Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

RSCPublishing

ARTICLE

Ru Alkylidene Compounds Bearing Tridentate, Dianionic Ligands: Lewis Acid Activation and Olefin Metathesis

Cite this: DOI: 10.1039/x0xx00000x

Adam M. McKinty and Douglas W. Stephan*

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The series of tridentate complexes of Ru-alkylidenes (L)Ru(CHPh)(SCH_2CH_2)$_2$E (E =O, L = SIMes 1, PCy_3 **2**, E = S, L = SIMes **3**, PCy_3 **4**; E = PPh **7**, L = PCy_3), (L)Ru(CHPh)(SC_6H_4)$_2$S (L = SIMes **5**, PCy_3 **6**), (L)Ru(CHPh) (OCH_2CH_2)$_2$O (L = SIMes **8**, PCy_3 **9**) were prepared an shown to react with one equivalent of BCl_3 to give the complexes (L)Ru(CHPh)Cl[E(CH_2CH_2S)$_2BCl_2$] (E = O, L = SIMes **10**, PCy_3 **11**, E = S, L = SIMes **12a/b,** PCy_3 **13**, E = PPh, L = PCy_3 **16**) and (L)Ru(CHPh)(SC_6H_4)$_2$O (L = SIMes **14**, PCy_3 **15**). In the case of **1** and **2** reaction with two equivalents of BCl_3 affording the corresponding cation via chloride abstraction. These cations coordinate MeCN to give the six coordinate Ru cation salts [(L)Ru(CHPh)(NCMe)(O(CH_2CH_2S)$_2BCl_2$)][BCl_4] L = SIMes **17**, PCy_3 **18**). The generated five coordinate cations derived from **2-9** via addition of two equivalents of BCl_3 were evaluated in standard preliminary tests for olefin metathesis catalysis.

Introduction

Olefin metathesis catalysis is a powerful reaction that has dramatically impacted synthetic organic methodology. Moreover, this technology has been exploited for a wide range of small molecules and pharmaceuticals as well as for polymers and hydride materials. The Schrock Mo-based catalysts are more active than Ru-based systems although early versions exhibited limited functional group tolerance.[1-7] Nonetheless, suitable ligand design has improved this and thus allowed a broader range of use.[8] Despite these advances, it is the Grubbs Ru alkylidene catalyst systems that have to date found wider applications in organic synthesis and commercial applications.[9-17] Indeed it is the Grubbs' second-generation catalyst architecture that's been the major focus of the proliferating variety of applications. Efforts to target catalyst modifications have exploited a variety of approaches, including variations of the N-heterocyclic carbene (NHC) ligand, the alkylidene fragment, and co-ligands. Of the over 300 variants known,[9-17] catalyst modifications have targeted extended catalyst lifetime, accelerated initiation[18-20] and specific selectivity issues.[21] Among the variants, replacement of the chlorides for either other anionic donors have received limited attention, although these systems generally exhibited lower catalyst activity.[22-25] Nonetheless, Fogg and co-workers[26] described the negative effects of such substitutions were overcome by sterically small, electronically weak donors such as OC_6F_5. More recently the groups of Hoveyda and Jensen have described Z-selective metathesis catalysts derived from Ru dithiolate complexes.[27-28] In an alternative approach the research groups of Nolan,[29] Dixneuf[30] and Fürstner[31-32] described active cationic Ru alkylidene species. In our own efforts we have combined these two ideas, synthesizing the tridentate ligand complex (SIMes)Ru(CHPh)(SCH_2CH_2)$_2$O (**1**).[33-34] While this species proved to be inactive in olefin metathesis catalysis, reaction of this species with two equivalents of BCl_3 demonstrated access to a cationic Ru alkylidene complex of the form [(SIMes)Ru(CHPh)(O(CH_2CH_2S)$_2$ BCl_2)][BCl_4] which proved to be an active catalyst.[33] In this paper, we further explore ligand perturbations accessing a range of tridentate ligand complexes and the subsequent reactions with one and two equivalents of BCl_3 ultimately providing access to Ru-alkylidene cations. Preliminary assessment of these species in standard olefin metathesis catalysis is also described.

Experimental section

All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing a Vac Atmospheres glove box and a Schlenk vacuum-line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks. All solvents were thoroughly degassed after purification (repeated freeze-pump-thaw cycles). CD_2Cl_2 was dried over CaH_2 and vacuum transferred into a Schlenk flask equipped with a Teflon-valve stopcock. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 25 °C on Varian 300 and 400 MHz and Bruker 400 MHz spectrometers. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal (^{1}H, ^{13}C) or relative to an external standard (^{31}P: 85% H_3PO_4). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. All chemicals were obtained from Aldrich and used as received unless stated. Pro-

ligands were synthesized by the addition of two equivalents of n-BuLi or KOtBu to the corresponding dithiol or diol. ($LiSCH_2CH_2)_2PPh$ and $(LiSC_6H_4)_2O$ were prepared according to by modification of a literature procedure.[35]

Synthesis of (L)Ru(CHPh)($SCH_2CH_2)_2O$ (L = SIMes 1, PCy_3 2) and (L)Ru(CHPh)($SCH_2CH_2)_2S$ (L = SIMes 3, PCy_3 4), (L)Ru(CHPh)($SC_6H_4)_2S$ (L = SIMes 5, PCy_3 6), (PCy_3)Ru(CHPh)($SCH_2CH_2)_2PPh$ 7, (L)Ru(CHPh)($OCH_2CH_2)_2O$ (L = SIMes 8, PCy_3 9) These compounds were prepared in a similar fashion and thus only one preparation is detailed.

(SIMes)(PCy_3)$RuCl_2$(CHPh) (0.326 g, 0.384 mmol) in MeCN (5 mL) was added to ($LiSCH_2CH_2)_2O$.2THF (0.144 g, 0.489 mmol) in MeCN (5 mL) and toluene (10 mL) and stirred for 16 h. All volatiles were removed from the dark brown solution. CH_2Cl_2 (5mL) was added to give a dark brown solution which was filtered through Celite. Upon concentration to dryness, the resulting dark brown solid was washed with hexane (20 mL) and dried to yield a black-red solid. (0.243 g, 99%).

1: ^{1}H NMR (CD_2Cl_2): 14.85 (s, 1H, Ru=CH), 7.14 (t, 1H, $^3J_{HH}$ = 8 Hz, p-H, Ph), 6.97-7.05 (m, 4H, Ph), 6.86 (s, 4H, Mes), 3.92 (s, 4H, Im), 3.65 (m, 2H, CH_2), 2.82 (m, 2H, CH_2), 2.45 (s, 12 H, CH_3), 2.32-2.41 (m, 4H, CH_2), 2.23 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 210.0 (Ru=CH), 153.7 (ipso-C, Ph), 137.9 (ipso-C, NCN), 137.4 (ipso-C, Mes), 137.3 (ipso-C, Mes), 127.3 (CH, Ph), 128.8 (CH, Mes), 125.0 (CH, Ph), 124.7 (CH, p-C, Ph), 77.6 (CH_2), 51.8 (CH_2, Im), 31.6 (CH_2), 20.6 (CH_3, Mes), 19.1 (CH_3, Mes). Anal. Calc. for $C_{32}H_{40}N_2ORuS_2$: C, 60.63; H, 6.36; N, 4.42. Found: C, 60.19; H, 5.97; N, 4.30.

