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Roles of Neutral and Anionic Ruthenium Polyhydrides in the Catalytic Hydrogenation of Ketones and Arenes

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Abstract: *fac*-$[RuH_3(PPh_3)_3]^-$ (**1**) and $[RuH_4(PPh_3)_3]$ (**3**) have been shown to coexist through the equilibrium **1** + ROH $\rightleftharpoons$ **3** + RO^-, for which $K_{eq} \approx 0.13$ for cyclohexanol in THF. The following reactions have been characterized: (1) **3** + cyclohexanone → $[RuH_2(PPh_3)_3]$ (**4**) + cyclohexanol. (2) **4** + H_2 → $[RuH_4(PPh_3)_3]$. The combination of these reactions constitutes a catalytic cycle for the hydrogenation of cyclohexanone, in which (1) is the rate-determining step. The $[RuH_3(PPh_3)_3]^-$-catalyzed hydrogenation of cyclohexanone is preceded by an induction period during which the catalyst precursor apparently is converted to $[RuH_4(PPh_3)_3]$. A catalytic cycle analogous to that for cyclohexanone was established for the hydrogenation of 9-methylanthracene (An′) to 1,2,3,4-H_4-An′. For this substrate also $[RuH_4(PPh_3)_3]$ is a more active catalyst than $[RuH_3(PPh_3)_3]^-$.

The anionic hydrido(phosphine)ruthenate complex $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ originally synthesized and characterized by Pez, Grey, and Corsi,[1] was reported to be an effective catalyst or catalyst precursor for the hydrogenation of arenes such as anthracene,[2] as well as of polar compounds such as ketones, aldehydes, esters, and nitriles.[3]

In the course of our earlier investigation of the mechanism of hydrogenations of anthracene, we found that, in the presence of H_2, $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ is rapidly converted to *fac*-$[RuH_3(PPh_3)_3]^-$. The latter reacts further to form bis(phosphine) complexes, including $[RuH(PPh_3)_2(\text{anthracene})]^-$ and $[RuH_5(PPh_3)_2]^-$, which probably constitute the catalytic intermediates in the reaction.[4]

It has been suggested[3,5] that the catalytic activity of anionic complexes such as $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ for the hydrogenation of polar compounds such as ketones is promoted by their nucleophilic reactivity, a key step being the transfer of a hydride ion from the ruthenium hydride to the substrate. The products of hydrogenation of ketones and esters are alcohols. In view of this and of the marked susceptibilities of anionic ruthenium hydride complexes to protonation, the nature of the catalysts and mechanisms of these catalytic reactions were unclear. In this paper we report the results of a study of the coordination chemistry of anionic and neutral hydrido(phosphine)ruthenium complexes relevant to the catalytic hydrogenation of ketones and arenes and of the kinetics of catalytic hydrogenation. We also compare the catalytic properties of the neutral and anionic complexes $[RuH_4(PPh_3)_3]$ and $[RuH_3(PPh_3)_3]^-$ in respect of the hydrogenation both of a ketone and an arene.

Experimental Section

Physical Measurements. ^1H, ^2H, and ^{31}P NMR spectra were determined with the University of Chicago 500-MHz Varian 400-MHz and Nicolet 200-MHz NMR spectrometers, respectively. Chemical shifts are expressed in parts per million upfield from $Si(cH_3)_4$ (^1H), $Si(CD_3)_4$ (^2H), and 85% H_3PO_4 (^{31}P). Infrared spectra were recorded with a Perkin-Elmer 283 or Nicolet MX-5 FTIR spectrophotometer. H_2 uptake kinetic measurements were made using a constant pressure gas uptake apparatus,[6] modified with Kelva-glass seals at the points of brass tubing–O-seal-glass attachment. The hydrogenation of cyclohexanone and of 9-methylanthracene was monitored with a Perkin-Elmer 330 capillary gas chromatograph interfaced with a PE Sigma 30 data station.[7]

Materials. General Data. All manipulations were conducted with rigorous exclusion of air and moisture using a high vacuum line (10^{-4}–10^{-5} torr), an argon-filled Schlenck line, and a nitrogen-filled glovebox (Vacuum Atmospheres). Solvents and reagents were stored in the glovebox.

Solvents and Organic Reagents. Hexane was distilled under nitrogen from Na/K alloy. Other solvents were distilled from Na/benzophenone. Cyclohexanone was distilled from anhydrous B_2O_3 under argon, stirred over fresh B_2O_3, degassed, and transferred in a high vacuum line. Cyclohexanol was stirred over potassium cyclohexyloxide, freeze–pump–thaw degassed, and transferred in a high vacuum line. Potassium cyclohexyloxide and diphenylmethoxide were prepared from the corresponding alcohols according the Morton and Claff,[8] substituting K-$[HBEt_3]$ for KNH_2 as the base. Triphenylphosphine was recrystallized from hot hexane. 9-Methylanthracene was recrystallized twice from anhydrous ether. 1,2,3,4-Tetrahydro-9-methylanthracene (H_4-An′) was prepared by the selective hydrogenation of 9-methylanthracene (An′).[3b] 1,2,3,4,5,6,7,8-Octahydro-9-methylanthracene (H_8-An′) was prepared from 1,2,3,4,5,6,7,8-octahydroanthracene by chloromethylation, followed by hydrogenation over Pd/C.[9]

K[*fac*-$[RuH_3(PPh_3)_3]$][4] **(1)** was prepared according to the procedure of Chan and Shieh[10] and recrystallized from 1:1 (v/v) THF/hexane.

$[RuH_2(N_2)(PPh_3)_3]$[11] **(2).** To a stirred suspension of 1.08 g (0.98 mmol) of $[RuHCl(PPh_3)_3]$ in THF (20 mL) was added 0.98 mL of 1.0 M $K[HBEt_3]$ in THF. After the solution was stirred for 40 h at room temperature, the KCl precipitate was filtered and 10 mL of hexane added. Filtration resulted in the isolation of 0.68 g (71%) of crude product that was further purified by dissolution in benzene (20 mL), filtration, and addition to hexane (20 mL) to precipitate the pure product: yield 0.4 g (42%); ^1H NMR (toluene-d_8, 200 MHz) δ −12.5 (tdd, $J_{P_bH_b} \approx 27$ Hz, $J_{P_aH_a} \approx 15$ Hz, $J_{H_aH_b} \approx 6$ Hz, 1 H, RuH_b), −8.1 (dtd, $J_{P_aH_a} \approx 75$ Hz, $J_{P_bH_a} \approx 30$ Hz, 1 H, RuH_a), 6.95 (m, 27 H, meta and para aryl protons), 7.27 (br t, $J \approx 7$ Hz, 18 H, ortho aryl protons of P_aPh_3), 7.43 (m, 12 H, ortho aryl protons of P_bPh_3); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 44.5 (t, $J_{P_aP_b} \approx 16$ Hz, 1 P, P_b), 56.8 (d, 2 P, P_a); IR (Nujol) ν_{Ru-H} 1920 (w), 1957 (m) cm^{-1}, ν_{N-N} 2156 (s) cm^{-1}.

