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Synthesis and reactivity of ruthenium tridentate bis-phosphinite ligand complexes†

Michael J. Sgro and Douglas W. Stephan*

The tridentate ligands $E(CH_2CH_2OPiPr_2)_2$ (E = NH **1**, E = S **2**) were employed in the synthesis of a number of ruthenium complexes. Reaction of these ligands with $(Ph_3P)_3RuCl_2$ afforded the dimers $[Ru(HN(CH_2CH_2OPiPr_2)_2)Cl(\mu\text{-}Cl)]_2$ (**3**) and $[(Ru(E(CH_2CH_2OPiPr_2)_2))_2(\mu\text{-}Cl)_3][X]$ (E = NH, X = PF_6 **4**, E = S, X = Cl **5**), respectively. Using $(Ph_3P)_3RuHCl$ in reactions with **1** gave $Ru(NH(CH_2CH_2OPiPr_2)_2)(PPh_3)HCl$ (**6**) while addition of pyridine and **2**, gave $Ru(S(CH_2CH_2OPiPr_2)_2)(py)HCl$ (**7**). Treatment of **6** or **7** with $NaBPh_4$ resulted in the formation of the η^6-arene complexes $RuH(E(CH_2CH_2OPiPr_2)_2)_2(\eta^6\text{-}C_6H_5BPh_3)$ (E = NH **8**, E = S **9**) while reactions with $K[B(C_6F_5)_4]$ gave the salts $[RuH(E(CH_2CH_2OPiPr_2)_2)(L)][B(C_6F_5)_4]$ (E = NH, L = PPh_3 **10**, E = S, L = py **12**). Compounds **6** and **7** react with CO giving $RuH(HN(CH_2CH_2OPiPr_2)_2)(CO)Cl$ (**15**) and $[RuH(S(CH_2CH_2OPiPr_2)_2(py)(CO)]Cl$ (**16**) respectively, while reaction of **6**, **10** or **12** with dihydrogen gave $RuH(HN(CH_2CH_2OPiPr_2)_2)(H_2)Cl$ (**18**) and $RuH(E(CH_2CH_2OPiPr_2)_2)(L)(H_2)][B(C_6F_5)_4]$ (E = NH, L = PPh_3 **19**, E = S, L = py **20**). The complexes **4–12**, **15** and **16** are shown to catalyze the dehydrogenation of HMe_2NBH_3.

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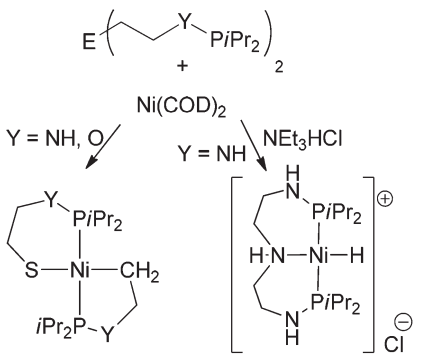
Introduction

Since the pioneering work by Shaw more than thirty years ago the field of pincer and more generally tridentate ligand chemistry has flourished.[1–6] Such complexes have found applications as sensors, switches and catalysts as well as displaying interesting reactivity including the oxidative addition of both C–halogen[7–9] and C–H bonds,[10,11] the activation of dinitrogen and the homolytic cleavage of H_2.[12,13] Much of the progress made with such systems has been described in published reviews.[14–16]

More recently, Milstein *et al.* have demonstrated that Ru complexes containing tridentate ligands such as $(C_5H_3N)(CH_2PtBu_2)_2$ or $(C_5H_3N)(CH_2PtBu_2)(CH_2NEt_2)$ are effective in a variety of catalytic transformations[17] including water splitting,[18] reversible NH activation[19] and the hydrogenation of carbonates, carbamates and formates.[20] In addition, Schneider *et al.* have utilized related Ru complexes of the ethyl linked NP_2 ligand for the reduction of N_3^- to NH_3,[21] as well as the dehydrogenation of amine-boranes.[22,23] While POP complexes of ruthenium have also received considerable attention and have exhibited reactivity with amine-boranes similar to the PNP analogue,[24] PSP complexes have received less attention.[25,26]

In our own efforts, we have been exploring both bis-phosphinite or aminophosphine donors with various neutral central donors.[27–30] For example, Ni complexes of the ligands $S(CH_2CH_2EPiPr_2)_2$ (E = O, NH) have recently been reported to undergo irreversible oxidative addition of the C–S bond to give a Ni alkyl-thiolate complex (Scheme 1). In contrast, the corresponding Ni(0) complexes of the ligand $HN(CH_2CH_2EPiPr_2)_2$ (E = NH) are readily oxidized to give Ni(II)-tridentate chelate hydride complexes. Analogous oxidative addition methods have also been used to prepare similar Pd and Pt halide, hydride, alkyl or aryl-complexes.[31] Herein, we report the synthesis of a series of Ru-complexes containing bis-phosphinite



Scheme 1 Reactions of aminophosphine tridentate ligands with $Ni(COD)_2$.

Department of Chemistry, University of Toronto, Toronto, ON, Canada.
E-mail: dstephan@chem.utoronto.ca

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ligands with central NH or S donors. The differing reactivity resulting from the change in central donor is explored and the reactivity of the resulting complexes with CO, H_2 and HMe_2NBH_3 are probed. The implications of such modifications for further applications in catalysis are considered.

Experimental section

General considerations

All preparations were performed under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and inert atmosphere glove boxes. Solvents (THF, CH_2Cl_2, Et_2O, hexane and pentane) were purified employing a Grubbs' type column system manufactured by Innovative Technology. Solvents were stored in the glove box over 4 Å molecular sieves. ^{1}H, ^{11}B{^{1}H} ^{13}C{^{1}H}, ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer or an Agilent 600 MHz spectrometer. ^{1}H and ^{13}C NMR were internally referenced to deuterated CD_2Cl_2 (δ = 5.32 ppm (^{1}H), 53.84 ppm (^{13}C)) and C_6D_5Br (δ = 6.94 ppm (^{1}H), 122.167 ppm (^{13}C)) relative to Me_4Si. NMR samples were prepared in the glove box, capped and sealed with parafilm. ^{11}B, ^{19}F and ^{31}P resonances were referenced externally to ($BF_3{\cdot}Et_2O$), $CFCl_3$ and 85% H_3PO_4, respectively. ^{1}H–^{13}C HSQC experiments were carried out using conventional pulse sequences to aid in the assignment of peaks in the ^{13}C{^{1}H} NMR spectroscopy. Coupling constants (J) are reported as absolute values. All glassware was dried overnight at 120 °C and evacuated for 1 hour prior to use. Combustion analyses were performed in-house employing a Perkin Elmer 2400 Series II CHNS Analyzer. In cases where the sensitivity of a compound precluded elemental analysis or HRMS, spectral data are deposited in the ESI.† CD_2Cl_2 and C_6D_5Br were purchased from the Cambridge Isotope Laboratories and were dried over CaH_2, distilled, degassed and stored under N_2 in a glove box. $Ru(PPh_3)_3Cl_2$ and $Ru(PPh_3)_3HClCO$ were obtained from Strem Chemicals Inc. $Ru(PPh_3)_3HCl$ was prepared according to literature procedure.[32] $ClPiPr_2$, Et_3N, $S(CH_2CH_2OH)_2$ were obtained from Aldrich Chemical Co. The ligand **2** was prepared as previously reported.[28]

Synthesis of NH((CH$_2$)$_2$OPiPr$_2$)$_2$ (1). A 250 mL round bottom Schlenk flask was charged with 1.5 mL of 2,2′-thiodiethanol (1.03 g, 9.79 mmol) and 100 mL of THF and stirred under nitrogen. Et_3N (9.98 g, 13.75 mL, 97.96 mmol) was added to the flask and the reaction mixture was stirred for 30 minutes. Neat iPr_2PCl (3.12 mL, 19.6 mmol) was added to the stirring solution drop wise over 5 minutes giving a cloudy white solution. The reaction mixture was stirred for an additional 24 hours before being dried *in vacuo*. The white solid was then combined with toluene and stirred before being filtered through Celite. The clear colourless solution was dried *in vacuo* giving the desired product as a liquid in 77% yield (2.54 g, 7.54 mmol). ^{1}H NMR (CD_2Cl_2; δ ppm) 3.74 (d of t, $^3J_{HH}$ 6 Hz, $^3J_{HP}$ 7 Hz, 4H, –CH_2–O), 2.73 (t, 4H, $^3J_{HH}$ 6 Hz, $^3J_{HP}$ 7 Hz, –CH_2–), 1.66 (sept of d, 4H, $^3J_{HH}$ 7 Hz, $^2J_{HP}$ 2 Hz, (CH$_3$)$_2$CH), 1.51 (bs, 1H, NH), 1.05 (d of d, 12H, $^3J_{HH}$ 7 Hz, $^2J_{HP}$ 10 Hz, (CH_3)$_2$CH), 1.00 (d of d, 12H, $^3J_{HH}$ 7 Hz, $^2J_{HP}$ 15 Hz, (CH_3)$_2$CH). ^{13}C{^{1}H} NMR (CD_2Cl_2; δ ppm) 72.28 (d, $^2J_{CP}$ 19 Hz, –CH_2–O), 51.16 (d, $^3J_{CP}$ 7 Hz, CH_2), 28.43 (d, $^1J_{CP}$ 17 Hz, (CH$_3$)$_2$CH)), 18.16 (d, $^2J_{CP}$ 21 Hz, (CH_3)$_2$CH), 17.17 (d, $^2J_{CP}$ 9 Hz, (CH_3)$_2$CH)). ^{31}P{^{1}H} NMR (CD_2Cl_2; δ ppm) 152.28 (s).

Synthesis of [Ru(NH((CH$_2$)$_2$OPiPr$_2$)$_2$)Cl(μ-Cl)]$_2$ (3). A solution of **1** and CH_2Cl_2 (70 mg, 0.209 mmol; 4 mL) was added to a brown suspension of $Ru(PPh_3)_3Cl_2$ in CH_2Cl_2 (200 mg, 0.209 mmol; 4 mL) giving no immediate change. The reaction mixture was allowed to stir for 12 h before at which point a yellow suspension was obtained. The reaction mixture was filtered and the bright yellow solid was washed with hexane (2 × 5 mL) and diethyl ether (1 × 5 mL). The yellow solid was then dried and the product was collected in an 95% yield (101 mg, 0.106 mmol). The yellow solid was not soluble enough in any solvent to obtain satisfactory NMR spectra, but yellow crystals were obtained by adding CH_2Cl_2 to a sample of the product, heating it and then allowing it to cool. EA: $C_{32}H_{74}O_4P_4S_2Ru_2Cl_4$: Calc'd: C, 37.71; H, 7.32; N, 2.75; Found: C, 38.05; H, 7.46; N, 3.15. **3**: $P\bar{1}$, a = 8.7890(8) Å, b = 10.408(1) Å, c = 13.796(1) Å, α = 91.428(4)°, β = 106.792(3)°, γ = 114.206(3)°, V = 1087.0(2) Å^3, Z = 1, data (>2σ) = 4575, variables = 225, R(>2σ) = 0.0208, R(all) = 0.0510, GOF = 1.039.

