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HYDRIDO(PHOSPHINE)RUTHENATE COMPLEXES AND THEIR ROLE IN THE CATALYTIC HYDROGENATION OF ARENES *

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Summary

Starting with the potassium salt of $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ (**1**), the following reactions in THF were identified: (1) **1** + H_2 → *fac*-$[RuH_3(PPh_3)_3]^-$ (**2**); (2) **1** + 1,4-Ph_2-1,3-butadiene → $[RuH(PPh_3)_2$(1,4-Ph_2-1,3-butadiene)$]^-$ (**3**) + PPh_3; (3) **3** + 4H_2 → $[RuH_5(PPh_3)_2]^-$ (**4**) + 1,4-Ph_2-butane; (4) **4** + 1-hexene → $[RuH_3(PPh_3)_2]^-$ (**5**) + hexane; (5) **4** + L → $[RuH_3(PPh_3)_2L]^-$ + H_2 (L = CO, PPh_3, PMe_2Ph); (6) **2** + 1,5-anthracene (A) → $[RuH(PPh_3)_2A]^-$ (**7**) + 0.5 (1,2,3,4-H_4A) + PPh_3; (7) **4** + 5 C_2H_4 → $[Ru(PPh_3)(PPh_2C_6H_4)(C_2H_4)_2]^-$ (**8**) + 3C_2H_6; (8) **4** + 2A → **7** + 1,2,3,4-H_4A; (9) **7** + 4H_2 → **4** + 1,2,3,4-H_4A. Reactions 8 and 9 constitute a catalytic cycle for the hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene.

Introduction

The orthometallated anionic ruthenium hydride complex, $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$, recently synthesized by Pez, Grey et al. [1], has been reported to be an effective homogeneous catalyst or catalyst precursor for the hydrogenation of a variety of substrates, including the highly selective hydrogenation of polynuclear aromatic compounds, for example, of anthracene to 1,2,3,4-tetrahydroanthracene [2,3]. The origin of this selectivity was of some interest, particularly in the light of earlier reports of different selectivities for other homogeneous hydrogenation catalysts, for example, $HCo(CO)_4$ which catalyzes the hydrogenation of anthracene exclusively to 9,10-dihydroanthracene [4,5]. In this paper we report the results of studies on the coordination chemistry of $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ and derivatives thereof, notably encompassing reactions with H_2 and with anthracene. These studies have led to the synthesis and characterization of several new hydrido(phosphine)ruthenate complexes and to the elucidation of at least some aspects of the mechanism of the catalytic hydrogenation of anthracene [6].

* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

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Experimental

Physical measurements. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker 270 MHz, Bruker 90 MHz, and Nicolet 200 MHz FT spectrometers, respectively. Chemical shifts are reported relative to $Si(CH_3)_4$ (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P). All NMR spectra were determined in THF-d_8, dried over Na-benzophenone and transferred on a high vacuum line into a flame dried glass storage vessel. Infrared spectra were recorded on a Perkin–Elmer 283 spectrophotometer (Nujol mulls) or a Nicolet MX-S FTIR spectrophotometer (THF solution spectra). GLC measurements, to monitor the hydrogenation of anthracene, were performed on a Varian Aerograph 920 instrument equipped with a thermal conductivity detector using either a 15 ft × 1/4″ 20% FFAP on chromosorb W 40/60 column at 220°C or a 20% SE-30 on chromosorb P 60/80 column at 160°C.

Materials and procedures. All manipulations were carried out with the rigorous exclusion of air and water on a high vacuum line (10^{-4}–10^{-5} torr) or in a nitrogen-filled glovebox (Vacuum atmospheres). Solvents were dried from Na/benzophenone, distilled under nitrogen and stored in the glovebox. Anthracene and all *trans*-1,4-diphenyl-1,3-butadiene were twice recrystallized from THF and toluene, respectively, under air- and moisture-free conditions. 1,3-Cyclohexadiene and 1-hexene were distilled from CaH_2 onto $LiAlH_4$, degassed and transferred in the high vacuum line. Triphenylphosphine was recrystallized from dry hexane and stored under nitrogen. Hydrogen (ultra-high purity), carbon monoxide (research grade), 90% ^{13}C labeled carbon monoxide and ethylene (C.P. grade) were used without further purification. Deuterium (Air Products, 99.99%) was passed through a molecular sieve drying column (high pressure) before use.