2: dark red solid, Yield: 98%. ^{1}H NMR (CD_2Cl_2): 13.68 (d, $^3J_{PH}$ = 12 Hz, 1H, Ru=CH), 7.27 (m, 2H, Ph), 7.14 (m, 3H, Ph), 3.84 (m, 2H, CH_2), 3.21 (m, 2H, CH_2), 2.74 (m, 4H, CH_2), 2.11, 1.98, 1.74, 1.61, 1.50, 1.19 (all m, 33 H, C_6H_{11}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 208.0 (Ru=CH), 153.3 (ipso-C, Ph), 128.2 (CH, Ph), 125.6 (CH, Ph), 125.4 (CH, Ph), 78.0 (CH_2), 35.9 (d, $^1J_{PC}$ = 24 Hz, ipso-C of C_6H_{11}), 32.4 (CH_2), 30.0 (m-C of C_6H_{11}), 28.3 (d, $^2J_{PC}$ = 10 Hz, o-C, C_6H_{11}), 26.9 (p-C C_6H_{11}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 65.6. Anal. Calc. for $C_{29}H_{47}OPRuS_2$: C, 57.30; H, 7.79. Found: C, 56.92; H, 7.55

3: a dark red solid, Yield: 98%). ^{1}H NMR (CD_2Cl_2): 14.41 (s, 1H, Ru=CH), 7.19 (t, $^3J_{HH}$ = 7 Hz 1H, p-H, Ph), 7.07 (t, $^3J_{HH}$ = 7 Hz 2H, m-H, Ph), 6.88 (d, $^3J_{HH}$ = 8 Hz 2H, o-H, Ph), 6.80 (s, 4H, CH, Mes), 3.99 (s, 4H, CH_2, Im), 3.22 (m, 2H, CH_2), 3.00 (m, 2H, CH_2), 2.52 (s, 12H, CH_3, Mes), 2.24 (m, 2H, CH_2), 2.19 (s, 6H, CH_3, Mes), 1.73 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 211.2 (Ru=CH), 138.1 (ipso-C, Ph), 137.8 (ipso-C, NCN), 137.7 (ipso-C, Mes), 129.2 (CH, Mes), 127.25.2 (CH, Ph), 127.1 (CH, Ph), 125.1 (CH, p-C, Ph), 52.4 (CH_2), 44.6 (CH_2, Im), 34.8 (CH_2), 21.0 (CH_3, Mes), 19.7 (CH_3, Mes). Anal. Calc. for $C_{32}H_{40}N_2RuS_3$•CH_2Cl_2: C, 53.94; H, 5.76; N, 3.81. Found: C, 55.69; H, 5.96; N, 3.81.[36]

4: a dark red solid, Yield: 97%. ^{1}H NMR (CD_2Cl_2): 13.48 (d, $^3J_{PH}$ = 19 Hz, 1H, Ru=CH), 7.12 (m, 3H, Ph), 6.93 (m, 2H, Ph), 3.41 (m, 2H, CH_2), 3.24 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 2.28, 2.04, 1.73, 1.57, 1.19 (all m, C_6H_{11}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 235.2 (d, $^2J_{PC}$ = 15 Hz, Ru=CH), 157.0 (ipso-C, Ph), 127.5 (CH, Ph), 125.8 (CH, Ph),125.4 (CH, Ph), 45.2 (CH_2), 36.3 (CH_2), 35.2 (d, $^1J_{PC}$ = 19.8 Hz, ipso-C of C_6H_{11}, 30.0 (m-C of C_6H_{11}, 28.4 (d, $^2J_{PC}$ = 10 Hz, o-C of C_6H_{11}, 26.9 (p-C of C_6H_{11}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 41.7. Anal. Calc. for $C_{29}H_{47}PRuS_3$: C, 55.83; H, 7.59. Found: C, 55.71; H,7.33.

5: red solid, Yield: 86%. ^{1}H NMR (CD_2Cl_2): 15.60 (s, 1H, Ru=CH), 7.41 (d, $^3J_{HH}$ = 8 Hz 2H, Ph), 6.91 (m, 8H, Ph, Mes), 6.79 (m, 5H, Ph), 6.64 (m, 2H, Ph), 4.08 (s, 4H, CH_2, Im), 2.51 (s, 12 H, CH_3, Mes), 2.22 (s, 6H, CH_3, Mes). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 209.1 (Ru=CH), 153.1 (ipso-C, Ph), 151.5 (ipso-C, Ph) 139.5 (ipso-C, NCN), 138.0 (ipso-C, Mes), 137.2 (ipso-C, Mes), 131.3 (CH, Ph), 129.2 (CH, Ph), 128.9 (CH, Ph), 128.1 (CH, Ph), 126.1 (CH, Mes), 127.4 (CH, Ph), 125.2 (CH, p-C, Ph), 122.9 (CH, Ph), 121.5 (CH, Ph), 114.8 (CH, Ph), 51.8 (CH_2, Im), 20.7 (CH3, Mes), 19.0 (CH_3, Mes). Anal. Calc. for $C_{40}H_{40}N_2ORuS_2$•CH_2Cl_2: C, 60.43; H, 5.19; N, 3.44. Found: C, 61.08; H, 5.78; N, 2.88.

6: a red solid Yield: 97%. ^{1}H NMR (CD_2Cl_2): 14.69 (d, $^3J_{PH}$ = 15 Hz, 1H, Ru=CH), 7.48 (d, $^3J_{HH}$ = 8 Hz, 2H, Ph), 7.48 (m, 3H, Ph), 6.90 (m, 4H, Ph), 6.82 (t, $^3J_{HH}$ = 7 Hz, 2H, Ph), 6.72 (m, 2H, Ph), 2.15, 2.02, 1.77, 1.55, 1.19 (all m, C_6H_{11}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 192.2 (Ru=CH), 154.0 (ipso-C, Ph), 152.2 (ipso-C, Ph), 139.1 (ipso-C, Ph), 132.1 (CH, Ph), 130.1 (CH, Ph), 127.9 (CH, Ph), 126.3 (CH, Ph), 125.3 (CH, Ph), 124.0 (CH, Ph), 122.7 (CH, Ph), 115.9 (CH, Ph), 36.0 (d, $^1J_{PC}$ = 25 Hz, ipso-C of C_6H_{11}, 31.62 (m-C of C_6H_{11}), 30.09 (p-C of C_6H_{11}), 28.19 (d, $^2J_{PC}$ = 10 Hz, o-C of C_6H_{11}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 68.6. Anal. Calc. for $C_{37}H_{47}OPRuS_2$: C, 63.13; H, 6.73. Found: C, 62.52; H, 6.30.[36]

7: a dark red solid, Yield: 89%. X-ray quality crystals were grown from a CH_2Cl_2/CH_3CN solution. ^{1}H NMR (CD_2Cl_2): 13.31 (dd, $^3J_{PH}$ = 23 Hz, $^3J_{PH}$ = 2 Hz, 1H, Ru=CH), 7.04 (m, 5H, PPh), 6.94 (d, $^3J_{HH}$ = 7 Hz 2H, Ph), 6.71 (m, 3H, Ph), 3.07 (m, 2H, CH2), 2.93 (m, 2H, CH_2), 2.47 (m, 5H, CH_2, C_6H_{11}), 2.15 (m, 2H, CH_2), 2.20, 1.86, 1.72, 1.33 (all m, C_6H_{11}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 235.9 (appt, $^2J_{PC}$ = 13 Hz, Ru=CH), 155.7 (dd, $^3J_{PC}$ = 11 Hz, 4 Hz, ipso-C, Ph), 130.7 (d, $^2J_{PC}$ = 9 Hz, CH, PPh), 128.56 (CH, PPh), 128.55 (d, $^1J_{PC}$ = 267 Hz, CH, PPh), 127.65 (d, $^3J_{PC}$ = 9 Hz, CH, PPh), 127.1 (CH, Ph), 126.0 (CH, Ph),125.0 (CH, Ph), 34.2 (m, CH_2), 31.5 (m, CH_2), 29.5 (m-C of C_6H_{11}), 28.0 (d, $^1J_{PC}$ = 9 Hz, ipso-C of C_6H_{11}), 27.7 (d, $^2J_{PC}$ = 9 Hz, o-C of C_6H_{11}), 26.6 (p-C of C_6H_{11}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 114.7 (d, $^2J_{PP}$ = 331 Hz), 28.9 (d, $^2J_{PP}$ = 331 Hz). Anal. Calc. for $C_{35}H_{52}P_2RuS_2$: C, 60.06; H, 7.49. Found: C, 59.58; H, 7.32.