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(7) The conditions for the capillary GLC analyses of cyclohexanone and cyclohexanol in the temperature programmed mode were as follows: $T_{detector} = T_{injector} = 250$ °C; temperature (1) = 32 °C; time (1) = 1.0 min; rate (1) = 4 °C min^{-1}; temperature (2) = 60 °C; time (2) = 0 min; rate (2) = 30 °C min^{-1}; temperature (3) = 180 °C. The conditions for the capillary GLC analyses for An′, H_4-An′, and H_8-An′ were as follows: $T_{detector} = T_{injector} = 350$ °C; temperature (1) = 150 °C; time (1) = 1.0 min; rate (1) = 20 °C min^{-1}; temperature (2) = 3.0 min; rate (2) = 20 °C min^{-1}; temperature (3) = 250 °C.

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[RuH$_4$(PPh$_3$)$_3$][11] (**3**) was prepared in situ by shaking or stirring a $\lesssim$0.02 M solution of [RuH$_2$(H$_2$)(PPh$_3$)$_3$] in THF or toluene under H_2 (1 atm) for ca. 2 min at room temperature: ^{1}H NMR (toluene-d_8, −50 to +30 °C) δ −7.05 (br s, 4 H, RuH), 6.85 (br t, $J \approx 7$ Hz, 18 H, meta aryl protons), 6.95 (br t, $J \approx 7$ Hz, 9 H, para aryl protons), 7.35 (br m, 18 H, ortho aryl protons); ^{31}P{^{1}H} NMR (toluene-d_8) δ 61.5 (br s, 3 P); ^{1}H NMR (THF-d_8) δ −7.47 (br s, 4 H, RuH), 6.94 (br t, $J \approx 7$ Hz, 18 H, meta aryl protons), 7.10 (br t, $J \approx 7$ Hz, 9 H, para aryl protons), 7.14 (br m, 18 H, ortho aryl protons); ^{31}P{^{1}H} NMR (THF-d_8, −80 to +30 °C) δ 58.0 (br s, 3 P).

[RuH$_2$(PPh$_3$)$_3$(THF)][12] (**4**) was prepared in situ as follows.[13] In a flask with a T-stopcock connected to two side arms, one with an Ace O-ring ball joint and an S-stopcock and the other with an inner ground glass joint, was placed 0.23 g (0.23 mmol) of [RuHCl(PPh$_3$)$_3$·toluene] and 9.4 mg (0.24 mmol) of KH. The flask was then sealed by using the S-stopcock that was connected to a solvent vessel containing 5 mL of THF-d_8. The sealed flask was attached to a high vacuum line, and evacuated, and the solvent was degassed at −78 °C and transferred to the reaction vessel. The flask was stirred for 4 days during which the color of the solution changed from burgundy to orange-yellow: ^{1}H NMR (THF-d_8, −50 to +30 °C) δ −10.2 (br q, $J_{P\text{-}H} \approx 39.5$ Hz, 2 H, RuH), 6.94 (m, 27 Hz, meta and para aryl protons), 7.31 (br t, $J \approx 7$ Hz, 18 H, ortho aryl protons); ^{31}P{^{1}H} NMR (THF-d_8, 25 °C) δ 57.6 (s, 3 P); ^{31}P{^{1}H} NMR (THF-d_8, −80 °C) δ 58 (br s, 1 P, P$_b$), 60.5 (br s, 2 P, P$_a$); IR (Nujol) $\nu_{Ru\text{-}H}$ 1920 (m), 1960 (w) cm^{-1}. **4** exhibited a marked tendency to disproportionate in THF solution to yield [RuH$_2$(PPh$_3$)$_4$] and a dihydride bis(phosphine) complex (by NMR), presumably [RuH$_2$(PPh$_3$)$_2$(THF)$_2$].

[RuH$_2$(PPh$_3$)$_3$] (**4′**) was prepared in sity by the same procedure as **4** but with toluene instead of THF as solvent: ^{31}P{^{1}H} NMR (toluene-d_8, −90 to +30 °C) δ 61.5 (br s, 3 P). An alternative procedure, involving reaction of [RuH$_3$(PPh$_3$)$_4$] (1.5×10^{-3} M) with cyclohexanone (2.7×10^{-3} M) in toluene-d_8, yielded a ligated analogue of **3**, [RuH$_2$(PPh$_3$)$_3$L] (**4″**) where L = cyclohexanone or cyclohexanol: ^{1}H NMR (toluene-d_8, 25 °C) δ −10.2 (q, $J_{P\text{-}H} \approx 39$ Hz, 2 H, RuH), 6.95 (m, 36 H, ortho and meta aryl protons), 7.30 (br t, $J \approx 7$ Hz, 9 H, para aryl protons); ^{31}P{^{1}H} NMR (toluene-d_8, 25 °C) δ 58.5 (br s, 3 P); ^{31}P{^{1}H} (toluene-d_8, −80 °C) δ 59.5 (br s, 1 P, P$_b$), 61.5 (m, 2 P, P$_a$). Because of their tendency to disproportionate to [RuH$_2$(PPh$_3$)$_4$] and [RuH$_2$(PPh$_3$)$_2$(L)$_2$] (?), **4′** and **4″** could not be isolated or further characterized.

Stoichiometric Reactions. These were studied in toluene-d_8 or THF-d_8 by mixing reagent solutions in the desired proportions. Reactions were monitored by ^{1}H NMR. The reactions of **1** with alcohols were monitored under hydrogen and other reactions in evacuated and sealed NMR tubes. The reactions of **3** (generated in situ by phosphine dissociation from [RuH$_2$(PPh$_3$)$_4$]) with N_2 and cyclohexanone (under argon) were monitored by ambient- and low-temperature ^{1}H and ^{31}P NMR. To initiate the reaction of **4** with H_2, the argon atmosphere was replaced by H_2. The reactions with D_2 were monitored by ^{1}H and ^{2}H NMR.