Synthesis of [(Ru(NH((CH$_2$)$_2$OPiPr$_2$)$_2$))$_2$(μ-Cl)$_3$][PF$_6$] (4). A suspension of **3** in CH_2Cl_2 (100 mg, 0.098 mmol; 4 mL) was prepared and solid $NaPF_6$ (17 mg, 0.098 mmol) was added giving no immediate change. The reaction mixture was stirred for 24 h at which point the cloudy yellow mixture was filtered through Celite and dried to a yellow solid. The solid was re-dissolved in CH_2Cl_2 and pentane was layered on top of the yellow solution. The product was isolated as orange-yellow crystals in an 86% yield (95 mg, 0.084 mmol). ^{1}H NMR (CD_2Cl_2, δ ppm) 4.15 (m, 6H, CH_2), 3.95 (m, 6H, CH_2), 3.75 (m, 2H, $^3J_{HH}$ 7.3 Hz, CH(CH$_3$)$_2$), 3.66 (m, 2H, $^3J_{HH}$ 7.3 Hz, CH(CH$_3$)$_2$), 2.99 (bs, 1H, NH), 2.96 (bs, 1H, NH), 2.76 (m, 2H, CH_2), 2.55 (m, 2H, $^3J_{HH}$ 7 Hz, CH(CH$_3$)$_2$), 2.36 (m, 2H, CH_2), 2.29 (m, 2H, $^3J_{HH}$ 7 Hz, CH(CH$_3$)$_2$), 1.35 (m, 42H, CH(CH_3)$_2$), 1.14 (m, 6H, $^3J_{HH}$ 7 Hz, $^3J_{HP}$ 17 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 64.19 (d, J_{CP} 3 Hz, CH_2), 63.60 (d, J_{CP} 4 Hz, CH_2), 52.74 (d, J_{CP} 4 Hz, CH_2), 52.69 (d, J_{CP} 4 Hz, CH_2), 37.80 (d, $^1J_{CP}$ 32 Hz, CH(CH$_3$)$_2$), 37.12 (d, $^1J_{CP}$ 32 Hz, CH(CH$_3$)$_2$), 34.14 (d, $^1J_{CP}$ 20 Hz, CH(CH$_3$)$_2$), 33.86 (d, $^1J_{CP}$ 21 Hz, CH(CH$_3$)$_2$), 21.46 (s, CH(CH$_3$)$_2$), 19.64 (d, $^2J_{CP}$ 5 Hz, CH(CH$_3$)$_2$), 19.37 (d, $^2J_{CP}$ 5 Hz, CH(CH$_3$)$_2$), 19.14 (d, $^2J_{CP}$ 7 Hz, CH(CH$_3$)$_2$), 18.70 (d, $^2J_{CP}$ 7 Hz, CH(CH$_3$)$_2$), 17.83 (d, $^2J_{CP}$ 6 Hz, CH(CH$_3$)$_2$), 17.74 (d, $^2J_{CP}$ 3 Hz, CH(CH$_3$)$_2$), 16.31 (d, $^2J_{CP}$ 4 Hz, CH(CH$_3$)$_2$). ^{19}F{^{1}H} NMR (CD_2Cl_2, δ ppm) −74.41 (d, $^1J_{FP}$ 710 Hz, PF_6). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ ppm) 177.58 (d, $^2J_{PP}$ 37 Hz), 171.50 (d, $^2J_{PP}$ 37 Hz), −144.54 (sept, $^1J_{PF}$ 710 Hz, PF_6); EA: $C_{32}H_{74}O_4P_5N_2Ru_2Cl_3F_6$: Calc'd: C, 34.04; H, 6.61; N, 2.48; Found: C, 33.77; H, 6.24; N, 2.25. **4**: $P2_12_12_1$, a = 14.310(1)Å, b = 15.520(1) Å, c = 22.333(2) Å, α = 90°, β = 90°, γ = 90°, V = 4959.7(7) Å^3, Z = 8, data (>2σ) = 10407, variables = 527, R(>2σ) = 0.0304, R(all) = 0.0695, GOF = 1.022.

Synthesis of [(Ru(S((CH$_2$)$_2$OPiPr$_2$)$_2$)Cl)$_2$(μ-Cl)]$_2$[Cl] (5). A solution of **2** and CH_2Cl_2 (74 mg, 0.209 mmol; 2 mL) was added to a brown suspension of $(PPh_3)_3RuCl_2$ in CH_2Cl_2

(200 mg, 0.209 mmol; 4 mL) immediately giving a clear orange solution. The reaction mixture was allowed to stir for 12 h before the solvent was removed *in vacuo* leaving an orange solid. The crude product was washed with hexane (2 × 5 mL) and diethyl ether (1 × 5 mL). The solid was then crystallized by layering cyclohexane on top of an orange solution of the product in CH_2Cl_2. The product was isolated as yellow-orange crystals in an 85% yield (93 mg, 0.088 mmol). ^{1}H NMR (CD_2Cl_2, δ ppm) 4.56 (m, 2H, CH_2), 4.43 (m, 2H, CH_2), 4.27 (m, 2H, CH_2), 4.08 (m, 2H, CH_2), 3.77 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*$(CH_3)_2$), 3.59 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*$(CH_3)_2$), 2.90 (m, 4H, CH_2), 2.64 (m, 2H, CH_2), 2.56 (m, 2H, CH_2), 2.49 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*$(CH_3)_2$), 2.37 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*$(CH_3)_2$), 1.33 (m, 48H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 64.05 (d, J_{CP} 5 Hz, CH_2), 63.99 (d, J_{CP} 4 Hz, CH_2), 37.77 (d, $^1J_{CP}$ 30 Hz, *C*H$(CH_3)_2$), 36.57 (d, $^1J_{CP}$ 25 Hz, *C*H$(CH_3)_2$), 34.49 (d, $^1J_{CP}$ 26 Hz, *C*H$(CH_3)_2$), 34.22 (d, J_{CP} 4 Hz, CH_2), 34.11 (d, $^1J_{CP}$ 21 Hz, *C*H$(CH_3)_2$), 34.09 (s, CH_2), 20.75 (d, $^2J_{CP}$ 2 Hz, CH(*C*H$_3)_2$), 19.74 (d, $^2J_{CP}$ 7 Hz, CH$(CH_3)_2$), 19.42 (d, $^2J_{CP}$ 1 Hz, CH(*C*H$_3)_2$), 19.37 (s, CH(*C*H$_3)_2$), 19.26 (d, $^2J_{CP}$ 6 Hz, CH(*C*H$_3)_2$), 18.43 (d, $^2J_{CP}$ 5 Hz, CH(*C*H$_3)_2$), 17.50 (d, $^2J_{CP}$ 3 Hz, CH(*C*H$_3)_2$), 16.80 (d, $^2J_{CP}$ 2 Hz, CH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ ppm) 167.83 (d, $^2J_{PP}$ 34 Hz), 166.14 (d, $^2J_{PP}$ 34 Hz); EA: $C_{32}H_{72}O_4P_4S_2Ru_2Cl_4$. 1/2 C_6H_{12}: Calc'd: C, 38.38; H, 7.18; Found: C, 38.54; H, 7.24.

Synthesis of RuH(NH((CH$_2$)$_2$OPiPr$_2$)$_2$)(PPh$_3$)Cl (6). A solution of **1** and CH_2Cl_2 (73 mg, 0.216 mmol; 4 mL) was added to a purple suspension of $(PPh_3)_3$RuHCl in CH_2Cl_2 (200 mg, 0.216 mmol; 4 mL) giving no immediate change. The mixture was allowed to stir overnight giving a slightly cloudy yellow orange mixture. The mixture was filtered through Celite and the yellow-orange solution was dried to a yellow solid. The crude product was washed with hexane (2 × 5 mL) and diethyl ether (1 × 5 mL) before the volatiles were removed *in vacuo.* The yellow product was then re-dissolved in CH_2Cl_2 and pentane was layered on top. The purified product was obtained as yellow crystals in 82% yield (131 mg, 0.177 mmol). ^{1}H NMR (CD_2Cl_2, δ ppm) 8.02 (m, 6H, *o*-C_6H_5 PPh_3), 7.27 (m, 9H, *m*,*p*-C_6H_5 PPh_3), 4.44 (m, 2H, CH_2), 4.00 (m, 3H, CH_2 and NH), 3.43 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 1.74 (sept, 2H, $^3J_{HH}$ 7.1 Hz, C*H*$(CH_3)_2$), 1.11 (sept, 2H, $^3J_{HH}$ 7 Hz, C*H*$(CH_3)_2$), 0.98 (m, 12H, $^3J_{HH}$ 7 Hz, CH(C*H*$_3)_2$), 0.89 (m, 6H, $^3J_{HH}$ 7 Hz, CH(C*H*$_3)_2$), 0.85 (m, 6H, $^3J_{HH}$ 7 Hz, CH(C*H*$_3)_2$), −17.48 (q, 1H, $^3J_{HP}$ 22 Hz, Ru–H). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 140.72 (d, J_{CP} 38 Hz, C*ipso* PPh_3), 136.18 (d, J_{CP} 10 Hz, *o-C* PPh_3), 129.26 (d, J_{CP} 2 Hz, *p-C* PPh_3), 127.16 (d, J_{CP} 8 Hz, *m-C* PPh_3), 65.36 (s, CH_2), 47.24 (bs, CH_2), 34.62 (t, J_{CP} 14 Hz, *C*H$(CH_3)_2$), 33.02 (t, J_{CP} 7 Hz, *C*H$(CH_3)_2$), 18.51 (s, CH(*C*H$_3)_2$), 18.27 (s, CH(*C*H$_3)_2$), 17.29 (t, J_{CP} 3 Hz, CH(*C*H$_3)_2$), 17.35 (s, CH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ ppm) 164.66 (d, $^2J_{PP}$ 28 Hz, OP(CH(CH$_3)_2)_2$), 60.29 (t, $^2J_{PP}$ 28 Hz, PPh_3); EA: $C_{34}H_{53}O_2P_3NRuCl$: Calc'd: C, 55.37; H, 7.25; N, 1.90; Found: C, 55.62; H, 7.54; N, 1.87. **6**: *C*2/*c*, a = 21.9644(8) Å, b = 17.3583(8) Å, c = 20.1248(9) Å, V = 7672.8(6) Å^3, Z = 8, data (>2σ) = 5894, variables = 383, R(>2σ) = 0.0431, R(all) = 0.0917, GOF = 0.936.

Synthesis of RuH(S((CH$_2$)$_2$OPiPr$_2$)$_2$)(py)Cl (7). A solution of **2** and CH_2Cl_2 (77 mg, 0.216 mmol; 4 mL) was added to a purple suspension of $(PPh_3)_3$RuHCl in CH_2Cl_2 (200 mg, 0.216 mmol; 4 mL) giving no immediate change. Neat pyridine (0.5 mL) was then added and the solution lightened to a cloudy green-brown mixture. The mixture was allowed to stir overnight giving a yellow-orange solution that was dried to a yellow solid. The crude product was washed with hexane (2 × 5 mL) and diethyl ether (1 × 5 mL) before the volatiles were removed *in vacuo.* The yellow product was then re-dissolved in CH_2Cl_2 and pentane was layered on top. The purified product was obtained as yellow crystals in 84% yield (104 mg, 0.182 mmol). ^{1}H NMR (CD_2Cl_2, δ ppm) 10.12 (d, 1H, $^3J_{HH}$ 5 Hz, Ar-H C_1), 8.59 (d, 1H, $^3J_{HH}$ 5 Hz, Ar-H C_5), 7.48 (t, 1H, $^3J_{HH}$ 7 Hz, Ar-H C_3), 7.10 (bt, 1H, Ar-H C_2), 6.80 (bt, 1H, Ar-H C_4), 5.40 (m, 2H, C*H*$_2$), 4.05 (m, 2H, C*H*$_2$), 2.69 (m, 2H, C*H*$_2$), 2.56 (m, 2H, C*H*$_2$), 2.16 (m, 2H, $(CH_3)_2$C*H*), 1.39 (m, 2H, $(CH_3)_2$C*H*), 1.19 (m, 12H, $(CH_3)_2$CH), 1.06 (m, 6H, $(CH_3)_2$CH), 0.95 (m, 6H, $(CH_3)_2$CH), −20.55 (bs, 1H, Ru–H). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 160.92 (bs, Ar-C C_1), 156.45 (bs, Ar-C C_5), 135.11 (s, Ar-C C_3), 124.05 (s, Ar-C C_2), 123.35 (s, Ar-C C_4), 66.50 (s, CH_2), 39.09 (s, CH_2), 32.34 (bs, $(CH_3)_2$*C*H), 30.08 (bs, $(CH_3)_2$*C*H), 18.22 (bs, $(CH_3)_2$CH), 17.80 (bs, $(CH_3)_2$CH), 17.50 (bs, $(CH_3)_2$CH), 16.46 (bs, $(CH_3)_2$CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ ppm) 159.18 (s); EA: $C_{21}H_{42}O_2P_2NSRuCl$: Calc'd: C, 44.16; H, 7.41; N, 2.45; Found: C, 44.11; H, 7.64; N, 2.91. **7**: *Pnma*, a = 11.0475(2) Å, b = 17.0485(4) Å, c = 17.8434(3) Å, α = 90°, β = 90°, γ = 90°, V = 2607.31(10) Å^3, Z = 4, data (>2σ) = 2625, variables = 148, R(>2σ) = 0.0241, R(all) = 0.0577, GOF = 1.043.

