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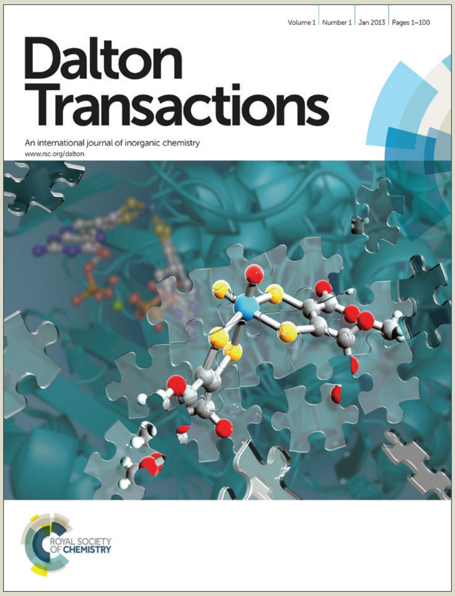

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ARTICLE TYPE

Reactions of Ruthenium Hydrides with Ethyl-Vinyl Sulfides

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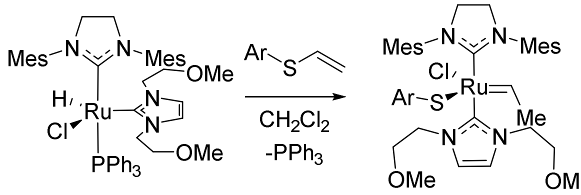
The Ru-hydride precursors $(Im(OMe)_2)(PPh_3)_2RuHCl$ (**1**) and $(Me_2Im(OMe)_2)(PPh_3)_2RuHCl$ (**2**) reacted with ethyl-vinyl-sulfide to give $((MeOCH_2CH_2)C_3H_2N_2(CH_2CH(OMe))RuCl(PPh_3)_2$ (**3**) and $((MeOCH_2CH_2)C_3Me_2N_2(CH_2CH(OMe))RuCl(PPh_3)_2$ (**4**), respectively. Dissolution of (**4**) in C_6D_6 prompts formation of $((MeOCH_2CH_2)C_5H_6N_2(CHCH)RuCl(PPh_3)_2$ (**5**). The analogous reactions of the *bis*-carbene Ru-hydride precursors $(Im(OMe)_2)(IMes)(PPh_3)RuHCl$ (**6**), $(Im(OMe)_2)(SIMes)(PPh_3)RuHCl$ (**7**) and $(Im(OMe)_2)(IMes\text{-}Cl_2)(PPh_3)RuHCl$ (**8**) gave $((MeOCH_2CH_2)C_3H_2N_2(CHCH)RuCl(PPh_3)(NHC)$ (NHC = IMes (**9**), SIMes (**10**), IMes-Cl_2 (**11**), respectively. The formation of compounds (**3**)-(**5**) and (**9**)-(**11**) is thought to go through an initial insertion of the vinyl-fragment into the Ru-H prompting subsequent C-H activation and loss of diethyl sulfide. This yields (**3**) and (**4**), while subsequent loss of methanol yields (**5**) and (**9**)-(**11**).

INTRODUCTION

The indisputable value of olefin metathesis in natural product synthesis, polymer, and pharmaceutical chemistry,[1] prompted the award of the 2005 Nobel prize to Grubbs, Shrock and Chauvin.[1d, 1e, 2] While the Schrock based systems are highly active,[1e] it is the stability, activity and broad applications of the "Grubbs' catalysts" $(Cy_3P)_2Cl_2RuCHPh$[3] and $(Cy_3P)(SIMes)Cl_2RuCHPh$[4] that has led to a range of commercial applications. Nonetheless, efforts continue to develop new strategies to related derivatives. The incorporation of pendant donors in the Grubbs-Hoveyda[5] modification has been reported, while Fogg and coworkers[6] have developed Ru-mono- or bidentate aryloxide derivatives and we have recently reported the tridentate dithiolate ligand derivative $(O(CH_2CH_2S)_2)(SIMes)RuCHPh$. Interestingly this latter species in inactive in metathesis, but is activated by the addition of the Lewis acid BCl_3.[7]



Scheme 1 Reaction of Ru-hydride with aryl-vinyl-sulfide.

A variety of methods to synthesize Ru-alkylidenes[8] have been reviewed comprehensively by Fogg. For example, reactions of Ru precursors with cyclopropenes,[9] sulfur-ylides,[10] dihalomethanes[11] and diazomethanes[12] afford routes to Ru-alkylidenes. Alternatively, Ru-allenylidene, indenylidene,[13] vinylidene[11c] or cumulenylidenes[14] provide alternative structures that also effect olefin metathesis. In seeking an alternative synthetic strategy to reactive Ru-alkylidenes, we have recently reported the reactions of aryl-vinyl-sulfides with Ru-hydrides.[15] This reaction affords the installation of both an alkylidene and a thiolate ligand simultaneously (Scheme 1). In continuing the development of this strategy we have explored the reaction of Ru-hydrides with ethyl-vinyl-sulfide. These systems are shown to react in a different fashion ultimately effecting the C-H activation of the ligand substituents.

