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Spectroscopic Investigation of the Reactivity of Cp*Ru(P^{i}Pr$_2$Ph)X toward H$_2$ and Silanes: Formation in Solution of Cp*Ru(P^{i}Pr$_2$Ph)(H)$_3$ and Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$Y (Y = Halide, OR, and SiR'$_3$)

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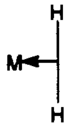
Reaction of Cp*RuLX (L = P^{i}Pr$_2$Ph; X = Br, I, OSiPh$_3$, NHPh, and OCH$_2$CF$_3$, called OR$_f$) with H$_2$ gives, at –60 °C, Cp*RuLX(H)$_2$, where the two hydride ligands are assigned cisoid positions using ^{1}H NMR spectra. These molecules (except X = Br and I) react with additional H$_2$ to give Cp*RuL(H)$_3$ and liberate HX. Mechanistic possibilities are discussed. Reaction of Cp*RuL(OR$_f$) with HSiR$_3$ (R = Me, Ph, OMe) gives Cp*RuL(H)$_2$SiR$_3$ and (R$_f$O)SiR$_3$. Reaction of Cp*RuL(OR$_f$) with H$_2$SiPh$_2$ gives the two products Cp*RuL(H)$_2$(SiXPh$_2$) (X = H and OR$_f$). Reversible equilibria make these species unstable toward isolation. Mechanistic studies are consistent with the presence of a common intermediate, for which H$_2$SiPh$_2$ and HSi(OR$_f$)Ph$_2$ compete.

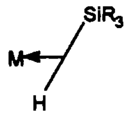
Introduction

We have studied compounds of the general form Cp*Ru(L)X (X = Br, I, OR$_f$, OSiPh$_3$, OSiMe$_2$Ph, NHPh; L = PPr$^i{}_2$Ph, PCy$_3$) to establish whether the 15-electron fragment Cp*RuP forms a single or a multiple bond to X.[1] The consequence of these would be to produce a 16- or an 18-valence[2] electron ground state for Cp*Ru(L)X. Our conclusion from structural studies (i.e., Ru/X bond lengths) is that there is considerable multiple bond character, yet these molecules rapidly add Lewis bases (e.g., CO and ethylene). For this reason, Cp*Ru(L)X is termed *operationally* unsaturated or "π-stabilized unsaturated".

Our next step was to examine the reactivity of molecules of this class toward σ bonds of reactant partners. We report here the results for H$_2$[1] and silanes, H-SiR$_3$. These are relatively weak reagents (e.g., they show no tendancy to react with conventional 18-electron compounds without thermal or photodissociation of a ligand), and each offers the potential to form a σ-bond complex (**A** or **B**) with retention of the reagent σ bond.



A



B

The pseudooctahedral geometry expected for a d^6 Cp*Ru(L)X(L) species (L = H$_2$ or R$_3$SiH) would seem to make retention of the ligand σ bond especially favorable. Indeed, the d^6 electron configuration is the most common electronic environment for discovering complexes containing intact H$_2$ as a ligand,[3] and this has been used to explain why the d^4 dihydride alternative is not adopted for species like Ru(H)$_2$(H$_2$)(PPh$_3$)$_3$[4] and HRu(H$_2$)(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2{}^+$.[5] The work reported here also provides insights into the effect of the electron donor power of the group X on the Lewis acidity and the reducing power of the molecule Cp*Ru(L)X.

Experimental Section

General Procedures. All manipulations were carried out under an N$_2$ atmosphere using standard Schlenk techniques. All glassware was flame dried under vacuum prior to use. Solid transfers were accomplished in a Vacuum Atmospheres Corp. glovebox. Toluene, pentane, and diethyl ether were distilled under nitrogen from K/benzophenone and degassed (freeze/pump/thaw) prior to use. Toluene-d_8 was distilled from NaK prior to use and stored in the glovebox. Tricyclohexylphosphine (97%, Aldrich), H$_2$ (99.8%, Air Products), diphenylsilane (98%, Aldrich), trimethoxysilane (95%, Aldrich), triphenylsilane (97+%, Hüls), trimethylsilane (97+%, Hüls), and chlorotrimethylsilane (98%, Aldrich) were used as received without further purification. Cp*Ru(P^{i}Pr$_2$Ph)(Cl) was made by following the procedure for Cp*Ru(PR$_3$)(Cl) {PR$_3$ = PCy$_3$, P^{i}Pr$_3$}.[6] P^{i}Pr$_2$Ph,[7] Tl(OCH$_2$CF$_3$),[8] K(OSiPh$_3$),[9] and Li(NHPh),[10] were synthesized according to published procedures.

All NMR measurements were made in toluene-d_8 and the ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on a Nicolet NT360 spectrometer at 361.1, 146.2, 90.8, and 339.7 MHz. Positive ^{1}H NMR chemical shifts are downfield of TMS (0.0 ppm). Negative ^{31}P NMR chemical shifts are upfield from external 85% H$_3$PO$_4$ (0.0 ppm). Fluorine chemical shifts are referenced to CCl$_3$F; negative chemical shifts are upfield of this reference. All positive ^{29}Si chemical shifts are downfield of TMS (0.0 ppm) and were measured on a Bruker AM500 spectrometer at 99.4 MHz.

The Cp*RuL(H)$_2$X species reported here are generally unstable to vacuum and isolation because they are constituents of a rapidly reverisble equilibrium. As such, NMR is desirable as a nonperturbing method of characterization and of equilibrium mole ratios.

Reactions of Cp*Ru(PR$_3$)(X) with H$_2$. NMR tubes (3-mL total volume) were charged with Cp*Ru(PR$_3$)(X)[8] (0.10 mmol) dissolved in 0.5 mL of toluene-d_8. These were degassed and filled to 1 atm with H$_2$ (ca. 0.10 mmol). Within minutes after thawing, these solutions changed to colors of red and brown (OR$_f$) or green (halide).

X = Br. ^{1}H NMR (25 °C): δ 7.7–7.0 (m, 5H, Ph), 2.38 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.60 (br singlet, 15 H, C$_5$Me$_5$), 0.90 (two overlapping dd, 12H, C(CH$_3$)$_2$), –6.00 (d, J_{PH} = 30 Hz, 2H,

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RuH). ^{31}P NMR (25 °C): δ82.7 (s). Selected ^{1}H NMR (−80 °C): 1.58 (s, 15H, C_5Me_5), δ −5.5 and −6.5 (each is broad, each 1H, Ru–H). ^{31}P NMR (−80 °C): 82.2 (s).

Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(I). ^{1}H NMR (25 °C): δ 7.7–7.0 (m, 5H, Ph), 2.40 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.69 (s, 15, C_5Me_5), 1.24 and 0.73 (each a dd, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 6H, $C(CH_3)_2$), −7.00 (d, J_{PH} = 29 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 82.3 (s). Selected ^{1}H NMR (−80 °C): δ 1.61 (s, 15H, C_5Me_5), −6.55 and −7.35 (each a d, J_{PH} = 26, 34 Hz, each 1H, RuH). ^{31}P NMR (−80 °C): δ 81.6 (s).

Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(OCH$_2$CF$_3$). ^{1}H NMR (25 °C): δ 7.5–7.0 (m, 5H, Ph), 3.98 (q, J_{HF} = 9 Hz, 2H, OCH_2CF_3), 2.05 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.95 (s, 15H, C_5Me_5), 0.93 and 0.68 (each a dd, J_{PH} = 16 Hz, J_{HH} = 7 Hz, 6H, $C(CH_3)_2$), −10.50 (d, J_{PH} = 29 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 52.8 (s). Selected ^{1}H NMR (−85 °C): δ 1.98 (s, 15H, C_5Me_5), −10.00 and −10.85 (each a d, J_{PH} = 27, 45 Hz, each 1H, RuH).

Cp*Ru(PCy$_3$)(H)$_2$(OSiPh$_3$). ^{1}H NMR (25 °C): δ 7.6–7.1 (m, 15H, Ph), 2.20–1.19 (m, 33H, Cy), 2.11 (s, 15H, C_5Me_5), −11.95 (d, J_{PH} = 25 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 50.6 (s).

Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(NHPh). ^{1}H NMR (25 °C): δ 7.7–7.0 (m, 10H, Ph), 4.24 (broad, 1H, N*H*Ph), 2.42 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.52 (s, 15H, C_5Me_5), 1.08 and 0.88 (each a dd, J_{PH} = 14 Hz, J_{HH} = 7 Hz, 6H, $C(CH_3)_2$), −10.74 (d, J_{PH} = 24 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 76.6 (s).

Elevated Pressure H$_2$ Reactions. Typically, 3.0-mL NMR tubes fitted with Teflon closures were charged with 0.5 mL solution (toluene-d_8) containing 0.05–0.10 mmol of Cp*Ru(P^{i}Pr$_2$Ph)(X). These solutions were subjected to five degassing cycles. This evacuated tube was then opened to a large volume (1 L) of H_2 and the tube was cooled to −196 °C to cool the hydrogen inside. The NMR tube was then closed and warmed to room temperature, yielding a pressure of 2–3 atm (0.2–0.4 mmol).

Reaction of Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$) with Silanes. In the drybox, a 10-mL pentane solution containing 2 equiv of liquid silane were added to a 100-mL flask charged with Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$)[11] (0.10 mmol) dissolved in 25 mL of pentane. The purple solution changed to a reddish brown color within 1 min. Excess solvent was removed *in vacuo* to yield brown oils.

In the case of trimethylsilane 2 equiv was added to the flask containing Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$) from a calibrated gas manifold.

Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(SiPh$_3$). ^{1}H NMR (25 °C): δ 8.1–6.9 (m, 20H, Ph), 2.09 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.32 (s, 15H, C_5Me_5), 0.95 and 0.61 (each a dd, J_{PH} = 16 Hz, J_{HH} = 7 Hz, 6H, $C(CH_3)_2$), −11.41 (d, J_{PH} = 29 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 78.4 (s). Selected ^{1}H NMR (−60 °C): δ 1.32 (s, 15H, C_5Me_5), −11.11 and −11.52 (each a d, J_{PH} = 25, 33 Hz, each 1H, RuH).

Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(SiMe$_3$). ^{1}H NMR (25 °C): δ 7.6–7.0 (m, 5H, Ph), 2.02 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.66 (s, 15H, C_5Me_5), 0.99 and 0.74 (each a dd, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 6H, $C(CH_3)_2\}$, 0.52 (s, 9H, Si(Me)$_3$), −12.33 (d, J_{PH} = 29 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 82.5 (s). Selected ^{1}H NMR (−80 °C): δ 1.56 (s, 15H, C_5Me_5), 0.83 (s, 9H, Si(Me)$_3$), −11.90 and −12.53 (each a d, J_{PH} = 26, 33 Hz, each 1H, RuH).

Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(Si(OMe)$_3$). ^{1}H NMR (25 °C): δ 7.4–7.0 (m, 5H, Ph), 3.67 (s, 9H, Si(OMe)$_3$), 2.35 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.67 (s, 15H, C_5Me_5), 1.11 and 0.77 (each a dd, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 6H, $C(CH_3)_2$), −12.21 (d, J_{PH} = 29 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 79.5 (s). ^{1}H NMR (−80 °C): δ 7.8–7.0 (m, 5H, Ph), 3.79 (s, 9H, Si(OMe)$_3$), 1.65 (s, 15H, C_5Me_5), 1.29, 1.07, 0.92, 0.52 (each a dd, J_{PH} = 17–12 Hz, J_{HH} = 7 Hz, 3H, $C(CH_3)_2$), 2.62 and 2.01 (each a d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 1H, CH), −11.76 and −12.55 (each a dd, J_{PH} = 27, 30 Hz, J_{HH} = 10 Hz, each 1H, RuH). ^{31}P NMR (−80 °C): δ 77.9 (s).

Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(SiHPh$_2$). ^{1}H NMR (25 °C): δ 7.9–7.0 (m, 15H, Ph), 5.90 (s, 1H, SiH), 2.41 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.51 (s, 15H, C_5Me_5), 0.91 and 0.66 (each a dd, J_{PH} = 16 Hz, J_{HH} = 7 Hz, 6H, $C(CH_3)_2$), −11.52 (d, J_{PH} = 29 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 80.1 (s). ^{29}Si NMR (25 °C): δ 25.9 (d, J_{SiH} = 182 Hz). ^{29}Si{^{1}H} NMR (25 °C): δ 25.9 (d, J_{SiP} = 10 Hz). Selected ^{1}H NMR (−60 °C): δ 1.48 (s, 15H, C_5Me_5), −11.12 and −11.78 (each a d, J_{PH} = 25, 30 Hz, each 1H, RuH).

Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(Si(OCH$_2$CF$_3$)Ph$_2$). ^{1}H NMR (25 °C): δ 8.1–7.0 (m, 15H, Ph), 3.69 (q, J_{HF} = 9 Hz, 2H, OCH_2CF_3), 2.03 (d of septets, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 2H, CH), 1.31 (s, 15H, C_5Me_5), 1.22 and 0.83 (each a dd, J_{PH} = 16 Hz, J_{HH} = 7 Hz, 6H, $C(CH_3)_2$), −11.14 (d, J_{PH} = 29 Hz, 2H, RuH). ^{31}P NMR (25 °C): δ 77.8 (s). ^{29}Si NMR (25 °C): δ 59.9 (s). Selected ^{1}H NMR (−60 °C): δ 3.81 and 3.56 (each a br s, 1H, OCH_2CF_3), 1.26 (s, 15H, C_5Me_5), −10.80 and −11.32 (each a d, J_{PH} = 26, 29 Hz, each 1H, RuH).

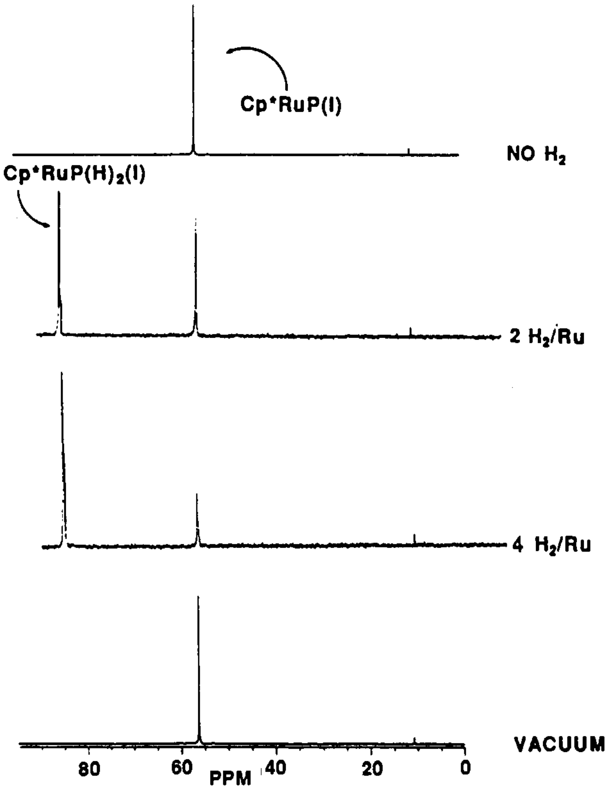


Figure 1. ^{31}P{^{1}H} NMR spectra (toluene, 25 °C) of Cp*Ru(P^{i}Pr$_2$Ph)I under varying mole ratios of H_2:Ru. The bottom spectrum was run after subjecting the 4:1 sample to vacuum.

Spectroscopic Data for Silyl Ethers. (MeO)$_3$SiOCH$_2$CF$_3$. ^{1}H NMR: δ 3.76 (q, J_{HF} = 9 Hz, 2H, OCH_2CF_3), 3.38 (s, 9H, OMe). ^{29}Si{^{1}H} NMR: δ −80.1 (s).

Me$_3$SiOCH$_2$CF$_3$. ^{1}H NMR: δ 3.49 (q, J_{HF} = 9 Hz, 2H, OCH_2CF_3), 0.19 (s, 9H, Me). ^{29}Si{^{1}H} NMR: δ 22.9 (s).

Ph$_3$SiOCH$_2$CF$_3$. ^{1}H NMR: δ 8.1–7.2 (m, 15H, Ph), 3.77 (q, J_{HF} = 9 Hz, 2H, OCH_2CF_3). ^{29}Si{^{1}H} NMR: δ −17.6 (s).

HSi(OCH$_2$CF$_3$)Ph$_2$. ^{1}H NMR: δ 7.6–7.1 (m, 10H, Ph), 5.48 (s, 1H, SiH), 3.61 (q, J_{HF} = 9 Hz, 2H, OCH_2CF_3). ^{29}Si{^{1}H} NMR: δ 51.7 (s).

Results

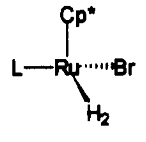
Reaction of H$_2$ with Cp*Ru(P^{i}Pr$_2$Ph)X (X = Cl, Br, I). Cp*RuLCl (L = P^{i}Pr$_2$Ph) shows no evidence (^{31}P NMR) for reaction with 2 atm of H_2 at −80 °C in toluene-d_8. However, within 5 min of exposure of Cp*RuPBr to H_2 (Ru:H_2 ratio of 1:2) at 25 °C in toluene-d_8 some adduct forms. This is also evident by a color change from blue to green-blue. The ^{31}P{^{1}H} NMR spectrum shows reactant and product in a mole ratio of 7:1. The equilibrium between these species is slow on the ^{31}P NMR scale, as well as (*vide infra*) the ^{1}H NMR time scale. Cooling this solution to −80 °C does not appreciably alter the reactant-to-product ratio. After this solution was subjected to vacuum, the ^{31}P NMR spectrum showed complete conversion to blue Cp*RuLBr. Adduct formation (eq 1) is thus reversible. The iodide analog, Cp*RuLI, rapidly (<5 min) takes up H_2 (Figure 1). Under 2 mol of H_2 per Ru in toluene-d_8 at 25 °C, the reactant:product ratio is 1:1, and the solution color is blue-green. At a H_2:Ru mole ratio of 4:1, the product:reactant ratio (by ^{31}P NMR) is 3:1. Again, cooling to −80 °C does not appreciably alter the degree of binding of H_2. Intermittent evacuation of the NMR

$$\mathrm{Cp^*RuL(X) + H_2 \rightleftharpoons Cp^*RuLH_2(X)} \qquad (1)$$

$$\mathrm{X = Br, I}$$

tube shifts the equilibrium (eq 1) completely back to Cp*RuLI. Since ($\sigma + \pi$) donor power of the halides decreases along the series Cl > Br > I,[8] it appears that internal π-donation inhibits H_2 binding.