$K[RuH_2(PPh_3)_2(PPh_2C_6H_4)]$ (1) A modification [7,8] of the method of Pez et al. [1] was used for the preparation of $K[RuH_2(PPh_3)_2(PPh_2C_6H_4)]$ (**1**).

fac-$K[RuH_3(PPh_3)_3]$ (2) [11]. Crude **1** (3.0 g) was slurried in toluene (25 ml) and THF (5–10 ml) was added slowly until all the yellow solid dissolved. This mixture was filtered through a cellite pad to remove KCl. The filtrate was added to a 3 oz. Fischer and Porter aerosol reaction vessel and stirred under 4 atm of hydrogen at 25°C for 4 days. The yellow solid was filtered and washed with diethyl ether. Yield: 2.5 g, 83%.

Anal. Found: C, 69.35; H, 5.43; P, 9.79; Ru, 10.57; K, 4.48. $C_{54}H_{48}P_3KRu$ calcd.: C, 69.74; H, 5.20; P, 9.99; Ru, 10.87; K, 4.20%.

^{1}H NMR (THF-d_8): δ −9.53 (m, 3H), 6.70 (m, 18H), 6.79 (m, 9H), 7.15 ppm (m, 18H); $^{31}P\{^{1}H\}$ NMR (THF-d_8): δ 65.9 ppm (m, 3P); IR (Nujol): 1857 and 1815 cm^{-1} (RuH); IR (THF): 1835 cm^{-1} (RuH).

$K[RuH(PPh_3)_2(1,4\text{-}Ph_2\text{-}1,3\text{-}butadiene)]$ (3). A slurry of **1** (5.00 g, 5.39 mmol) and all *trans*-1,4-Ph_2-1,3-butadiene (1.65 g, 8.00 mmol) in toluene (125 ml) was stirred vigorously at 90°C. The solids dissolved after several minutes, followed by the precipitation of a thick mass of yellow product. The mixture was heated for a total of 45 min, cooled to room temperature, filtered, and washed with diethyl ether. Yield: 3.90 g, 83%.

^{1}H NMR (THF-d_8): δ −15.44 (dd, 1H, RuH), 0.07 (m, 1H), 0.92 (m, 1H), 4.19 (br s, 1H), 4.37 (br s, 1H), 6.26–8.06 (40H, phenyl protons) ppm; $^{31}P\{^{1}H\}$ NMR (THF-d_8): δ 67.9 (br s, 1P), 71.4 (br s, 1P) ppm (both signals split into the expected doublets upon selective decoupling from aromatic protons); IR (Nujol): 1910 cm^{-1} (RuH).

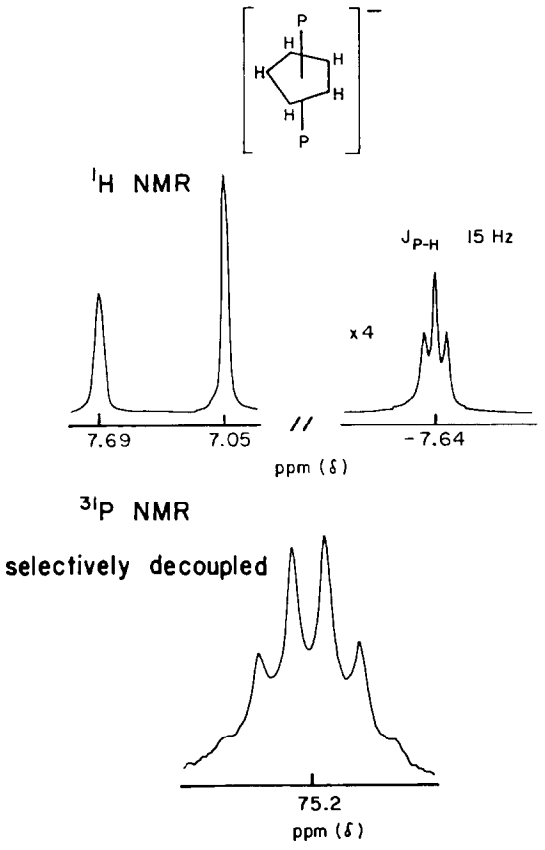


Fig. 1. ^{1}H and ^{31}P NMR spectra of $[RuH_5(PPh_3)_2]^-$.

$K[RuH_5(PPh_3)_2]$ (4). A slurry of **3** (1.00 g) in THF (7.5 ml) and hexane (15 ml) in a 3 oz. Fischer and Porter aerosol reaction vessel was pressurized to 4 atm of hydrogen and heated to 65°C. For the reaction to proceed to completion vigorous stirring was required. When the initially yellow solids turned light tan or white (2–5 h) the mixture was cooled to room temperature, filtered, and washed with hexane. Yield: 0.57–0.75 g, 74–97%.