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 (THF, toluene, pentane, hexanes, CH_2Cl_2) and stored over molecular sieves. Some solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks and degassed accordingly (C_6H_6, C_6D_6, CD_2Cl_2). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 25 °C on Bruker 400 MHz and Bruker 500 MHz spectrometers. Chemical shifts were 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). 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. Ethyl vinyl sulfide was purchased from Sigma Aldrich and used as received. SIMes, IMes,[16] IMes-Cl$_2$[17] were prepared according to literature procedures. (Im(OMe)$_2$)(IMes)(PPh$_3$)RuHCl **1**, (Me$_2$Im(OMe)$_2$)(PPh$_3$)$_2$RuHCl **2**, (Im(OMe)$_2$)(IMes)(PPh$_3$)RuHCl **6**, (Im(OMe)$_2$)(SIMes)(PPh$_3$) RuHCl **7** were prepared as previously reported.[18]

Synthesis of ((MeOCH$_2$CH$_2$)C$_3$H$_2$N$_2$(CH$_2$CH(OMe))RuCl (PPh$_3$)$_2$ (3) Ethyl vinyl sulfide (24 µL, 0.236 mmol) was added to a solution of (**1**) (0.100 g, 0.118 mmol) in 5 mL C$_6$H$_6$ at room temperature. The solution was then stirred for 6 hours before the solvent was concentrated to 1 mL and 15 mL of pentane was added which caused a light orange precipitate to form. The solid was collected by filtration, washed with pentane and dried under high vacuum (0.080 g, 80%). X-ray quality crystals were grown from benzene/pentane at 25 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.71(br s, 10H, P*Ph*$_3$), 7.39 (m, 1H, P*Ph*$_3$), 7.03 (br s, 19H, P*Ph*$_3$), 6.33 (d, $^3J_{HH}$ = 2 Hz, 1H, Im-C*H*), 6.29 (m, 1H, Ru-C*H*OMe), 5.83 (d, $^3J_{HH}$ = 2 Hz, 1H, Im-C*H*), 3.54 (br s, 4H, NC*H*$_2$C*H*$_2$OMe + O(C*H*$_3$)), 3.45 (m, 1H, NC*H*$_2$C*H*$_2$OMe), 2.77 (s, 3H, O(C*H*$_3$)), 2.55 (dd, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 5 Hz, 1H, NC*H*$_2$CHOMe), 2.48 (m, 2H, NC*H*$_2$C*H*$_2$OMe), 2.37 (dd, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 5 Hz, 1H, NC*H*$_2$CHOMe). ^{31}P{^{1}H} NMR (161 MHz, C$_6$D$_6$): δ 41.9 (d, $^2J_{PP}$ = 319 Hz, *P*Ph$_3$), 35.7 (d, $^2J_{PP}$ = 319 Hz, *P*Ph$_3$). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$): δ 192.8 (t, $^2J_{PC}$ = 14 Hz, N*C*N), 138.0 (d, $^2J_{PC}$ = 12 Hz, PPh$_3$), 134.7 (br s, PPh$_3$), 134.1 (d, $^1J_{PC}$ = 20 Hz, PPh$_3$), 129.0 (PPh$_3$), 128.8 (d, $^3J_{PC}$ = 7 Hz, PPh$_3$), 128.5 (PPh$_3$), 120.4 (Im-*C*H), 116.7 (Im-*C*H), 82.5 (t, $^2J_{PC}$ = 6Hz, NCH$_2$*C*HOMe), 71.1 (N*C*H$_2$CH$_2$OMe), 58.8 (O(*C*H$_3$)), 58.1 (O(*C*H$_3$)), 57.9 (N*C*H$_2$CHOMe), 49.2 (NCH$_2$*C*H$_2$OMe). Elemental Analysis for C$_{45}$H$_{45}$ClN$_2$O$_2$P$_2$Ru: C, 64.01; H, 5.37; N, 3.32. Found: C, 63.90; H, 5.71; N, 3.45.

Synthesis of ((MeOCH$_2$CH$_2$)C$_3$Me$_2$N$_2$(CH$_2$CH(OMe))RuCl (PPh$_3$)$_2$ (4) Ethyl vinyl sulfide (24 µL, 0.234 mmol) was added to a solution of (**2**) (0.140 g, 0.161 mmol) in 5 mL CH$_2$Cl$_2$ at room temperature. The solution was then stirred for 6 hours before the solution was filtered over celite and the solvent was concentrated to 1 mL. Pentane (15 mL) was added while stirring to precipitate a red solid which was collected on a frit and dried under high vacuum (0.071 g, 51%). X-ray quality crystals were grown from benzene/hexane at 25 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.90(br s, 6H, P*Ph*$_3$), 7.11-6.88 (br m, 24H, P*Ph*$_3$), 6.35 (ddd, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $^3J_{PH}$ = 4 Hz, 1H, Ru-C*H*OMe), 3.59 (m, 2H, NC*H*$_2$C*H*$_2$OMe), 3.42 (s, 3H, O(C*H*$_3$)), 2.76 (s, 3H, O(C*H*$_3$)), 2.73-2.64 (m, 2H, NC*H*$_2$C*H*$_2$OMe + NC*H*$_2$CHOMe), 2.61 (dt, $^2J_{HH}$ = 10 Hz, $^3J_{HH}$ = 5 Hz, 1H, NC*H*$_2$CHOMe), 2.22 (dd, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 7 Hz, 1H, NC*H*$_2$CHOMe), 1.47 (s, 3H, Me$_2$Im(OMe)$_2$-4,5-C*H*$_3$), 1.27 (s, 3H, Me$_2$Im(OMe)$_2$-4,5-C*H*$_3$). ^{31}P{^{1}H} NMR (161 MHz, C$_6$D$_6$): δ 40.8 (d, $^2J_{PP}$ = 315 Hz, *P*Ph$_3$), 33.0 (d, $^2J_{PP}$ = 315 Hz, *P*Ph$_3$). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$): δ 134.6 (t, $^2J_{PC}$ = 6 Hz, PPh$_3$), 134.2 (d, $^1J_{PC}$ = 18 Hz, PPh$_3$), 129.2 (PPh$_3$), 127.7 (t, $^3J_{PC}$ = 4 Hz, PPh$_3$), 124.6 (Im-4,5-C$_{ipso}$), 122.6 (Im-4,5-C$_{ipso}$), 80.6 (t, $^2J_{PC}$ = 6Hz, NCH$_2$*C*HOMe), 71.3 (N*C*H$_2$CH$_2$OMe), 58.5 (O(*C*H$_3$)), 58.1 (O(*C*H$_3$)), 56.1 (N*C*H$_2$CHOMe), 46.4 (NCH$_2$*C*H$_2$OMe), 9.2 (Me$_2$Im-4,5-*C*H$_3$), 8.9 (Me$_2$Im-4,5-*C*H$_3$), N*C*N peak not observed. Elemental Analysis for C$_{47}$H$_{49}$ClN$_2$O$_2$P$_2$Ru•(CH$_2$Cl$_2$)$_{0.5}$: C, 62.36; H, 5.51; N, 3.06. Found: C, 62.14; H, 5.76; N, 3.28.