8: a dark red solid. Yield: 90%. ^{1}H NMR (CD_2Cl_2): 16.23 (s, 1H, Ru=CH), 7.58 (d, $^3J_{HH}$ = 8 Hz 2H, Ph), 7.18 (m, 3H, Ph), 6.87 (s, 4H, CH, Mes), 3.78 (m, 4H, CH_2), 3.44 (s, 4H, CH_2, Im), 3.18 (m, 4H, CH_2), 2.57 (s, 12 H, CH_3, Mes), 2.19 (s, 6H, CH_3, Mes). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 212.4 (Ru=CH), 153.3 (ipso-C, Ph), 138.7 (ipso-C, NCN), 137.5 (ipso-C, Mes), 137.4 (ipso-C, Mes), 128.5 (CH, Ph), 128.2 (CH, Mes), 124.6 (CH, Ph), 123.6 (CH, p-C, Ph), 79.4 (CH2), 70.7 (CH_2), 51.4 (CH_2, Im), 20.7 (CH_3, Mes), 18.4 (CH_3, Mes). Anal. Calc. for $C_{32}H_{40}N_2O_3Ru$: C, 63.87; H, 6.70; N, 4.66. Found: C, 63.30 H, 6.43 N, 4.25.[36]

9: a red solid, Yield: 90%. ^{1}H NMR (CD_2Cl_2): 15.72 (d, $^3J_{PH}$ = 15 Hz, 1H, Ru=CH), 7.91 (d, $^3J_{HH}$ = 8 Hz 2H, Ph), 7.31 (m, 3H, Ph), 4.19 (m, 2H, CH_2), 3.96 (m, 2H, CH_2), 3.39 (m, 2H, CH_2), 2.96 (m, 2H, CH_2), 2.44, 2.22, 1.87, 1.67, 1.65 (all m, C_6H_{11}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 208.0 (Ru=CH), 128.6 (Ph), 128.2 (Ph), 126.4 (Ph), 124.7

(Ph), 79.5 (CH2), 72.1 (CH2), 33.2 (d, $^{1}J_{PC}$ = 26 Hz, ipso-C of C_6H_{11}), 28.8 (m-C of C_6H_{11}), 27.7 (d, $^{2}J_{PC}$ = 10 Hz, o-C of C_6H_{11}), 26.5 (p-C of C_6H_{11}). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): 64.8. Anal. Calc. for $C_{29}H_{47}O_3PRu$: C, 60.50; H, 8.23. Found: C, 59.94 H, 7.83.

Synthesis of (L)Ru(CHPh)Cl[O(CH$_2$CH$_2$S)$_2$BCl$_2$] (L = SIMes 10, PCy$_3$ 11), (L)Ru(CHPh)Cl[S(CH$_2$CH$_2$S)$_2$BCl$_2$] (L = SIMes 12a/b, PCy$_3$ 13), (L)Ru(CHPh)(SC$_6$H$_4$)$_2$O (L = SIMes 14, PCy$_3$ 15), (PCy$_3$)Ru(CHPh)(SCH$_2$CH$_2$)$_2$PPh 16, These compounds were prepared in a similar fashion and thus only one preparation is detailed.

To a CH_2Cl_2 solution (1 mL) of **1** (0.020 g, 0.032 mmol) was added BCl_3 in hexanes (1 M, 32 µL, 0.032 mmol). The brown solution immediately turned dark green. All volatiles were removed, and the resulting dark solid was washed with CH_3CN (2 mL) and dried to yield the blue-green solid **10** (0.022 g, 92%).

10: X-Ray quality crystals were grown from a CH_2Cl_2/CH_3CN solution.^{1}H NMR (CD_2Cl_2): 17.68 (s, 1H, Ru=CH), 8.09 (br, 2H, o-H of Ph) 7.56 (t, $^{3}J_{HH}$ = 8 Hz, 1H, p-H, Ph), 7.24 (t, $^{3}J_{HH}$ = 8 Hz, 2H, m-H of$_6$ Ph), 7.03 (s, 2H, CH, Mes), 6.56 (s, 2H, CH, Mes), 4.84 (m, 1H, CH_2), 3.84 (m, 2H, CH_2, Im), 3.74 (m, 1H, CH_2), 3.64 (m, 2H, CH_2, Im), 3.01, 2.80, 2.62 (all m, 1H, CH_2), 2.52 (s, 6 H, CH_3, Mes), 2.34 (m, 2H, CH_2), 2.25 (s, 6 H, CH_3, Mes), 2.20 (s, 6 H, CH_3, Mes), 2.17 (m, 1H, CH_2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 308.9 (Ru=CH), 214.6 (ipso-C, Ph), 152.0 (ipso-C, NCN), 138.5 (CMe, Mes), 137.6 (ipso-C, Mes), 137.4 (ipso-C, Mes), 132.7 (o-CH, Ph), 130.7 (p-CH, Ph), 129.6, 129.3 (CH, Mes), 127.0 (m-CH, Ph), 70.3, 68.1 (CH_2), 52.2, 53.8 (CH_2, Im), 30.6, 26.5 (CH_2), 20.7 (CH_3, Mes), 19.1 (CH_3, Mes), 18.7 (CH_3, Mes). ^{11}B NMR (CD_2Cl_2): 11.5. Anal. Calc. for $C_{32}H_{40}BCl_3N_2ORuS_2$•$CH_2Cl_2$: C, 47.41; H, 5.06; N, 3.35. Found: C, 48.05 H, 5.36; N, 3.78.[36]

11: a green solid. Yield: 89%. X-Ray quality crystals were grown from a CH_2Cl_2/CH_3CN solution. ^{1}H NMR (CD_2Cl_2): 18.93 (d, $^{3}J_{PH}$ = 12 Hz, 1H, Ru=CH), 8.87 (d, $^{3}J_{HH}$ = 8 Hz, 2H, o-H of Ph), 7.74 (t, $^{3}J_{HH}$ = 8 Hz, 1H, p-H of Ph), 7.51 (t, $^{3}J_{HH}$ = 8 Hz, 2H, m-H of Ph), 5.05, 4.56, 4.19, 3.82, 3.13, 3.00, 2.89, 2.78 (all m, 1H, CH_2), 2.12, 1.88, 1.82-1.64, 1.52, and 1.21-1.13 (all m, C_6H_{11}). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 277.4 (Ru=CH), 153.1 (ipso-C, Ph), 132.7 (CH, Ph), 131.8 (CH, Ph), 128.4 (CH, Ph), 71.2, 68.6 (CH_2), 36.2 (d, $^{1}J_{PC}$ = 19 Hz, ipso-C of C_6H_{11}), 33.2, 30.6 (CH_2), 29.5 (m-C of C_6H_{11}), 27.9 (o-C of C_6H_{11}), 26.4 (p-C of C_6H_{11}). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): 35.54. ^{11}B NMR (CD_2Cl_2): 11.1 (s).Anal. Calc. for $C_{29}H_{47}BCl_3OPRuS_2$: C, 48.04; H, 6.53. Found: C, 47.83 H, 6.62.

12: a blue-green solid. Yield: 93%. X-Ray quality crystals were grown from a CH_2Cl_2/CH_3CN solution. **12a:12b** ratio is 1:1. ^{1}H NMR (CD_2Cl_2): 17.20 (Ru=CH, **12a**), 16.30 (Ru=CH, **12b**), 7.61 (m, 2H, o-H of Ph) 7.43 (m, 1H, p-H, Ph), 7.34 (m, 2H, m-H of Ph), 7.12 (s, 2H, CH, Mes), 7.04 (s, 1H, CH, Mes) 6.58 (s, 1H, CH, Mes), 3.90 (m, 2H, CH_2, Im), 3.77 (m, 2H, CH_2, Im), 3.51, 3.31, 3.20 (all m, 1H, CH_2), 2.97 (m, 2H, CH_2) 2.65, 2.60, 2.49, 2.40, 2.33, 2.28 (all s, 3 H, CH_3, Mes), 2.06 (m, 1H, CH_2), 1,85 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 152.7, 150.4, 138.7, 138.6, 137.7,137.3, 131.7, 131.2, 129.6,129.5, 128.3 (all Ph, Mes), 65.6 (CH_2, Im), 52.1, 51.9, 42.2, 40.5, 39.4, 35.4, 31.5, 31.2, 28.5, 26.8, 25.5 (all CH2), 20.8, 20.6, 19.3, 19.0, 18.8, 18.7 (CH_3, Mes). ^{11}B NMR (CD_2Cl_2): 12.0, 9.9. Anal. Calc. for $C_{32}H_{40}BCl_3N_2RuS_3$: C, 50.10; H, 5.26; N, 3.65. Found: C, 49.46 H, 5.14; N, 3.39.[36]

13: a green solid. Yield: 93%. ^{1}H NMR (CD_2Cl_2): 17.96 (d, $^{3}J_{PH}$ = 15 Hz, 1H, Ru=CH), 8.34 (d, $^{3}J_{HH}$ = 9 Hz, 2H, o-H of C_6H_5), 7.65 (t, $^{3}J_{HH}$ = 8 Hz, 1H, p-H of C_6H_5), 7.40 (t, $^{3}J_{HH}$ = 8 Hz, 2H, m-H of C_6H_5), 3.66, 3.13, 2.95 (all m, 1H, CH_2), 2.55 (m, 5H, CH_2), 2.05, 1.88, 1.75-1.45, and 1.18 (all m, C_6H_{11}). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 275.3 (Ru=CH), 154.8 (ipso-C, Ph), 132.2 (CH, Ph), 131.8 (CH, Ph), 128.8 (CH, Ph), 39.3, 39.0 (CH_2), 36.7 (d, $^{1}J_{PC}$ = 19.3 Hz, ipso-C C_6H_{11}, 30.2, 30.03 (CH_2), 27.8 (m-C of C_6H_{11}), 27.6 (o-C of C_6H_{11}), 26.6 (p-C of C_6H_{11}). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): 34.9. ^{11}B NMR (CD_2Cl_2): 9.9 (s). Anal. Calc. for $C_{29}H_{47}BCl_3PRuS_3$: C, 47.00; H, 6.39. Found: C, 46.89 H, 6.46.