Kinetic Measurements. Stoichiometric Reaction of 3 with Cyclohexanone. Toluene-d_8 solutions, containing the desired initial concentrations of cyclohexanone and of **3** (generated in situ by reaction of H_2 with **2**), were sealed in NMR tubes. The ensuing reaction was monitored under pseudo-first-order conditions (excess cyclohexanone) by ^{1}H NMR using toluene-d_7 as an internal standard. Pseudo-first-order rate constants $(k_{\mathrm{stoich}})_{\mathrm{obsd}}$ were calculated by nonlinear least-squares fitting of the kinetic data over at least 3 half-lives to the rate law

$$-d[\mathrm{RuH_4(PPh_3)_3}]/dt = (k_{\mathrm{stoich}})_{\mathrm{obsd}}[\mathrm{RuH_4(PPh_3)_3}] \qquad (1)$$

Low-Pressure Catalytic Reactions. A flask containing a toluene[14] solution of the reactants, prepared as above, was evacuated and connected to the gas-uptake apparatus. The flask was equipped with an externally-driven stir bar. The system was evacuated and then pressurized with H_2 to nearly the desired manometer reading. The reaction vessel was opened to the gas-uptake apparatus and the system equilibrated to the desired temperature by immersion in a large thermostated bath. The experiment was started by closing the stopcocks to the monometer and to the constant-pressure ballast. The volume of H_2 taken up was determined by measuring the displacement of a piston in the calibrated gas burette. The volume of H_2 (corrected to 1 atm) was converted to a pseudo-zero-order rate constant $(k_{\mathrm{cat.}})_{\mathrm{obsd}}$, using eq 2, (where the stoichiometric factor n = 1 for cyclohexanone and 2 for 9-methylanthracene), where $-dV(H_2)/dt$ is the rate of uptake of H_2 (corrected to 1 atm), R is the molar gas constant, T is the temperature (K), [Ru] is the concentration of [RuH$_4$(PPh$_3$)$_3$] (M), and V_{soln} is the volume of solution (3 mL).

$$(k_{\mathrm{cat.}})_{\mathrm{obsd}} = -dV(H_2)/dt/nRTV_{\mathrm{soln}}[\mathrm{Ru}] \qquad (2)$$

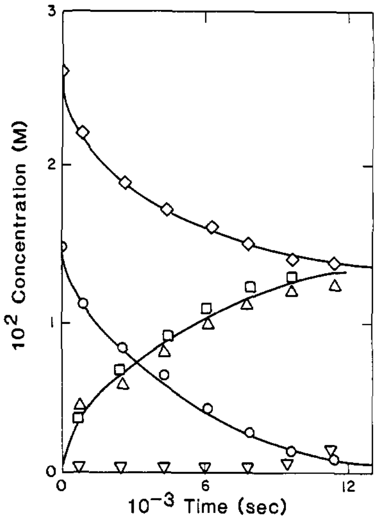

Figure 1. Reaction of [RuH$_4$(PPh$_3$)$_3$] with cyclohexanone in THF at 45 °C: ◇, cyclohexanone; □, cyclohexanol; ○, [RuH$_4$(P$_3$)]; △, [RuH$_2$P$_3$L]; ▽, [RuH$_2$P$_4$] + [RuH$_2$P$_2$L$_2$] (L = THF).

High-Pressure Catalytic Reactions. Weighed amounts of **1** or **2** (which generates **3** in situ by reaction with H_2) were added to 10 mL of THF in a Fisher-Porter bottle (85 mL) equipped with a magnetic stir bar, followed by addition of aliquots of stock solutions of cyclohexanone or 9-methyl anthracene and an internal standard (n-dodecane). The sealed vessel was cooled to −78 °C, evacuated, and pressurized with H_2 at room temperature. The partial pressure of H_2 was calculated by subtracting the solvent partial pressure from the total pressure which was monitored with a gauge. The bottle was immersed in a thermostated oil bath and the reaction solution stirred. Samples were removed at measured time intervals by means of a gas-tight syringe, quenched in air, passed over silica to remove inorganic constituents, and injected into a gas chromatograph equipped with a fused silica capillary column.[7] Peak areas were determined by digital integration and converted to concentrations by comparison with the internal standard.

Results and Discussion

Hydrogenation of Cyclohexanone. Stoichiometric Reactions. Addition of 0.018 M cyclohexanol to a THF-d_8 solution containing 0.020 M K[RuH$_3$(PPh$_3$)$_3$]$^-$ yielded, after a few minutes, a solution containing (by ^{1}H NMR) 0.015 M [RuH$_3$(PPh$_3$)$_3$]$^-$, 0.005 M [RuH$_4$(PPh$_3$)$_3$], 0.013 M c-C$_6$H$_{11}$OH, and 0.005 M [c-C$_6$H$_{11}$O$^-$]. A solution of the same composition was obtained starting from 0.020 M [RuH$_4$(PPh$_3$)$_3$] and 0.018 M [c-C$_6$H$_{11}$O$^-$]. This demonstrates the reversibility of reaction 3 and yields a value of ca. 0.13 for K_3^{eq}.

$$[\mathrm{RuH_3(PPh_3)_3}]^- + \text{c-}\mathrm{C_6H_{11}OH} \underset{}{\overset{K_3^{\mathrm{eq}}}{\rightleftharpoons}} [\mathrm{RuH_4(PPh_3)_3}] + \text{c-}\mathrm{C_6H_{11}O^-} \qquad (3)$$

Addition of an excess of cyclohexanone to a toluene-d_8 solution of [RuH$_4$(PPh$_3$)$_3$] resulted in quantitative reaction according to eq 4 (L = C$_6$H$_{10}$O or C$_6$H$_{11}$OH) (Figure 1), followed at longer times by extensive disproportionation of [RuH$_2$(PPh$_3$)L] into [RuH$_2$(PPh$_3$)$_4$] and [RuH$_2$(PPh$_3$)$_2$L$_2$].

$$[\mathrm{RuH_4(PPh_3)_3}] + \text{c-}\mathrm{C_6H_{10}O} \xrightarrow{k_4} [\mathrm{RuH_2(PPh_3)_3L}] + \text{c-}\mathrm{C_6H_{11}OH} \qquad (4)$$

Under pseudo-first-order conditions (c-C$_6$H$_{10}$O in excess) the kinetics conformed to the rate law of eq 1 (Figure 2). Values

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[13] This synthesis of **4**, which utilizes potassium hydride as the reducing agent, yields results similar to those for the original synthesis employing sodium methoxide[12] but avoids a side reaction that yields [RuH$_2$(CO)(PPh$_3$)$_3$]. In THF, the products of both preparations were unstable to disproportionation to give mixtures (by ^{1}H and ^{31}P NMR) of [RuH$_2$(PPh$_3$)$_3$(THF)], [RuH$_2$(PPh$_3$)$_4$], and [RuH$_2$(PPh$_3$)$_2$(THF)$_2$] (in the ratio 8:1:1). The last, relatively unreactive, species exhibited a ^{1}H NMR triplet signal (δ −24.9 ($J_{P\text{-}H} \approx 30$ Hz)) and two temperature-dependent ^{31}P resonances (δ 76.0 (s, 2 P at 25 °C), 81.8 (1 P), 71.8 (1 P at −80 °C)). The use of toluene as solvent avoids this complication but the reaction is extremely slow.