Synthesis of ((MeOCH$_2$CH$_2$)C$_3$Me$_2$N$_2$(CHCH)RuCl(PPh$_3$)$_2$ (5) A solution of (**4**) (0.060 g, 0.068 mmol) in 3 mL C$_6$H$_6$ was left stirring for 24 hours before the solvent was concentrated to 1 mL and pentane was added while stirring to precipitate a yellow solid which was collected on a frit and dried under high vacuum (0.045 g, 77%).^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.67 (d, $^3J_{HH}$ = 5 Hz, 1H, RuC*H*CHN),7.44 (br s, 12H, P*Ph*$_3$), 7.29 (br m, 6H, P*Ph*$_3$), 7.23 (br m, 12H, P*Ph*$_3$), 5.66 (dt, $^3J_{HH}$ = 5 Hz, $^4J_{PH}$ = 3 Hz, 1H, RuCHC*H*N), 3.63 (t, $^3J_{HH}$ = 6 Hz 2H, NC*H*$_2$C*H*$_2$OMe), 3.01 (t, $^3J_{HH}$ = 6 Hz, 2H, NC*H*$_2$C*H*$_2$OMe) 2.93 (s, 3H, O(C*H*$_3$)), 1.71 (s, 3H, Me$_2$Im(OMe)$_2$-4,5-C*H*$_3$), 1.42 (s, 3H, Me$_2$Im(OMe)$_2$-4,5-C*H*$_3$). ^{31}P{^{1}H} NMR (161 MHz, CD$_2$Cl$_2$): δ 36.7 (s, *P*Ph$_3$). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$): δ 135.6 (t, $^2J_{PC}$ = 19 Hz, Ru*C*HCHN), 134.6 (t, $^2J_{PC}$ = 6 Hz, PPh$_3$), 134.2 (d, $^1J_{PC}$ = 18 Hz, PPh$_3$), 129.2 (PPh$_3$), 127.6 (t, $^3J_{PC}$ = 4 Hz, PPh$_3$), 125.2 (Im-4,5-C$_{ipso}$), 124.6 (br s, RuCH*C*HN), 122.6 (Im-4,5-C$_{ipso}$), 71.8 (N*C*H$_2$CH$_2$OMe), 58.7 (O(*C*H$_3$)), 46.4 (NCH$_2$*C*H$_2$OMe), 9.2 (Me$_2$Im-4,5-*C*H$_3$), 8.9 (Me$_2$Im-4,5-*C*H$_3$), N*C*N peak not observed. Elemental Analysis for C$_{46}$H$_{45}$ClN$_2$OP$_2$Ru•(C$_5$H$_{12}$)$_{0.5}$: C, 66.47; H, 5.87; N, 3.20. Found: C, 66.49; H, 6.18; N, 2.98.

Synthesis of (Im(OMe)$_2$)(IMes-Cl$_2$)(PPh$_3$)RuHCl (8) IMes-Cl$_2$ (0.174 g, 0.472 mmol) in 5 mL THF was added to a solution of (**1**) (0.200 g, 0.236 mmol) in 5 mL of THF and the mixture was heated at 60 °C for 48 h. All volatiles were removed in 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 (0.147 g, 65%). X-ray quality crystals were grown from toluene/pentane at 25 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.48 (t, $^3J_{HH}$ = 8 Hz, 6H, P*Ph*$_3$), 6.96 (m, 5H, P*Ph*$_3$ + Mes-C*H*), 6.90 (m, 8H, P*Ph*$_3$ + Mes-C*H*), 6.68 (br s, 1H, Im(OMe)$_2$-C*H*), 6.67 (d, $^3J_{HH}$ = 2 Hz, 1H, Im(OMe)$_2$-C*H*), 4.61 (ddd, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 4 Hz, $^3J_{HH}$ = 2 Hz, 1H, Im(OMe)$_2$-C*H*$_2$), 3.88 (m, 1H, Im(OMe)$_2$-C*H*$_2$), 2.91 (s, 3H, Im(OMe)$_2$-C*H*$_3$), 2.87 (m, 1H, Im(OMe)$_2$-C*H*$_2$), 2.81-2.57 (m, 13H, Im(OMe)$_2$-C*H*$_3$ + Mes-C*H*$_3$ + Im(OMe)$_2$-C*H*$_2$) 2.36-2.15 (m, 10H, Im(OMe)$_2$-C*H*$_2$ + Mes-C*H*$_3$), 2.05 (br s, 3H, Mes-C*H*$_3$), -28.11(d, $^2J_{PH}$ = 25 Hz, 1H, Ru-*H*). ^{31}P{^{1}H} NMR (161 MHz, C$_6$D$_6$): δ 43.2 (s, PPh$_3$). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, partial): δ 140.7 (d, $^1J_{PC}$ = 31 Hz, C$_{ipso}$, PPh$_3$), 134.9 (d, $^2J_{PC}$ = 11 Hz, *o*-C, PPh$_3$), 129.4 (br s, C$_{ipso}$)128.3 (Mes-*C*H), 128.2 (d, $^4J_{PC}$ = 2 Hz, *p*-C, PPh$_3$), 127.6 (d, $^3J_{PC}$ = 8 Hz, *m*-C, PPh$_3$), 120.0 (Im(OMe)$_2$-*C*H), 118.8 (Im(OMe)$_2$-*C*H), 72.4 (Im(OMe)$_2$-*C*H$_2$), 71.3 (Im(OMe)$_2$-*C*H$_2$), 58.2 (Im(OMe)$_2$-*C*H$_3$), 57.9 (Im(OMe)$_2$-*C*H$_3$), 48.1 (Im(OMe)$_2$-*C*H$_2$), 47.4 (Im(OMe)$_2$-*C*H$_2$), 21.3 (br s, Mes-*C*H$_3$), 18.2 (br s, Mes-*C*H$_3$). Elemental Analysis for C$_{48}$H$_{54}$Cl$_3$N$_4$O$_2$PRu•C$_6$H$_{14}$: C, 62.15; H, 6.57; N, 5.37. Found: C, 62.64; H, 6.43; N, 5.45.