14: a green solid. Yield: 83%. ^{1}H NMR (CD_2Cl_2): 17.75 (s, 1H, Ru=CH), 7.60 (t, $^{3}J_{HH}$ = 7 Hz 1H, Ph), 7.40 (m, 5H, Ph), 7.31 (m, 2H, Ph), 7.13 (m, 3H, Ph), 7.06 (m, 3H, Ph, Mes), 6.82 (m, 1H, Ph), 6.04 (s, 2H, Mes), 3.83 (m, 1H, CH_2, Im), 3.68 (m, 1H, CH_2, Im), 3.48 (m, 2H, CH_2, Im), 2.59 (s, 6 H, CH_3, Mes), 2.18 (s, 6H, CH_3, Mes), 2.05 (s, 6H, CH_3, Mes).$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 289.9 (Ru=CH), 212.4, 183.7, 161.4, 160.4, 151.3, 138.6, 137.6, 137.3, 136.6, 134.1, 131.3, 130.2, 129.6, 129.4, 129.1, 128.5, 128.3, 126.8, 126.1, 125.7, 125.0, 123.0, 120.2, 52.2 (CH_2, Im), 20.8 (CH_3, Mes), 19.0 (CH_3, Mes), 18.5 (CH_3, Mes). ^{11}B NMR (CD_2Cl_2): 14.7. Anal. Calc. for $C_{40}H_{40}N_2ORuS_2BCl_3$: C, 56.71; H, 4.76; N, 3.31. Found: C, 56.48; H, 4.62; N, 3.10.

15: a blue-green solid. Yield 87%. ^{1}H NMR (CD_2Cl_2): 18.85 (d, $^{3}J_{PH}$ = 12 Hz, 1H, Ru=CH), 8.54 (d, $^{3}J_{HH}$ = 8 Hz, 2H, Ph), 7.74 (m, 3H, Ph), 7.57-7.37 (m, 6H, Ph), 7.20 (m, 2H, Ph), 2.40, 2.07, 1.80, 1.62, 1.43 (all m, C_6H_{11}). $^{13}C\{^{1}H\}$ NMR (Partial) (CD2Cl=): 154.6, 131.9, 131.2, 130.9, 128.7, 126.7, 123.1, 122.2, 121.2, 118.1, 116.3, 35.3, 31.6, 29.7, 29.1, 27.8, 27.7, 27.5 27.2 26.9, 26.3. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): 36.51. 11B NMR (CD_2Cl_2): 12.11. Anal. Calc. for $C_{37}H_{47}BCl_3OPRuS_2$: C, 54.12; H, 5.77. Found: C, 53.94 H, 5.62.

16: a dark green solid. Yield: 93%. **The compound exists as a mixture of isomers (16a, 16b in ratio: 9:1).** ^{1}H NMR (CD_2Cl_2): 18.06 (d, $^{3}J_{PH}$ =7 Hz, Ru=CH, **16b**), 17.32 (dd, $^{3}J_{PH}$ = 17 Hz, $^{3}J_{PH}$ = 11 Hz, Ru=CH, **16**a), 7.80 (m, Ph), 7.76 (m, Ph), 7.64 (m, Ph), 7.59 (m, Ph), 7.55 (m, Ph), 7.43 (m, Ph), 7.35 (m, Ph), 7.26 (m, Ph), 7.17 (m, Ph), 7.11 (m, Ph), 6.99 (m, Ph), 4.63 (m, CH_2, 5-3a), 4.39 (m, CH_2, **16a**), 4.19 (m, CH_2, **16a**), 4.05 (m, CH_2, **16a**), 3.61 (m, CH_2, **16b**), 3.17 (m, CH_2, **16b**), 2.89 (m, CH_2, **16b**), 2.82 (m, CH_2, **16b**), 2.49 (m, C_6H_{11}), 2.16 (m, C_6H_{11}), 1.87 (m, C_6H_{11}), 1.68 (m, C_6H_{11}), 1.32 (m, C_6H_{11}). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 153.3, 151.1, 137.3, 134.9, 133.3, 131.9, 131.5, 130.6, 130.2, 129.7, 129.2, 128.8, 128.6, 128.4, 128.1, 128.0, 127.9, 127.6, 127.1, 126.4 (all Ph), 37.6 (CH_2), 35.8 (CH_2), 35.7 (CH_2), 34.1 (CH_2), 31.3 (d, $^{1}J_{PC}$ = 30 Hz, C_6H_{11}), 30.9 (CH_2), 30.6 (CH_2), 30.1 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 27.7 (d, $^{3}J_{PP}$ = 4 Hz, C_6H_{11}), 27.2 (d, $^{2}J_{PP}$ = 11 Hz, C_6H_{11}), 26.5 (CH_2), 25.7 (CH_2). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): 81.5 (d, $^{2}J_{PP}$ = 255 Hz, PPh, **12b**), 75.8 (d, $^{2}J_{PP}$ = 26 Hz, PPh, **12a**), 29.6 (d, $^{2}J_{PP}$ = 26 Hz, PCy$_3$, **12a**), 26.9 (d, $^{2}J_{PP}$ = 257 Hz, PCy$_3$, **12b**). ^{11}B NMR (CD_2Cl_2): 10.7. Anal. Calc. for $C_{35}H_{52}BCl_3P_2RuS_2$: C, 51.45; H, 6.41. Found: C, 51.03; H, 6.88.

Synthesis of [(L)Ru(CHPh)(NCMe)(O(CH$_2$CH$_2$S)$_2$BCl$_2$)][BCl$_4$] L = SIMes 17, PCy$_3$ 18) These compounds were prepared in a similar fashion and thus only one preparation is detailed.

To a CH_2Cl_2 solution (1 mL) of 5-3 (0.050 g, 0.069 mmol) was added BCl_3 in hexanes (1 M, 69 μL, 0.069 mmol). The green solution immediately turned darker green. To this, MeCN (0.30 mL) was added and the solution turned dark red. All volatiles were removed and the dark red solid was dissolved in CH_2Cl_2 (1 mL) and filtered. Pentane (5 mL) was added and a dark red precipitate formed. The solid was collected, washed with pentane (2 x 2 mL) and dried in vacuo to yield a dark red solid, **18** (0.053 g, 87%).

17: red solid. (0.034 g, 94%). X-Ray quality crystals were grown from a CH_2Cl_2 solution layered with pentane.^{1}H NMR (CD_2Cl_2): 17.26 (s, 1H, Ru=CH), 7.64 (m, 3H, *o*-H and *p*-H of C_6H_5) 7.38 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-H of C_6H_5), 7.00 (s, 2H, CH, Mes), 6.77 (s, 2H, CH, Mes), 4.02 (m, 1H, CH_2), 3.83 (br, 5H, 1H, CH_2 and CH_2, Im), 3.46 (m, 2H, CH_2, Im), 3.21 (m, 1H, CH_2), 2.66 (m, 3H, 3 × CH, CH_2), 2.53 (s, 6 H, CH_3, Mes), 2.47 (s, 3H, CH_3CN), 2.27 (s, 6 H, CH_3, Mes), 2.25 (s, 6 H, CH_3, Mes). ^{13}C{^{1}H} NMR (CD_2Cl_2): 208.5 (*ipso*-C, Ph), 151.7 (*ipso*-C, NCN), 140.1 (CMe, Mes), 137.5 (*ipso*-C, Mes), 136.9 (Mes), 136.4 (Mes), 134.1 (*o*-CH, Ph), 131.8 (*p*-CH, Ph) 130.3, 129.9 (CH, Mes), 129.1 (*m*-CH, Ph), 70.4, 69.5 (CH_2), 54.1, 53.1 (CH_2, Im), 34.5, 33.9 (CH_2), 22.8 (CH_3, Mes), 19.0 (CH_3, Mes), 18.8 (CH_3, Mes), 14.2 (CH_3, CH_3CN). ^{11}B NMR (CD_2Cl_2): 11.4 (BS_2Cl_2), 6.9 (BCl_4). Anal. Calc. for $C_{34}H_{43}B_2Cl_6N_3ORuS_2$: C, 44.91; H, 4.77; N, 4.62. Found: C, 44.52 H, 4.60; N, 4.27.