Synthesis of RuH(E((CH$_2$)$_2$OPiPr$_2$)$_2$)(η^6-C$_6$H$_5$BPh$_3$) E = NH (8), S (9). The preparations of these compounds were completed in a similar fashion thus only the preparation of one of them is described. A yellow solution of **6** in THF was prepared (60 mg, 0.081 mmol; 4 mL) and set stirring. Solid $NaBPh_4$ was added (28 mg, 0.081 mmol) giving a cloudy orange mixture. Within four hours the reaction mixture had lightened to pale yellow. The mixture was allowed to stir for 24 h at which point the cloudy colorless solution was dried. The solid was extracted with CH_2Cl_2 and filtered through Celite to remove NaCl. The clear colorless solution was then concentrated and cyclohexane was layered on top of the CH_2Cl_2 layer. The product was obtained as white blocks in 87% yield (54 mg, 0.071 mmol) after the solution was decanted to remove PPh_3. **8**: ^{1}H NMR (CD_2Cl_2, δ ppm) 7.42 (d, 6H, $^3J_{HH}$ 7 Hz, *o*-C_6H_5 BPh_4), 7.08 (t, 6H, $^3J_{HH}$ 7 Hz, *m*-C_6H_5 BPh_4), 6.96 (t, 3H, $^3J_{HH}$ 7 Hz, *p*-C_6H_5 BPh_4), 5.83 (d, 1H, $^3J_{HH}$ 6 Hz, *p*-C_6H_5(η^6-Ph) BPh_4), 5.76 (t, 2H, $^3J_{HH}$ 6 Hz, *m*-C_6H_5(η^6-Ph) BPh_4), 5.52 (d, 2H, $^3J_{HH}$ 6 Hz, *o*-C_6H_5(η^6-Ph) BPh_4), 3.88 (m, 2H, CH_2), 3.54 (m, 2H, CH_2), 2.82 (m, 4H, CH_2), 2.08 (m, 2H, $^3J_{HH}$ 7.1 Hz, C*H*$(CH_3)_2$), 1.72 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*$(CH_3)_2$), 1.26 (m, 6H, $^3J_{HH}$ 7 Hz, CH(C*H*$_3)_2$), 1.21 (m, 6H, $^3J_{HH}$ 7 Hz, CH(C*H*$_3)_2$), 1.08 (m, 6H, $^3J_{HH}$ 7 Hz, CH(C*H*$_3)_2$), 0.60 (m, 6H, $^3J_{HH}$ 7 Hz, CH(C*H*$_3)_2$), −10.20 (t, 1H, $^3J_{HP}$ 35 Hz, Ru–H). NH not observed. ^{11}B{^{1}H} NMR (CD_2Cl_2, δ ppm) −8.17 (s, BPh_4). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 136.60 (s, BPh_4), 126.46 (s, BPh_4), 123.54 (s, BPh_4), 96.26 (bs, (η^6-Ph) BPh_4), 92.86 (bs, (η^6-Ph) BPh_4), 89.10 (bs, (η^6-Ph) BPh_4), 69.90 (m, CH_2), 51.38 (m, CH_2), 36.98 (t, $^1J_{CP}$ 14 Hz, *C*H$(CH_3)_2$), 33.71 (t, $^1J_{CP}$ 12 Hz, *C*H$(CH_3)_2$), 18.90 (s,

$CH(CH_3)_2$), 18.73 (s, $CH(CH_3)_2$), 18.46 (bs, $CH(CH_3)_2$) C*ipso* for either type of Ph on BPh_4 not located. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 174.57 (s, $OP(CH(CH_3)_2)_2$). EA: $C_{40}H_{58}BNO_2P_2Ru$: Calc'd: C, 63.32; H, 7.71; N, 1.85; Found C, 63.36; H, 7.83; N, 1.95. **8**: $P2_1/n$, a = 13.6707(6) Å, b = 13.3994(5) Å, c = 21.0170(8) Å, α = 90°, β = 93.096(1)°, γ = 90°, V = 3844.3(3) Å^3, Z = 4, data (>2σ) = 7230, variables = 436, R(>2σ) = 0.0288, R(all) = 0.0711, GOF = 1.023.

9: The product was obtained as white blocks in 53% yield (45 mg, 0.056 mmol) after the purple solution was decanted off to remove the colored by-product. ^1H NMR (CD_2Cl_2, δ ppm) 7.43 (d, 6H, $^3J_{HH}$ 7.34 Hz, *o*-C_6H_5 BPh_4), 7.09 (t, 6H, $^3J_{HH}$ 7 Hz, *m*-C_6H_5 BPh_4), 6.97 (t, 3H, $^3J_{HH}$ 7 Hz, *p*-C_6H_5 BPh_4), 5.81 (d, 3H, *p*/*m*-$C_6H_5(\eta^6$-Ph) BPh_4), 5.54 (d, 2H, $^3J_{HH}$ 5.4 Hz, *o*-$C_6H_5(\eta^6$-Ph) BPh_4), 3.98 (m, 2H, CH_2), 3.83 (m, 2H, CH_2), 2.80 (m, 2H, CH_2), 2.69 (m, 2H, CH_2), 2.09 (m, 2H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 1.71 (m, 2H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 1.26 (m, 12H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 1.10 (m, 6H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 0.65 (m, 6H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), −10.29 (t, 1H, $^3J_{HP}$ 35 Hz, Ru–H). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, δ ppm) −8.23 (s, BPh_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 136.55 (s, BPh_4), 126.48 (s, BPh_4), 123.62 (s, BPh_4), 96.33 (bs, η^6-BPh_4), 93.27 (t, J_{CP} 4 Hz, η^6-BPh_4), 89.02 (m, η^6-BPh_4), 68.94 (t, J_{CP} 5 Hz, CH_2), 37.07 (t, $^1J_{CP}$ 12 Hz, $CH(CH_3)_2$), 35.19 (t, J_{CP} 4 Hz, CH_2), 34.16 (t, $^1J_{CP}$ 13 Hz, $CH(CH_3)_2$), 19.02 (s, $CH(CH_3)_2$), 18.82 (d, J_{CP} 3 Hz, $CH(CH_3)_2$), 18.56 (s, $CH(CH_3)_2$). C*ipso* for either type of Ph on BPh_4 not located. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 174.88 (s, $OP(CH(CH_3)_2)_2$). EA: $C_{40}H_{57}BSO_2P_2Ru{\cdot}1/2C_6H_{12}$: Calc'd: C, 63.12; H, 7.77; Found C, 63.03; H, 7.96. **9**: $P\bar{1}$, a = 13.117(2) Å, b = 13.357(2) Å, c = 13.641(2) Å, α = 86.498(6)°, β = 86.588(6)°, γ = 71.613(6)°, V = 2261.7(5) Å^3, Z = 2, data (>2σ) = 6684, variables = 476, R(>2σ) = 0.0315, R(all) = 0.0760, GOF = 1.051.

Synthesis of $[RuH(E((CH_2)_2OPiPr_2)_2)(L)][B(C_6F_5)_4]$ E = NH, L = PPh_3 (10), E = S, L = py (12). The preparations of these compounds were completed in a similar fashion thus only the preparation of one of them is described. A pale yellow solution of **6** and THF (75 mg, 0.102 mmol; 4 mL) was prepared and solid $K[B(C_6F_5)_4]$ (73 mg, 0.102 mmol) was added. No immediate change is observed but after approximately 4 h a cloudy orange solution is obtained. The reaction mixture was stirred for 24 h at which point the solvent was removed *in vacuo*. The solid was extracted with CH_2Cl_2 and filtered through a plug of Celite. The clear orange solution was dried and the foamy solid was washed with hexane (3 × 5 mL). **10**: The orange solid was obtained in 78% yield (109 mg, 0.079 mmol). ^1H (CD_2Cl_2, δ ppm) *isomer* (a) 7.59 (m, 5H, Ar-H PPh_3), 7.46 (m, 10H, Ar-H PPh_3), 4.01 (m, 2H, CH_2), 3.91 (m, 2H, CH_2), 3.53 (m, 2H, CH_2), 3.29 (m, 2H, CH_2), 2.01 (m, 2H, $CH(CH_3)_2$), 1.35 (m, 2H, $CH(CH_3)_2$), 1.17 (m, 12H, $CH(CH_3)_2$), 0.76 (m, 12H, $CH(CH_3)_2$), −30.04 (d of t, 1H, $^2J_{HP}$ 30, 20 Hz, Ru–H); *isomer* (b) 7.59 (m, 5H, Ar-H PPh_3), 7.46 (m, 10H, Ar-H PPh_3), 3.91 (m, 2H, CH_2), 3.43 (m, 2H, CH_2), 3.13 (m, 1H, CH_2 and 1H $CH(CH_3)_2$), 2.59 (m, 2H, CH_2), 2.57 (m, 1H, $CH(CH_3)_2$), 2.31 (m, 1H, CH_2), 1.35 (m, 12H, $CH(CH_3)_2$ and 2H, $CH(CH_3)_2$), 0.99 (m, 12H, $CH(CH_3)_2$) −30.04 (d of t, 1H, $^2J_{HP}$ 29.6 and 19.8 Hz, Ru–H). Both NMR above are partial assignment. $^{11}B\{^1H\}$ (CD_2Cl_2, δ ppm) −16.64 (s). $^{13}C\{^1H\}$ (CD_2Cl_2, δ ppm) 148.17 (dm, $^1J_{CF}$ 240 Hz, *o*-C_6F_5), 138.94 (dm, $^1J_{CF}$ 250 Hz, *p*-C_6F_5), 136.47 (dm, $^1J_{CF}$ 237 Hz, *m*-C_6F_5), 134.04 (d, J_{CP} 12 Hz, Ar-C PPh_3), 131.38 (bs, Ar-C PPh_3 (a)), 131.10 (bs, Ar-C PPh_3 (b)), 129.31 (d, J_{CP} 10 Hz, Ar-C PPh_3(a)), 128.75 (d, J_{CP} 9 Hz, Ar-C PPh_3 (b)), 67.05 (s, CH_2 (a)), 66.70 (s, CH_2 (b)), 52.84 (s, CH_2 (a)), 52.65 (s, CH_2 (b)), 32.91 (bm, $CH(CH_3)_2$ (a)), 31.85 (t, J_{CP} 12 Hz, $CH(CH_3)_2$ (b)), 30.90 (t, J_{CP} 14 Hz, $CH(CH_3)_2$ (b)), 19.57 (s, $CH(CH_3)_2$), 19.28 (s, $CH(CH_3)_2$), 18.80 (s, $CH(CH_3)_2$), 18.71 (s, $CH(CH_3)_2$), 18.44 (s, $CH(CH_3)_2$), 17.38 (s, $CH(CH_3)_2$), 16.97 (s, $CH(CH_3)_2$), 16.67 (s, $CH(CH_3)_2$). $^{19}F\{^1H\}$ (CD_2Cl_2, δ ppm) −134.13 (bs, *o*-F), 164.62 (t, $^3J_{FF}$ 21 Hz, *p*-F), −168.50 (bt, $^3J_{FF}$ 18 Hz, *m*-F). $^{31}P\{^1H\}$ (CD_2Cl_2, δ ppm) *isomer* (a) (major) 184.21 (m, $OP(CH(CH_3)_2)_2$), 43.40 (m, PPh_3); *isomer* (b) (minor) 172.97 (m, $OP(CH(CH_3)_2)_2$), 55.90 (m, PPh_3). ESI-TOF HI-RES MS $[C_{34}H_{53}O_2P_3NRu]^+$ m/z = 702.2327 (theoretical 702.2359).

12: Red solid was obtained in 83% yield (133 mg, 0.109 mmol). ^1H (CD_2Cl_2, δ ppm) 8.43 (d, 2H, $^3J_{HH}$ 7 Hz, *o*-Ar-H Py), 7.75 (t, 1H, $^3J_{HH}$ 7 Hz, *p*-Ar-H Py), 7.28 (d, 2H, $^3J_{HH}$ 7 Hz, *m*-Ar-H Py), 4.23 (m, 4H, CH_2), 2.78 (m, 2H, CH_2), 2.32 (m, 2H, CH_2), 2.23 (m, 2H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 1.56 (m, 2H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 1.23 (m, 6H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 1.10 (m, 12H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 0.93 (m, 6H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), −29.71 (bm, 1H, Ru–H). $^{11}B\{^1H\}$ (CD_2Cl_2, δ ppm) −16.64 (s). $^{13}C\{^1H\}$ (CD_2Cl_2, δ ppm) 148.60 (dm, $^1J_{CF}$ 238 Hz, *o*-C_6F_5), 138.68 (dm, $^1J_{CF}$ 247 Hz, *p*-C_6F_5), 137.94 (s, Ar-C Py), 136.79 (dm, $^1J_{CF}$ 250 Hz, *m*-C_6F_5), 125.91 (s, Ar-C Py), 68.95 (s, CH_2), 39.03 (s, CH_2), 31.07 (t, J_{CP} 11 Hz, $CH(CH_3)_2$), 29.23 (t, J_{CP} 14 Hz, $CH(CH_3)_2$), 18.46 (t, J_{CP} 5 Hz, $CH(CH_3)_2$), 18.04 (s, CH $(CH_3)_2$), 17.86 (s, $CH(CH_3)_2$), 16.11 (s, $CH(CH_3)_2$). $^{19}F\{^1H\}$ (CD_2Cl_2, δ ppm) −134.15 (bs, *o*-F), 164.55 (t, $^3J_{FF}$ 18 Hz, *p*-F), −168.47 (bt, $^3J_{FF}$ 16 Hz, *m*-F). $^{31}P\{^1H\}$ (CD_2Cl_2, δ ppm) 163.82 (s, $OP(CH(CH_3)_2)_2$). ESI-TOF HI-RES MS $[C_{21}H_{42}O_2P_2NSRu]^+$ m/z = 536.1449 (theoretical 536.1434).