Proton NMR studies of each of these adducts show two inequivalent isopropyl methyl groups and one hydride doublet at 25 °C. This is due to intramolecular fluxionality. It is not associated with rapid (on the NMR time scale) H_2 dissociation (eq 1) since these equilibrium mixtures show separate Cp* and ^{i}Pr ^{1}H NMR signals for Cp*RuLX and Cp*RuLH_2(X) at 25 °C. The intramolecular site exchange is slowed at –80 °C, where it becomes possible to establish the molecular structure. The bromo complex shows two hydride chemical shifts (1:1 intensity) at low temperature, thereby ruling out either an H_2 complex (C)[12] or a *trans* Ru(IV) species (D). A *cis*-square-pyramidal Ru(IV) species (E, X = Br) is in agreement with the observations. In the case of Cp*RuL(H)$_2$I, the resolution of the –80 °C ^{1}H NMR spectrum is sufficient to see doublet structure in each of the hydride resonances (H^a and H^b), due to distinct P–Ru–H coupling constants (26 and 34 Hz). These static spectra are also consistent with structure E in that the ^{i}Pr groups now show a total of four methyl chemical shifts. Thus, there is no molecular mirror plane of symmetry containing the Ru–P bond.



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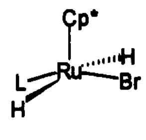

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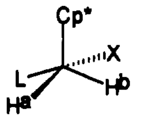

E

Reaction of H_2 with Cp*Ru(L)(OR_f). Addition of <2 H_2 to a solution of Cp*Ru(P^{i}Pr$_2$Ph)(OR_f) in toluene-d_8 also gives an adduct. The adduct is fluxional at 25 °C, showing a hydride doublet and only two isopropyl methyl chemical shifts. At –80 °C, the fluxionality is slowed to the point where two unit intensity hydride doublets (P–Ru–H coupling; $^2J_{HH'}$ is not resolved) are observed. At –80 °C, four isopropyl methyl signals are resolved. These aspects of structure and nonrigidity are analogous to those in the halide complexes and thus the "adduct" is *cis*-Cp*RuP(H)$_2$(OR_f) (E, with X = OR_f). What is different is the subsequent reactivity observed for the OR_f example: excess H_2 causes the production of R_fOH (^{1}H NMR evidence) and Cp*Ru(P^{i}Pr$_2$Ph)(H)$_3$.[13] The latter is a classical trihydride;[14,15] once its temperature-dependent and non-first-order ^{1}H NMR pattern (AB_2X at low temperature) are recognized, its identity follows readily. It is important to recognize that reductive elimination of alcohol is not a (spontaneous) unimolecular process (eq 2), but requires the presence of H_2. If the reaction of Cp*RuL(OR_f) is carried out at 25 °C and with excess H_2 (>2 H_2 per Ru), then only Cp*RuL(H)$_3$ and R_fOH are observed. Excess H_2 reacts with Cp*RuL(H)$_2$(OR_f) even at –60 °C to give Cp*RuL(H)$_3$ and R_fOH. On the other hand, evacuating a solution containing Cp*RuL(H)$_2$(OR_f) reverses the H_2 oxidative addition, and regenerates Cp*RuL(OR_f).

$$\mathrm{Cp^*RuL(H)_2(OR_f)} \nrightarrow \mathrm{Cp^*RuLH + R_fOH} \qquad (2)$$

A solution which contains both Cp*RuL(H)$_2$(OR_f) and R_f-OH shows variable ^{31}P and hydride NMR chemical shifts for the dihydride. These vary (5 ppm downfield in ^{31}P NMR in the presence of 20 equiv of R_fOH) with the concentration of alcohol present and are attributed to hydrogen bonding of free alcohol to the coordinated alkoxide. While the ^{31}P NMR resonance shifts only 0.2 ppm in the presence of equimolar R_fOH, the alkoxy methylene protons move 1 ppm upfield. Since alkoxide in Cp*RuL(H)$_2$(OR_f) is a pure σ ligand, its high (two lone pair) electron density makes it a good participant in a hydrogen bond.

Other Hydrogenolysis Reactions. Reaction of equimolar H_2 with Cp*Ru(PCy$_3$)(OSiPh$_3$) or Cp*Ru(P^{i}Pr$_2$Ph)(NHPh) in toluene-d_8 at 25 °C produces the corresponding Cp*RuL(H)$_2$X and Cp*RuL(H)$_3$, as well as Ph$_3$SiOH or aniline, respectively. Additional H_2 causes further conversion, to leave only the corresponding Cp*RuL(H)$_3$ and HX. The first (oxidative addition) step is again reversible: evacuation of a solution containing either Cp*RuL(H)$_2$X species regenerates Cp*RuLX. For either of the above species, there is no coalescence of either ^{1}H or ^{31}P NMR signals for the species Cp*RuLX and Cp*RuL(H)$_2$X when they are together in toluene-d_8 at 25 °C; any exchange between these is slow on the NMR time scale.

Reaction of Cp*RuL(OR_f) with Tertiary Silanes. Reaction of Cp*RuL(OR_f) with two equivalents of HSiR$_3$ (R = OMe, Me or Ph) at 25 °C in pentane gives, within 15 min, complete conversion to the corresponding Cp*RuL(H)$_2$(SiR$_3$). The ^{1}H NMR spectrum of each reaction also showed signals consistent with formation of R$_3$SiOR$_f$ (eq 3). Vacuum transfer of the volatiles from the HSi(OMe)$_3$ reaction permitted additional confirmation (*via* ^{1}H NMR spectroscopy) of the formation of (MeO)$_3$SiOR$_f$. The ^{29}Si{^{1}H} NMR spectrum of this volatile product is a singlet at –80.1 ppm, while the ^{29}Si NMR signal of Cp*RuL(H)$_2$Si(OMe)$_3$ was observed as a singlet at –55.2 ppm. The corresponding values observed for R_fOSiPh$_3$ and Cp*RuL(H)$_2$(SiPh$_3$) are –17.6 and –8.5 ppm. For Cp*RuL(H)$_2$(SiMe$_3$), the ^{29}Si resonance was a doublet ($^2J_{PSi}$ = 8 Hz) at 10.7 ppm, with R_fOSiMe$_3$ observed at 22.9 ppm. A previous relevant report is the reaction of HSiMe$_2$Ph with *trans*-Ir(PPh$_3$)$_2$CO(OMe) to yield Ir(H)$_2$(PPh$_3$)$_2$CO(SiMe$_2$Ph) and (MeO)SiMe$_2$Ph.[16]

$$\mathrm{Cp^*RuL(OR_f) + 2\,HSiR_3} \rightarrow \mathrm{Cp^*RuL(H)_2(SiR_3) + R_3SiOR_f} \qquad (3)$$