18: X-Ray quality crystals were grown from a CH_2Cl_2 solution layered with pentane. ^{1}H NMR (CD_2Cl_2): 18.66 (d, $^3J_{PH}$ = 9 Hz, 1H, Ru=CH), 8.36 (d, $^3J_{HH}$ = 8 Hz, 2H, *o*-H of C_6H_5), 7.91 (t, $^3J_{HH}$ = 7 Hz, 1H, *p*-H of C_6H_5), 7.71 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-H of C_6H_5), 4.66 (m, 2H, CH_2), 4.50 (m. 1H, CH_2), 4.37 (m, 2H, CH_2), 4.25 (m, 1H, CH_2), 3.95 (m, 2H, CH_2), 2.65 (s, 3H MeCN) 2.09, 1.95, 1.89-1.77, and 1.26-1.15 (all m, C_6H_{11}). ^{11}B NMR (CD_2Cl_2): 11.7 (s, S_2BCl_2), 6.98 (s, BCl_4). ^{13}C{^{1}H} NMR (CD_2Cl_2): 152.0 (*ipso*-C, Ph), 134.7 (CH, Ph), 131.9 (CH, Ph), 129. 6 (CH, Ph), 75.2, 70.5 (CH_2), 36.7 (d, $^1J_{PC}$ = 18.9 Hz, *ipso*-C of C_6H_{11}), 33.4, 31.6 (CH_2), 29.5 (*m*-C of C_6H_{11}), 27.7 (*o*-C of C_6H_{11}), 26.0 (*p*-C of C_6H_{11}), 13.9 (CH_3, CH_3CN). ^{31}P{^{1}H} NMR (CD_2Cl_2): 36.1. Anal. Calc. for $C_{31}H_{50}B_2Cl_6NOPRuS_2$: C, 42.15; H, 5.71; N, 1.59. Found: C, 42.28 H, 5.51; N, 1.10.

General Metathesis Catalysis Procedures: Catalyst Generation The required amount of pre-catalyst (5 mol%) was weighed out and dissolved in CD_2Cl_2 and 2 equivalents of BCl_3 was added and the mixture allowed to stand for 5 min. The solutions were placed in an NMR tube equipped with a septa. For Ring Closing Metathesis, diethyl diallyl malonate (40 μL, 0.165 mmol) was added via the septum and solution was mixed. For ring opening polymerization, 1,5-cyclooctadiene (50 μL, 0.40 mmol) was added and in the case of cross metathesis a mixture of 5-hexenyl acetate (20 μL, 0.12 mmol) and methyl acrylate (10 μL, 0.11 mmol) was added. In each case, reaction progress was monitored by ^{1}H NMR every 2 min. Reaction progress was determined by integration of the olefinic peaks of the starting material versus the product.

X-Ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data for crystals of 10 were collected on a Bruker Apex II diffractometer. The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

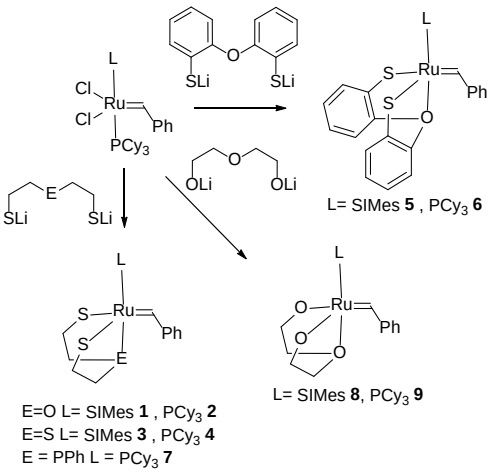
Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[37] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine.[38] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\sigma (F_o-F_c)^2$, where the weight σ is defined as $4F_o^2/2\sigma (F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C-H atom positions were calculated and allowed to ride on the carbon to which they were bonded, assuming a C-H bond length of 0.95Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they were bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information.

Results and discussion

Synthesis: The syntheses of (L)Ru(CHPh)(SCH$_2$CH$_2$)$_2$O (L = SIMes **1**, PCy$_3$ **2**) and (L)Ru(CHPh)(SCH$_2$CH$_2$)$_2$S (L = SIMes **3**, PCy$_3$ **4**) and (L)Ru(CHPh)(SC$_6$H$_4$)$_2$O (L = SIMes **5**, PCy$_3$ **6**) (Scheme 1) were prepared in a similar fashion involving the reaction of the dilithiated dithiolate ligand with the respective starting materials (L)RuCl$_2$(CHPh)(PCy$_3$) (L = SIMes, PCy$_3$).[33] It should be noted that we previously communicated an alternative methodology employed the reactions of thioacetals with Ru(0) synthons to prepare these compounds.[34]

In an analogous fashion, the species (LiSCH$_2$CH$_2$)$_2$PPh[35] was generated via a literature procedure and reacted with (PCy$_3$)$_2$RuCl$_2$(CHPh) in THF (Scheme 1). The resulting dark brown solution showed two doublets at 114.7 and 28.9 ppm in the ^{31}P{^{1}H} NMR spectrum with a $^2J_{PP}$ of 332 Hz suggesting a *trans*-orientation of the phosphine fragments. The alkylidene signal in the ^{1}H NMR spectrum shifts to 13.3 ppm and appears as a doublet of doublets due to coupling to both phosphines. The alkylidene carbon gives rise to an apparent triplet at 239.5 ppm in the ^{13}C NMR with a two bond coupling constant of 13 Hz. These data are consistent with the formation of **7** as (PCy$_3$)Ru(CHPh)(SCH$_2$CH$_2$)$_2$PPh. Interestingly attempts to react this SPS ligand and base with (SIMes)(PCy$_3$)RuCl$_2$(CHPh) led only to intractable mixtures of products with loss of the alkylidene fragment.

The structure of **7** was unambiguously confirmed *via* an X-ray crystallographic study (Figure 1). The Ru-PCy_3 and Ru-PPh distances are 2.4462(6) Å and 2.2869(7) Å respectively while the Ru-S bonds are 2.3004(7) Å and 2.2876(6) Å. The P-Ru-P angle and S-Ru-S angles are is 172.47(2)° and 130.94(3)° and the C-Ru-S angles are 119.12(8)° and 109.73(8)°. The Ru-C distance in **7** is 1.873(2) Å; slightly longer than the corresponding Ru-C distance of 1.853(3) Å previously reported for **1**. This is presumably a reflection of the more electron rich Ru center in **7** versus **1**. The structure of **7** is similar to that reported for **1** although, the S-Ru-S angle in **7** is significantly smaller than in **1** (147.35(4)°).[33] These metric parameters are consistent with a description of the geometry of **7** as a distorted trigonal bipyramidal geometry at Ru. Interestingly in the solid state, the phenyl substituents on P and the alkylidene fragment are oriented in a parallel fashion suggestive of pi-stacking.



Scheme 1. Synthesis of **1-7**.

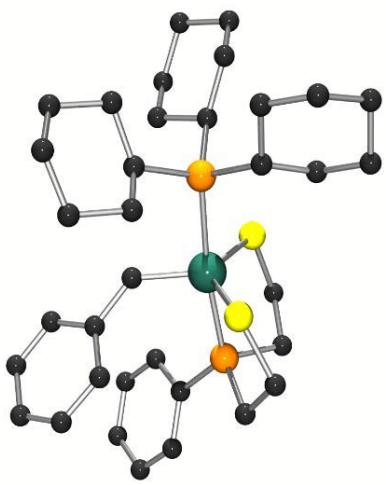


Figure 1. POV-ray depiction of **7**; C: black, S: yellow, P: orange, Ru: teal.