^{1}H NMR (THF-d_8) (Fig. 1): δ −7.64 (t, 5H, J(P–H) 15 Hz), 7.05 (br s, 18H), 7.69 (br s, 12H) ppm; ^{31}P{^{1}H} NMR (THF-d_8): δ 75.2 ppm (s, 2P, splits into the expected sextet upon selective decoupling from aromatic protons); IR (Nujol): 1750 cm^{-1} (s, b, RuH).

$K[RuH_3P_2]$ (5). A solution of **4** (0.63 g, 0.94 mmol) in THF (7.5 ml) was treated with 1-hexene (0.25 ml, 2 mmol) at room temperature for 10 min. Hexane (25 ml) was added to the solution resulting in the precipitation of a dark yellow solid which was filtered and washed with hexane. Yield: 0.53 g, 85%. The ^{1}H NMR spectrum indicated ca. 3% contamination with $K[RuH_5(PPh_3)_2]$ which was not eliminated by the addition of excess 1-hexene.

^{1}H NMR (THF-d_8) (Fig. 2): δ −13.38 (tt, 1H, H^3, J(P–H) 21 Hz, J(H–H) 7 Hz), −8.08 (m, 2H, $H^{1,2}$), 6.96 (m, 18H), 7.35 (m, 12H) ppm; ^{31}P{^{1}H} NMR

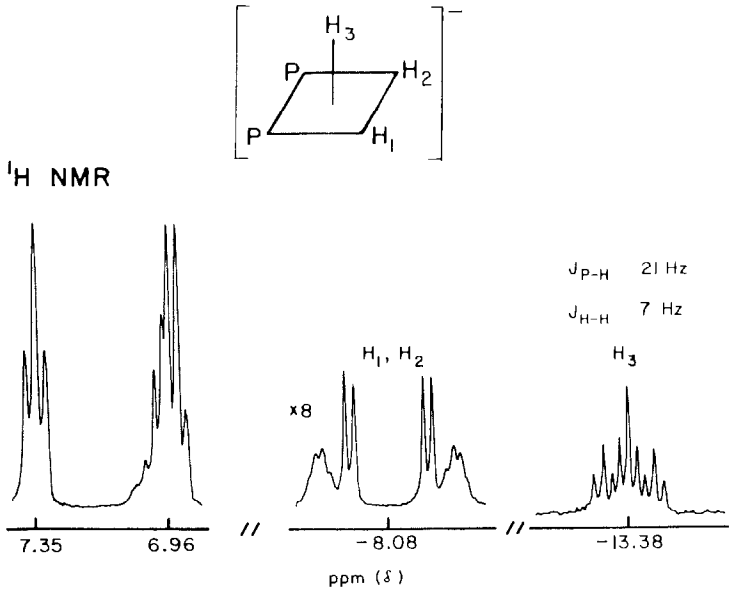


Fig. 2. ^{1}H NMR spectrum of $[RuH_3(PPh_3)_2]^-$.

(THF-d_8): δ 62.6 (br s, 2P) ppm; IR (THF): 2100 (s, sh, RuH), 1940 (shoulder, RuH), 1880 (shoulder, RuH), 1780 cm^{-1} (m, br, RuH).

K[RuH$_3$(PPh$_3$)$_2$(CO)] (6). A 50 ml flask was charged with **4** (0.35 g) dissolved in THF (3.5 ml). The solution was stirred under 1 atm of carbon monoxide at room temperature for 1 h. Hexane (14 ml) was added to the pale yellow solution resulting in the precipitation of a light yellow solid. The solid was filtered and washed with hexane. Yield: 0.32 g, 88%.

^{1}H NMR (THF-d_8): δ −9.00 (m, 2H, H^{1,2}), −7.77 (tt, 1H, H^{3}, J(P–H) 23 Hz, J(H–H) 6.8 Hz), 6.92 (m, 18H), 7.36 (m, 12H) ppm; ^{31}P {^{1}H} NMR (THF-d_8): δ 62.6 (br s, 2P) ppm; IR (THF): 1900 (s, br, CO), 1835 cm^{-1} (shoulder).

A sample of K[RuH$_3$(PPh$_3$)$_2$(^{13}CO)] was prepared by the method described above using 90% ^{13}C labeled carbon monoxide.

^{31}P{^{1}H} NMR (THF-d_8) (Fig. 3): 62.6 (d, 2P, J(P–C) 7.4 Hz) ppm; ^{13}C{^{1}H} NMR (THF-d_8): δ 123.1 ppm (t, 1C, J(P–C) 7.4 Hz); IR (THF): 1903 (shoulder), 1858 cm^{-1} (s, br, CO).