In the ^{1}H NMR spectrum (25 °C), the dihydride products each showed a Cp* singlet, two ^{i}Pr methyl chemical shifts, one methine signal, and a hydride doublet (due to P–Ru–H coupling). Cooling the sample from the HSiMe$_3$ reaction to –80 °C causes the hydride doublet to resolve into two doublets, with J_{PH} values of 26 and 30 Hz. This is consistent with these molecules undergoing rapid hydride fluxionality at 25 °C. Also resolved at –80 °C are four ^{i}Pr methyl chemical shifts, indicating that there is no mirror plane of symmetry containing the Ru–P bond. Taken together, these observations are consistent with a four-legged piano-stool structure with the hydrides cisoid (E, with X = SiR$_3$).[17] The fluxional process, which cannot involve dissociation of either P^{i}Pr$_2$Ph or H_2, must pass through a transition state or intermediate with a mirror plane of symmetry containing Ru, P, Si, and the Cp* ring centroid. Both F ("planar") and G require consideration as a transition state or intermediate, respectively, in this fluxional process.

Since the 1:2 stoichiometry of eq 3 implies the occurrence of two hydrogen transfers, we have sought evidence for intermediates by studying reactions at equimolar reagent ratios. Upon mixing equimolar Cp*RuL(OR_f) and HSi(OMe)$_3$ at 25 °C in toluene-

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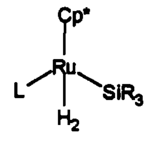
(12) Rapid rotation of coordinated H_2 on the chemical shift time scale is universally observed, since the rotational barrier is typically less than 3 kcal/mol.[3]

(13) This overall reaction was reported for Cp*Ru(PCy$_3$)(OMe). See: Chaudret, B.; Duteil, A.; He, X. D. *J. Organomet. Chem.* **1990**, *391*, C45.

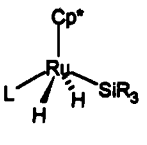
(14) (a) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308. (b) A structure determination of Cp*Ru(PPh$_3$)(H)$_3$ shows that coordinated H_2 is not present. See: Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1987**, *6*, 1569.

(15) Selected spectroscopic data for Cp*Ru(P^{i}Pr$_2$Ph)(H)$_3$ (25 °C). ^{1}H NMR: δ 1.96 (s, 15H, C$_5$Me$_5$), 0.99 and 0.78 (each a dd, J_{PH} = 12 Hz, J_{HH} = 7 Hz, 6H, C(CH$_3$)$_2$), –10.77 (d, J_{PH} = 22 Hz, 3H, RuH). ^{31}P{^{1}H} NMR: δ 92.7 (s).

(16) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939.



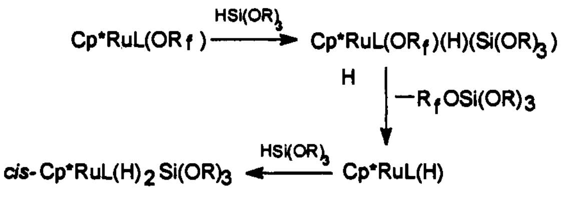
F



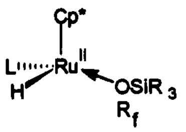
G

d_8, one immediately observes resonances consistent with equimolar amounts of Cp*RuL(OR$_f$), Cp*RuL(H)$_2$Si(OMe)$_3$, and (MeO)$_3$SiOR$_f$. When this reaction was repeated by combining the reagents (equimolar) in a cold NMR tube at −78 °C and recording (within 5 min of mixing) NMR spectra in a probe precooled to −80 °C, both ^{1}H and ^{31}P nuclei revealed only Cp*RuL(OR$_f$), Cp*RuL(H)$_2$Si(OMe)$_3$, (MeO)$_3$SiOR$_f$, and unreacted HSi(OMe)$_3$. Over the next 30 min at −80 °C, all of the silane was consumed, leaving only Cp*RuL(OR$_f$), Cp*RuL(H)$_2$Si(OMe)$_3$, and (Me$_3$O)$_3$SiOR$_f$. Scheme I shows a proposed mechanism, and the intermediate H is evidently extremely short-lived. To enable reductive elimination of (RO)$_3$SiOR$_f$ from H, this intermediate must have the (RO)$_3$Si and OR$_f$ groups cisoid.

Scheme I

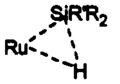


Given that I is an authentic 16-electron hydride (i.e., devoid of π-stabilized unsaturation) it might be considered unattractive (unlikely) as a species formed rapidly at −78 °C. Thus, we consider alternative, *bimolecular* routes from H to product. These could be direct attack of HSiR$_3$ on H ("σ bond metathesis"),[18] with concurrent displacement of (RO)$_3$SiOR$_f$, or direct attack after η^5- → η^3-Cp* rearrangement.[19] Alternatively, the electron-rich (pure σ Ru-O bond) OR$_f$ in H could effect nucleophilic attack (S$_N$2) on silicon of the incoming HSi(OR)$_3$.[20] Yet another alternative to highly unsaturated I would be J, the product of silyl migration to the electron-rich OR$_f$ ligand.



J

Reaction of Cp*RuL(OR$_f$) with Secondary Silanes. Studies with a difunctional silane are mechanistically enlightening. A pentane solution of Cp*RuL(OR$_f$) reacts with 1 mol of H$_2$SiPh$_2$ (25 °C, 15 min) to yield, after removal of solvent, a brown oil which exhibits two ^{31}P{^{1}H} NMR singlets of equal intensity. The ^{1}H NMR spectrum of this oil is consistent with the presence of two *cis*-Cp*RuL(H)$_2$(SiXPh$_2$) products, where X = H or OR$_f$. Detected are an RuSi*H*Ph$_2$ singlet (5.86 ppm) and a quartet due to RuSi(OC*H*$_2$CF$_3$)Ph$_2$, as well as signals due to HSi(OR$_f$)Ph$_2$.[21] The ^{29}Si NMR spectrum of the silyl groups attached to ruthenium, when proton *coupled*, shows a doublet ($^1J_{SiH}$ = 182 Hz) at 25.9 ppm and a singlet at 59.9 ppm. No Si–P coupling was observed, nor was there any Si–H coupling (expected[22] magnitude 30–65 Hz) due to incipient interactions of the sort shown in K (i.e., η^2-H-SiR$_3$).