Stirring the related pro-ligand $(LiOCH_2CH_2)_2O$ with $(SIMes)(PCy_3)RuCl_2(CHPh)$ resulted in the isolation of the red compound **8**. (Scheme 1). The alkylidene proton **8** is seen at 16.23 ppm in the ^1H NMR spectrum. An X-ray crystallographic study confirmed the formulation and structure of **8** as $(SIMes)Ru(CHPh)(OCH_2CH_2)_2O$ (Figure 2). In the solid state, one of the alkyl arms is disordered over two positions. The alkylidene fragment gives rise to a Ru-C bond length of 1.830(3) Å, while the Ru-O(ether) and Ru-C(carbene) bond lengths are 2.194(1) Å and 1.983(2) Å respectively giving rise to a O-Ru-C angle of 165.18(2)°. The Ru-O(alkoxy) bond lengths are observed to be 1.944(3) Å to 2.020(4) Å. These parameters describe the distorted trigonal bipyramidal geometry, again similar to **1** and **7**.

In a related fashion, the *bis*-alkoxy-ether ligand was reacted with $(PCy_3)_2RuCl_2(CHPh)$ to give **9**. The doublet assigned to the alkylidene proton is observed at 15.72 ppm in the ^1H NMR spectrum with a $^3J_{PH}$ of 15 Hz. Four multiplets from 4.19 to 2.96 ppm arise from the ethylene linkers in the backbone of the tridentate ligand. A singlet at 64.8 ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum and signal at 192.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum is attributed to the alkylidene carbon. These are consistent with the formulation of **9** as $(PCy_3)Ru(CHPh)(OCH_2CH_2)_2O$.

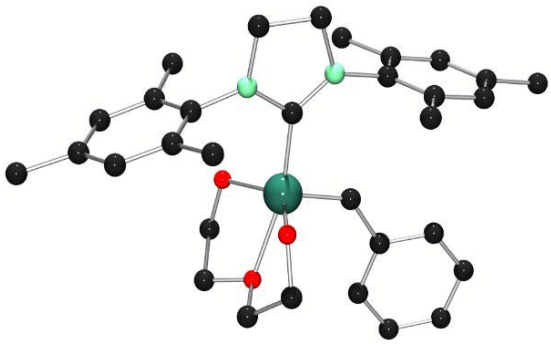


Figure 2. POV-ray depiction of **8**; C: black, O: red, N: green/blue, Ru: teal.

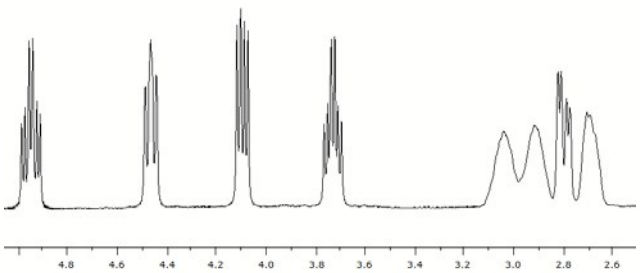


Figure 3. Expansion of methylene region of ^1H NMR spectrum of **11**.

Reactions with BCl_3: In a separate communication, we showed that compound **1** reacts with one equivalent of BCl_3 resulting in a product $(SIMes)Ru(CHPh)Cl[O(CH_2CH_2S)_2BCl_2]$ **10** in which a BCl_2 fragment bridges between the two thiolate ligands and a chloride that is transferred from boron to ruthenium making the ruthenium centre six-coordinate (Scheme 2).[33] Herein, we explore the analogous reactions of **2-9**. The reaction of compound **2** with BCl_3 results in a color change from red to green, affording a green solid $(PCy_3)Ru(CHPh)Cl[O(CH_2CH_2S)_2BCl_2]$ **11** in 89% isolated yield (Scheme 2). Compound **11** exhibits a downfield doublet for the alkylidene at 18.9 ppm in the ^1H NMR spectra with a C-P coupling constant of 12 Hz. The signals attributable to the methylene protons

on the ligand backbone give rise to inequivalent resonances, suggesting loss of symmetry (Figure 3). The ^{31}P signal is seen at 35.5 ppm and a new boron sharp singlet is seen at 11.1 ppm in the ^{11}B spectrum, characteristic of a four coordinate boron.

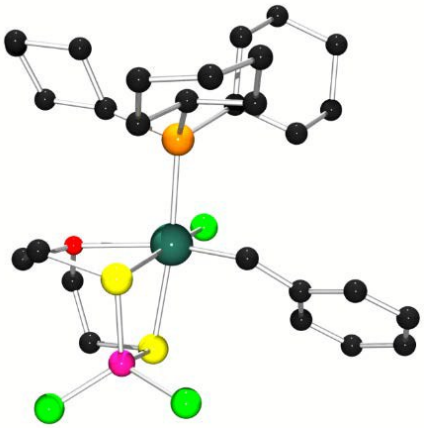


Figure 4. POV-ray depiction of **11**; C: black, O: red, S: yellow, P: orange, Ru: teal, B: pink, Cl: green.

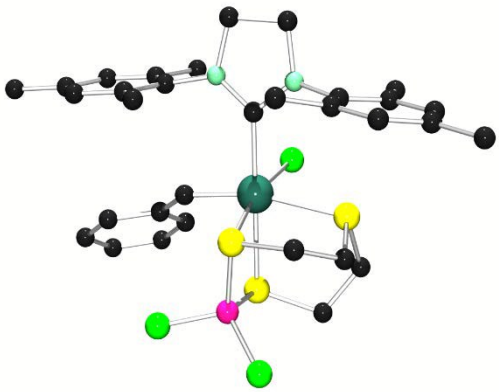
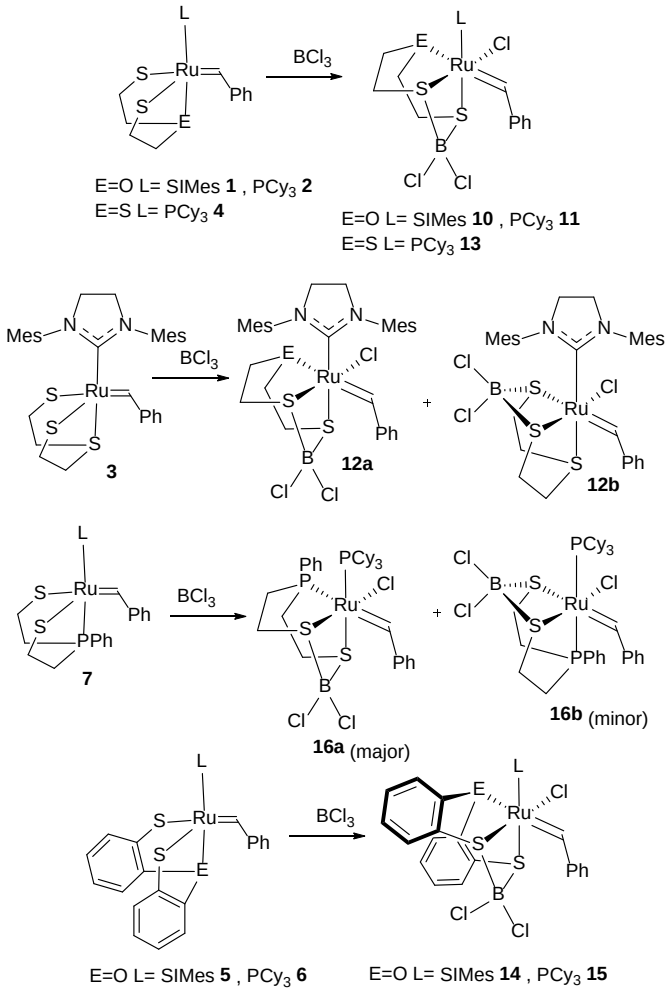


Figure 5. POV-ray depiction of **12a**; C: black, N: blue-green, S: yellow, P: orange, Ru: teal.