K[RuH(PPh$_3$)$_2$(anthracene)] (7). One arm of a H-shaped flask was charged with **4** (1.27 g, 1.90 mmol), anthracene (0.70 g, 3.93 mmol) and THF (15 ml). The mixture was stirred at room temperature for 24 h and then heated at 65°C for 30 min. After cooling to room temperature, the volume of solvent was reduced by 50% in vacuo. Hexane (75 ml) was placed in the other arm of the H-flask and the H-flask was evacuated. The hexane slowly (24 h) diffused into the product solution by placing the H-flask arm in an ice bath. The layered solution was allowed to mix at 0°C for 2 days and then at room temperature for 2 days yielding a dark red solid. The solution was removed by syringe, hexane (50 ml) was added, and the solid was broken up by agitation and freeze-thaw cycles, filtered and dried in vacuo. Yield: 1.29 g, 81%.

^{1}H NMR (THF-d_8): δ −14.1 (t, 1H, RuH, J(P–H) 24 Hz), 2.43 (d, 2H, H^{1,4}), 4.65 (br s, 2H, H^{2,3}), 5.38 (s, 2H, H^{9,10}), 6.52 (m, 4H, H^{5,6,7,8}), 6.87 7.60 (m, 30H,

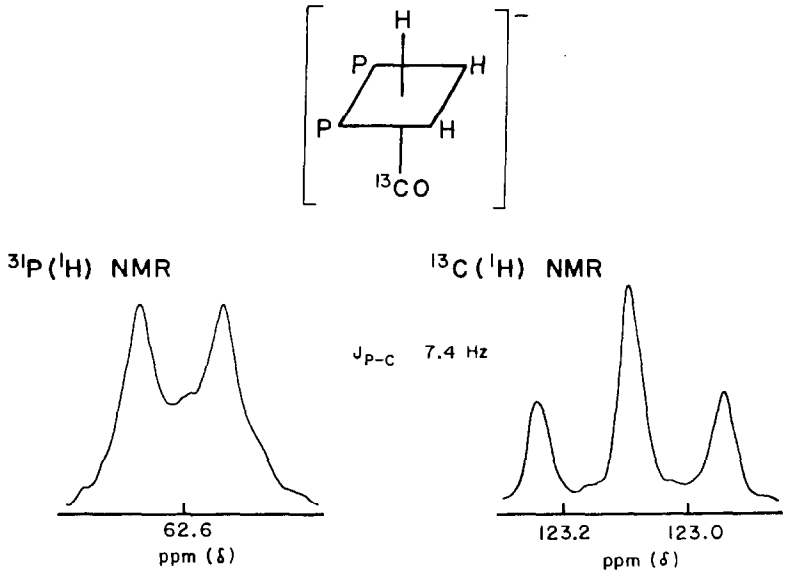


Fig. 3. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of $[RuH_3(PPh_3)_2(^{13}CO)]^-$.

PPh_3 H) ppm; $^{31}P\{^1H\}$ NMR (THF-d_8): δ 69.8 ppm (s, 2P; splits into the expected doublet upon selective decoupling from aromatic protons); IR (Nujol): 1850 cm^{-1} (m, b, RuH).

K[Ru(PPh$_3$)(PPh$_2$C$_6$H$_4$)(C$_2$H$_4$)$_2$] (8). A 50 ml flask was charged with **4** (0.20 g) and THF (1.5 ml). An atmosphere of ethylene was admitted and the solution was stirred at room temperature for 1 h. Hexane (10 ml) was added resulting in the precipitation of a yellow microcrystalline product. The product was filtered and washed with hexane.

^1H NMR (THF-d_8): δ 1.40 (br, 8H, 2 C_2H_4), 6.38–7.54 ppm (m, 29H, phenyl protons); $^{31}P\{^1H\}$ NMR (THF-d_8) δ −12.7 (d, 1P, $PPh_2C_6H_4$, J(P–P) = 16 Hz), 55.6 ppm (d, 1P, PPh_3).

Kinetic measurements. The catalytic hydrogenation of anthracene was monitored in Fischer–Porter pressure bottles (3 oz.). The bottle was charged in an inert atmosphere box, sealed, attached to a copper vacuum line and flushed with H_2 through several pressurization-release cycles. After introducing the desired H_2 pressure the bottle was placed in a thermostatted bath (75.0 ± 0.2°C) and stirred. Samples were withdrawn periodically with an airtight syringe through a septum connected to the bottle through a ball valve. Exposure to air quenched the reaction and resulted in precipitation of a ruthenium-containing solid. After removal of the precipitate by filtration, the solution was analyzed by GLC. The measurements encompassed the concentration ranges, 5.2×10^{-4} to 1.5×10^{-3} *M* **2**, 0.7 to 2 *M* anthracene and 1.5 to 5 atm H_2.