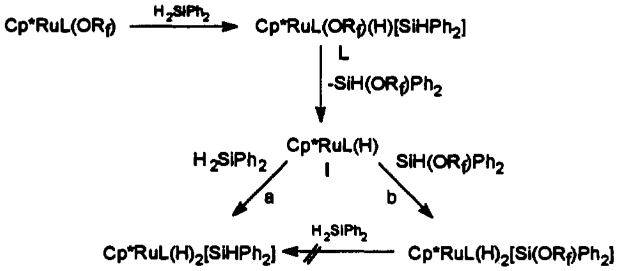


K

Of particular significance is the observation that H$_2$SiPh$_2$ does not convert Cp*RuL(H)$_2$(SiOR$_f$Ph$_2$) into Cp*RuL(H)$_2$(SiHPh$_2$) in toluene, even over a period of 1 h at 90 °C. Once formed, these molecules (which are coordinatively *saturated*) are therefore inert to interconversion by added silane.

On the other hand, when the mole ratio of Cp*RuL(OR$_f$) to H$_2$SiPh$_2$ at the time of the initial reaction was changed to 1:5, the mole ratio of Cp*RuL(H)$_2$(SiXPh$_2$) changed to 1:2 for X = OR$_f$ to X = H. Analogously, when the Cp*RuL(OR$_f$):H$_2$SiPh$_2$ mole ratio was reduced to 2:1, unreacted Cp*RuL(OR$_f$) was accompanied by Cp*RuL(H)$_2$(SiXPh$_2$) in a mole ratio of 1 (X = H) to 1 (X = OR$_f$). These results indicate that partitioning between the X = H and X = OR$_f$ products occurs at some reaction intermediate and that H$_2$SiPh$_2$ is in competition with another reagent (HSi(OR$_f$)Ph$_2$) for capture of this intermediate. This is nicely accommodated by a small elaboration of Scheme I, shown as Scheme II. Species I is the 16-electron transient common to both Scheme I and II, and it is captured by two competitive bimolecular processes, a and b of Scheme II. As the concentration

Scheme II



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(17) In contrast to the situation in square-planar and octahedral complexes, the transoid $^2J_{PH}$ coupling constant is *not* much larger than the cisoid $^2J_{PH}$ value in a four-legged piano-stool compound CpM(H)(PR$_3$)L$_2$. In fact, there is evidence that the cisoid J is larger than the transoid one. However, examples are known, for square-pyramidal compounds, of cisoid (16 Hz) and transoid (8 Hz) coupling constants of nearly equal magnitude, and coupling constants assigned as transoid vary from zero to 30 Hz, while those assigned as cisoid vary from 16 to 75 Hz.[34–39] This warning has also been sounded elsewhere recently. See: Casey, C. P.; Tanke, R. S.; Hazin, P. N.; Kemnitz, C. R.; McMahon, R. J. *Inorg. Chem.* **1992**, *31*, 5474. This confusing situation may arise because the H–M–H angles in Cp*MLL′(H)$_2$ species can vary greatly with variation in repulsion between L and L′ and especially between L or L′ and the Cp* ring. Thus, the names transoid and cisoid may encompass such a wide variation in H–M–H angles (and J values) that stereochemical assignment based on J values becomes unreliable. In this regard, it is decisive to note that the *trans*- and (two) *cis*-H-Ir-P angles in Cp*Ir(PMe$_3$)(H)$_3^+$ are[35] 98.3(4)° *vs* 74.7(4) and 75.8(3)° (i.e., *very* similar). Our J_{PH} values are similar to each other and are thus not compelling for stereochemical asignment. We prefer to decide stereochemistry based on the number of hydride chemical shifts in Cp*Ru(H)$_2$L(SiR$_3$). We consistently see two chemical shifts (and resolve $^2J_{HH}$ = 10 Hz in Cp*RuL(H)$_2$[Si(OMe)$_3$]), which is inconsistent with a transoid structure but consistent with cisoid stereochemistry. Our assignment is also required by the observation of four methyl chemical shifts for the ^{i}Pr methyl groups in Cp*Ru(P^{i}Pr$_2$Ph)(H)$_2$(SiMe$_3$). However, for an alternative stereochemistry in a closely related molecule, see: Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1992**, 1201.

(18) σ-Bond metathesis probably demands an empty orbital on the metal, making this mechanism less attractive for our 18-electron Ru(IV) species **H**. There is, however, one postulate of σ-bond metathesis for a saturated iridium compound. See: Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079.

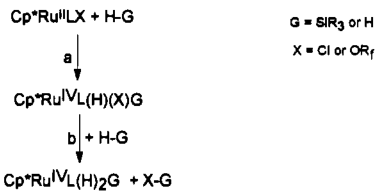
(19) A ring slip mechanism was suggested for the *phosphine*-induced elimination of alcohol from Cp*Ir(PPh$_3$)(H)(OEt): Glueck. D. S.; Newman Wilson, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462.

(20) Corriu, R. J. P. *J. Organomet. Chem.* **1990**, *400*, 81.

(21) HSi(OR$_f$)Ph$_2$ was independently synthesized from HSiClPh$_2$ and TlOR$_f$ to confirm its spectral parameters.

(22) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. See also: Wang, W.; Eisenberg, R. *Organometallics* **1992**, *11*, 908, and references therein.

Scheme III



(i.e., mole ratio Si:Ru) of H_2SiPh_2 rises, path a becomes more important. To the extent that the chemistry of a difunctional silane also reflects that of $HSiR_3$, the results summarized in Scheme II suggest that the initial molecule of silyl ether formed in either mechanism *departs the coordination sphere to a significant extent before or while the second molecule of Si–H reagent attacks.*

Other Ligand Exchanges. The Si–Cl bond energy might be strong enough to allow SiH/RuCl redistribution. In fact, reaction of Cp*RuLCl with Me_3SiH (1:3 mole ratio) in toluene-d_8 gives quantitative conversion (<5 h, 25 °C) to Cp*RuL$(H)_2(SiMe_3)$ and Me_3SiCl. The presumed intermediate Cp*RuL(Cl)(H)$(SiMe_3)$ therefore does not survive at 25 °C in the presence of Me_3SiH.[23] This contrasts with the lack of reactivity of Cp*Ru$(P^iPr_3)(Cl)(SiH_2Ph)H$ toward $PhSiH_3$.[6]

Discussion

The facility with which all of these reactions occur supports the idea that all Cp*RuLX species, while possessing varying degrees of Ru/X multiple bonding, are operationally unsaturated: the approach of H_2 or a silane effectively "displaces" a lone pair to the group X. This also supports the idea that the many high-temperature C-H activation reactions involving[24] CpRu$(PR_3)_2(CH_3)$ begin with PR_3 dissociation, which has a high activation energy because CH_3 lacks a lone pair.