Synthesis of $[RuH(NH((CH_2)_2OPiPr_2)_2)(PPh_3)(CH_3CN)][B(C_6F_5)_4]$ (11). An orange solution of **10** and CH_2Cl_2 was prepared (70 mg, 0.051 mmol; 2 mL) and set stirring in a 4 dram vial. Neat acetonitrile (2.09 mg, 0.051 mmol) was added giving no immediate change. The reaction mixture was stirred for 24 h at which point a pale yellow solution was obtained. The stir bar was removed and pentane was layered on top of the CH_2Cl_2 mixture. **11**: The product was obtained as very faint yellow to colorless crystals once the solvent was decanted in 62% yield (45 mg, 0.032 mmol). ^1H (CD_2Cl_2, δ ppm) 7.59 (m, 6H, *o*-Ar-H PPh_3), 7.41 (m, 3H, *p*-Ar-H PPh_3), 7.36 (m, 6H, *m*-Ar-H PPh_3), 4.43 (m, 2H, CH_2), 4.04 (m, 2H, $^3J_{HH}$ 6.4 Hz, CH_2), 3.48 (bs, 1H, NH), 2.98 (m, 2H, CH_2), 2.68 (m, 2H, CH_2), 2.10 (bs, 3H, CH_3CN), 1.77 (m, 2H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 1.57 (m, 2H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 1.00 (m, 18H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), 0.77 (m, 6H, $^3J_{HH}$ 7 Hz, $CH(CH_3)_2$), −14.36 (q, 1H, $^3J_{HP}$ 21 Hz, Ru–H). $^{11}B\{^1H\}$ (CD_2Cl_2, δ ppm) −16.6 (s). $^{13}C\{^1H\}$ (CD_2Cl_2, δ ppm) 148.58 (dm, $^1J_{CF}$ 237 Hz, *o*-C_6F_5), 138.65 (dm, $^1J_{CF}$ 247 Hz, *p*-C_6F_5), 136.67 (dm, $^1J_{CF}$ 239 Hz, *m*-C_6F_5), 134.70 (d, J_{CP} 10 Hz, Ar-C PPh_3), 130.50 (d, J_{CP} 2 Hz, Ar-C PPh_3), 128.07 (d, J_{CP} 9 Hz, Ar-C PPh_3), 63.95 (s, CH_2), 47.52 (s, CH_2), 34.90 (t, $^1J_{CP}$ 14 Hz, $CH(CH_3)_2$), 32.49 (t, $^1J_{CP}$ 9 Hz, $CH(CH_3)_2$),

18.94 (t, J_{CP} 2 Hz, CH(CH_3)$_2$), 18.32 (s, CH(CH_3)$_2$), 17.76 (s, CH(CH_3)$_2$), 17.51 (t, J_{CP} 2 Hz, CH(CH_3)$_2$), 4.92 (bs, CH_3CN). $^{19}F\{^1H\}$(CD_2Cl_2, δ ppm) −134.06 (bs, *o*-F), −164.65 (t, $^3J_{FF}$ 21 Hz, *p*-F), −168.53 (bt, $^3J_{FF}$ 18 Hz, *m*-F). $^{31}P\{^1H\}$ (CD_2Cl_2, δ ppm) 165.13 (d, $^2J_{PP}$ 26 Hz, OP(CH(CH_3)$_2$)$_2$), 61.96 (d, $^2J_{PP}$ 26 Hz, PPh_3). EA: $C_{60}H_{56}O_2P_3N_2RuF_{20}B$: Calc'd: C, 50.65; H, 3.97; N, 1.97; Found C, 50.23; H, 4.10; N, 2.06. **11**: $P\bar{1}$, a = 12.7350(6) Å, b = 14.0486(7) Å, c = 16.8712(9) Å, α = 92.955(2)°, β = 92.820(2)°, γ = 92.267(2)°, V = 3008.1(3) Å^3, Z = 2, data (>2σ) = 9277, variables = 807, R(>2σ) = 0.0542, R(all) = 0.1271, GOF = 1.024.

Synthesis of [RuH(HN((CH$_2$)$_2$OPiPr$_2$)$_2$)(CO)$_2$][B(C$_6$F$_5$)$_4$] (13). An orange solution of **10** in THF (140 mg, 0.102 mmol; 4 mL) was prepared in a 25 mL bomb. The solution was degassed using three freeze–pump–thaw cycles and was charged with 1 atm of CO. The solution fades from red to pale yellow over 12 h at which point the solvent was removed giving an off white solid. The sample was re-dissolved in CH_2Cl_2 and pentane was layered on top of the pale yellow solution. The product was obtained as colorless crystals in 87% yield (104 mg, 0.088 mmol). Two isomers observed by NMR major (a), minor (b) in 8 : 2 ratio. ^1H NMR (CD_2Cl_2, δ ppm) 4.24 (m, 2H, $^3J_{HH}$ 7 Hz, CH_2), 3.99 (m, 2H, $^3J_{HH}$ 7 Hz, CH_2), 2.85 (m, 2H, $^3J_{HH}$ 7 Hz, CH_2), 2.73 (m, 3H, $^3J_{HH}$ 7 Hz, CH_2, N*H*), 2.53 (m, 2H, $^3J_{HH}$ 7 Hz, J_{HP} 7 Hz, (CH$_3$)$_2$C*H*), 2.28 (sept, 2H, $^3J_{HH}$ 7 Hz, (CH$_3$)$_2$C*H*), 1.32 (m, 24H, $^3J_{HH}$ 7 Hz, (CH_3)$_2$CH), −5.39 (t, 1H, $^2J_{HP}$ 20 Hz, Ru–H (a)), −5.69 (t, 1H, $^2J_{HP}$ 21 Hz, Ru–H (b)). $^{11}B\{^1H\}$ (CD_2Cl_2, δ ppm) −16.62 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 197.34 (m, CO), 197.04 (m, CO), 148.74 (dm, $^1J_{CF}$ 240 Hz, *o*-C_6F_5), 138.84 (dm, $^1J_{CF}$ 245 Hz, *p*-C_6F_5), 136.90 (dm, $^1J_{CF}$ 249 Hz, *m*-C_6F_5), 67.80 (s, CH_2 (a)), 67.29 (s, CH_2 (b)), 57.17 (t, J_{CP} 4 Hz, CH_2 (a)), 55.70 (t, J_{CP} 4 Hz, CH_2 (b)), 33.08 (t, J_{CP} 14 Hz, (CH$_3$)$_2$C*H*), 32.10 (t, J_{CP} 18 Hz, (CH$_3$)$_2$C*H*), 18.23 (t, J_{CP} 1 Hz, (CH_3)$_2$CH (a)), 17.47 (t, J_{CP} 5 Hz, (CH_3)$_2$CH (b)) 17.09 (t, J_{CP} 4 Hz, (CH_3)$_2$CH (a)), 16.87 (t, J_{CP} 3 Hz, (CH_3)$_2$CH (a)). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, δ ppm) −133.13 (bd, *o*-F), −163.60 (t, $^3J_{FF}$ 21 Hz, *p*-F), −167.50 (bt, $^3J_{FF}$ 18 Hz, *m*-F). $^{31}P\{^1H\}$ (CD_2Cl_2, δ ppm) 166.34 (s, $PiPr_2$ (b)), 162.35 (s, $PiPr_2$ (a)). IR stretching Frequency CO; 2055 cm^{-1}, 2001 cm^{-1}. EA: $C_{42}H_{38}O_4P_2NRuBF_{20}$: Calc'd: C, 42.92; H, 3.26; N, 1.19; Found C, 42.67; H, 3.25; N, 1.12.

Synthesis of [RuH(S((CH$_2$)$_2$OPiPr$_2$)$_2$)(py)CO][B(C$_6$F$_5$)$_4$] (14). A red solution of **12** in THF (100 mg, 0.082 mmol; 4 mL) was prepared in a 25 mL bomb. The solution was degassed using three freeze–pump–thaw cycles and was charged with 1 atm of CO. The solution fades from red to pale yellow over 12 h at which point the solvent was removed giving an off white solid. The sample was re-dissolved in CH_2Cl_2 and pentane was layered on top of the pale yellow solution. The product was obtained as colorless crystals in 83% yield (85 mg, 0.068 mmol). ^1H NMR (CD_2Cl_2, δ ppm)) 8.80 (bs, 1H, Ar-H Py), 8.77 (b, 1H, Ar-H Py), 8.64 (d, 1H, $^3J_{HH}$ 5 Hz, Ar-H Py) 7.73 (t, 1H, $^3J_{HH}$ 8 Hz, Ar-H Py), 7.21 (b, 2H, Ar-H Py), 4.34 (m, 4H, CH_2), 2.65 (m, 2H, (CH$_3$)$_2$C*H*), 2.51 (m, 4H, CH_2), 1.25 (m, 20H, (CH$_3$)$_2$C*H* and (CH_3)$_2$CH), 0.93 (m, 6H, (CH_3)$_2$CH), −4.26 (t, 1H, $^2J_{HP}$ 22 Hz, Ru–H). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, δ ppm) −16.6 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 202.16 (m, CO), 160.21 (b, Ar-C, Py), 157.60 (b, Ar-C, Py), 148.79 (dm, $^1J_{CF}$ 237 Hz, *o*-C_6F_5), 138.84 (dm, $^1J_{CF}$ 244 Hz, *p*-C_6F_5), 138.62 (s, Ar-C, Py), 136.87 (dm, $^1J_{CF}$ 240 Hz, *m*-C_6F_5), 126.71 (b, Ar-C, Py), 126.34 (b, Ar-C, Py), 66.98 (b, CH_2), 38.32 (b, CH_2), 31.42 (b, (CH$_3$)$_2$C*H*), 18.16 (b, (C*H*$_3$) $_2$CH), 16.72 (b, (CH_3)$_2$CH). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, δ ppm) −133.09 (bd, *o*-F), −163.66 (t, $^3J_{FF}$ 21 Hz, *p*-F), −167.53 (bt, $^3J_{FF}$ 18 Hz, *m*-F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 165.86 (bs, $PiPr_2$). IR (CO); 1953 cm^{-1}. EA: $C_{46}H_{42}O_3P_2SRuF_{20}NB{\cdot}2CH_2Cl_2$: Calc'd: C, 40.79; H, 3.28; N, 0.99; Found C, 41.05; H, 2.72; N, 0.81.

Synthesis of RuH(NH((CH$_2$)$_2$OPiPr$_2$)$_2$)(CO)Cl (15). A solution of **1** and CH_2Cl_2 (89 mg, 0.262 mmol; 4 mL) was added to a gray suspension of $RuH(PPh_3)_3(CO)Cl$ in CH_2Cl_2 (250 mg, 0.262 mmol; 4 mL) giving no immediate change. After approximately five minutes a very pale yellow solution was obtained. The reaction mixture was stirred for 12 h at which point the mostly colourless, clear solution was dried. The white solid was washed with hexane (3 × 5 mL) and the remaining volatiles were removed *in vacuo*. The white product was obtained in 88% yield (116 mg, 0.230 mmol). ^1H NMR (CD_2Cl_2, δ ppm)) 4.16 (m, 2H, CH_2), 4.01 (m, 2H, CH_2), 3.46 (bs, 1H, NH), 2.74 (m, 6H, CH_2, C*H*(CH$_3$)$_2$), 2.19 (m, 2H, CH_2), 1.36 (m, 12H, $^3J_{HH}$ 7 Hz, CH(CH_3)$_2$), 1.24 (m, 6H, $^3J_{HH}$ 7 Hz, CH(CH_3)$_2$), 1.11 (m, 6H, $^3J_{HH}$ 7 Hz, CH(CH_3)$_2$), −14.68 (t, 1H, $^3J_{HP}$ 22 Hz, Ru–H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 205.38 (t, $^2J_{CP}$ 16 Hz, CO), 66.51 (s, CH_2), 57.22 (t, J_{CP} 4 Hz, CH_2), 31.65 (t, J_{CP} 10 Hz, *C*H(CH$_3$)$_2$), 30.27 (t, J_{CP} 18 Hz, *C*H(CH$_3$)$_2$), 18.27 (s, CH(*C*H$_3$)$_2$), 17.79 (t, J_{CP} 3 Hz, CH(*C*H$_3$)$_2$), 17.41 (s, CH(*C*H$_3$)$_2$), 16.84 (s, CH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 160.98 (s, OP(CH(CH$_3$)$_2$)$_2$). IR (CO); 1930 cm^{-1}. EA: $C_{17}H_{38}O_3P_2NRuCl$: Calc'd: C, 40.58; H, 7.62; N, 2.79; Found C, 41.02; H, 7.61; N, 2.77. **14**: *C*2/*c*, a = 18.4105(7) Å, b = 20.4109(8) Å, c = 15.1460(6) Å, α = 90°, β = 126.075(1)°, γ = 90°, V = 4600.1(3) Å^3, Z = 8, data (>2σ) = 4698, variables = 230, R(>2σ) = 0.0198, R(all) = 0.0489, GOF = 1.023.