The kinetics of the reaction of *fac*-K[$RuH_3(PPh_3)_3$] (**2**) with anthracene (eq. 1) were measured by monitoring the formation of $[RuH(PPh_3)_2(\text{anthracene})]^-$ spectrophotometrically at 540 to 590 nm. The measurements encompassed the concentration ranges, ca. 1×10^{-3} *M* **2** and 1×10^{-2} to 7×10^{-2} *M* anthracene.

The kinetics of the reaction of K[$RuH_3(PPh_3)_3$] (**2**) with D_2 (eq. 2) in THF-d_8 were followed by monitoring the disappearance of **2** using ^1H NMR (2–4 atm D_2).

The reaction was found to be fully reversible; treatment of $[RuD_3(PPh_3)_3]^-$ with H_2 resulted in the quantitative regeneration of **2**.

Results and discussion

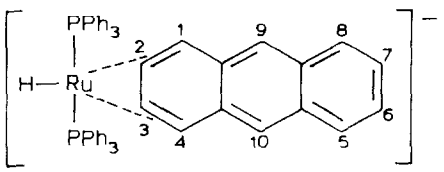
General. The ruthenate complexes described in this paper are extremely air and water sensitive in both the solid state and in solution. Solubility of the complexes was negligible in all solvents with which they did not react except ethers such as THF and glyme. Tetrahydrofuran solutions were thermally stable except for $K[RuH_5(PPh_3)_2]$ and $K[RuH_3(PPh_3)_2]$ solutions which decomposed over a period of several hours.

Reactions of tris(phosphine) complexes. $K[RuH_2(PPh_3)_2(PPh_2C_6H_4)]$ reacts with H_2 under mild conditions to form *fac*-$K[RuH_3(PPh_3)_3]$ (**2**). The ^1H NMR signal at δ −9.53 ppm due to the three Ru-bonded protons corresponds to a six-peak multiplet resembling that previously reported for *fac*-$[IrH_3(PPhEt_2)_3]$ and analyzed by computer simulation as an AA'A''XX'X'' pattern [12]. Recently Chan and Shieh [11] reported the crystal structure of **2** and a synthesis which permits a much more facile entry into hydrido(phosphine)ruthenate chemistry.

fac-$K[RuH_3(PPh_3)_3]$ reacts with anthracene in THF (eq. 1) to form $K[RuH(PPh_3)_2(anthracene)]$ (**7**), a probable intermediate in the hydrogenation of anthracene.

$$fac\text{-}[RuH_3(PPh_3)_3]^- + 1,5\text{-anthracene} \rightarrow [RuH(PPh_3)_2(anthracene)]^- + 0.5\ (1,2,3,4\text{-tetrahydroanthracene}) + PPh_3 \qquad (1)$$

The ^1H NMR spectrum of **7** resembles that reported for $[Fe(CO)_3(anthracene)]$ [13] and is interpreted in terms of an analogous structure. An excess of anthracene was required to drive reaction 1 to completion, thus hampering isolation of pure product. The reaction of $K[RuH_5(PPh_3)_2]$ with anthracene provided a more convenient synthetic route to **7** (vide infra).



(**7**)

Reaction 1 exhibits the same rate law as the isotopic exchange of **2** with D_2 (eq. 2), i.e., $-d[\mathbf{2}]/dt = k_3[\mathbf{2}]$, where $k_3 = 7.6 \times 10^{-4}\ s^{-1}$ at 65°C, independent of the H_2 (or anthracene) concentration. This implies that both reactions proceed through a common unimolecular rate-determining step, namely, the reductive elimination of H_2 to form the common intermediate $[RuH(PPh_3)_3]^-$, an isomer of **1** (eq. 3). Reactions 1 and 2 are much faster than the exchange reactions of **2** with phosphines (e.g., replacement of PPh_3 by PEt_3 or $P(OMe)_3$), ruling out PPh_3 dissociation as the rate-determining step.

$$\underset{(\mathbf{2})}{fac\text{-}[RuH_3(PPh_3)_3]^-} \xrightarrow{D_2} [RuHD_2(PPh_3)_3]^- \left(\xrightarrow{D_2} [RuD_3(PPh_3)_3]^-\right) \qquad (2)$$

fac-$[RuH_3(PPh_3)_3]^-$
(2)

$$\xrightarrow[-H_2]{k_3} [RuH(PPh_3)_3]^- \begin{cases} \xrightarrow[-PPh_3]{\text{anthracene}} [RuH(PPh_3)_2(\text{anthracene})]^- & (3a) \\ \xrightarrow[D_2]{} [RuHD_2(PPh_3)_3]^- & (3b) \end{cases}$$