The examples of H–G bond cleaveage below 25 °C reported here are summarized in Scheme III. The mechanism of step b is challenging, since the metal complex is saturated.

Possible mechanisms when H–G is a silane have been discussed above and we will discuss Ru-O hydrogenolysis below. Step a occurs because the Cp*Ru^{II}L moiety is quite electron-rich for all X. Step b occurs because of the strength of the X-G bond and/or the four-electron destabilization[25] (d_π/X lone-pair repulsion) in Cp*RuL(H)(X)G. The multiple appearance of Ru(IV) in this scheme clearly indicates that we underestimated the electron-rich character of Cp*RuLX species at the outset of this work. The $d^6 \rightarrow d^4$ redox change is accessible here with even weak oxidants. The same is true for the protonation of Cp*RuL_2H species,[26] where the (low-temperature) kinetic product is a dihydrogen complex (Ru(II)), but this readily rearranges to Cp*$Ru^{IV}L_2(H)_2^+$.

It is clear that $\Delta G°$ for loss of H_2 from a species Cp*RuL$(H)_2$X (i.e., the reverse of eq 1) shows a systematic dependence on X. When X has lone pairs (halides, OR_f, $OSiPh_3$, NHPh), the free-energy change is less positive than when X is H or SiR_3. This trend is clearly correlated with the presence or absence of lone pairs on X, to the point where H_2 dissociation is undetectable when X is a pure σ-bonding group. For example, we find that Cp*Ru$(PPh_3)(H)_3$ shows no exchange under 1 atm D_2 over 48 h at 25 °C. These results are in accord with the quantitative determination of E_a[27] for eq 4, where E_a ranges from 29 kcal/mol for X = OH to over 47 kcal/mol for X = H.

$$\mathrm{Cp^*Ru(PMe_3)_2X \rightarrow Cp^*Ru(PMe_3)X + PMe_3} \qquad (4)$$

Stereochemistry of Cp*Ru$(PR_3)(H)_2$X. The dihydride compounds reported here show a distinct preference for the stereoisomer in which the hydride ligands are *cis*. This stands in contrast to the compounds CpRu$(PR_3)_2(H)_2^+$,[26] which have the hydrides *trans*. One cannot explain our *cis* stereochemistry as due to an avoidance of two strong σ ligands being opposed (*trans*), since the same would then apply to the bis(phosphine) compounds. Although hydride ligands are small, and two can perhaps occupy the least volume when they are *cis*, it is hard to imagine that mutual repulsions among Cp*, PR_3, and X are smaller when the hydrides are *cis* than when they are *trans*. Moreover, this argument also applies equally well to bis(phosphine) compounds, yet they are not *cis*. It could be argued that incipient (thus weak) H/H attractive interactions could cause the *cis* isomer to be preferred, yet we find no significant (i.e., >30 Hz) J_{HH} coupling in these molecules.

What differentiates Cp*RuL$(H)_2$X from the bis(phosphine) cations, is that the electron-rich character of the purely σ-bonded groups X creates a repulsion with the electron-rich hydride ligands, and that such repulsions are fewer in number in the *cis* than in the *trans* isomer.[28]

Reversibility of Hydrogenolysis. We have argued that a four-electron destabilization reduces the bond strength of these (and certain other) late transition metal/ligand bonds. Thus the facile hydrogenolysis reported here becomes understandable in its contrast to early transition metal alkoxides and amides. We were, nevertheless, surprised that products as Bronsted acidic as Ph_3SiOH and CF_3CH_2OH were eliminated, in spite of the potential that these could protonate Cp*RuL$(H)_3$. We anticipated that this protonation product, Cp*RuLH_4^+ (possibly containing coordinated H_2), could easily reform Cp*RuL$(H)_2$(OR) by the mechanism shown in eq 5. In fact, we showed that 100 equiv of

$$\mathrm{Cp^*RuLH_4^+ \rightleftharpoons H_2 + Cp^*RuLH_2^+ \xrightarrow{RO^-} Cp^*RuL(H)_2(OR)} \qquad (5)$$

R_fOH (and the absence of added H_2) will reverse the hydrogenolysis reaction; the yield (*in situ*) of Cp*RuL$(H)_2(OR_f)$ is 30%. Moreover, subjecting a 1:1 solution of Cp*RuL$(H)_3$ and R_fOH to vacuum at 25 °C completely reverses the oxidative addition of H_2 and regenerates Cp*RuL(OR_f). This means that these reactions are nearly thermoneutral.[29]

Mechanism of Ru–O Bond Hydrogenolysis. While it is interesting that Cp*RuL$(H)_2$(OR) does not spontaneously and unimolecularly eliminate alcohol, it is problematic to understand the mechanism by which H_2 promotes alcohol production. The problem centers on how (eq 6) H_2 can interact with the apparently

$$\mathrm{Ru–OR + H–H \rightarrow Ru–H + H–OR} \qquad (6)$$

saturated species Cp*RuL$(H)_2$(OR). In early transition metal chemistry (i.e., d^0 metals), a "σ-bond metathesis" mechanism is proposed. However, this reaction *requires* an empty metal orbital, yet such is absent here for Ru(IV).

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(23) For the conversion of $[Cp^*Ru(OMe)]_2$ to $(Cp^*RuCl)_4$ using Me_3SiCl, see: Kölle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383.

(24) Lehmkuhl, H.; Bellenbaum, M.; Grundke, J. *J. Organomet. Chem.* **1987**, *330*, C23. Lehmkuhl, H.; Schwickardi, R.; Mehler, G.; Krüger, C.; Goddard, R. *Z. Anorg. Allg. Chem.* **1991**, *606*, 141 and references therein.

(25) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

(26) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675. Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161.

(27) Compare Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. M. *Organometallics* **1988**, *8*, 379.

(28) A reviewer proposes that the *cis* isomer is preferred because *trans* hydrides suffer a high *trans* influence (mutual competition for one metal orbital). Since the *trans* ∠H–M–H is typically less than 100° (see data in ref 17), the *trans* designation is not very descriptive ("diagonal" is better), and a strong *trans* influence is not certain. The matter of angular deformation in four-legged piano stools was analyzed recently: Lin, Z.; Hall, M. B. *Organometallics* **1993**, *12*, 19.