[14] Because THF attacked the seals of the gas-uptake apparatus, toluene was used as the solvent in this reactions and, to permit comparison, in the stoichiometric reactions of **3** with cyclohexanone. Since **1** is insoluble in toluene, the rates of the [RuH$_3$P$_3$]$^-$- and [RuH$_4$P$_3$]-catalyzed reactions were compared in Fisher-Porter bottle experiments using THF as solvent.

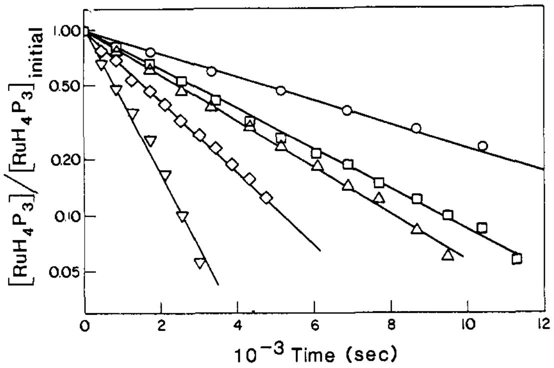

Figure 2. Kinetic plots for the reaction of $[RuH_4(PPh_3)_3]$ (1.5×10^{-2} M) with cyclohexanone in toluene-d_8 at 20.5 °C. [Cyclohexanone]: ○, 0.12 M; □, 0.18 M; △, 0.21 M; ◇, 0.34 M; ▽, 0.54 M.

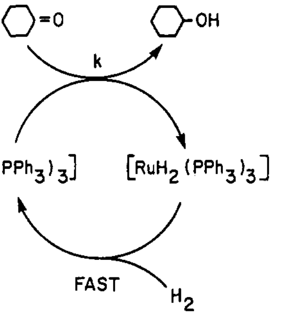

Figure 3. Catalytic cycle for the $[RuH_4(PPh_3)_3]$-catalyzed hydrogenation of cyclohexanone.

Table I. Kinetic Data for the Reaction of $[RuH_4(PPh_3)_3]$ in Toluene-d_8 according to Eq 4

$10^2[RuH_4(PPh_3)_3]$, M	$[c\text{-}C_6H_{10}O]$, M	temp, °C	$10^4(k_{stoich})_{obsd}$, s^{-1}	10^3k_4, $M^{-1}\ s^{-1}$
0.5	0.12	20.5	1.42	1.2
1.0	0.12	20.5	1.32	1.1
1.5	0.12	20.5	1.55	1.3
1.5	0.16	24.8	2.7	1.7
1.0	0.16	44.7	16	10.0
1.5	0.12	20.5	1.55	1.3
1.5	0.18	20.5	2.53	1.4
1.5	0.21	20.5	2.83	1.4
1.5	0.34	20.5	4.35	1.3
1.5	0.54	20.5	8.17	1.5

of $(k_{stoich})_{obsd}$ over a range of temperatures and of C_6H_{10} concentrations are listed in Table I. $(k_{stoich})_{obsd}$ is seen to be proportional to the $C_6H_{10}O$ concentrations, and, thus, the kinetics conform to the overall second-order rate law (eq 5), where $k_4 = (1.7 \pm 0.1) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 24.8 °C.

$$-d[RuH_4(PPh_3)_3]/dt = (k_{stoich})_{obsd}[C_6H_{10}O] = k_4[RuH_4(PPh_3)_3][C_6H_{10}O] \quad (5)$$

Reaction of $[RuH_2(PPh_3)_3L]$ with H_2. Reaction of $[RuH_2(PPh_3)_3(THF)]$ with H_2 (1 atm) in THF at 25 °C resulted in rapid (<5 min) conversion to $[RuH_4(PPh_3)_3]$ (>70% by ^1H and ^{31}P NMR), according to eq 6. Other $[RuH_2(PPh_3)_3L]$ adducts, notably $[RuH_2(PPh_3)_3(N_2)]$, also were found to react rapidly with H_2 to form $[RuH_4(PPh_3)_3]$ in quantitative yield (also reported by Knoth[10]).

$$[RuH_2(PPh_3)_3L] + H_2 \rightarrow [RuH_4(PPh_3)_3] + L \quad (6)$$

Catalytic Hydrogenation. Reactions 4 and 6 constitute a catalytic cycle for the hydrogenation of cyclohexanone (Figure 3). To establish whether this is the only catalytic mechanism, the kinetics of the $[RuH_4(PPh_3)_3]$-catalyzed reaction were determined by the gas-uptake method described earlier. The initial rates of uptake of H_2 exhibited pseudo-zero-order kinetics (Figure 4), yielding values of $(k_{cat.})_{obsd}$ according to eq 2. These are listed in Table II and are seen to be proportional to the cyclohexanone concentration, yielding a catalytic rate law (eq 7) essentially identical with that for the stoichiometric reaction of $[RuH_4(PPh_3)_3]$ with cyclohexanone (eq 5).

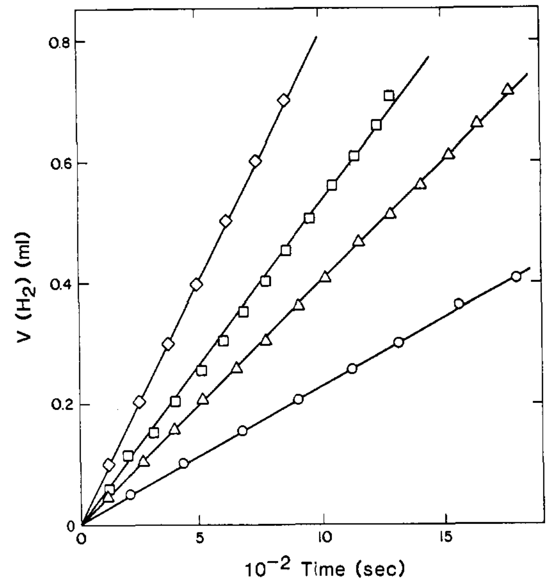

Figure 4. H_2 gas uptake plots for the $[RuH_4(PPh_3)_3]$-catalyzed hydrogenation of cyclohexanone in toluene at 20.5 °C (0.64 atm of H_2; 0.015 M $[RuH_4(PPh_3)_3]$). [Cyclohexanone]: ○, 0.158 M; △, 0.281 M; □, 0.371 M; ◇, 0.541 M.