In an attempt to prepare an easily isolable bis(phosphine) complex, **1** was treated with a variety of diolefins in THF at 65°C and the reactions were followed by ^1H NMR. 2,5-Norbornadiene, 1,3-cyclooctadiene, 1,5-cyclooctadiene (which isomerized to 1,3-cyclooctadiene), 1,5-hexadiene, 1,3-butadiene, and all *trans*-2,4-hexadiene either failed to react significantly or yielded mixtures of products. An excess of 1,3-cyclohexadiene reacted with **1** to form **2**, cyclohexane, and benzene. Whereas the homogeneously catalyzed disproportionation of 1,3-cyclohexadiene to cyclohexene and benzene has been reported previously [14] this is the first case of which we are aware in which the products are cyclohexane and benzene. Two new monohydrides appeared as intermediates during the course of the disproportionation. One has been identified as $[RuH(PPh_3)_2(\text{cyclohexadiene})]$ by comparison with an authentic sample (vide infra); the nature of the other hydride is unknown.

The only reaction of **1** with a diolefin leading to an isolable bis(phosphine) complex was with all *trans*-1,4-Ph_2-1,3-butadiene (eq. 4).

$$K\left[\overline{RuH_2(PPh_3)_2(PPh_2C_6H_4)}\right] + 1,4\text{-}Ph_2\text{-}1,3\text{-butadiene} \rightarrow K[RuH(PPh_3)_2(1,4\text{-}Ph_2\text{-}1,3\text{-butadiene})] + PPh_3 \quad (4)$$

The importance of the electron withdrawing phenyl substituents on the diolefin is emphasized by our inability to obtain analogous products with 1,3-butadiene and all *trans*-2,4-hexadiene. Unlike $[IrH(P\text{-}i\text{-}Pr_3)_2(\text{butadiene})]$ [15], which has been characterized crystallographically [16], the PPh_3 ligands of **3** are non-equivalent on the NMR time scale. More unusual is the apparently small value of $J(P-P)$ of 3 Hz. No splitting of the proton decoupled ^{31}P NMR resonances was observed at room temperature. At −43°C the resonances sharpened and a small splitting was observed in the narrower downfield resonance.

Ethanol reacts with **1** under N_2 at room temperature to yield the oxidized product, $[RuH_2N_2(PPh_3)_3]$, and with **2** to yield a mixture of $[RuH_2N_2(PPh_3)_3]$ and $[RuH_4(PPh_3)_3]$ [17]. These results are of interest in the light of the reported hydrogenation reactions (e.g., of esters) catalyzed by **1** which result in alcoholic products [2] and raise questions about whether the catalytic species in such reactions in fact are anionic complexes.

Reactions of bis(phosphine) complexes. $K[RuH(PPh_3)_2(\text{anthracene})]$ and $K[RuH(PPh_3)_2(1,4\text{-}Ph_2\text{-}1,3\text{-butadiene})]$ react rapidly with H_2 in THF at 25°C to yield $K[RuH_5(PPh_3)_2]$ (**4**), eq. 5 and 6. The latter reaction provides the most convenient route to isolation of the pentahydride. The NMR spectrum of **4** (Fig. 1), which was unchanged on cooling to −60°C, is consistent with a pentagonal bipyramidal structure or with a fluxional structure having a low activation barrier for interconversion.

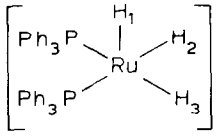
$$K[RuH(PPh_3)_2(\text{anthracene})] + 4H_2 \rightarrow K[RuH_5(PPh_3)_2] + \text{1,2,3,4-tetrahydroanthracene} \quad (5)$$
(7) (4)

$$K[RuH(PPh_3)_2(\text{1,4-Ph}_2\text{-1,3-butadiene})] + 4H_2 \rightarrow K[RuH_5(PPh_3)_2] + \text{1,4-diphenylbutane} \quad (6)$$
(3) (4)

