Supporting Information for:

A Facile Route to Ru-Alkylidenes

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General Considerations: All synthetic manipulations were carried out under an atmosphere of dry, O2-free N2 employing a VAC Atmospheres glove box and a Schlenk vacuum-line. Hexanes, pentane and dichloromethane were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Acetonitrile was dried over CaH2 and distilled. Dichloromethane-d2 was dried over CaH2 and benzene-d6 was dried over Na metal and vacuum-transferred into a Young bomb. All solvents were thoroughly degassed after purification (three freeze-pump-thaw cycles). NMR spectra were recorded at 25 °C on a Bruker Avance 400 MHz spectrometer unless otherwise noted. Commercially available substrates were obtained from Sigma-Aldrich and used without further purification. SiMes, Ru(cod)(cot), Ru(PPh3)3(H)2 and the thioacetal (S(CH2CH2S)2CHPh)2 were prepared according to literature procedures. Chemical shifts are given relative to SiMe4 and referenced to the residual solvent signal (1H, 13C) or relative to an external standard (31P: 85% H3PO4). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. 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.

A general procedure for the synthesis of thioacetals is as follows. A solution of p-toluenesulfonic acid (5 mg) in 200 mL of MeOH was heated to 55 °C in a 3-neck round bottom flask fitted with a condenser, addition funnel and septum. A solution of 2-Mercaptoethyl ether (1.065 g, 7.7 mmol) and benzaldehyde (0.817 g, 7.7 mmol) in 150 mL MeOH was added drop wise from the addition funnel over 4 hours. The mixture was left at 55 °C overnight. The reaction mixture was cooled and filtered through a plug of alumina to remove the acid. All volatiles were removed and the white solid was dissolved in 10 mL of toluene. The solution was ran through an alumina plug to remove any oligomers that may have formed and all volatiles were removed from the filtrate.
Thioacetal 1 was crystallized from CH$_2$Cl$_2$ and obtained as colorless needles. (1.65 g, 95%). $^1$H NMR (C$_6$D$_6$): 7.22 (s, 2H, Ph), 6.84 (t, 2H, Ph), 6.75 (t, 1H, Ph), 5.80 (s, 1H, CH), 3.50 (m, 2H, CH$_2$), 2.90 (m, 2H, CH$_2$), 2.50 (m, 2H, CH$_2$), 2.05 (m, 2H, CH$_2$). $^{13}$C($^1$H) NMR (C$_6$D$_6$): 143.2 (ipso-Ph), 128.7 (Ph), 128.0 (Ph), 127.8 (Ph), 127.6 (Ph), 72.7 (CH$_2$), 59.2 (S$_2$CHPh), 33.2 (CH$_2$). Analysis calculated for C$_{11}$H$_{14}$OS$_2$: C, 58.37; H, 6.23. Found: C, 57.94; H, 6.38.

Thioacetal 3 was crystallized from CH$_2$Cl$_2$ and obtained as colorless needles. (2.26 g, 91%). $^1$H NMR (C$_6$D$_6$): 7.61 (m, 2H, Ph), 7.01 (m, 2H, Ph), 6.93 (m, 3H, Ph), 6.84 (m, 2H, Ph), 6.64 (m, 4H, Ph), 5.84 (s, 1H, S$_2$CHPh). $^{13}$C($^1$H) NMR (C$_6$D$_6$): 155.4, 140.4, 132.3, 130.3, 129.9, 128.8, 128.1, 127.8, 124.6, 123.0, 119.1 (all Ph), 61.3 (S$_2$CH). Analysis calculated for C$_{19}$H$_{14}$OS$_2$: C, 70.77; H, 4.38. Found: C, 70.46; H, 4.11.

**General procedure for synthesis of Ru alkylidyne complexes**

Procedure 1: Ru(cod)(cot) (20 mg, 0.063 mmol), PCy$_3$ (20 mg, 0.070 mmol) and thioacetal 1 (14 mg, 0.063 mmol) were mixed and heated in C$_6$H$_6$ at 50°C for 4 h. The solution was cooled to room temperature and the solvent was removed in vacuo. The resulting solid was washed with hexanes and recrystallized from CH$_2$Cl$_2$ and pentane to give 4 as a red solid.