The structure of **11** was determined unambiguously to be $(PCy_3)Ru(CHPh)Cl[O(CH_2CH_2S)_2BCl_2]$ by an X-ray crystallographic study (Figure 4). The ether donor which was *trans* to the PCy_3 in the precursor **2** is now *trans* to the alkylidene and the Ru-O bond distance is 2.3554(9) Å. One of the thiolates which is bridged by the BCl_2 fragment is *trans* to phosphine and the other is *trans* to chloride, affording an overall pseudo-octahedral geometry at Ru. The apparent rearrangement of the tridentate chelate is most likely a result of the strong *trans* effect of the alkylidene in this six coordinate product. The axial Ru-S bond distance *trans* to P is 2.3702(4) Å while the Ru-S bond *trans* to Cl is 2.4622(4) Å. The geometry of **11** is similar to that reported for **10**. It is interesting to note that the Ru-O distance in **11** is significantly longer than that in **10** (2.300(2) Å). At the same time, the Ru-S distances in **10** (2.3444(7) Å, 2.4105(7) Å)[33] are shorter than those seen in **11**.

Compound **3** also reacts with BCl_3, revealing the formation of two isomeric products, **12a** and **12b** in a ratio of 1:1 (Scheme 2). The isolated green solid displays two downfield shifted resonances for the alkylidene protons in the ^{1}H NMR spectrum at 17.20 and 16.30 ppm, as well as two sharp singlets at 12.0 and 9.9 ppm in the ^{11}B NMR spectrum, consistent with the presence of two four-coordinate boron environments. X-ray quality crystals of one of the isomers, **12a** were used to confirm its molecular structure as $(SIMes)Ru(CHPh)Cl[S(CH_2CH_2S)_2BCl_2]$ (Figure. 5). The Ru-S thiolate bond lengths are 2.3557(5) and 2.5027(5) Å with a S-Ru-S angle of 78.21(2)°. The B-S bond lengths are 1.950(2) Å and 1.960(2) Å Å with as S-B-S angle of 103.3(1)°. The Ru-Cl bond length is 2.4350(5) Å and the two Cl remaining on the B resulting in B-Cl distances of 1.844(3) Å and 1.850(2) Å. Analogous to **11**, the tridentate ligand in **12a** is oriented such that the thioether in **12a** is *trans* to the alkylidene at a Ru-S bond distance of 2.4919(5) Å and Ru-C(alkylidene) and Ru-C(NHC) distances are 1.909(2) Å and 2.081(2) Å respectively.



Scheme 2 Reactions with 1 equivalent of BCl_3.

The reorientation of the S_3-ligand in **12a** such that the thioether donor occupies the position *trans* to the alkylidene is observed. The BCl_2 fragment bridges the two thiolates restricting them to adopt *cis* coordination sites, with concurrent transfer of chloride to Ru. The resulting six coordinate species adopts a distorted octahedral

geometry. Presumably the *trans* influence of the strongly donating alkylidene ligand prompts the reorientation resulting in the weakest donor, the thioether, to be located in the position *trans* to the alkylidene. The NHC donor has a similar but slightly weaker trans influence than the alkylidene and thus the minor isomer **12b** is thought to be the species in which the thioether donor is *trans* to the NHC.

Compound **4** reacts with BCl_3 to give $(PCy_3)Ru(CHPh)Cl[S(CH_2CH_2S)_2BCl_2]$ **13** (Scheme 2) as evidenced by the downfield proton signal at 17.96 ppm and ^{13}C NMR signal at 275.3 ppm, attributable to the alkylidene fragment. In addition, the $^{31}P\{^1H\}$ NMR signal at 34.9 ppm and the ^{11}B resonance at 9.9 ppm are consistent with the formation of a single isomer of **13**, in contrast to **12**.

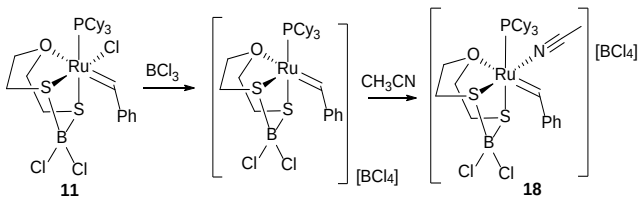
Similarly, **5** and **6** react with BCl_3 to give $(L)Ru(CHPh)(SC_6H_4)_2O$ (L = SIMes **14**, PCy_3 **15** respectively (Scheme 2). The spectroscopic data for these products show the typical parameters, with alkylidene signal in the ^1H NMR spectra at 17.74 ppm and 18.9 ppm, and the characteristic ^{11}B shifts at 14.7 and 12.1 ppm respectively.

The reaction of **7** with BCl_3 proceeds to give two isomers of $(PCy_3)Ru(CHPh)(SCH_2CH_2)_2PPh$, **16a** and **16b** in a ratio of 9:1 (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum shows two sets of two doublets, one at 81.5 and 26.9 ppm and a second at 75.8 and 29.6 ppm. The former resonances for **16a** exhibit a P-P coupling constant of 226 Hz, whereas the latter has a coupling constant of only 26 Hz. This suggestion one isomer presents a *trans*-phosphine disposition, while in the latter case the phosphine donors are *cis* in **16b**. Similarly the alkylidene region of the ^1H NMR spectrum also displays two signals; a doublet at 18.2 ppm (J_{PH} = 7 Hz) and a doublet of doublets at 17.4 ppm (J_{PH} = 17, 11 Hz). Oddly the ^{11}B NMR spectrum shows only a sharp singlet at 10.7 ppm, suggesting B environments in the two isomers are similar.

Finally, efforts to react complexes **8** and **9** with one equivalent of BCl_3 appeared to react similarly. While preliminary spectroscopic characterization of the reaction mixtures suggest that these reaction proceeds in a similar manner, these products could not be isolated cleanly.

Compound **10** has been shown to react with a second equivalent of BCl_3 resulting in the abstraction of chloride from Ru and the generation of the $[BCl_4]$ anion and formally five-coordinate Ru center $[(SIMes)Ru(CHPh)(O(CH_2CH_2S)_2BCl_2)][BCl_4]$.[33] Although this salt was not isolable, addition of MeCN afforded $[(SIMes)Ru(CHPh)(NCMe)(O(CH_2CH_2S)_2BCl_2)][BCl_4]$ **17**.[33] In a similar fashion, reaction of **11** with a second equivalent of BCl_3 generated $[(PCy_3)Ru(CHPh)(O(CH_2CH_2S)_2BCl_2)][BCl_4]$ which was isolated as $[(PCy_3)Ru(CHPh)(NCMe)(O(CH_2CH_2S)_2BCl_2)][BCl_4]$ **18** (Scheme 3). This species exhibited a resonance attributed to the alkylidene proton in the ^1H NMR at 18.66 ppm, together with a small shift in the ^{31}P NMR signal to 36.1 ppm. Two peaks in the ^{11}B NMR spectrum at 11.8 and 7.0 ppm are attributable to the BCl_2 fragment and the $[BCl_4]$ anion. An X-ray crystallographic study confirmed the structure of **18** (Figure 6). The geometry remains a distorted octahedral about Ru, similar to **10**. The Ru-P bond lengthens slightly to 2.4080(9) Å while the Ru-S bonds shorten to 2.441(1) Å and 2.3596(9) Å with a S-Ru-S angle of 79.55(3)°. The Ru-O, Ru-C and Ru-N bonds are 2.292(2), 1.874(3) Å and 2.053(3) Å respectively. The N-Ru-C and N-Ru-O angles are 98.2(1)° and 89.7(1)°, respectively. The B-S bond lengths are 1.967(5) and 1.950(4) Å and the S-B-S angle is 103.3(2)º. The B-Cl bond length of the coordinated borate are 1.841(4) Å and 1.811(5) Å with a Cl-B-Cl angle of 112.0(2)°.

The isolation and full characterization of **17** and **18** demonstrates that two equivalents of BCl_3 reacts with the precursors **1** or **2** to generate a cationic five coordinate Ru-alkylidene complex which then coordinates an equivalent of acetonitrile. We have shown that compound **1** and **10** were inactive in metathesis catalysis, but that the five coordinate precursor to **17** was an active catalyst in a standard assessments of olefin metathesis. The present synthesis of compounds **2-9** prompted us to probe the utility of these species as precursors to related catalysts.