$K[RuH_5(PPh_3)_2]$ displays a rich and diverse chemistry which is outlined in eq. 7–11. $K[RuH_5(PPh_3)_2]$ reacts with a stoichiometric amount of anthracene to form **7** in quantitative yield (eq. 7), thus providing a convenient synthetic route to the anthracene complex. The corresponding reaction with 1,3-cyclohexadiene yields the thermally unstable diene adduct $K[RuH(PPh_3)_2(\text{1,3-cyclohexadiene})]$ together with cyclohexane and cyclohexene. Reaction of **4** with 1-hexene (eq. 8) resulted in partial dehydrogenation and formation of $K[RuH_3(PPh_3)_2]$, whose NMR spectrum (Fig. 2) is consistent with structure **5**. It is probable that the "vacant" coordination site is occupied by a THF molecule, the resulting structure being analogous to that of $K[RuH_3(PPh_3)_2(CO)]$.

$$K[RuH_5(PPh_3)_2] + 2\ \text{anthracene} \rightarrow K[RuH(PPh_3)_2(\text{anthracene})] + \text{1,2,3,4-tetrahydroanthracene} \quad (7)$$

$$K[RuH_5(PPh_3)_2] + \text{1-hexene} \rightarrow K[RuH_3(PPh_3)_2] + \text{hexane} \quad (8)$$
(5)



(**5**)

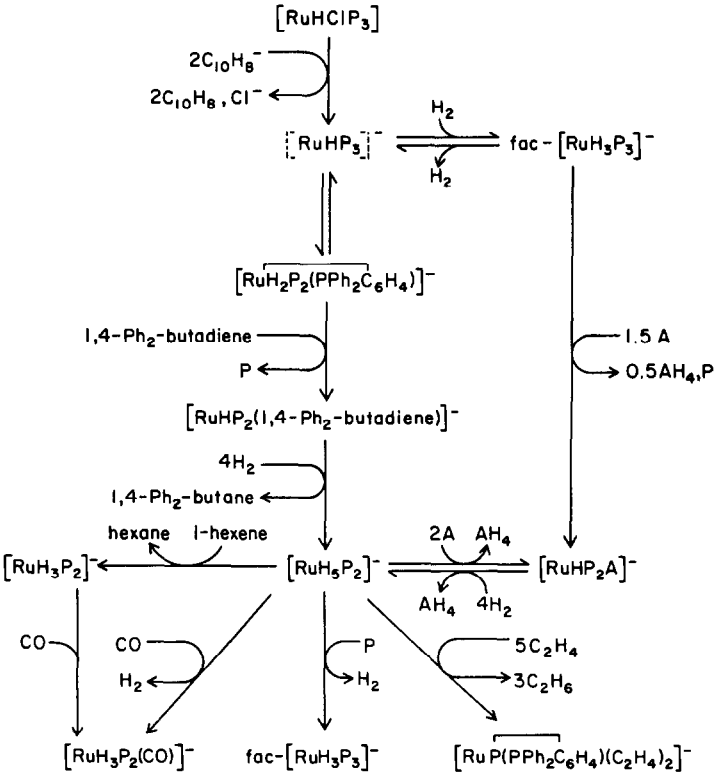
The reaction of **4** with CO and with phosphines (P = PPh_3, PMe_2Ph) proceeds rapidly at room temperature to yield $K[RuH_3(PPh_3)_2(CO)]$ (**6**) and $K[RuH_3(PPh_3)_2P]$, respectively (eq. 9, 10). Ethylene (1 atm) reacts with **4** at room temperature yielding the orthometallated complex $K[\overline{Ru(PPh_3)(PPh_2C_6H_4)}(C_2H_4)_2]$ (**8**), eq. 11. These reactions reveal an interesting pattern reflecting the abilities of various olefins to dehydrogenate $K[RuH_5(PPh_3)_2]$ to different degrees; 1-hexene removes 2 H atoms, 1,3-cyclohexadiene (and anthracene) removes 4 H atoms, and ethylene removes 6 H atoms, one being transferred from an *ortho*-phenyl position.

$$K[RuH_5(PPh_3)_2] + CO \rightarrow K[RuH_3(PPh_3)_2(CO)] + H_2 \quad (9)$$

$$K[RuH_5(PPh_3)_2] + P \rightarrow K[RuH_3(PPh_3)_2P] + H_2 \quad (10)$$

$$K[RuH_5(PPh_3)_2] + 5C_2H_4 \rightarrow K[\overline{Ru(PPh_3)_2(PPh_2C_6H_4)}(C_2H_4)_2] + 3C_2H_6 \quad (11)$$

As mentioned earlier, pale yellow THF solutions of $K[RuH_5(PPh_3)_2]$ and $K[RuH_3(PPh_3)_2]$ decompose over a period of several hours at room temperature to form dark red solutions. The decomposition was greatly accelerated by the addition of ethanol or water. The isolated product was soluble in non-polar solvents such as



SCHEME 1. Summary of hydrido(phosphine)ruthenate chemistry. (P = triphenylphosphine, A = anthracene, AH_4 = 1,2,3,4-tetrahydroanthracene).