Procedure 2: To a C$_6$H$_6$ (1 mL) solution of Ru(PPh$_3$)$_3$(H)$_2$ (20 mg, 0.022 mmol) was added PCy$_3$ (9 mg, 0.033 mmol) and the thioacetal 1 (6 mg, 0.026 mmol). The mixture was heated at 50 °C in an oil bath for 4 h and the yellow solution turned dark red as bubbles evolved. Pentane was added to the solution resulting in the precipitation of the red product, 4 which was washed with pentane. The product was recrystallized from CH$_2$Cl$_2$ and pentane.

Procedure 3: To a C$_6$H$_6$ (1 mL) solution of Ru(PPh$_3$)$_3$(H)$_2$ (20 mg, 0.022 mmol) was added thioacetal 1 (6 mg, 0.026 mmol). The mixture was heated at 50°C in an oil bath for 4 h and the yellow solution turned dark red as bubbles evolved. A solution of SIMes (10 mg, 0.033 mmol) in C$_6$H$_6$ was added and the reaction was heated for another 30 min. Pentane was added to the solution resulting in the precipitation of the red product 7 which was washed with pentane. The product was recrystallized from CH$_2$Cl$_2$ and pentane.

**Synthesis of (O(CH$_2$CH$_2$S)$_2$RuCHPh(PCy$_3$) (4)**
Isolated as a red solid in 73% yield (28 mg, 0.046 mmol) by procedure 1 and 89% yield (12 mg, 0.020 mmol) by procedure 2 as a red solid. $^1$H NMR (CD$_2$Cl$_2$): 13.68 (d, $^3$J$_{PH}$ = 11.8 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, 2 × CH$_2$), 2.11, 1.98, 1.74, 1.61, 1.50, 1.19 (all m, 33H, P(C$_6$H$_{11}$)$_3$). $^{13}$C {$^1$H} NMR (CD$_2$Cl$_2$): 208.0 (Ru=CH), 153.3 (ipso-C, Ph), 128.2 (2 × CH, Ph), 125.6 (CH, Ph), 125.4 (2 × CH, Ph), 78.0 (2 × CH$_2$), 35.9 (d, $^1$J$_{PC}$ = 24.2 Hz, ipso-C of P(C$_6$H$_{11}$)$_3$), 32.4 (2 × CH$_2$), 30.0 (m-C of P(C$_6$H$_{11}$)$_3$), 28.3 (d, $^2$J$_{PC}$ = 10.3 Hz, o-C of P(C$_6$H$_{11}$)$_3$), 26.9 (p-C of P(C$_6$H$_{11}$)$_3$). $^{31}$P {$^1$H} NMR (CD$_2$Cl$_2$): 65.6.

Analysis calculated for C$_{29}$H$_{47}$OPRuS$_2$: C, 57.30; H, 7.79. Found: C, 56.92; H, 7.55.

$^1$H NMR (CD$_2$Cl$_2$)
$^{13}\text{C}^{1\text{H}}$ NMR (CD$_2$Cl$_2$)
Synthesis of (S(CH$_2$CH$_2$S)$_2$RuCHPh(PCy$_3$) 5