Synthesis of [RuH(S((CH$_2$)$_2$OPiPr$_2$)$_2$)(py)CO][Cl] (16). A sample of **7** was dissolved in CH_2Cl_2 (100 mg, 0.187 mmol; 5 mL) and transferred to a 50 mL tube bomb. The yellow solution was degassed using three the freeze–pump–thaw cycles. The solution was thawed and 1 atm of CO was added immediately giving a pale yellow solution. The mixture was stirred under CO for 12 h at which point the very pale yellow solution was concentrated and pentane was layered on top of the CH_2Cl_2 solution. The product was obtained as white crystals in 79% yield (89 mg, 0.148 mmol). ^1H NMR (CD_2Cl_2, δ ppm)) 8.70 (bs, 1H, Ar-H Py), 8.65 (d, 1H, $^3J_{HH}$ 5 Hz, Ar-H Py), 7.85 (bt, 1H, $^3J_{HH}$ 8 Hz, Ar-H Py), 7.28 (bs, 2H, Ar-H Py), 4.39 (m, 4H, CH_2), 2.73 (m, 4H, CH_2), 2.42 (m, 2H, CH_2), 1.43 (m, 2H, (CH$_3$)$_2$C*H*), 1.26 (m, 18H, (CH_3)$_2$CH), 0.94 (m, 6H, (CH_3)$_2$CH), −4.25 (t, 1H, $^2J_{HP}$ 21 Hz, Ru–H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 202.41 (bm, CO), 159.99 (b, Ar-C, Py), 157.34 (b, Ar-C, Py), 138.66 (s, Ar-C, Py), 126.39 (b, Ar-C, Py), 67.55 (b, CH_2), 38.02 (b, CH_2), 31.40 (b, (CH$_3$)$_2$C*H*), 16.71 (b, (C*H*$_3$)$_2$CH), 15.48 (b, (C*H*$_3$)$_2$CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ ppm) 165.05 (s). IR (CO); 1966 cm^{-1}. EA: $C_{22}H_{42}O_3P_2SRuClN{\cdot}0.5CH_2Cl_2$: Calc'd: C, 42.11; H, 6.76; N, 2.18; Found C, 41.64; H, 6.31; N, 2.13.

Synthesis of [RuH(S((CH$_2$)$_2$OPiPr$_2$)$_2$)(py)CO][PF$_6$] (17). A pale yellow solution of **16** in CH_2Cl_2 (50 mg, 0.084 mmol;

4 mL) was prepared in a 4 dram vial and was wrapped in Al-foil. Solid $AgPF_6$ (21 mg, 0.084 mmol) was added to the stirring solution immediately giving a cloudy gray mixture. The reaction was stirred for 12 h at which point it was filtered through Celite to a pale yellow solution and dried. The sample was re-dissolved in CH_2Cl_2 and pentane was layered on top of the pale yellow solution. The product was obtained as colorless crystals in 87% yield (52 mg, 0.073 mmol). ^{1}H NMR (CD_2Cl_2, δ ppm) 8.80 (bs, 1H, Ar-H Py), 8.70 (d, 1H, $^3J_{HH}$ 5 Hz, Ar-H Py), 7.83 (bt, 1H, $^3J_{HH}$ 8 Hz, Ar-H Py), 7.29 (bs, 2H, Ar-H Py), 4.42 (m, 4H, CH_2), 2.63 (m, 4H, CH_2), 2.41 (m, 2H, CH_2), 1.29 (m, 20H, $(CH_3)_2CH$ and $(CH_3)_2CH$), 0.99 (m, 6H, $(CH_3)_2CH$), −4.20 (t, 1H, $^2J_{HP}$ 21.0 Hz, Ru–H). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 160.00 (b, Ar-C, Py), 157.38 (b, Ar-C, Py), 138.54 (s, Ar-C, Py), 126.34 (b, Ar-C, Py), 67.06 (b, CH_2), 38.07 (b, CH_2), 31.02 (b, $(CH_3)_2CH$), 16.56 (b, $(CH_3)_2CH$), 15.79 (b, $(CH_3)_2CH$). Could not locate CO by ^{13}C. ^{19}F{^{1}H} NMR (CD_2Cl_2, δ ppm) −74.37 (d, $^1J_{FP}$ 710 Hz, PF_6). ^{31}P{^{1}H} (CD_2Cl_2, δ ppm) 165.72 (bs, $PiPr_2$), −144.50 (sept, $^1J_{PF}$ 710 Hz, PF_6). IR (CO); 1975 cm^{-1}. EA: $C_{22}H_{42}O_3P_3SRuF_6N$: Calc'd: C, 37.27; H, 5.98; N, 1.98; Found C, 36.73; H, 5.78; N, 1.92. **16**: $P\bar{1}$, a = 8.830(2) Å, b = 13.451(2) Å, c = 15.359(2) Å, α = 81.154(7)°, β = 74.718(7)°, γ = 74.475(7)°, V = 1688.7(5) Å^3, Z = 2, data (>2σ) = 4520, variables = 361, R(>2σ) = 0.0896, R(all) = 0.2672, GOF = 1.047.

Synthesis of $RuH(NH((CH_2)_2OPiPr_2)_2)(H_2)Cl$ (18). A sample of **6** was dissolved in CD_2Cl_2 and transferred to a J-Young NMR tube. The yellow solution was degassed using three freeze–pump–thaw cycles. The solution was frozen once more in liquid nitrogen and H_2 was added. The solution quickly changes from yellow to colorless once thawed and the product is observed in quantitative yield by NMR. ^{1}H NMR (CD_2Cl_2, δ ppm)) 4.12 (m, 2H, $^3J_{HH}$ 7 Hz, CH_2), 3.99 (m, 2H, $^3J_{HH}$ 7 Hz, CH_2), 3.58 (m, 1H, NH), 2.97 (m, 4H, CH_2), 2.58 (sept, 2H, $^3J_{HH}$ 7 Hz, C$H(CH_3)_2$), 1.93 (sept, 2H, $^3J_{HH}$ 7 Hz, C$H(CH_3)_2$), 1.27 (m, 6H, $^3J_{HH}$ 7 Hz, CH(CH_3)$_2$), 1.15 (m, 6H, $^3J_{HH}$ 7 Hz, CH(CH_3)$_2$), 1.09 (m, 6H, $^3J_{HH}$ 7 Hz, CH(CH_3)$_2$), 0.90 (m, 6H, $^3J_{HH}$ 7 Hz, CH(CH_3)$_2$), −12.52 (t, 3H, $^3J_{HP}$ 17 Hz, Ru–H(H_2)). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 65.93 (s, CH_2), 59.11 (t, J_{CP} 3.05 Hz, CH_2), 29.58 (t, J_{CP} 9.16 Hz, C$H(CH_3)_2$), 28.06 (t, J_{CP} 17 Hz, C$H(CH_3)_2$), 18.88 (s, CH(CH_3)$_2$), 18.50 (bs, CH(CH_3)$_2$), 17.86 (t, J_{CP} 5 Hz, CH(CH_3)$_2$), 16.03 (s, CH(CH_3)$_2$). [Free PPh_3 also observed]. ^{31}P{^{1}H} NMR (CD_2Cl_2, δ ppm) 173.51 (s, OP(CH(CH_3)$_2$)$_2$). If the sample is heated or allowed to stand for extended periods of time decomposition to **3** is observed.

Synthesis of $[RuH(E((CH_2)_2OPiPr_2)_2)(L)(H_2)][B(C_6F_5)_4]$ E = NH, L = PPh_3 (19), E = S, L = py (20). The preparations of **19** and **20** were completed in a similar fashion thus only the preparation of one of them is described. **19**: A sample of **10** was dissolved in CD_2Cl_2 and transferred to a J-Young NMR tube. The orange solution was degassed 3 times using the freeze–pump–thaw method. The solution was frozen once more in liquid nitrogen and H_2 was added. The solution quickly changes from orange to a very pale yellow once thawed and the product is observed in quantitative yield by NMR spectroscopy. **19**: ^{1}H NMR (CD_2Cl_2, δ ppm) 7.52 (m, 15H, Ar-H PPh_3), 4.26 (m, 2H, CH_2), 4.06 (m, 2H, CH_2), 3.89 (bs, 1H, NH), 3.01 (m, 2H, CH_2), 2.88 (m, 2H, CH_2), 2.32 (m, 2H, C$H(CH_3)_2$), 1.57 (m, 2H, C$H(CH_3)_2$), 1.30 (m, 6H, CH(CH_3)$_2$), 1.08 (m, 6H, CH(CH_3)$_2$), 0.99 (m, 6H, CH(CH_3)$_2$), 0.56 (m, 6H, $^3J_{HH}$ 7 Hz, CH(CH_3)$_2$), −12.10 (bm, 3H, Ru–H and Ru–H_2). ^{11}B{^{1}H} NMR (CD_2Cl_2, δ ppm) −16.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 148.16 (dm, $^1J_{CF}$ 238.13 Hz, o-C_6F_5), 138.24 (dm, $^1J_{CF}$ 248 Hz, p-C_6F_5), 136.30 (dm, $^1J_{CF}$ 248 Hz, m-C_6F_5), 133.36 (b, Ar-C PPh_3), 130.92 (b, Ar-C PPh_3), 129.22 (b, Ar-C PPh_3), 66.12 (bm, CH_2), 59.04 (bm, CH_2), 33.71 (bm, C$H(CH_3)_2$), 30.60 (bm, C$H(CH_3)_2$), 19.69 (bm, CH(CH_3)$_2$), 18.48 (bm, CH(CH_3)$_2$), 17.65 (bm, CH(CH_3)$_2$), 17.07 (bm, CH(CH_3)$_2$), 16.12 (bm, CH(CH_3)$_2$). ^{19}F{^{1}H} NMR (CD_2Cl_2, δ ppm) −133.09 (bs, o-F), 163.72 (t, $^3J_{FF}$ 21 Hz, p-F), −167.57 (bt, $^3J_{FF}$ 17 Hz, m-F). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ ppm) 162.13 (m, OP(CH$(CH_3)_2)_2$), 36.49 (m, PPh_3).

20: The solution quickly changes from red to a very pale orange once thawed and the product is observed in quantitative yield by NMR. ^{1}H NMR (CD_2Cl_2, δ ppm) 8.93 (d, 2H, $^3J_{HH}$ 6 Hz, o-Ar-H Py), 7.86 (t, 1H, $^3J_{HH}$ 6 Hz, p-Ar-H Py), 7.37 (d, 2H, $^3J_{HH}$ 6 Hz, m-Ar-H Py), 4.33 (m, 2H, $^3J_{HH}$ 6 Hz, CH_2), 4.27 (m, 2H, $^3J_{HH}$ 6 Hz, CH_2), 3.03 (m, 2H, $^3J_{HH}$ 6 Hz, CH_2), 2.68 (m, 2H, $^3J_{HH}$ 6 Hz, CH_2), 2.13 (m, 2H, $^3J_{HH}$ 6 Hz, C$H(CH_3)_2$), 1.74 (m, 2H, $^3J_{HH}$ 6.1 Hz, C$H(CH_3)_2$), 1.13 (m, 6H, $^3J_{HH}$ 6 Hz, CH(CH_3)$_2$), 1.05 (m, 6H, $^3J_{HH}$ 6 Hz, CH(CH_3)$_2$), 0.77 (m, 6H, $^3J_{HH}$ 6 Hz, CH(CH_3)$_2$), 0.67 (m, 6H, $^3J_{HH}$ 6 Hz, CH(CH_3)$_2$), −11.31 (t, 3H, $^2J_{HP}$ 12 Hz, Ru–H). ^{11}B{^{1}H} NMR (CD_2Cl_2, δ ppm) −15.0 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ ppm) 156.26 (bs, Ar-C Py), 148.63 (dm, $^1J_{CF}$ 244 Hz, o-C_6F_5), 138.66 (dm, $^1J_{CF}$ 250 Hz, p-C_6F_5), 138.65 (s, Ar-C Py), 136.86 (dm, $^1J_{CF}$ 253 Hz, m-C_6F_5), 128.72 (s, Ar-C Py), 126.42 (s, Ar-C Py), 66.99 (s, CH_2), 38.96 (t, J_{CP} 3 Hz, CH_2), 30.20 (t, J_{CP} 17 Hz, C$H(CH_3)_2$), 29.96 (t, J_{CP} 11 Hz, C$H(CH_3)_2$), 18.54 (s, CH(CH_3)$_2$), 17.00 (t, J_{CP} 5 Hz, CH(CH_3)$_2$), 16.53 (s, CH(CH_3)$_2$), 15.74 (s, CH(CH_3)$_2$). ^{19}F{^{1}H} NMR (CD_2Cl_2, δ ppm) −133.17 (bs, o-F), 163.55 (t, $^3J_{FF}$ 21 Hz, p-F), −167.46 (bt, $^3J_{FF}$ 17 Hz, m-F). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ ppm) 169.87 (s, OP(CH$(CH_3)_2)_2$).