(29) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

We have considered a mechanism which begins with a pre*equilibrium* phosphine elimination (eq 7), and have attempted to probe this by treatment of $Cp^*Ru(P^iPr_2Ph)(H)_2(OR_f)$ with

$$Cp^*Ru(P^iPr_2Ph)(H)_2OR_f \rightleftharpoons \underset{\textbf{M}}{Cp^*Ru(H)_2(OR_f)} + P^iPr_2Ph \qquad (7)$$

$2PCy_3$. In fact, we observe no change after two weeks at 25 °C. This result rules out preequilibrium dissociation of phosphine, since intermediate **M** should be captured by PCy_3 to give $Cp^*Ru(PCy_3)(H)_2(OR_f)$.[30] In the context of π-stabilization of unsaturation, the proposed species $Cp^*Ru(H)_2(OR_f)$ has special appeal because of potential alkoxide π-donation, yet it is apparently not a kinetically significant species.

We have also evaluated a mechanism which begins by a pre*equilibrium* alcohol reductive elimination (eq 2). However, qualitative rate observations at low temperature show that added R_fOH (5:1, 10:1, and 20:1 mole ratios) does not slow the rate of alcohol elimination by H_2 from $Cp^*RuL(H)_2(OR_f)$. We are left to conclude that the hydrogenolysis mechanism involves H_2 attack on an $(\eta^3\text{-}C_5Me_5)RuL(H)_2(OR_f)$ species, or on a weakly bonded $Cp^*RuL(H)(R_fOH)$ species analogous to **J**.

The nature of the hydrogenolysis reaction raises the question of whether the alcohol proton in the product originates from $Cp^*RuL(H)_2(OR_f)$ or from the attacking H_2. Unfortunately, the observed rapid exchange of $Cp^*RuL(H)_2(OR_f)$ with D_2 renders the obvious experiment (eq 8) technically impossible.

$$Cp^*RuL(H)_2(OR_f) + D_2 \rightarrow R_fOX + ... \qquad (8)$$

$$X = H \text{ or } D?$$

We have examined a coordinatively saturated ("pure-σ") alkoxide for possible Ru-OR_f hydrogenolysis by a four-center transition state without prior H_2 coordination to Ru itself. Treatment of $Cp^*RuL(CO)(OR_f)$ with 1 atm H_2 at 25 °C for 1 week (eq 9) gives no reaction. Since $Cp^*RuL(CO)H$ is a member of a known class of molecules (and thus not thermodynamically implausible), this would suggest that this reaction fails for kinetic reasons. We propose that it is the lack of coordinated hydride which causes eq 9 to fail, and thus that it is a coordinated hydride of $Cp^*RuL(H)_2(OR_f)$ that becomes the alcohol proton (i.e., *this* is the mechanistic feature lacking in eq 9).[31]

$$Cp^*RuL(CO)(OR_f) + H_2 \xrightarrow{?} Cp^*RuL(CO)H + R_fOH \qquad (9)$$

One early theme of late-transition metal alkoxide chemistry is that such M-OR bonds are weak. This has now been refuted,[32] but based entirely on data for square-planar d^8 compounds. For those, O → M π-donation is somewhat unfavorable since the d_{z^2} orbital is doubly occupied. Indeed, from the available structural data for such compounds (Ir^I and Pt^{II}), it is concluded that there is no evidence for π-donation.

As we generalize, from the present work, to include d^6 species, it is clear that the M/OR bond can be strong or weak, multiple or single, depending on the ligand set and geometry. Thus, the absence of unimolecular alcohol dissociation (eq 10) results from the high energy of the authentically-unsaturated $Cp^*Ru(L)H$ species, even though $Cp^*Ru(L)(H)_2(OR)$ has a nearly pure Ru–O single bond (i.e., is "weak"). However, this Ru(IV) compound is now "prepared" to eliminate alcohol in a bimolecular encounter with H_2, which simultaneously furnishes the ligands needed to form the trihydride product (eq 11). The first mole of H_2 thus "activates" the (stronger) Ru/O multiple bond in $Cp^*Ru(L)(OR)$ by converting it to a single bond and by increasing the Bronsted basic character of the oxygen (localization of two lone pairs on oxygen). The overall hydrogenolysis reaction (i.e., Ru + $2H_2$) is thus substrate-promoted. The weakness of the Ru/O single bond in $Cp^*Ru(L)(H)_2(OR)$ is accentuated by the fact that there is a repulsive (destabilizing) interaction between the several filled d_π orbitals and the two oxygen lone pairs. Such "four-electron destabilization" is, with increasing frequency, being recognized as a decisive factor in organometallic chemistry.

$$Cp^*Ru(L)(H)_2(OR) \nrightarrow Cp^*Ru(L)H + ROH \qquad (10)$$

$$Cp^*Ru(L)(H)_2(OR) + H_2 \rightarrow Cp^*Ru(L)(H)_3 + ROH \qquad (11)$$

The ready hydrogenolysis of Ru–$OSiR_3$ bonds reported here, and the reversibility of these transformations, suggests that Ru(II) (as well as other transition metals with >4 d electrons) should readily undergo conversion to Ru–H and –OH groups on silica and alumina supports. The generation of metal hydrides of these metals bound to surfaces is thus readily understood.

There are limits to Ru/O bonds which can be split with a mild reagent like H_2. Given that $[Cp^*Ru(H)_2]_2$ is a known compound,[33] we have attempted the hydrogenolysis shown in eq 12.

$$[Cp^*Ru(OR_f)]_2 + 3\,H_2 \xrightarrow{?} [Cp^*Ru(H)_2]_2 + 2\,R_fOH \qquad (12)$$

After 72 h at 25 °C under 1 atm H_2 (H_2:Ru = 15:1), all $[Cp^*Ru(OR_f)]_2$ is recovered unchanged. This reaction cannot be kinetically limited by steric factors. Moreover, the μ_2-OR_f oxygens are pyramidal, suggesting the presence of lone pairs and thus Bronsted basicity. Consequently, the failure of this reaction probably resides in it being thermodynamically unfavorable.

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(30) Note also that the observation of P–Ru–H coupling at low temperature indicates that eq 7, if it occurs at all, is slower than the observed hydrogenolysis reaction.

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