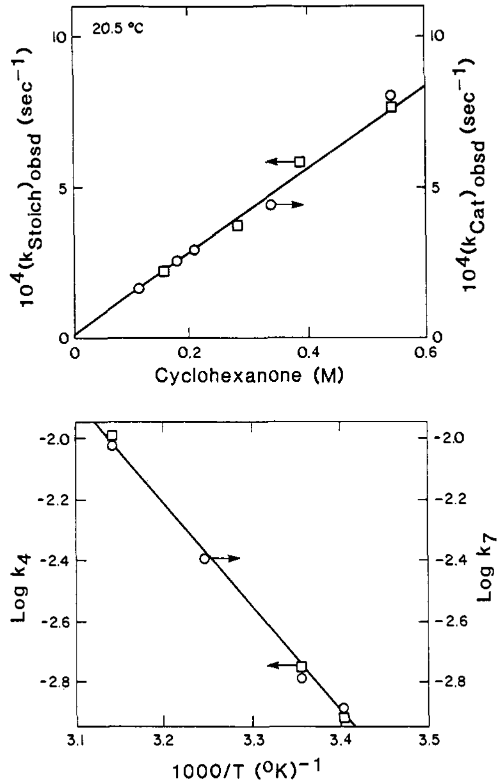

Figure 5. Comparison of the rate constants for the stoichiometric reaction of $[RuH_4(PPh_3)_3]$ with cyclohexanone (eq 4) and the $[RuH_4(PPh_3)_3]$-catalyzed hydrogenation of cyclohexanone in toluene: □, stoichiometric reaction; ○, catalytic reaction.

$$-d[C_6H_{10}O]/dt = (k_{cat.})_{obsd}[C_6H_{10}O] = k_7[RuH_4(PPh_3)_3][C_6H_{10}O] \quad (7)$$

The agreement between $(k_{stoich})_{obsd}$ and $(k_{cat.})_{obsd}$ (hence, between k_4 and k_7) is demonstrated by Figure 5. From the temperature dependence of k_4 (or k_7) the following activation parameters are deduced: $\Delta H_4^{\ddagger} = 15.0 \pm 1$ kcal/mol; $\Delta S_4^{\ddagger} = -34.2 \pm 3$ cal/(mol K).

Table II. Kinetic Data for the $[RuH_4(PPh_3)_3]$-Catalyzed Hydrogenation of Cyclohexanone in Toluene

$10^2[RuH_4(PPh_3)_3]$, M	$[c\text{-}C_6H_{10}O]$, M	H_2 press, atm	temp, °C	$10^4[-dV(H_2)/dt]$,[a] mL s^{-1}	$10^4(k_{cat})_{obsd}$, s^{-1}	10^3k_7, M^{-1} s^{-1}
0.3	0.158	0.64	44.7	3.9	16.4	10.4
0.6	0.158	0.64	44.7	6.4	13.6	8.6
0.9	0.158	0.64	44.7	11	15.0	9.5
1.2	0.158	0.64	44.7	13	14.0	8.9
1.5	0.158	0.64	44.7	18	16.0	10.1
0.9	0.158	0.32	24.8	1.6	2.4	1.5
0.9	0.158	0.64	24.8	1.7	2.5	1.6
0.9	0.158	0.21	44.7	11.3	16.2	10.2
0.6	0.158	0.21	44.7	7.0	15.0	9.5
0.9	0.158	0.64	44.7	11.0	15.0	9.5
0.6	0.040	0.64	44.7	0.88	1.9	4.8
0.6	0.158	0.64	44.7	6.4	13.6	8.6
0.6	0.322	0.64	44.7	15.0	32.0	9.9
0.6	0.482	0.64	44.7	21.7	46.2	9.6
0.6	0.643	0.64	44.7	22.7	48.3	7.5
1.5	0.158	0.64	20.5	2.2	2.1	1.3
1.5	0.281	0.64	20.5	3.9	3.6	1.3
1.5	0.371	0.64	20.5	5.3	4.9	1.3
1.5	0.541	0.64	20.5	8.3	7.7	1.4
1.5	0.158	0.64	20.5	2.2	2.1	1.3
0.9	0.158	0.64	34.8	4.3	6.3	4.0
0.9	0.158	0.64	44.7	10.8	15.3	9.7

[a] Corrected to 1 atm.

The catalytic hydrogenation of cyclohexanone clearly proceeds by the mechanism of Figure 3 in which the reaction between $[RuH_4(PPh_3)_3]$ and cyclohexanone is the rate-determining step. The detailed mechanism of this step is unclear since $[RuH_4(PPh_3)_3]$ is coordinately saturated. A rate-determining or preequilibrium loss of H_2 is difficult to reconcile with the observed kinetics unless the inverse $[H_2]$ dependence of the latter step is compensated by an H_2-dependent subsequent step, e.g., eq 8–11.

$$[RuH_4(PPh_3)_3] \rightleftharpoons [RuH_2(PPh_3)_3] + H_2 \qquad (8)$$

$$[RuH_2(PPh_3)_3] + c\text{-}C_6H_{10}O \rightleftharpoons [RuH_2(PPh_3)_3(c\text{-}C_6H_{10}O)] \qquad (9)$$

$$[RuH_2(PPh_3)_3(c\text{-}C_6H_{10}O)] + H_2 \rightarrow [RuH_2(PPh_3)_3(c\text{-}C_6H_{11}OH)] \xrightarrow[\text{fast}]{H_2} [RuH_4(PPh_3)_3] + c\text{-}C_6H_{11}OH \qquad (10)$$

$$c\text{-}C_6H_{10}O + H_2 \xrightarrow{[RuH_4(PPh_3)_3]} c\text{-}C_6H_{11}OH \qquad (11)$$

In accord with this it was found that $[RuH_4(PPh_3)_3]$ undergoes rapid substitution (presumably by loss of H_2), e.g., by N_2 or PPh_3, to form $[RuH_2(PPh_3)_3(N_2)]$ or $[RuH_2(PPh_3)_4]$, respectively (reaction with N_2 complete (>80% by NMR), in less than 5 min at 45 °C). We also attempted to establish dissociation of H_2 from $[RuH_4P_2]$ by exchange with D_2, but the results were not entirely conclusive. Exchange with 4.4 atm of D_2 to form $RuD_4(PPh_3)_3$ was fast (≲5 min) and complete at 85 °C. At 35 °C, exchange was still fast (no change after 12 min) but incomplete (ca. 20%), possibly because of depletion of the dissolved D_2 and slow diffusion. Reversibility of the exchange reaction was confirmed by reequilibrating with H_2 to regenerate $[RuH_4(PPh_3)_3]$. The exchange reaction was unaffected by addition of 0.25 equiv of PPh_3 (higher PPh_3 results in conversion to $[RuH_2(PPh_3)_4]$), implying that exchange does not proceed by PPh_3 dissociation.