Procedure for catalytic dehydrogenation reactions

A sample of HMe_2NBH_3 (7.4 mg, 0.126 mmol) was weighed out in a 2 dram push top vial and 1 mL of C_6D_5Br was added. The solution was added to the appropriate amount of ruthenium complex in a two dram push top vial equipped with a magnetic stir bar and the reaction mixture stirred for 24 h in a N_2 glovebox. The reaction was transferred to a NMR tube and immediately frozen in Liq-N_2. The sample was thawed at the NMR spectrometer and ^{11}B NMR was used to monitor reaction progress. Analogous reactions were run in tandem and one of the samples was quenched with 0.5 mL of CH_3CN before freezing. The productivities obtained in either fashion were found to be in good agreement. For the reactions followed at varying intervals the mixture was transferred to a sealed J-Young NMR tube and frozen until the first NMR experiment was ready to be run.

X-ray crystallography

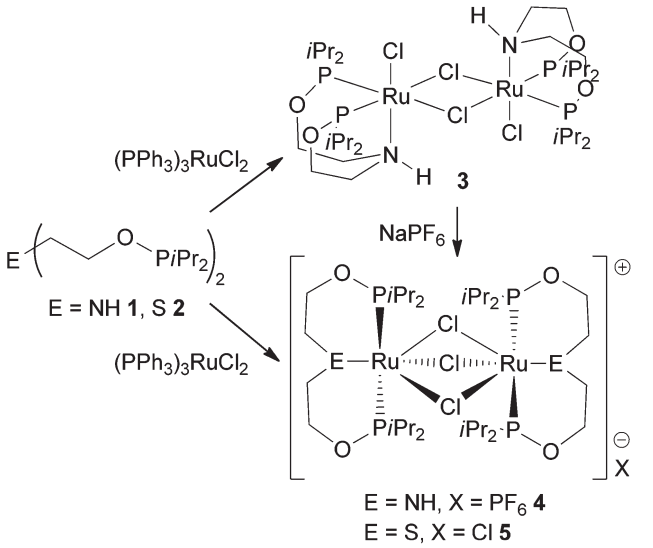
Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N_2

stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II and Bruker SMART diffractometers employing Mo Kα radiation (λ = 0.71073 Å). Data collection strategies were determined using Bruker Apex software and optimized to provide >99.5% complete data to a 2θ value of at least 55°. 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 multi-scan method (SADABS). Non-hydrogen atomic scattering factors were taken from the literature tabulations.[33] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. 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 $\omega(F_o - F_c)^2$ where the weight ω 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 are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C-atom to which they are 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.

Results and discussion

The tridentate ligands $HN(CH_2CH_2OPiPr_2)_2$ (**1**) and $S(CH_2CH_2OPiPr_2)_2$ (**2**) are readily prepared in high yields from the reaction of $ClPiPr_2$ with a mixture of the corresponding diol and triethylamine in THF.[28] Following work-up, the ligands can be used without further purification. Reaction of a solution of **1** in CH_2Cl_2 with $Ru(PPh_3)_3Cl_2$ yielded a yellow suspension. The product (**3**) was insoluble and could not be characterized by NMR spectroscopy at room temperature. However, slow cooling of a hot suspension of the solid in CH_2Cl_2 afforded single crystals of **3**. The solid state structure revealed that **3** is the dimer $[Ru(NH(CH_2CH_2OPiPr_2)_2)Cl(\mu\text{-}Cl)]_2$ comprised of two equivalent Ru centers bridged by two chloride atoms (Scheme 2, Fig. 1). Of the four remaining coordination sites, three are filled by the ligand **1** in a facial coordination mode and one is occupied by a terminal chloride. The most notable feature of the molecule is the close contact of 2.52(1) Å between the terminal Cl and the NH proton of the adjacent Ru. This lies within the sum of the van der Waals radii of the atoms and suggests Cl···HN hydrogen bonding.

Addition of $NaPF_6$ to a suspension of **3** in CH_2Cl_2 allowed for the isolation of $[(Ru(NH(CH_2CH_2OPiPr_2)_2))_2(\mu\text{-}Cl)_3][PF_6]$ **4**



Scheme 2 Synthesis of **3–5**.

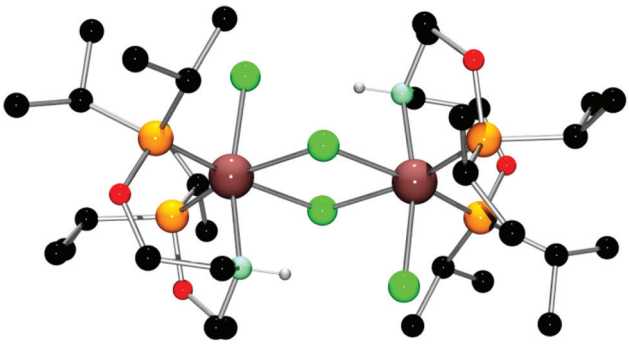


Fig. 1 POV-ray depiction of the molecular structure of **3**. C: black, O: red, P: orange, N: aquamarine, Cl: green, H: gray, Ru: salmon; all H-atoms except the NH are omitted for clarity.

as a yellow solid in 86% yield (Scheme 2). The $^{31}P\{^1H\}$ spectrum shows two doublets at 177.6 ppm and 171.5 ppm with a coupling constant of 37 Hz suggesting two inequivalent phosphorus environments with a *cis* disposition. The ^1H NMR spectrum was consistent with an asymmetric ligand environment as each methylene group of the ethyl linkers are inequivalent. Similarly, the methine resonances of the iso-propyl groups are inequivalent. Single crystals of **4** were analyzed by X-ray diffraction revealing a C_2 symmetric dimeric structure similar to **3** but with three chlorine atoms bridging the two metal centres (Fig. 2). The overall charge of the bimetallic cation is balanced by a PF_6 counter-ion.

The analogous combination of **2** and $(PPh_3)_3RuCl_2$ in CH_2Cl_2 gives the orange solid $[(RuS(CH_2CH_2OPiPr_2)_2))_2(\mu\text{-}Cl)_3][Cl]$ (**5**) in 85% yield (Scheme 2). The $^{31}P\{^1H\}$ and ^1H NMR spectra are similar to those observed for **4** with the most notable features being the two doublets centred at 167.8 ppm and 166.1 ppm with a coupling constant of 34 Hz in the $^{31}P\{^1H\}$ NMR spectrum. These data are consistent with the formulation of **5** as the *S* analogue of **4**.

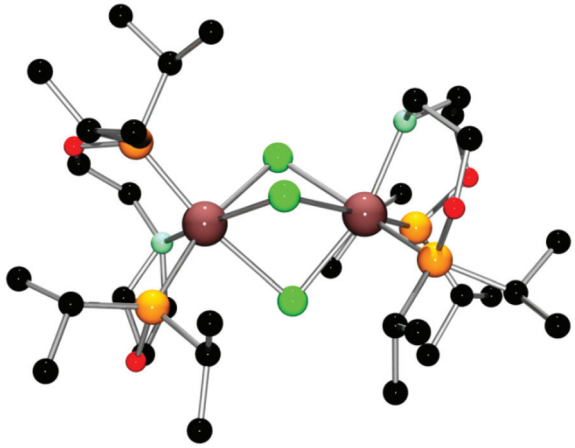
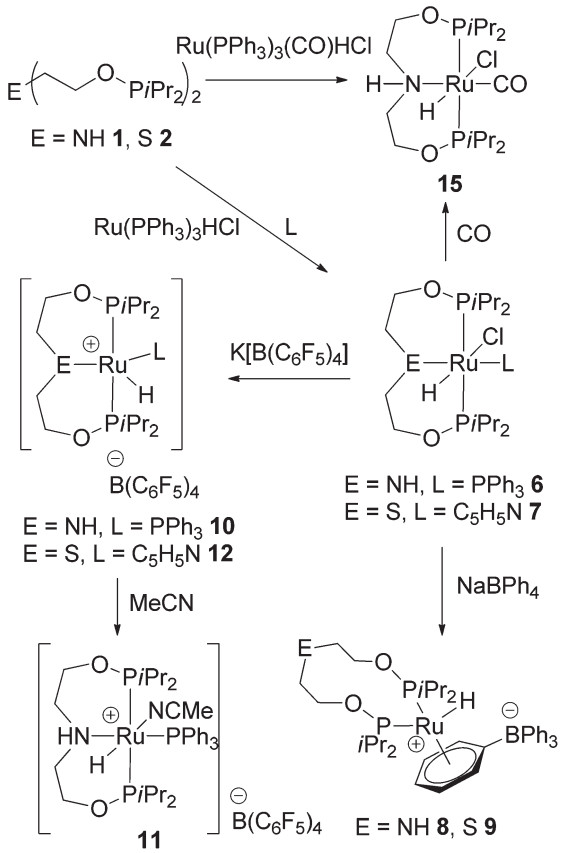


Fig. 2 POV-ray depiction of the molecular structure of the cation of **4**. C: black, O: red, P: orange, N: aquamarine, Cl: green, H: gray, Ru: salmon; hydrogen atoms are omitted for clarity.

The combination of a solution of **1** with a purple suspension of $Ru(PPh_3)_3HCl$ in CH_2Cl_2 affords the yellow solid $Ru(NH(CH_2CH_2OPiPr_2)_2)(PPh_3)HCl$ **6** in 82% yield (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **6** shows a doublet at 164.7 ppm and a triplet at 60.3 ppm, in a 2 : 1 ratio, with a coupling constant of 28 Hz, consistent with the presence of three phosphine donors in two inequivalent environments. The ^1H NMR spectrum contains a pseudo quartet (a doublet of triplets) centred at −17.5 ppm, four resonances arising from inequivalent geminal protons of the ethyl linkers, two signals for the methine protons and four signals for the methyl protons of the iso-propyl groups. In addition, the ^1H resonance for the NH proton was observed at 4.00 ppm while aryl protons were observed at 8.02 and 7.27 ppm consistent with the presence of PPh_3. A single crystal X-ray study of **6** confirmed coordination of **1** to Ru in a meridional fashion, with a hydride occupying the position *trans* to a chloride and a PPh_3 completing the coordination sphere, *trans* to the central NH (Fig. 3). The Ru–H and Ru–Cl distances were found to 1.56(3) Å and 2.5785(8) Å, respectively while the Ru–N distance of 2.234(2) Å, lies in the range expected for PNP systems.[34,35] The iso-propyl groups of the phosphines are sterically crowded by the PPh_3 ligand resulting in a P–Ru–P bite angle of 159.08(3)°. Additionally, the proton from the central NH is located on the same side of the molecule as the chloride group with a Cl···HN distance of 2.93(1) Å, just within the sum of the van der Waals radii indicating the possibility of a weak hydrogen bonding interaction locking the molecule in one conformation.

The corresponding reaction of **2** with $Ru(PPh_3)_3HCl$ afforded a complex mixture of products. However, addition of pyridine to the mixture gave $Ru(S(CH_2CH_2OPiPr_2)_2)(py)HCl$ (**7**) in 84% yield (Scheme 3). This species gave rise to a $^{31}P\{^1H\}$ NMR signal at 159.2 ppm and a ^1H resonance at −20.6 ppm. An additional feature of the ^1H NMR spectrum is a set of five resonances each integrating to one proton from 6.80–10.12 ppm characteristic of coordinated pyridine. Results from single crystal X-ray diffraction of **7** yielded a molecular



Scheme 3 Synthesis of **6–13** and **15**.