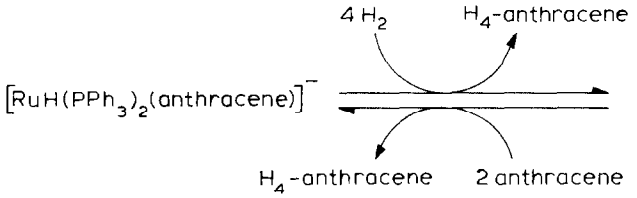
toluene. We have not fully characterized this material but its solubility and NMR spectrum suggest that it probably is a neutral cluster.

The chemistry of hydridoruthenate complexes that we have described is summarized in Scheme 1. An interesting parallel exists between this chemistry and that of corresponding neutral iridium complexes. In the case of almost all the new ruthenate complexes a neutral iridium analogue has previously been reported (and in most instances structurally characterized). Thus, $[IrH_2(PPh_3)_2(PPh_2C_6H_4)]$ [18], *fac*-$[IrH_3P_3]$ (P = PEt_2Ph [12], PMe_2Ph [19,20]), $[IrH(P\text{-}i\text{-}Pr_3)_2(C_4H_6)]$ [15,16], $[IrH_5(PEt_2Ph)_2]$ [21], and $[Ir(PPh_3)_2(PPh_2C_6H_4)(C_2H_4)_2]$ [15,22] are direct analogues of **1**, **2**, **3**, **4**, and **8**, respectively. Caulton et al. also have recently reported the preparation of *fac*-$K[OsH_3(PMe_2Ph)_3]$ [23].

Catalytic hydrogenation of anthracene. We have confirmed that **1** serves as a catalyst or catalyst precursor for the hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene (and, more slowly, for the further hydrogenation to 1,2,3,4,5,6,7,8-octahydroanthracene) as previously reported [3]. Preliminary studies, which are continuing, reveal that the kinetics are approximately first order in Ru, first order in anthracene, and zero order in H_2. Compounds **2**, **3**, **4** and **7** also were found to serve as catalyst precursors for the hydrogenation of anthracene with rates that, in some cases, were initially higher than that obtained with **1** but ultimately leveled off at approximately the same value, suggesting that they give rise to a common catalytic

mechanism. In the light of the chemistry that we have described it seems likely that, under the conditions of the reaction, the orthometallated precursor **1** is converted rapidly and irreversibly to other species (notably **2**, **4** and **7**) and so is not directly involved in the catalytic mechanism. It further seems likely that the species that are encompassed by the catalytic cycle contain only two phosphine ligands per Ru, as do the active catalytic precursors **4** and **7**.

The combination of reactions 5 and 7, as depicted by eq. 12, corresponds to a catalytic cycle for the hydrogenation of anthracene and, thus, clearly constitutes one demonstrated mechanism for this reaction.



(12)

The determination of whether this is the only mechanism will require further kinetic studies, which now are in progress, on the overall catalytic reaction as well as on the several component steps that we have identified. It also remains to be established to what extent the chemistry that we have identified is relevant to the catalysis by **1**, or derivatives thereof, of the hydrogenation of other substrates such as ketones, nitriles, and esters [2].

The selectivity exhibited by this catalyst system for the hydrogenation of anthracene (reflected in the formation of 1,2,3,4-tetrahydroanthracene) differs from that previously found for the $HCo(CO)_4$-catalyzed hydrogenation which yields 9,10-dihydroanthracene and which has been interpreted in terms of a free radical mechanism [4,5]. In this connection it is noteworthy that the same selectivity (i.e., to 1,2,3,4-tetrahydroanthracene) now has been observed for cationic ($[Rh(Ph_2PCH_2CH_2PPh_2)(MeOH)_2]^+$) [24], neutral ($[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$) [25] and anionic ($[RuH_5(PPh_3)_2]^-$) catalysts and probably reflects the ability of the catalyst, in each case, to hydrogenate anthracene while coordinated in a "diene" (i.e., 1,2,3,4-η^4) mode.

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8 The large number of successive synthetic steps involved in the preparation of these compounds required optimization of the yield of each step. $RuCl_2(PPh_3)_3$ [9] was prepared in 100% yield by using one-half the amount of solvent recommended. This product (rather than $RuCl_2(PPh_3)_4$) was converted to $RuHCl(PPh_3)_3$ [10] in 83% yield and was used for the preparation of $K[RuH_2(PPh_3)_2(PPh_2C_6H_4)]$ without further purification.
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