Synthesis of ((MeOCH$_2$CH$_2$)C$_3$H$_2$N$_2$(CHCH) RuCl(PPh$_3$)(IMes) (9) Ethyl vinyl sulfide (14.0 µL, 0.138 mmol) was added to a solution of (**6**) (0.100 g, 0.112 mmol) in 5 mL

C_6H_6 at room temperature. The solution was then stirred for 48 hours before the solvent was concentrated to 1 mL. Pentane (15 mL) was layered and left overnight at room temperature yielding red crystals. The pentane was decanted and the crystals were dried under high vacuum (0.076 g, 79%). X-ray quality crystals were grown from benzene/hexane at 25 °C.^{1}H NMR (400 MHz, C_6D_6): δ 7.75 (dd, $^3J_\mathrm{HH}$ = 5 Hz, $^3J_\mathrm{PH}$ = 1 Hz, 1H, RuC*H*CHN), 7.32 (ddd, $^3J_\mathrm{PH}$ = 10 Hz, $^3J_\mathrm{HH}$ = 8 Hz, $^4J_\mathrm{HH}$ = 2 Hz, 6H, C_6*H*$_5$, PPh$_3$), 7.06-6.92 (m, 11H, (9H) PPh$_3$ + (2H) Mes-C*H*), 6.86 (br s, 2H, Mes-C*H*), 6.69 (d, $^3J_\mathrm{HH}$ = 2 Hz, 1H, Im-C*H*), 6.45 (d, $^3J_\mathrm{HH}$ = 2 Hz, 1H, Im-C*H*), 6.12 (br s, 2H, IMes-C*H*), 6.09 (dd, $^3J_\mathrm{HH}$ = 5 Hz, $^4J_\mathrm{PH}$ = 2 Hz, 1H, RuCHC*H*N), 4.97 (m, 1H, NC*H*$_2$C*H*$_2$OMe), 2.97 (m, 1H, NC*H*$_2$C*H*$_2$OMe), 2.91 (m, 1H, NC*H*$_2$C*H*$_2$OMe), 2.84 (s, 3H, O(C*H*$_3$)), 2.47 (app dt, $^2J_\mathrm{HH}$ = 10 Hz, $^3J_\mathrm{HH}$ = 2 Hz, 1H, NC*H*$_2$C*H*$_2$OMe), 2.79-2.05 (br s, 18H, Mes-C*H*$_3$). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6): δ 38.4 (s, *P*Ph$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 185.9 (d, $^2J_\mathrm{PC}$ = 16 Hz, N*C*N), 160.2 (d, $^2J_\mathrm{PC}$ = 12 Hz, Ru*C*HCHN), 137.8 (C$_\mathrm{ipso}$), 137.5 (C$_\mathrm{ipso}$), 134.6 (d, $^2J_\mathrm{PC}$ = 11 Hz, P*Ph*$_3$), 134.2 (d, $^1J_\mathrm{PC}$ = 20 Hz, P*Ph*$_3$), 129.3 (Mes-*C*H), 128.6 (Mes-*C*H), 127.6 (d, $^3J_\mathrm{PC}$ = 9 Hz, P*Ph*$_3$), 124.4 (d, $^4J_\mathrm{PC}$ = 2 Hz, RuCH*C*HN), 122.9 (IMes-C*H*), 122.8 (IMes-C*H*), 118.7 (Im-*C*H), 114.5 (Im-*C*H), 73.0 (N*C*H$_2$CH$_2$OMe), 58.0 (O(*C*H$_3$)), 48.5 (N*C*H$_2$CH$_2$OMe), 21.2 (br s, Mes-*C*H$_3$), 19.8 (br s, Mes-*C*H$_3$). Elemental Analysis for $C_{47}H_{50}ClN_4OPRu•(C_6H_6)_{0.5}$: C, 67.21; H, 5.98; N, 6.27. Found: C, 66.90; H, 6.28; N, 6.22.