Exchange with D_2 was accompanied by extensive incorporation of deuterium into the ortho phenyl positions of the PPh_3 ligands. When a THF solution of $[RuH_2D_2(PPh_3)_3]$ (prepared by reaction of D_2 with $[RuH_2(PPh_3)(N_2)]$ at −78 °C) was warmed to 30 °C, intramolecular scrambling with the ortho phenyl hydrogens (monitored by ^2H NMR; Figure 6) was observed to proceed according to a first-order rate law with a first-order rate constant of $(2.5 \pm 0.2) \times 10^{-1}$ s^{-1}. The statistically corrected equilibrium ratio $([C–D]/[C–H])/([Ru–D]/[Ru–H])$ was found to be 2.2, consistent with the higher C–H(D) zero-point energy compared with Ru–H(D).

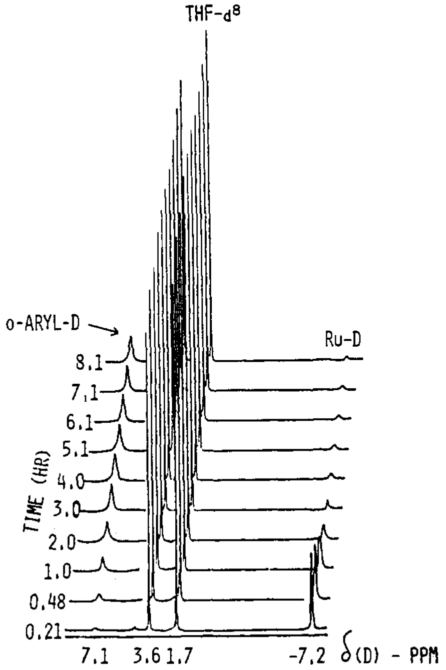

Figure 6. ^2H NMR spectra depicting the intramolecular scrambling of deuterium from $[RuH_2D_2(PPh_3)_3]$ into the ortho phenyl positions of the PPh_3 ligands in THF at 32 °C (7.5×10^{-3} M $[RuH_2D_2(PPh_3)_3]$).

Comparison of the Catalytic Activities of $[RuH_4(PPh_3)_3]$ and $[RuH_3(PPh_3)_3]^-$. Grey, Pez, and Wallo[3] reported that $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ (which is rapidly converted by reaction with H_2 to $[RuH_3(PPh_3)_3]^-$ [4]) is an effective catalyst or catalyst precursor for the hydrogenation of polar compounds such as ketones, esters, and nitriles. They suggested that this catalytic activity might be promoted by the anionic character of the catalyst that enhances its effectiveness as a hydride donor (i.e., to a carbonyl group). Accordingly, it was of some interest to compare the catalytic activities of $[RuH_4(PPh_3)_3]$ and $[RuH_3(PPh_3)_3]^-$ for the hydrogenation of cyclohexanone. Surprisingly, in view of the rationale cited above, $[RuH_3(PPh_3)_3]^-$ was found not be an effective catalyst for the hydrogenation of cyclohexanone. When added initially (Figure 7), an induction period was observed, following which catalytic hydrogenation proceeded at a rate identical with that of the $[RuH_4(PPh_3)_3]$-catalyzed reaction. Apparently $[RuH_3(PPh_3)_3]^-$ itself is inactive but is converted during the induction period to $[RuH_4(PPh_3)_3]$ by cyclohexanol

Table III. Kinetic Data for the $[RuH_4(PPh_3)_3]$-Catalyzed Hydrogenation of 9-Methylanthracene (An′) in Toluene at 55 °C

$10^3[RuH_4(PPh_3)_3]$, M	[An′], M	H_2 press, atm	$10^3[dV(H_2)/dt]$,^{a} mL s^{-1}	$10^3(k_{cat})_{obsd}$, s^{-1}	10^3k_{12}, M^{-1} s^{-1}
1.5	0.48	0.71	1.1	4.5	9.5
3.0	0.48	0.71	1.6	3.3	6.8
3.0	0.48	0.71	1.5	3.2	6.6
6.0	0.48	0.71	3.3	3.4	7.2
9.0	0.48	0.71	5.2	3.6	7.5
6.0	0.12	0.71	1.1	1.2	9.7
6.0	0.24	0.71	2.4	2.5	10.3
6.0	0.48	0.71	3.3	3.4	7.2
6.0	0.60	0.71	5.3	5.5	9.2
6.0	0.72	0.71	6.2	6.3	8.8
3.0	0.48	0.20	1.7	3.5	7.2
3.0	0.48	0.45	1.8	3.6	7.5
3.0	0.48	0.71	1.8	3.6	7.5
3.0	0.48	0.71	1.7	3.5	7.2
3.0	0.48	0.84	1.8	3.6	7.2
				$(k_{12})_{mean}$	8.0

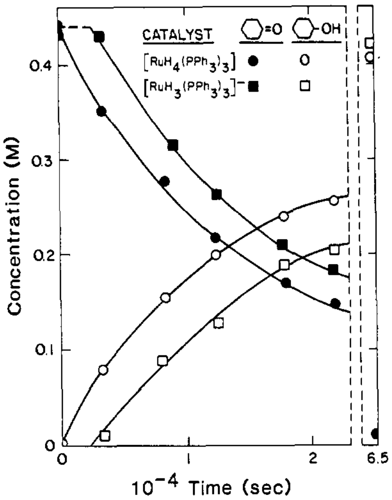

Figure 7. Rate plots for the $[RuH_4(PPh_3)_3]$- and $[RuH_3(PPh_3)_3]^-$-catalyzed hydrogenation of cyclohexanone in THF (5.4 × 10^{-3} M [Ru]; 4.0 atm of H_2; 45 °C).