Isolated in 87 % yield (12 mg, 0.019 mmol) following procedure 2 with thioacetal 2 as a dark red solid. X-ray quality crystals were grown from a CH$_2$Cl$_2$/CH$_3$CN solution. $^1$H NMR (CD$_2$Cl$_2$): 13.48 (d, $^3$J$_{PH}$ = 19.3 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, 33H, P(C$_6$H$_{11}$)$_3$). $^{13}$C$^{'1}$H} NMR (CD$_2$Cl$_2$): 235.2 (d, $^2$J$_{PC}$ = 14.8 Hz, Ru=CH), 157.0 (ipso-C, Ph), 127.5 (2 × CH, Ph), 125.8 (2 × CH, Ph), 125.4 (CH, Ph), 45.2 (2 × CH$_2$), 36.3 (2 × CH$_2$), 35.2 (d, $^1$J$_{PC}$ = 19.8 Hz, ipso-C of P(C$_6$H$_{11}$)$_3$), 30.0 (m-C of P(C$_6$H$_{11}$)$_3$), 28.4 (d, $^2$J$_{PC}$ = 10.25 Hz, o-C of P(C$_6$H$_{11}$)$_3$), 26.9 (p-C of P(C$_6$H$_{11}$)$_3$). $^{31}$P$^{'1}$H} NMR (CD$_2$Cl$_2$): 41.7. Analysis calculated for C$_{29}$H$_{47}$PRuS$_3$: C, 55.83; H, 7.59. Found: C, 55.71; H, 7.33.$^1$H NMR (CD$_2$Cl$_2$)

$^{31}$P$^{'1}$H} NMR (CD$_2$Cl$_2$)
Synthesis of \((\text{O(C}_6\text{H}_4\text{S})_2\text{RuCHPh(PCy}_3\text{)})\) 6

Isolated in 84\% (13 mg, 0.018 mmol) yield following procedure 2 with thioacetal 3 as a red solid. X-ray quality crystals were grown from a \(\text{CH}_2\text{Cl}_2\)
solution. $^1$H NMR (CD$_2$Cl$_2$): 14.69 (d, $^3$J$_{PH} = 14.7$ Hz, 1H, Ru=CH), 7.48 (d, $^3$J$_{HH} = 7.6$ Hz, 2H, Ph), 7.48 (m, 3H, Ph), 6.90 (m, 4H, Ph), 6.82 (t, $^3$J$_{HH} = 7.3$ Hz, 2H, Ph), 6.72 (m, 2H, Ph), 2.15, 2.02, 1.77, 1.55, 1.19 (all m, 33H, P(C$_6$H$_{11}$)$_3$). $^{13}$C$\{^1$H} NMR (CD$_2$Cl$_2$): 192.2 (Ru=CH), 154.0 (2 $\times$ ipso-C, Ph), 152.23 (ipso-C, Ph), 139.1 (2 $\times$ ipso-C, Ph), 132.1 (2 $\times$ CH, Ph), 130.1 (2 $\times$ CH, Ph), 127.9 (2 $\times$ CH, Ph), 126.3 (CH, Ph), 125.3 (2 $\times$ CH, Ph), 124.0 (2 $\times$ CH, Ph), 122.7 (2 $\times$ CH, Ph), 115.9 (2 $\times$ CH, Ph), 36.0 (d, $^1$J$_{PC} = 25.05$ Hz, ipso-C of P(C$_6$H$_{11}$)$_3$), 31.6 (m-C of P(C$_6$H$_{11}$)$_3$), 30.1 (p-C of P(C$_6$H$_{11}$)$_3$), 28.2 (d, $^2$J$_{PC} = 10.24$ Hz, o-C of P(C$_6$H$_{11}$)$_3$). $^{31}$P$\{^1$H} NMR (CD$_2$Cl$_2$): 68.6. Analysis calculated for C$_{37}$H$_{47}$OPRuS$_2$: C, 63.13; H, 6.73. Found: C, 62.52; H, 6.30.

$^1$H NMR (CD$_2$Cl$_2$)

$^{31}$P$\{^1$H} NMR (CD$_2$Cl$_2$)
Synthesis of (O(CH₂CH₂S)₂RuCHPh (SiMes) 7

Isolated in 86% yield (12 mg, 0.019 mmol) following procedure 3 as a red solid. Spectral data matches that of previous report.⁵
Synthesis of \((S(CH_2CH_2S)_2RuCHPh (SIMes) 8\)