Synthesis of ((MeOCH$_2$CH$_2$)C$_3$H$_2$N$_2$(CHCH) RuCl(PPh$_3$)(SIMes) (10) Ethyl vinyl sulfide (13.0 µL, 0.128 mmol) was added to a solution of (**7**) (0.100 g, 0.112 mmol) in 5 mL C_6H_6 at room temperature. The solution was then stirred for 16 hours before the solvent was concentrated to 1 mL and 15 mL of pentane was added to which caused a purple precipitate to form. The purple solid was collected by filtration, washed with pentane and dried under high vacuum (0.073 g, 76%). X-ray quality crystals were grown from benzene/pentane at 25 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.70 (d, $^3J_\mathrm{HH}$ = 5 Hz, 1H, RuC*H*CHN), 7.27 (t, $^3J_\mathrm{HH}$ = 8 Hz, 6H, C_6*H*$_5$, PPh$_3$), 7.04-6.90 (m, 13H, C_6*H*$_5$, PPh$_3$ + Mes-C*H*), 6.61 (d, $^3J_\mathrm{HH}$ = 2 Hz, 1H, Im-C*H*), 6.42 (d, $^3J_\mathrm{HH}$ = 2 Hz, 1H, Im-C*H*), 6.10 (dd, $^3J_\mathrm{HH}$ = 5 Hz, $^4J_\mathrm{PH}$ = 2 Hz, 1H, RuCHC*H*N), 4.95 (dt, $^2J_\mathrm{HH}$ = 14 Hz, $^3J_\mathrm{HH}$ = 3 Hz, 1H, NC*H*$_2$C*H*$_2$OMe), 3.44 (br m, 1H, SIMes-C*H*$_2$), 3.29 (br m, 1H, SIMes-C*H*$_2$), 3.09-2.96 (br m, 4H, SIMes-C*H*$_2$ + NC*H*$_2$C*H*$_2$OMe), 2.90 (dt, $^2J_\mathrm{HH}$ = 11 Hz, $^3J_\mathrm{HH}$ = 3 Hz, 1H, NC*H*$_2$C*H*$_2$OMe), 2.83 (s, 3H, O(C*H*$_3$)), 2.74 (s, 3H, Mes-C*H*$_3$), 2.43 (s, 6H, Mes-C*H*$_3$), 2.25 (s, 3H, Mes-C*H*$_3$), 2.14 (s, 3H, Mes-C*H*$_3$), 1.74 (s, 3H, Mes-C*H*$_3$). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6): δ 37.0 (s, *P*Ph$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 202.6 (NCN), 184.9 (d, $^2J_\mathrm{PC}$ = 15 Hz, N*C*N), 159.6 (d, $^2J_\mathrm{PC}$ = 15 Hz, Ru*C*HCHN), 137.6 (C$_\mathrm{ipso}$), 137.3 (C$_\mathrm{ipso}$), 136.3 (br, C$_\mathrm{ipso}$), 134.6 (d, $^2J_\mathrm{PC}$ = 11 Hz, P*Ph*$_3$), 130.4 (br, C$_\mathrm{ipso}$), 129.7 (Mes-*C*H), 128.6 (Mes-*C*H), 127.6 (d, $^3J_\mathrm{PC}$ = 9 Hz, P*Ph*$_3$), 124.2 (d, $^4J_\mathrm{PC}$ = 2 Hz, RuCH*C*HN), 118.9 (Im-*C*H), 114.5 (Im-*C*H), 72.9 (N*C*H$_2$CH$_2$OMe), 58.0 (O(*C*H$_3$)), 51.3 (br s, N*C*H$_2$CH$_2$N), 48.6 (N*C*H$_2$CH$_2$OMe), 21.3 (Mes-*C*H$_3$), 21.0 (Mes-*C*H$_3$), 20.4 (Mes-*C*H$_3$), 20.1 (Mes-*C*H$_3$), 19.9 (Mes-*C*H$_3$), 17.9 (Mes-*C*H$_3$). Elemental Analysis for $C_{47}H_{52}ClN_4OPRu•(C_6H_6)_{0.5}$: C, 67.06; H, 6.19; N, 6.26. Found: C, 66.69; H, 6.65; N, 6.25.

Synthesis of ((MeOCH$_2$CH$_2$)C$_3$H$_2$N$_2$(CHCH)RuCl(PPh$_3$) (IMes-Cl$_2$) (11) Ethyl vinyl sulfide (13.0 µL, 0.128 mmol) was added to a solution of (**8**) (0.100 g, 0.104 mmol) in 5 mL C_6H_6 at room temperature. The solution was then stirred for 48 hours before the solvent was concentrated to 1 mL. Pentane (15 mL) was layered and left overnight at room temperature yielding red crystals. The pentane was decanted and the crystals were dried under high vacuum (0.079 g, 82%). X-ray quality crystals were grown from benzene/hexane at 25 °C.^{1}H NMR (400 MHz, C_6D_6): δ 7.66 (dd, $^3J_\mathrm{HH}$ = 5 Hz, $^3J_\mathrm{PH}$ = 1 Hz, 1H, RuC*H*CHN), 7.27 (m, 6H, C_6*H*$_5$, PPh$_3$), 6.99 (m, 3H, C_6*H*$_5$, PPh$_3$), 6.94 (m, 6H, C_6*H*$_5$, PPh$_3$), 6.83 (br s, 2H, Mes-C*H*), 6.75 (br s, 2H, Mes-C*H*), 6.63 (d, $^3J_\mathrm{HH}$ = 2 Hz, 1H, Im-C*H*), 6.40 (d, $^3J_\mathrm{HH}$ = 2 Hz, 1H, Im-C*H*), 6.04 (dd, $^3J_\mathrm{HH}$ = 5 Hz, $^4J_\mathrm{PH}$ = 2 Hz, 1H, RuCHC*H*N), 4.89 (ddd, $^2J_\mathrm{HH}$ = 10 Hz, $^3J_\mathrm{HH}$ = 4 Hz, $^3J_\mathrm{HH}$ = 3 Hz, 1H, NC*H*$_2$C*H*$_2$OMe), 2.99 (m, 1H, NC*H*$_2$C*H*$_2$OMe), 2.86 (ddd, $^2J_\mathrm{HH}$ = 14 Hz, $^3J_\mathrm{HH}$ = 4 Hz, $^3J_\mathrm{HH}$ = 2 Hz, 1H, NC*H*$_2$C*H*$_2$OMe), 2.82 (s, 3H, O(C*H*$_3$)), 2.44 (app dt, $^2J_\mathrm{HH}$ = 10 Hz, $^3J_\mathrm{HH}$ = 3 Hz, 1H, NC*H*$_2$C*H*$_2$OMe), 2.16 (br s, 9H, Mes-C*H*$_3$), 2.11 (br s, 9H, Mes-C*H*$_3$). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6): δ 38.4 (s, *P*Ph$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 184.8 (d, $^2J_\mathrm{PC}$ = 16 Hz, N*C*N), 159.2 (d, $^2J_\mathrm{PC}$ = 12 Hz, Ru*C*HCHN), 137.2 (C$_\mathrm{ipso}$), 136.9 (C$_\mathrm{ipso}$), 134.4 (d, $^2J_\mathrm{PC}$ = 11 Hz, P*Ph*$_3$), 128.9 (Mes-*C*H), 128.8 (Mes-*C*H), 127.5 (d, $^3J_\mathrm{PC}$ = 9 Hz, P*Ph*$_3$), 124.4 (d, $^4J_\mathrm{PC}$ = 2 Hz, RuCH*C*HN), 118.8 (Im-*C*H), 114.5 (Im-*C*H), 72.6 (N*C*H$_2$CH$_2$OMe), 57.9 (O(*C*H$_3$)), 48.5 (N*C*H$_2$CH$_2$OMe), 21.1 (Mes-*C*H$_3$), 20.9 (Mes-*C*H$_3$), 17.8 (Mes-*C*H$_3$). Elemental Analysis for $C_{47}H_{48}Cl_3N_4OPRu$: C, 61.14; H, 5.24; N, 6.07. Found: C, 56.84; H, 5.74; N, 6.08.