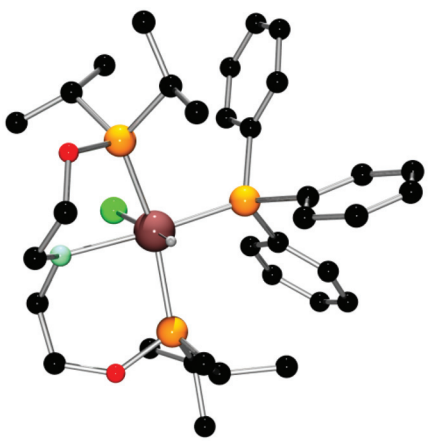


Fig. 3 POV-ray depiction of the molecular structure of **6**. C: black, O: red, P: orange, N: aquamarine, Cl: green, H: gray, Ru: salmon; hydrogen atoms except the Ru–H are omitted for clarity. Ru–$PiPr_2$ distances: 2.3595(9) Å, 2.3526(9) Å; Ru–PPh_3 distance: 2.2838(8) Å.

structure very similar to **6** where PPh_3 has been replaced by pyridine (Fig. 4). The Ru–H distance (1.49(3) Å) is shorter than in **6**. In contrast, the Ru–Cl distance of 2.5979(7) Å is slightly longer than in **6**. The most notable feature of **7** is the P–Ru–P bite angle is 164.30(3)°. The larger bite angle in **7** compared to **6** may result from the larger central donor S in combination with the smaller pyridine ligand.

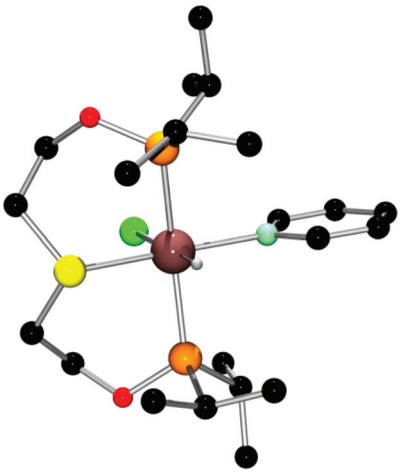


Fig. 4 POV-ray depiction of the molecular structure of **7**. C: black, O: red, P: orange, S: yellow, N: aquamarine, Cl: green, Ru: salmon; hydrogen atoms except the Ru–H are omitted for clarity. The Ru–P distances: 2.3098(5) Å, 2.3099(5) Å.

The addition of $NaBPh_4$ to a solution of **6** in THF gave rise to a white solid, **8** (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **8** shows a single resonance at 174.6 ppm consistent with the loss of PPh_3, while the $^{11}B\{^1H\}$ spectrum shows a upfield shifted singlet at −8.2 ppm arising from the BPh_4 counter-ion. The ^1H NMR spectrum shows a triplet hydride resonance at −10.2 ppm, downfield with respect to that of **6**, and 15 aromatic protons between 6.96 ppm and 7.42 ppm as well as three new signals at 5.83 ppm, 5.76 ppm and 5.52 ppm. A single crystal X-ray diffraction study confirmed the formulation of **8** as $RuH(HN(CH_2CH_2OPiPr_2)_2)(\eta^6\text{-}C_6H_5BPh_3)$. **8** has a zwitterionic piano-stool-type geometry with a cationic Ru centre coordinated to the two P centers of the ligand (**1**), a hydride and an η^6-bound phenyl ring of the BPh_4 anion (Fig. 5). The Ru–C bond distances range from 2.245(2) Å to 2.430(2) Å and are in accord with other examples of Ru complexes with η^6-bound BPh_4.[36] The Ru–H distance (1.55(2) Å) remains essentially unchanged relative to **6**.

The analogous reaction of **7** with $NaBPh_4$ proceeds in a similar manner to give white blocks of $[RuH(S(CH_2CH_2O\text{-}PiPr_2)_2)(\eta^6\text{-}C_6H_5BPh_3)]$ (**9**) in 53% yield (Scheme 3). Similar to

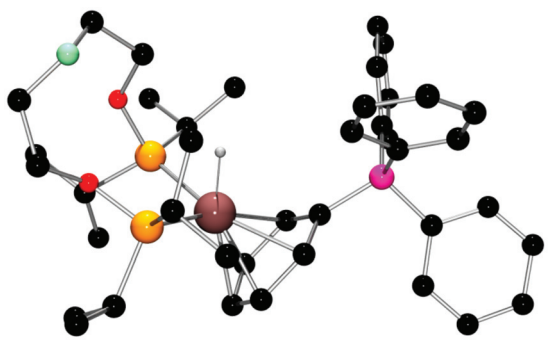


Fig. 5 POV-ray depiction of the molecular structure of **8**. C: black, O: red, P: orange, N: aquamarine, H: gray, B: pink, Ru: salmon; hydrogen atoms except the Ru–H are omitted for clarity. The Ru–P distances: 2.2670(5) Å, 2.3037(5) Å.

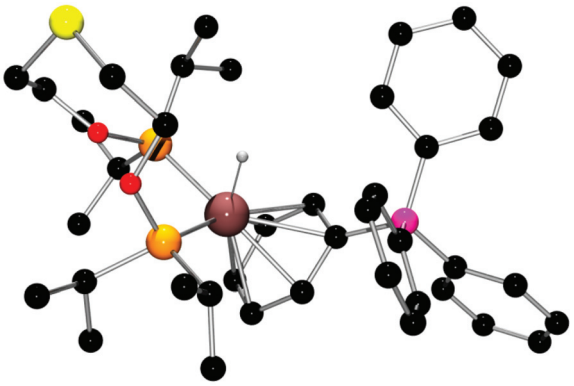


Fig. 6 POV-ray depiction of the molecular structure of **9**. C: black, O: red, P: orange, S: yellow, H: gray, B: Pink, Ru: light-blue; hydrogen atoms except the Ru–H are omitted for clarity. Ru–P distances: 2.2656(7) Å, 2.2939(7) Å.

8, a single resonance is observed in the in the $^{31}P\{^1H\}$ NMR spectrum at 174.9 ppm while the $^{11}B\{^1H\}$ NMR shows a singlet at −8.3 ppm. Additionally, the ^1H spectrum shows resonances at 5.81 ppm and 5.54 ppm indicative of an η^6-arene bound to Ru, and a corresponding triplet at −10.3 ppm for the hydride. The formulation of **9** was confirmed using single crystal X-ray diffraction (Fig. 6). The metrics within **9** were similar to those in **8** with the Ru–C distances ranging from 2.255(2) Å to 2.362(2) Å, and a Ru–H distance of 1.59(3) Å.

The corresponding reaction of **6** with $K[B(C_6F_5)_4]$ was carried out and yielded an orange solid $[RuH(HN(CH_2CH_2O\text{-}PiPr_2)_2)(PPh_3)][B(C_6F_5)_4]$ (**10**) (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **10** exhibited two sets of resonances attributable to two isomers present in a 70 : 30 ratio. The more abundant isomer consisted of resonances at 184.2 ppm and 43.4 ppm in a 2 : 1 ratio, while the minor product showed similar peaks at 173.0 ppm and 55.9 ppm. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra all revealed resonances consistent with the presence of two isomers, but surprisingly only one hydride resonance, a doublet of triplets at −30.0 ppm, was observed. The two isomeric forms observed are thought to arise from differing conformations of the central NH relative to the position of the Ru–H. The presence of two isomers of **10** contrasts with **6** and may result from the absence of hydrogen bonding between the NH and chloride noted for **3** and **6**. While **10** was not characterized in the solid state, high resolution mass spectrometry was consistent with the above formulation of the cation. Furthermore, addition of MeCN to **10** afforded the species $[RuH(HN(CH_2CH_2OPiPr_2)_2)(PPh_3)(NCMe)][B(C_6F_5)_4]$ (**11**) as evidenced by $^{31}P\{^1H\}$ and ^1H NMR spectroscopic data which are similar to that of **10**. The most noteworthy changes in the NMR spectra are the new signal at 2.10 ppm in the ^1H NMR spectrum attributable to bound MeCN and the large downfield shift from −30.0 ppm to −14.4 ppm for the hydride. The latter shift is consistent with the change from a vacant site *trans* to the H^- to one that is occupied by MeCN. The molecular structure of **11** was confirmed using X-ray crystallography (Fig. 7). The bond distances for the coordinated ligands distances are similar to those in **6**. Thus, despite the cationic nature of **10**,

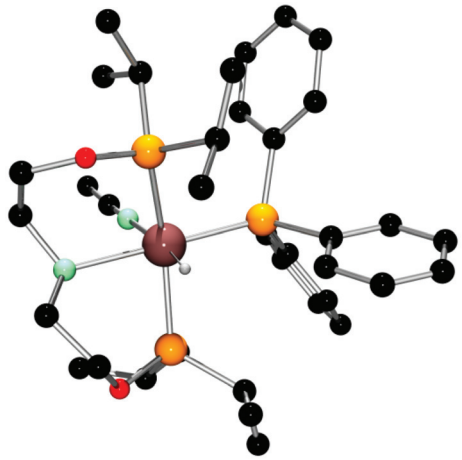


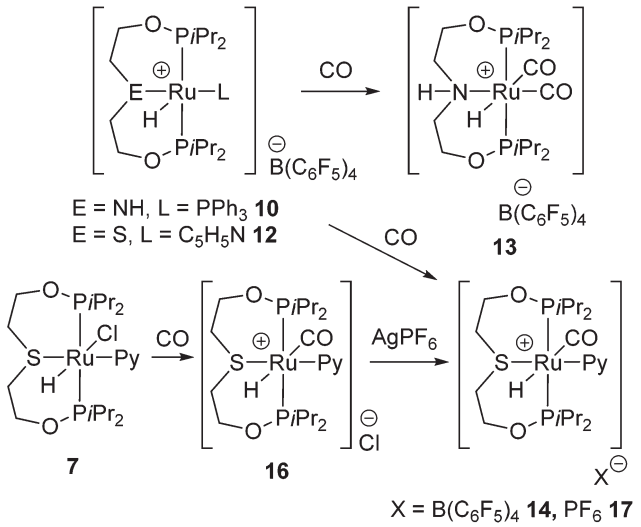
Fig. 7 POV-ray depiction of the molecular structure of the cation of **11**. C: black, O: red, P: orange, N: aquamarine, H: gray, Ru: salmon; hydrogen atoms except the Ru–H are omitted for clarity. Ru–$PiPr_2$ distances: 2.3297(9) Å, 2.355(1) Å, Ru–PPh_3 2.302(1) Å.

the metrical parameters are essentially unchanged likely a result of the sterics preventing stronger Ru–P bond formation. The Ru–N for the PNP ligand was found to be 2.240(3) Å while the MeCN donor gives rise to a Ru–N of 2.131(3) Å while the P–Ru–P bite angle is 156.46(4)°.

Reactivity with CO

Compound **10** reacts with 1 atm of CO resulting in a slow colour change from orange to pale yellow. *In situ* NMR experiments show three peaks in the $^{31}P\{^1H\}$ spectrum, two singlets at 166.3 ppm and 162.4 ppm in a 4 : 1 ratio, and one at −4.0 ppm, consistent with the liberation of PPh_3. The ^1H NMR spectrum displays two triplets in the hydride region at −5.4 ppm and −5.7 ppm in the same 4 : 1 ratio observed in the $^{31}P\{^1H\}$ NMR spectrum. These data infer the formation of two isomeric complexes related by inversion at nitrogen. Following work-up, a white solid **13** is obtained in 87% yield. The downfield shift compared to **10** is an indication of the coordination of a ligand *trans* to the hydride, with the chemical shift suggesting the *trans* ligand is CO. The IR spectrum of **13** which displays two equal intensity signals at 2055 and 2001 cm^{-1}, indicating inequivalent carbonyl ligands, suggests the formulation of **13** as $[RuH(HN(CH_2CH_2OPiPr_2)_2)(CO)_2][B(C_6F_5)_4]$ (Scheme 4). While single crystals of **13** were obtained, hydride-carbonyl disorder precluded a satisfactory refinement (see ESI†).

The corresponding reaction between **12** and CO undergoes a similar colour change over 12 h. Following work-up, compound **14** can be obtained in 83% yield. In this case, ^1H NMR data affirm that the bound pyridine is not displaced by CO, although the IR absorption at 1953 cm^{-1} demonstrates coordination of CO to the metal centre. The $^{31}P\{^1H\}$ NMR spectrum shows only a single singlet at 165.9 ppm indicating the two phosphines are bound in a symmetric manner, and the hydride signal in the ^1H NMR spectrum is seen at −4.3 ppm.



Scheme 4 Formation of the CO-complexes **13–17**.

These data support the formulation of **14** as $[RuH(S(CH_2CH_2O-PiPr_2)_2)(py)(CO)][B(C_6F_5)_4]$.