Scheme 3 Synthesis of **18**

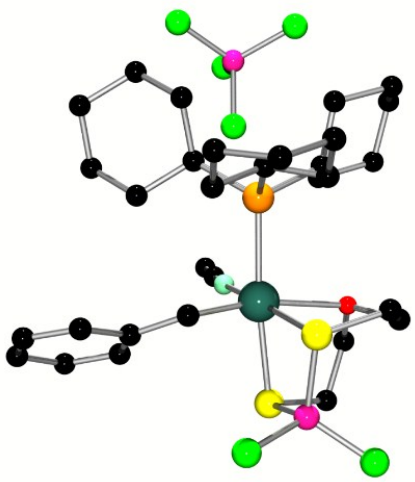
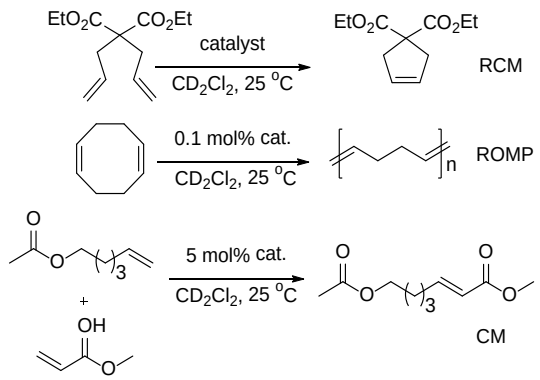


Figure 6. POV-ray depiction of **18**; C: black, N: blue-green, S: yellow, P: orange, Ru: teal, B: pink, Cl: green, O: red.

To this end, each of compounds **2-9**, were employed as a pre-catalyst, treated with two equivalents of BCl_3 and employed in standard olefin metathesis reactions including ring closing metathesis of diethyl diallylmallonate (RCM), ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene and cross metathesis (CM) of 5-hexenyl acetate and methyl acrylate (Scheme 4, see SI). In the case of RCM, the NHC containing catalysts are more active than the phosphine derivatives, consistent with known reactivity of the 1st and 2nd generations of Grubbs catalysts. The catalysts generated from **8** and **9** were clearly the most active, with the catalyst derived from **8**

mediating complete RCM of diethyl diallylmallonate in 8 min at a 5 mol% catalyst loading.

Interestingly, for both ROMP of 1,5-cyclooctadiene and CM of 5-hexenyl acetate and methyl acrylate only the catalysts that included an NHC were active. We note that a similar observation of activity for RCM and not ROMP has been reported for other cationic catalysts.[32] Nonetheless, 0.1 mol% catalysts derived from **5** and **8** were active for the ROMP test of the, achieving 86 and 96% polymerization after 40 and 30 min. respectively. Similarly, 5 mol% of the catalysts derived from **5** and **8** effected 74 and 31% formation of the heterocoupled product of cross metathesis of 5-hexenyl acetate and methyl acrylate. It is noteworthy that the ^{1}H NMR spectrum of the latter case showed complete consumption of 5-hexenyl acetate and thus the presence of a significant portion of the homocoupled metathesis product. In addition, it is noteworthy that compounds **17** and **18** were tested for ROMP and RCM at room temperature in CH_2Cl_2 at 5 mol% and 0.1 mol% respectively. These species were inactive, however, heating to 40C turned on catalysis, presumably by thermally effecting CH_3CN dissociation.



Scheme 4 Standard metathesis test reactions.

Conclusions

The present report extends a synthetic protocol to a series of tridentate ligand Ru-alkylidene derivatives. These species are shown to react with one and two equivalents of BCl_3 in a sequential fashion. Initially B-Cl cleavage generates six coordinate Ru species which react with the second equivalent of BCl_3 generates a five coordinate cation. Some of these latter species exhibit activity in standard olefin metathesis test reactions. Interestingly, the more reactive catalysts provide to be those incorporating NHC ligands. In addition the tridentate O3-ligands appears to be more active than the other ligand perturbations examined. This finding is directing our efforts to examine related alkoxide-chelate ligands targeting new avenues to reactive Ru-alkylidene species.

Acknowledgements

NSERC of Canada is thanked for financial support. DWS is grateful for the award of a Canada Research Chair.

Notes and references

Department of Chemistry, University of Toronto
80 St. George Street, Toronto, Ontario, M5S 3H6 (Canada).
E-mail: dstephan@chem.utoronto.ca

Electronic Supplementary Information (ESI) available: Spectroscopic data and catalytic data are deposited. X-ray crystallographic data are deposited in CCDC# 1413190-1413194. See DOI: 10.1039/b000000x/

1. R. R. Schrock, *J. Organomet. Chem.*, 1986, **300**, 249-262.
2. R. R. Schrock, *Polyhedron*, 1995, **14**, 3177-3195.
3. R. R. Schrock, *Top. Organomet. Chem.*, 1998, **1**, 1-36.
4. R. R. Schrock, *NATO ASI Series, Series C: Mathematical and Physical Sciences*, 1998, **506**, 357-380.
5. R. R. Schrock, *Tetrahedron*, 1999, **55**, 8141-8153.
6. A. H. Hoveyda and R. R. Schrock, *Chem.-Eur. J.*, 2001, **7**, 945-950.
7. A. H. Hoveyda and R. R. Schrock, *Comprehensive Asymmetric Catalysis, Supplement*, 2004, **1**, 207-233.
8. J. Heppekausen and A. Fürstner, *Angew. Chem. Int. Ed.*, 2011, **50**, 7829-7832.
9. R. H. Grubbs, *Polym. Prepr.*, 1991, **32**, 711-713.
10. R. H. Grubbs, *Polym. Prepr.*, 1991, **32**, 84-85.
11. W. Risse and R. H. Grubbs, *J. Mol. Catal.*, 1991, **65**, 211-217.
12. R. H. Grubbs, S. J. Miller and G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446-452.
13. R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413-4450.
14. R. H. Grubbs and D. M. Lynn, *Aqueous-Phase Organometallic Catalysis*, 1998, 466-476.
15. R. H. Grubbs and T. M. Trnka, *Ruthenium in Organic Synthesis*, 2004, 153-177.
16. C. W. Bielawski and R. H. Grubbs, *Prog. Polym. Sci.*, 2007, **32**, 1-29.
17. G. C. Vougioukalakis and R. H. Grubbs, *Chem Rev*, 2010, **110**, 1746-1787.
18. P. E. Romero and W. E. Piers, *J. Am. Chem. Soc.*, 2007, **129**, 1698-1704.
19. S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168-8179.
20. J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, **121**, 791-799.
21. B. K. Keitz, K. Endo, M. B. Herbert and R. H. Grubbs, *J. Am. Chem. Soc.*, 2011, **133**, 9686-9688.
22. S. Chang, L. Jones, C. Wang, L. M. Henling and R. H. Grubbs, *Organometallics* 1998, **17**, 3460.
23. M. S. Sanford, L. M. Henling, M. W. Day and R. H. Grubbs, *Angew. Chem., Int. Ed.* , 2000, **39**, 3451.
24. W. Buchowicz, J. C. Mol, M. Lutz and A. L. Spek, *J. Organomet. Chem.* , 1999, **588**, 205.
25. W. Buchowicz, F. Ingold, J. C. Mol, M. Lutz and A. L. Spek, *Chem. Eur. J.* , 2001, **7**, 2842.
26. J. C. Conrad, D. Amoroso, P. Czechura, G. P. A. Yap and D. E. Fogg, *Organometallics*, 2003, **22**, 3634-3636.
27. R. K. M. Khan, S. Torker and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2013, **135** 10258–10261.
28. G. Occhipinti, F. R. Hansen, K. W. Tornroos and V. R. Jensen, *J. Am. Chem. Soc.*, 2013, **135**, 3331-3334.
29. F. Boeda, H. Clavier and S. P. Nolan, *Chem. Commun.*, 2008, 2726-2740.
30. M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998 2249-2250.

31. A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard and P. H. Dixneuf, *Chem. Eur. J.* , 2000, **6**, 1847-1857.
32. A. Fürstner, M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, 1315-1316.
33. A. M. McKinty, C. Lund and D. W. Stephan, *Organometallics*, 2013, **32**, 4730-4732.
34. A. M. McKinty and D. W. Stephan, *Dalton Trans.*, 2014, **43**, 2710-2712.
35. J. Antonio Muñoz, L. Escriche, J. Casabó, C. Pérez-Jiménez, R. Kivekäs and R. Sillanpää, *Inorg. Chim. Acta*, 1997, **257**, 99-104.
36. Repeated attempts to obtain elemnetal analysis resulted in low carbon with satiusfactory H and N values. This is attributed to incomplete combustion and the partial formation of RuC.
37. D. T. Cromer and J. T. Waber, *Int. Tables X-Ray Crystallogr.*, 1974, **4**, 71-147.
38. G. M. Sheldrick, Bruker AXS Inc .Madison, WI, , 2000.

TOC Graphic