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

The Ru-hydride precursors (Im(OMe)$_2$)(PPh$_3$)$_2$RuHCl (**1**) and (Me$_2$Im(OMe)$_2$)(PPh$_3$)$_2$RuHCl (**2**), were prepared using previous published methodologies.{Wang, 2013 #3779;Lund, 2012 #9770} and subsequently reacted with ethyl-vinyl-sulfide. In the case of (**1**), the mixture of ethyl vinyl sulfide with a benzene solution of (**1**) was allowed to react for 6 hours resulting in an orange solution. After workup, compound (**3**) was isolated as a light orange solid in 80% yield (Scheme 2). The presence of diethyl sulfide as a by-product was confirmed by GC analysis of the reaction mixture. The ^{31}P{^{1}H} NMR spectrum revealed two doublets at 41.9 and 35.7 ppm with a coupling constant of 319 Hz indicative of two phosphines in a *trans* disposition. A multiplet at 6.29 ppm in the ^{1}H NMR spectrum, which integrates to one proton, was assigned to the Ru-C*H*OMe proton. The ^{13}C{^{1}H}

NMR spectrum displays a triplet at 82.5 with a $^{2}J_{PC}$ of 6 Hz which corresponds to the Ru-alkyl carbon. In addition to these NMR spectra, single crystals of **3** afforded the molecular structure determination (Fig. 1) which affirmed **3** as $((MeOCH_2CH_2)C_3H_2N_2(CH_2CH(OMe))RuCl(PPh_3)_2$. The distorted square pyramidal geometry about the ruthenium center consists of a square plane of two phosphine donors, the chloride and the carbon of the NHC with an alkyl carbon fragment occupying the pseudo-axial position. The corresponding Ru-Cl bond length was determined to be 2.4468(8) Å and the Ru-P bond lengths were found to be 2.3407(8) and 2.3515(8) Å. A Ru-C bond length of 1.961(3) Å was observed for the NHC carbon which is similar to previously reported bond lengths for Ru complexes employing such ligands.[15, 18] The Ru-C bond length for the alkyl fragment (2.061(7) Å) is slightly shorter than typical Ru-C single bonds.[19] Chelation of the two carbons to the Ru center leads to the formation of a five-membered metallo-ring with a C-Ru-C angle of 78.2(2) °. It is interesting to note that subjecting a solution of (**3**) in C_6D_6 to 4 atm of H_2 at room temperature leads to the quantitative reformation of (**1**).

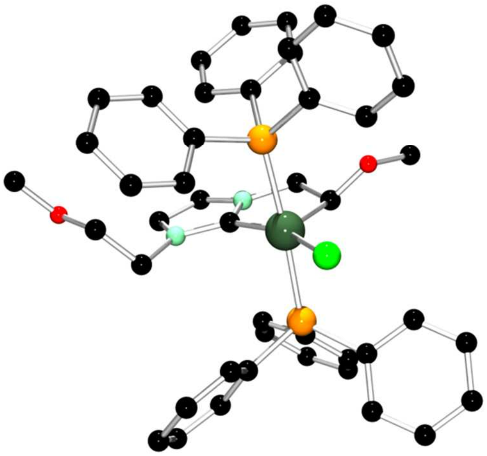


Figure 1 POV-ray depiction of the molecular structure of (**3**) Ru: dark green, O: red; Cl: green; N: aquamarine, P: orange, C: black. H-atoms omitted for clarity**.**

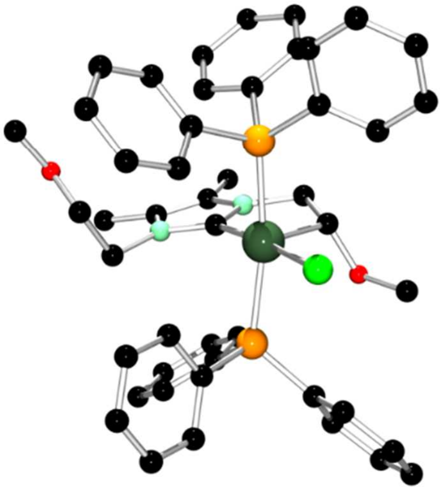
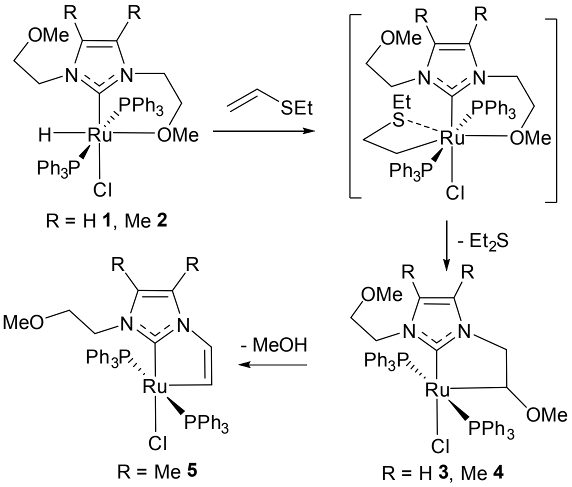


Figure 2 POV-ray depiction of the molecular structure of (**4**) Ru: dark green, O: red; Cl: green; N: aquamarine, P: orange, C: black. H-atoms omitted for clarity.