Compounds **6** and **7** also react with CO to yield the new species **15** and **16**. The $^{31}P\{^1H\}$ spectra show resonances at 161.0 and 165.1 ppm respectively. In the former case, liberated PPh_3 was also evidenced by the signal at −4 ppm. These products were isolated in 83 and 79% respectively. $^{13}C\{^1H\}$ NMR resonances at 205.4 and 202.4 ppm as well as IR absorptions at 1930 and 1965 cm^{-1} respectively are consistent with coordinated CO. The hydrides of **15** and **16** give rise to resonances at −14.7 and −4.3 ppm in ^1H NMR spectra. These data are consistent with the formulation of **15** as $RuH(HN-(CH_2CH_2OPiPr_2)_2)(CO)Cl$, where CO occupies the position *trans* to nitrogen, and **16** as $[RuH(S(CH_2CH_2OPiP_2)_2)(py)(CO)]Cl$, where CO is *trans* to the hydride (Scheme 4). Single crystal X-ray studies confirmed the formulation of **15** (Fig. 8). The Ru–P bond distances are shorter than those observed in **6** and

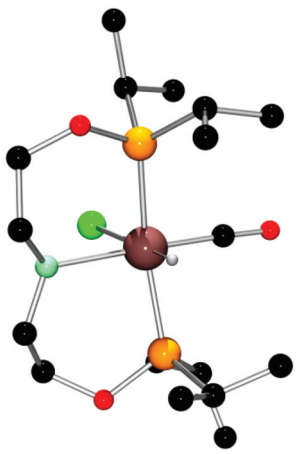


Fig. 8 POV-ray depiction of **15**; C: black, O: red, P: orange, N: aquamarine, Cl: green, H: gray, Ru: salmon; hydrogen atoms except the Ru–H are omitted for clarity. Ru–P distances: 2.3249(4) Å, 2.3282(4) Å.

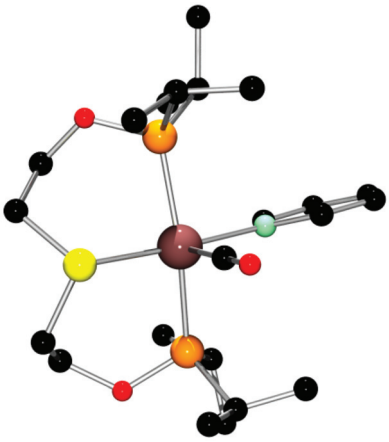


Fig. 9 POV-ray depiction of the cation of **17**; C: black, O: red, P: orange, S: yellow, N: aquamarine, hydrogen atoms are omitted for clarity. Ru–P distances: 2.359(2) Å, 2.360(2) Å.

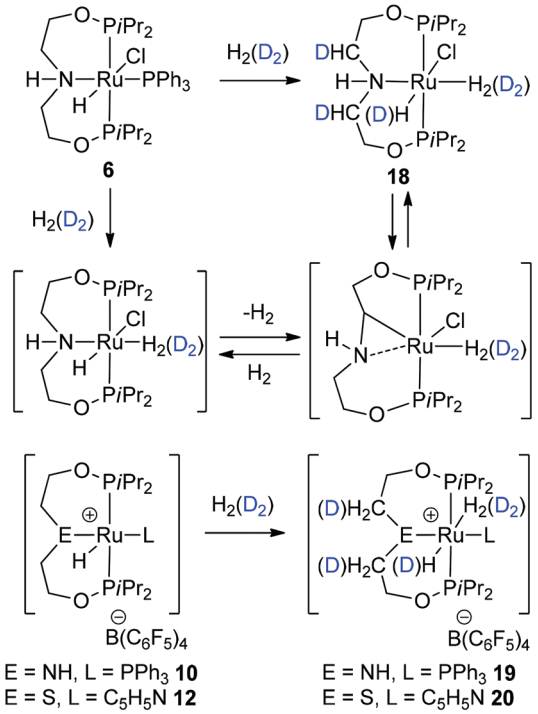
11 presumably a result of the presence of the π-accepting CO ligand. The corresponding P–Ru–P bite angle is increased to 166.82(2)° in comparison to **6**. The Ru–N distance of 2.218(1) Å is slightly longer than the analogous distance in **6** while the Ru–Cl distance in **15** is 2.5477(4) Å and the CO bond length is 1.154(2) Å.

Anion metathesis with $AgPF_6$ allowed the conversion of **16** to $[RuH(S(CH_2CH_2OPiPr_2)_2)(py)(CO)]PF_6$ **17** in 87% yield (Scheme 4). This species was crystallographically characterized (Fig. 9). In this case, the Ru–S distance is 2.360(3) Å and the CO bond length is 1.15(1) Å. The cationic species **15** and **17** are similar to Ru(PNP)(CO) complexes reported by Jia *et al.*[37]

The reactivity of **6** and **7** with CO differs in that PPh_3 is displaced from **6** whereas for **7** chloride is liberated and pyridine remains bound to the metal center. The presence of a weaker central donor in the tridentate ligand in **7** presumably combines with the diminished steric demands of pyridine to result in the retention of the pyridine ligand.

Reactivity with H_2/D_2

Exposure of **6** to 1 atm of H_2 results in the quantitative formation of $RuH(HN(CH_2CH_2OPiPr_2)_2)(H_2)Cl$ (**18**) (Scheme 5) as evidenced by the $^{31}P\{^1H\}$ spectrum which shows two singlets, one at 173.5 ppm and one at −4 ppm for free PPh_3. It is worth noting, that while the displacement of PPh_3 by H_2 has previously been observed in other systems, it is rare.[38–41] The ^1H NMR spectrum of **18** reveals a triplet at −12.5 ppm integrating to three protons. This suggests rapid exchange between the bound H_2 molecule and the hydride, an observation further supported by the analogous reaction with D_2 which resulted in deuterium incorporation into the hydride position. In addition, the selective incorporation of D into one of the geminal positions of the methylene groups adjacent to N was also observed (Fig. S3, ESI†). As hydride abstraction from the methylene groups adjacent N in related PNP systems[34] has been reported, as similar mechanism is proposed to account for the incorporation of deuterium into the corresponding site



Scheme 5 Reactions with H_2 or D_2.

in **18** (Scheme 5). The selective incorporation of deuterium at one of the methylene sites indicates that the reaction occurs from only one face of the molecule. It is also noted that deuterium is not incorporated into the NH group illustrating that the amine proton is not involved in the process. The H–D coupling constant of 5.4 Hz observed for **18** is relatively small and similar to values previously described for complexes in which dihydrogen ligands exchange with hydrides, suggesting the formation of isotopomers.[42] Using an analysis of these data described by Morris,[43] these data suggest a dihydrogen complex (see ESI†). While exchange precluded resolution of hydride and dihydrogen resonances even on cooling to −80 °C, T_1(min) measurements for **18** were carried out and showed T_1(min) of 86 ms at −60 °C on a 600 MHz spectrometer. While these data further affirm the hydride-dihydrogen nature of **18**, attempts to obtain an analytically pure sample were unsuccessful, presumably due to the facile loss of H_2 upon work-up.

Reaction of the cationic species **10** and **12** with H_2 proceed to give $[RuH(E(CH_2CH_2OPiPr_2)_2)(L)(H_2)][B(C_6F_5)_4]$ (E = NH, L = PPh_3 (**19**), E = S, L = py (**20**)) respectively (Scheme 5). The hydride resonance for **19** was observed at −12.1 ppm, consistent with coordination of a ligand *trans* to the hydride. A similar shift was observed in the ^1H NMR spectrum of **20** for the hydride resonance shifts to −11.3 ppm. The formation of the analogous species **19-d** and **20-d** from the reactions with D_2 showed deuterium incorporation in the ligand backbones similar to that described for **18** (Scheme 5). In the case of **20**, the H–D coupling experiments showed J_{HD} of 7.4 Hz suggesting a dihydrogen complex similar to that reported for

Table 1 TON of HMe_2NBH_3 to $[Me_2NBH_2]_2$ for Ru-catalysts **4–10**, **12**, **15** and **16** in 24 h

Catalyst	mol% Ru	TON
4	5	14
5	5	2
6	1	57
7	1	99
8	1	49
9	5	4
10	1	67
12	2.5	14
15	5	2
16	5	2

related POP complexes.[44] Although variable temperature NMR experiments for both **19** and **20** failed to resolve the dihydrogen and hydride signals, T_1(min) values of 44 ms (−35 °C) and 55 ms (−65 °C) were observed respectively, consistent with the dihydrogen complex formulations.

Reactivity with HMe_2NBH_3

The ruthenium complexes **4–12**, **15** and **16** were all shown to effect the dehydrogenation of HMe_2NBH_3 to $[Me_2NBH_2]_2$ in a fashion similar to that previously described for the complexes RuH($(C_5H_4PPh_2)_2$Fe)(ICy)Cl (ICy = $(CyN)_2C_3H_2$)[16] and RuH(N-$(CH_2CH_2PiPr_2)_2$)(PMe_3).[23,24] However, the catalytic competence of the present complexes was shown to vary dramatically (Table 1). To gain a better understanding of the differences in catalysis, the reactions of **6**, **8**, **10** and **12** with HMe_2NBH_3 were monitored using $^{31}P\{^1H\}$ NMR spectroscopy. In the cases of **6**, **10** and **12**, the spectra showed the formation of **18**, **19** and **20** respectively under catalytically relevant conditions. This suggests that these dihydrogen complexes are formed and are intermediates in the release of H_2 from the amine-borane.

Interestingly the consumption of HMe_2NBH_3 by **10** as followed by ^{11}B NMR spectroscopy was shown to yield the products of dehydrogenation including Me_2NBH_2, $[Me_2NBH_2]_2$ and $Me_2NBH_2NMe_2BH_3$ as evidenced by the known ^{11}B NMR signals, reported by Weller *et al.*[45] (Fig. 10). The consumption HMe_2NBH_3 is rapid at the beginning of the reaction and slows towards the end. Me_2NBH_2 is an intermediate that is formed and consumed while the species $HMe_2NBH_2NMe_2BH_3$ shows only very slow consumption over the course of 10 h in a sealed vessel, but is completely consumed in an open system. These results are analogous to those described in several other studies and suggest a similar mechanism of dehydrogenation in which $HMe_2NBH_2NMe_2BH_3$ is an intermediate en route to $[Me_2NBH_2]_2$.[24,46–50] The general trend in reactivity (Table 1) indicates that complexes containing NH as the central donor demonstrate greater activity than the *S*-substituted analogues. Interestingly even in the cases where the central donor was not coordinated (**8** and **9**), an amine-based ligand imparts greater reactivity. This suggests the possibility of participation of the NH fragment in the activation of HMe_2NBH_3. Nonetheless, this view is contradicted by the observation that **7** catalyzes the dehydrogenation more effectively than **6**.

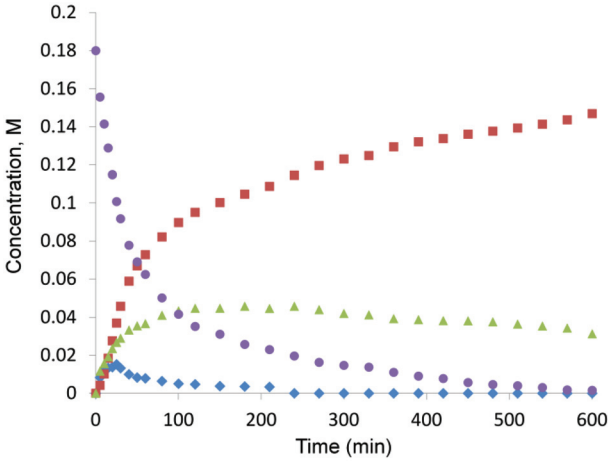


Fig. 10 Concentration–time plots for B-containing products of dehydrogenation using 2.5 mol% **10** and 0.18 M HMe_2NBH_3. Key: HMe_2NBH_3 (circles), Me_2NBH_2 (diamonds), $[Me_2NBH_2]_2$ (squares), $HMe_2NBH_2NMe_2BH_3$ (triangles).

Conclusions

A series of Ru complexes derived from tridentate bis-phosphinite ligands have been prepared and characterized. The reactivity of these species with CH_3CN, CO, H_2 and HMe_2NBH_3 has been described. The resulting Ru-carbonyl complexes and dihydrogen complexes have been characterized. These complexes are also shown to act as catalyst for the dehydrogenation of HMe_2NBH_3. Generally this reactivity demonstrates the subtle influences that steric demands of the donors and the electronic nature of the central donor can have on reactivity of these tridentate ligand complexes. The utility of these compounds as catalyst precursors for other processes of interest is continuing to be studied in our laboratories.

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