Isolated in 84 % yield (12 mg, 0.018 mmol) following procedure 3 using thioacetal 2 as a dark brown solid. X-ray quality crystals were grown from a CH\(_2\)Cl\(_2\)/CH\(_3\)CN solution. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): 14.41 (s, 1H, Ru=CH), 7.19 (t, 1H, \(p\)-H, Ph), 7.07 (t, 2H, \(m\)-H, Ph), 6.88 (d, 2H, \(o\)-H, Ph), 6.80 (s, 4H, 4 \(\times\) CH, Mes), 3.99 (s, 4H, 2 \(\times\) CH\(_2\), Im), 3.22 (m, 2H, CH\(_2\)), 3.00 (m, 2H, CH\(_2\)), 2.52 (s, 12H, 4 \(\times\) CH\(_3\), Mes), 2.24 (m, 2H, CH\(_2\)), 2.19 (s, 6H, 2 \(\times\) CH\(_3\), Mes), 1.73 (m, 2H, CH\(_2\)). \(^{13}\)C\(^\{^1\}H\) NMR (CD\(_2\)Cl\(_2\)): 211.2 (Ru=CH), 138.08 (ipso-C, Ph), 137.8 (ipso-C, NCN), 137.7 (ipso-C, Mes), 129.2 (4 \(\times\) CH, Mes), 127.3 (2 \(\times\) CH, Ph), 127.1 (2 \(\times\) CH, Ph), 125.1 (CH, \(p\)-C, Ph), 52.4 (2 \(\times\) CH\(_2\)), 44.6 (2 \(\times\) CH\(_2\), Im), 34.8 (2 \(\times\) CH\(_2\)), 21.0 (2 \(\times\) CH\(_3\), Mes), 19.7 (4 \(\times\) CH\(_3\), Mes). Analysis calculated for C\(_{32}\)H\(_{40}\)N\(_2\)RuS\(_3\)+CH\(_2\)Cl\(_2\) (In crystal lattice): C, 53.94; H, 5.76; N, 3.81. Found: C, 55.69; H, 5.96; N, 3.81.

\(^1\)H NMR (CD\(_2\)Cl\(_2\))

\(^{13}\)C\(^\{^1\}H\) NMR (CD\(_2\)Cl\(_2\))
Synthesis of (O(C₆H₄S)₂RuCHPh(SIMes)) 9

Isolated in 88% yield (14 mg, 0.019 mmol) following procedure 3 using thioacetal 3 as a red solid. ¹H NMR (CD₂Cl₂): 15.60 (s, 1H, Ru=CH), 7.41 (d, 2H, Ph), 6.91 (m, 8H, Ph, Mes), 6.79 (m, 5H, Ph), 6.64 (m, 2H, Ph), 4.08 (s, 4H, 2 × CH₂, Im), 2.51 (s, 12 H, 4 × CH₃, Mes), 2.22 (s, 6H, 2 × CH₃, Mes).

¹³C{¹H} NMR (CD₂Cl₂): 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 (2 × CH, Ph), 129.2 (2 × CH, Ph), 128.9 (2 × CH, Ph), 128.1 (2 × CH, Ph), 126.1 (4 × CH, Mes), 127.4 (2 × CH, Ph), 125.2 (CH, p-C, Ph), 122.9 (CH, Ph), 121.5 (2 × CH, Ph), 114.8 (2 × CH, Ph), 51.8 (2 × CH₂, Im), 20.7 (2 × CH₃, Mes), 19.9 (4 × CH₃, Mes). Analysis calculated for C₄₀H₄₀N₂ORuS₂+CH₂Cl₂: C, 60.43; H, 5.19; N, 3.44. Found: C, 61.08; H, 5.78; N, 2.88.

¹H NMR (CD₂Cl₂)
$^{13}\text{C}^{1\text{H}}$ NMR (CD$_2$Cl$_2$)

Synthesis of 2nd Gen. Grubbs Catalyst from 7
To a CH$_2$Cl$_2$ (3 mL) solution of 7 (20 mg, 0.032 mmol) was added PCy$_3$ (10 mg, 0.035 mmol) and PhC(O)Cl (7.7 µL, 0.066 mmol). The solution was stirred for 30 min and a color change from red to purple was observed. Hexanes was added to precipitate the product which was collected and washed with hexanes to give a purple solid in 93 % yield (25 mg, 0.029 mmol). Spectral data was identical to previous reports of 2nd Gen. Grubbs.$^6$