The corresponding reaction of (**2**) with ethyl vinyl sulfide in CH_2Cl_2 at room temperature results in the isolation of a red solid (**4**) in 69% yield (Scheme 2). Similar to (**3**), the $^{31}P\{^{1}H\}$ NMR spectrum revealed doublets at 40.8 and 33.0 ppm, while the ^{1}H NMR spectrum showed a doublet of doublet of doublet at 6.35 ppm and the corresponding carbon shift afforded a triplet at 80.6 ppm. An X-ray structure determination (Fig. 2) confirmed (**4**) to be $((MeOCH_2CH_2)C_3Me_2N_2(CH_2CH(OMe))RuCl(PPh_3)_2$, the analogue of (**3**). The geometry about the ruthenium center in (**4**) is directly analogous to (**3**) with a Ru-C_{NHC} distance of 1.986(3) Å and the Ru-C_{alkyl} bond length of 2.066(4) Å and the C-Ru-C angle of 79.2(2) °.



R = H **1**, Me **2**

R = Me **5**

R = H **3**, Me **4**

Scheme 2 Synthesis of compounds (**3**)-(**5**).

Interestingly, dissolution of (**4**) in C_6D_6 prompts formation of a new product (**5**) which gives rise to a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum at 36.7 ppm. Isolation of (**5**) after standing in benzene at room temperature for 24 hours gave a yellow solid in 77% yield. Loss of methanol from (**4**) was inferred by the ^{1}H NMR spectrum. Moreover, the ^{1}H NMR data showed a doublet at 7.67 ppm with a coupling constant of 5 Hz and a doublet of triplet at 5.66 with $^{3}J_{HH}$ of 5 Hz and $^{4}J_{PH}$ of 3 Hz. As each of these signals integrated to one proton, they were assigned to Ru-vinyl protons (RuC*H*C*H*N). The corresponding carbon signals were observed as a triplet at 135.6 ppm ($^{2}J_{PC}$ of 19 Hz) and a broad singlet at 124.6 ppm. These data were consistent with the formulation of (**5**) as $((MeOCH_2CH_2)C_5H_6N_2(CHCH)RuCl(PPh_3)_2$ (Scheme 2).

Exploring this reactivity further, the *bis*-carbene Ru-hydride precursors $(Im(OMe)_2)(IMes)(PPh_3)RuHCl$ (**6**), $(Im(OMe)_2)(SIMes)(PPh_3)RuHCl$ (**7**) and $(Im(OMe)_2)(IMes\text{-}Cl_2)(PPh_3)RuHCl$ (**8**) were prepared using previously published methodologies.{Dahcheh, 2014 #5794;Lund, 2012 #9770;Wang, 2013 #3779;Dahcheh, 2014 #5794;Lund, 2012 #9770;Wang, 2013 #3779} While (**6**) and (**7**) are known species, compound (**8**) is a new derivative and was prepared in 65% yield. The ^{1}H NMR spectrum of (**8**) revealed a doublet at -28.11 ppm with $^{2}J_{PH}$ of 25 Hz indicative of a hydride coupled to a single phosphine ligand.

The $^{31}P\{^1H\}$ NMR revealed a singlet at 43.2 ppm, while a single-crystal X-ray analysis of (**8**) revealed a five-coordinate square-pyramidal ruthenium where the base of the pyramid is formed by the two NHCs, chloride, and phosphine ligands and the hydride occupies the apex: thus, the formulation as (IMes-Cl_2)(Im(OMe)$_2$)(PPh_3)RuHCl (Fig. 3). The Ru-C distances for IMes-Cl_2 and Im(OMe)$_2$ were found to be 2.058(5) and 1.976(5) Å, respectively. The Ru-P and Ru-Cl distances of 2.314(1) and 2.452(1) Å, respectively, were observed. The Ru-H distance was determined to be 1.51(4) Å and the *cis* disposition of the carbene ligands in (**8**) results in a C-Ru-C angle of 97.3(2) °.

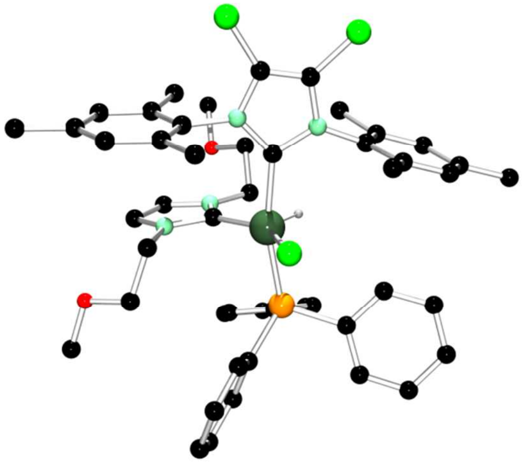


Figure 3 POV-ray depiction of the molecular structure of (**8**) Ru: dark green, O: red; Cl: green; N: aquamarine, P: orange, C: black, H: gray. H-atoms except for Ru-H omitted for clarity.

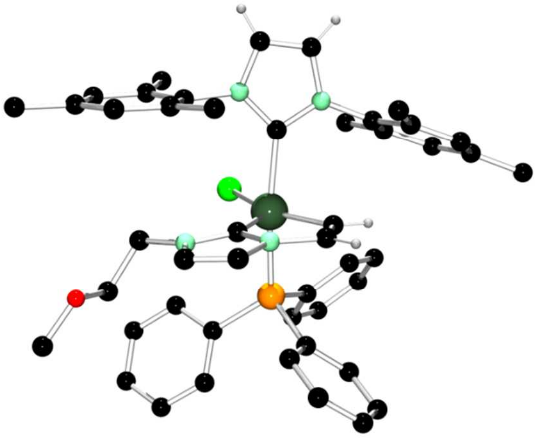


Figure 4 POV-ray depiction of the molecular structure of (**9**) Ru: dark green, O: red; Cl: green; N: aquamarine, P: orange, C: black, H: gray. H-atoms except for vinylic and IMes-CH protons omitted for clarity.