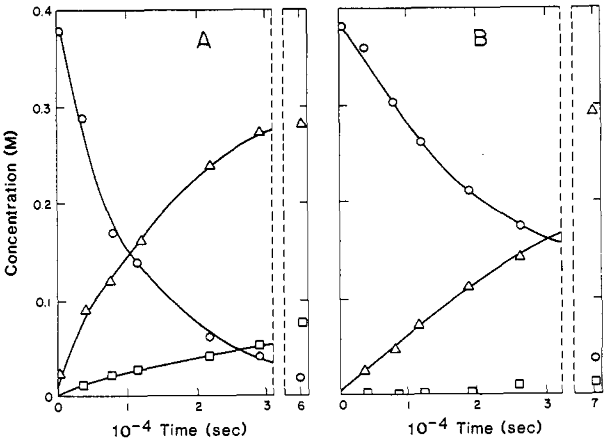

Figure 8. Rate plots for the (A) $[RuH_4(PPh_3)_3]$- and (B) $[RuH_3(PPh_3)_3]^-$-catalyzed hydrogenation of 9-methylanthracene (1.8 × 10^{-3} M [Ru]; 4.0 atm of H_2; 55 °C): ○, An′; △, H_4-An′; An′; □, H_8-An′.

(eq 3), whose initial formation is slow and autocatalytic. An explanation of the higher catalytic activity of $[RuH_4(PPh_3)_3]$ may be provided by its recent characterization as an η^2-dihydrogen complex, i.e., $[RuH_2(\eta^2\text{-}H_2)(PPh_3)_3]$.[15] The facility with which "RuH_4P_3" loses H_2 may be related to this, and, indeed, the corresponding loss of H_2 from $[RuH_3(PPh_3)_3]^-$ (as deduced from its rate of substitution or D_2 exchange) is much slower (7 × 10^{-4} s^{-1} at 65 °C).[4]

Hydrogenation of Arenes. $[RuH_4(PPh_3)_3]$ also was found to be an effective catalyst for the hydrogenation of 9-methylanthracene,[16] accompanied by formation of 1,2,3,4,5,6,7,8-octahydroanthracene (H_8-An′). By using the gas-uptake method previously described, the kinetics of the $[RuH_4(PPh_3)_3]$-catalyzed hydrogenation of An′ in toluene were found to obey a rate law (eq 12) similar to that for cyclohexanone (eq 7) and to that previously reported for the $[RuH_3(PPh_3)_3]^-$-catalyzed hydrogenation of anthracene.[4] The kinetic data are summarized in Table III and yield a value of 7.6 × 10^{-3} M^{-1} s^{-1} for k_{12} at 55 °C.

$$-d[An']/dt = (k_{cat.})_{obsd}[RuH_4(PPh_3)_4] = k_{12}[RuH_4(PPh_3)_3][An'] \quad (12)$$

The catalytic activities of $[RuH_4(PPh_3)_3]$ and $[RuH_3(PPh_3)_3]^-$ were compared directly by measuring the rates of hydrogenation of An′ at 55 °C under 4 atm of H_2 in THF solutions containing initially 0.38 M An′ and 1.8 × 10^{-2} M catalyst (Figure 8). The pseudo-first-order rate constants for the hydrogenation of An′ were determined to be 7.5 × 10^{-5} s^{-1} for $[RuH_4(PPh_3)_3]$ and 3.3 × 10^{-5} s^{-1} for $[RuH_3(PPh_3)_3]^-$. Although (in contrast to hydrogenation of cyclohexanone) $[RuH_3(PPh_3)_3]^-$ is itself a catalyst for the hydrogenation of An′, its activity is only about half that of $[RuH_4(PPh_3)_3]$. With the assumption of the same rate law as that for the toluene solution (eq 12), the values of k_{12} in THF were determined to be 4.1 × 10^{-3} M^{-1} s^{-1}, i.e., only about half that in toluene.

The $[RuH_4(PPh_3)_3]$-catalyzed hydrogenation of An′ yielded a somewhat higher fraction of H_8-An′ (~17%) than the $[RuH_3(PPh_3)_3]^-$-catalyzed reaction (<3%). It is of interest that no induction period is observed for the $[RuH_4(PPh_3)_3]$-catalyzed formation of H_8-An′ and that the ratio of H_4-An′ to H_8-An′ remained fairly constant (ca. 5:1) during the course of the reaction. This suggests that free H_4-An′ is not an intermediate in the formation of H_8-An′. This behavior exhibits some parallel with the "roll-over" reactions of $[IrH_2(PPh_3)_2S_2]$ and $[ReH_7(PPh_3)_2]$, reported by Crabtree[17] and Caulton.[18]

Some aspects of the mechanism of the $[RuH_3(PPh_3)_3]^-$-catalyzed hydrogenation of arenes, including the formation of the anthracene adduct $[RuH(PPh_3)_2(anthracene)]^-$, have previously been described.[4] The details of the mechanism of the $[RuH_4(PPh_3)_3]$-catalyzed reaction remain to be elucidated. Reaction of $[RuH_4(PPh_3)_3]$ with ca. 0.5 equiv of An′ in THF at 45 °C resulted in formation, after ca. 5 h, of a quantitative yield of

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(15) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124–3125.

(16) 9-Methylanthracene was used in these studies, instead of anthracene, because of its higher solubility and more convenient NMR characteristics.

(17) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107–113.

(18) DeWit, D. G.; Folting, K.; Streib, W. E.; Caulton, K. G. *Organometallics* **1985**, *48* 1149–1153.

H_4-An′ together with a mixture of ruthenium products, including $[\mathrm{RuH_2(PPh_3)_3(THF)}]$, $[\mathrm{RuH_2(PPh_3)_2(THF)_2}]$ and $[\mathrm{RuH_2(PPh_3)_4}]$, and with a small amount (0.05 equiv) of a product ($\delta_{\mathrm{Ru-H}}$ −19.6 ($J_{\mathrm{P-H}}$ = 30 Hz)) tentatively identified as $[\mathrm{RuH_2}(\eta^4\text{-An}')(\mathrm{PPh_3})_2]$. An analogous, η^4-complex $[\mathrm{RuH_2}(\eta^4\text{-DPB})(\mathrm{PPh_3})_2]$ (DPB = *trans,trans*-1,4-diphenylbutadiene) was obtained in ca. 30% yield by reacting $[\mathrm{RuH_4(PPh_3)_3}]$ with DPB in THF-d_8 at 25 °C according to eq 13.

$$[\mathrm{RuH_4(PPh_3)_3}] + 0.9\ \mathrm{DPB} \rightarrow 0.33[\mathrm{RuH_2(PPh_3)_3(THF)}] + 0.33[\mathrm{RuH_2(PPh_3)_4}] + 0.33[\mathrm{RuH_2}(\eta^4\text{-DPB})(\mathrm{PPh_3})_2] + 0.5[\text{1,4-diphenylbutane}] \quad (13)$$

