decomposition by forming face bridged $Ru_2(\mu Cl)_3$ dimers. Most of the systems reported showed slow initiation, where metathesis was done at elevated temperatures, but very good activities. The systems with $(OC_6F_5)^-$ or $(OC_6Br_5)^-$ showed very good activity. RCM tests showed that compounds **3-6** and **9-10** showed minimal activity at 25 °C while **9** and **10** showed modest activity at 45 °C (Table 2, entries 6 and 8). Conversions are improved with the addition of BCl_3. The highest activities were observed with **6**, **9** and **10** where one equivalent of BCl_3 is used at 45 °C, affording complete conversions after 2 hours (entries 15, 17, 19). Using 5 mol% of G1 at 25 °C results in 83% conversion to the ring-closed product after 30 minutes (entry 20) while, under the same conditions, G2 give 100% conversion (entry 21).

Similar trends were observed for CM reactions where the pre-catalysts **3-6** and **9-10** are inactive even upon warming to 45 °C (Table 3). Activities are enhanced with the addition of BCl_3, with the best conversions of 72% and 80% of the hetero-coupled product being obtained with **6** and **10** after 2 hours at 45 °C (entries 11 and 14). Using 2 mol% of G1 at 25 °C results in 20% conversion to the heterocoupled product after 3 hours (entry 15) while, under the same conditions, G2 gives 56% conversion (entry 16). It is worth noting that in addition to the desired heterocoupled product, the homocoupled by-product was also observed.

Table 3: Cross-Metathesis of 5-Hexenyl Acetate and Methyl Acrylate



Entry	Catalyst (2 mol%)	BCl_3 (mol%)	T (°C)	Time (h)	Conversion[a] (%)
1	**3**	0	45	24	0
2	**4**	0	45	24	0
3	**5**	0	45	24	0
4	**6**	0	45	24	0
5	**9**	0	45	24	0
6	**10**	0	45	24	0
7	**3**	2	25	2	48
8	**3**	2	45	2	42
9	**4**	2	45	24	32
10	**5**	2	45	2	28
11	**6**	2	45	4	72
12	**9**	2	45	4	60
13	**10**	2	25	6	79
14	**10**	2	45	2	80
15	**G1**	0	25	3	20
16	**G2**	0	25	3	56

[a] Conversions determined by ^{1}H NMR spectroscopy; conversions refer to hetero-coupled product.

The use of acids as additives in olefin metathesis to enhance catalysis has been previously demonstrated. Grubbs and coworkers have reported the use of HCl and $AlCl_3$ as phosphine scavengers which enhance the rate of catalysis when using the second generation catalyst.[29] Yang *et al.* has used Lewis acids, such as $Ti(OiPr)_4$, to deactivate diallylamines with basic N atoms to prevent binding to Ru and shutting off metathesis.[30] Monitoring the present reactions by ^{11}B NMR spectroscopy revealed a resonance at 6.9 ppm consistent with the presence of a $[BCl_4]$ anion. Thus BCl_3 is believed to abstract the halide generating a cationic Ru centre which is presumably stabilized by a hemi-labile ether arm of the NHC (see supporting information) The formation of this cation enhances reactivity. Interestingly the precatalyst are unstable in CH_2Cl_2 in the absence of BCl_3 over 24 hours, decomposing with loss of the alkylidene fragment. In contrast the cationic species are stable under similar conditions. Similarly, halide abstraction has been used with Ru-alkylidene precursors to enhance metathesis activity as was demonstrated by Hofmann and coworkers.[31] Cationic Ru-alkylidene complexes have also been reported for metathesis activity by the research groups of Nolan, Dixneuf and Fürstner.[32] We have also recently reported the use of BCl_3 as an activator for Ru-dithiolate alkylidene complexes where two equivalents are used to generate cationic complexes which were shown to be active metathesis catalysts.[7, 33]

CONCLUSION

We have prepared a series of derivatives of *bis*-mixed-carbene Ru-alkylidene complexes employing a facile, high-yielding, and inexpensive route using *bis*-mixed-carbene Ru-hydride species and aryl vinyl sulfides. These complexes exhibit modest metathesis activities, which are enhanced in the presence of the Lewis acid additive BCl_3. We are continuing to exploit reactions of vinyl sulfides with metal precursors to prepare new alkylidene complexes in a quest for new metathesis catalysts.

Notes and references

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‡ Crystallographic data have been deposited in the Cambridge Datbase CCDC#-1027918-1027922.

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