Subsequent reaction of these *bis*-carbene Ru-hydride species with ethyl vinyl sulfide was investigated. In the case of (**6**), the reaction results in the isolation of (**9**) as red crystals in 79% yield. Spectral data for (**9**) are consistent with the formulation as (($MeOCH_2CH_2$)$C_3H_2N_2$(CHCH)RuCl(PPh_3)(IMes). In particular, in the ^1H NMR spectrum, the two doublet of doublet at 7.75 and 6.09 ppm, with H-H and P-H couplings were assigned to Ru-vinyl protons (RuC*H*C*H*N). This was also consistent with the $^{13}C\{^1H\}$ NMR doublets at 160.2 and 124.4 ppm. X-ray data affirmed this formulation of (**9**) (Fig. 4) in which there is a distorted square pyramidal coordination sphere about ruthenium with the carbene carbon of the chelated NHC occupying the pseudo-axial position. The Ru-C_{NHC} and Ru-C_{IMes} bond lengths were found to be 1.940(3) Å and 2.114(2) Å, respectively, while the Ru-C_{vinyl} bond length is 2.033(3) Å and the vinyl C-C bond is 1.325(4) Å. The chelation of the two carbons at Ru gives a C-Ru-C angle of 75.7(1) °.

In a similar fashion, reaction of ethyl vinyl sulfide with (**7**) and (**8**) afforded (**10**) and (**11**) as purple and red solids in 76 and 82% yields, respectively (Scheme 3). In these cases, the generation of diethyl sulfide and methanol as by-products were confirmed by GC analysis and ^1H NMR spectroscopy, respectively. Compounds (**10**) and (**11**) gave rise to $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$signals similar to **9** inferring the formulation of (**10**) and (**11**) as (($MeOCH_2CH_2$)$C_3H_2N_2$(CHCH)RuCl(PPh_3)(NHC) (NHC = (SIMes (**10**), IMes-Cl_2 (**11**)). Crystallography data confirmed this formulation in the case of (**10**) (Fig. 5) as analogous to (**8**) and (**9**). The Ru-C_{NHC} and Ru-C_{SIMes} bond lengths of 1.940(2) Å and 2.113(2) Å, Ru-C_{vinyl} of 2.031(3) Å and chelate C-Ru-C angle of 75.7(1) ° are similar to those seen in (**9**).

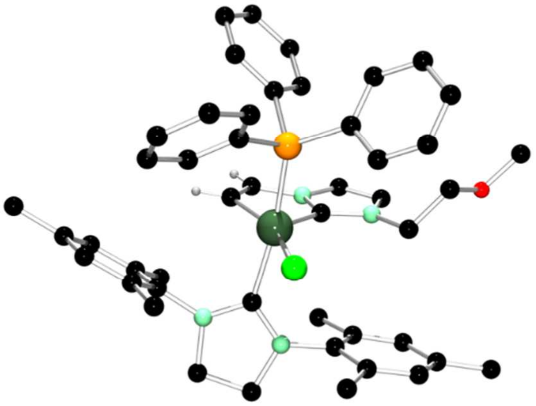
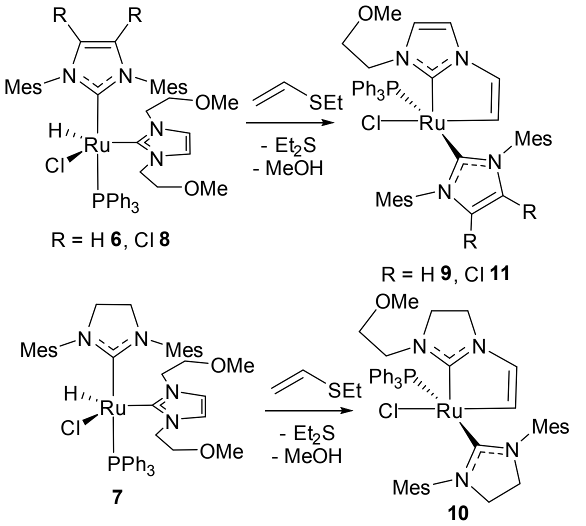


Figure 5 POV-ray depiction of the molecular structure of (**10**) Ru: dark green, O: red; Cl: green; N: aquamarine, P: orange, C: black, H: gray.. H-atoms except for vinylic protons omitted for clarity.



Scheme 3 Synthesis of compounds (**9**)-(**11**).

The formation of compounds (**3**)-(**11**) are thought to be initiated through the initial insertion of the vinyl-fragment into the Ru-H (Scheme 2). Donation from the thioether sulfur enhances electron density at Ru and prompts C-H activation of the pendant ether arm affording loss of diethyl sulfide. In this fashion compounds (**3**) and (**4**) are generated. Loss of methanol from (**4**) gives the *bis*-phosphine Ru-vinyl species (**5**). Compounds (**9**)-(**11**) are thought to form in a similar fashion, although the increased electron density on Ru derived from the additional carbene ligand facilitates loss of both Et_2S and MeOH.

Conclusion

This manuscript has described the reactions of a series of Ru-hydrides with ethyl-vinyl-sulfide. In contrast to the previously reported reactions with aryl-vinyl-sulfides which yield Ru-alkylidenes, these reactions proceed with initial loss of diethyl sulfide generating a Ru-alkyl species. In some cases, these reactions proceed further with loss of methanol to give Ru-vinyl derivatives. This unique reactivity pathway is attributed to the stronger donor character of the ethyl-sulfide derivative. The ability of the reactions of Ru-hydrides with vinyl-sulfides to provide access to Ru-alkylidene, alkyl and vinyl derivatives continues to be a subject of further development. Specifically we are targeting use of this reactivity in the synthesis of related compounds suitable for catalysis.

Notes and references

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‡ Crystallographic data have been deposited in the Cambridge Datbase CCDC 973557-973561.

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TOC GRAPHIC

Ru-hydride precursors containing the OCO-carbene ligand react with ethyl-vinyl-sulfide to give Ru alkyl and vinyl derivatives via an initial insertion of the vinyl-fragment into the Ru-H, subsequent C-H activation and loss of diethyl sulfide.