$[\mathrm{RuH_2}(\eta^4\text{-DPB})(\mathrm{PPh_3})_2]$ also was prepared by protonation of $[\mathrm{RuH}(\eta^4\text{-DPB})(\mathrm{PPh_3})_2]^-$ [4] with 1 equiv of H_2O although this reaction also produces some unidentified products. The NMR spectrum of $[\mathrm{RuH_2}(\eta^4\text{-DPB})(\mathrm{PPh_3})_2]$ suggests two nonequivalent phosphorus atoms and two equivalent hydrogens: ^{1}H NMR δ −11.9 (dd, $J_{\mathrm{P-H}}$ = 27 Hz, $J_{\mathrm{P'-H}}$ = 23 Hz, 2 H, RuH_2); $^{31}P\{^1H\}$ NMR δ 67.0 (d, $P_{\mathrm{P-P}}$ = 80 Hz, 1 P), δ 59.5 (d, 1P); each signal splits into the expected doublet of triplets upon selective decoupling of the aryl protons. $[\mathrm{RuH_2}(\eta^4\text{-DPB})(\mathrm{PPh_3})_2]$ was found to be unreactive toward H_2 and thus does not appear to be a catalytic intermediate.

Reaction of $[\mathrm{RuH_4(PPh_3)_3}]$ with an excess (ca. 4 equiv) of An′ resulted in formation, after ca. 4 h at 65 °C, of 1 equiv of H_4-An′ implying reduction of the ruthenium to Ru(0), possibly to $[\mathrm{Ru}(\eta^4\text{-An}')(\mathrm{PPh_3})_3]$ or $[\mathrm{Ru}(\eta^6\text{-An}')(\mathrm{PPh_3})_2]$. Analogues of both species have previously been reported, namely, $[\mathrm{Ru}(\eta^4\text{-C_4H_6})(\mathrm{PPh_3})_3]$[18] and $[\mathrm{Os}(\eta^6\text{-C_6H_6})(\mathrm{PPh_3})_2]$.[19]

We have confirmed earlier reports[18] that $[\mathrm{RuH_4(PPh_3)_3}]$ reacts with dienes, for example, 1,3-butadiene to form (after ca. 20 min at room temperature in C_6D_6) $[\mathrm{Ru}(\eta^4\text{-C_4H_6})(\mathrm{PPh_3})_3]$ (eq 14). The latter reacts more slowly (ca. 1.5 h) with more butadiene to form $[\mathrm{Ru}(\eta^4\text{-C_4H_6})_2(\mathrm{PPh_3})]$ (eq 15) [$^{31}P\{^1H\}$ NMR δ 67.9 ppm (br s)]. $[\mathrm{Ru}(\eta^4\text{-C_4H_6})(\mathrm{PPh_3})_3]$ reacts rapidly with H_2 to regenerate $[\mathrm{RuH_4(PPh_3)_3}]$. Equations 14 and 16 constitute a catalytic cycle for the hydrogenation of butadiene. On the other hand, $[\mathrm{Ru}(\eta^4\text{-C_4H_6})_2(\mathrm{PPh_3})]$ was found to be unreactive toward H_2 (or even toward PPh_3) and, thus, represents an unproductive dead end.

$$[\mathrm{RuH_4(PPh_3)_3}] + 2[1,3\text{-}\mathrm{C_4H_6}] \rightarrow [\mathrm{Ru}(\eta^4\text{-C_4H_6})(\mathrm{PPh_3})_3] + \mathrm{C_4H_{10}} \quad (14)$$

$$[\mathrm{Ru}(\eta^4\text{-C_4H_6})(\mathrm{PPh_3})_3] + 1,3\text{-}\mathrm{C_4H_6} \rightarrow [\mathrm{Ru}(\eta^4\text{-C_4H_6})_2(\mathrm{PPh_3})] + 2\mathrm{PPh_3} \quad (15)$$

$$[\mathrm{Ru}(\eta^4\text{-C_4H_6})(\mathrm{PPh_3})_3] + 4\mathrm{H_2} \rightarrow [\mathrm{RuH_4(PPh_3)_3}] + \mathrm{C_4H_{10}} \quad (16)$$

Concluding Remarks

These studies have revealed that $[\mathrm{RuH_4(PPh_3)_3}]$ is an effective and versatile catalyst for the hydrogenation of ketones and arenes and have served to elucidate some aspects of the mechanisms of these reactions and to identify and characterize some of the intermediates. In comparative studies we have failed to identify any distinctive properties or advantages of the anionic catalyst $[\mathrm{RuH_3(PPh_3)_3}]^-$, over the related neutral complex $[\mathrm{RuH_4(PPh_3)_3}]$, for the hydrogenation either of ketones or of arenes. Indeed, the latter was found to be the more effective catalyst for both reactions.

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[19] Werner, H.; Werner, R. *J. Organomet. Chem.* **1980**, *194*, C7.

Highly Stabilized Copper(III) Complexes

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Abstract: It has been possible to synthesize a family of copper complexes in the rare +III oxidation state by employing strongly donating polyanionic chelating (PAC) ligands containing organic *N*-amido and oxido donors. The X-ray crystal structure of one example, $[\mathrm{PPh_4}][\mathrm{Cu}(\eta^4\text{-}\mathbf{4})]\cdot 2\mathrm{H_2O}$ ($H_4\mathbf{4}$ = 1,2-bis(2-hydroxy-2-methylpropanamido)benzene), is reported. The metal center is found in a square-planar environment with normal bond distances and angles for the copper(III) formulation. Copper(III/II) couples are highly sensitive to ligand environments. This property is exploited to assess the relative donor properties of a series of PAC ligands containing *N*-amido, phenolato, and alkoxido donors. The possible noninnocence of the PAC ligands that contain aromatic groups is considered, and an approach for determining the best formal oxidation state assignments for the metal centers in potentially ambiguous cases is introduced. The trend in formal potentials as the aromatic groups of the PAC ligands are replaced by aliphatic groups indicates that oxidation of each copper(II) complex is metal-centered. The formal potentials of the copper(III/II) couples vary over a range of more than 1.1 V (−1.08 to +0.14 V vs. Fc^+/Fc). Alkoxide ligands are much stronger donors than phenoxide ligands. The copper(III) complexes of the more donating PAC ligands are considerably more stabilized (more negative formal potentials for copper(III/II) couples) than has been observed hitherto for complexes with first-row donor complements.

Interest in copper compounds of the rare +III oxidation state has mounted substantially in the last decade. Although few copper(III) compatible ligand environments have been discovered, a rich coordination chemistry has been developed for several systems.[2–9] A debate is in progress over the possible participation of copper(III) complexes in certain enzymatic processes.[10] In the specific case of galactose oxidase one side has copper(III) as

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