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Borohydride/Ethanol Reduction of $RuCl_3(PMe_2Ph)_3$

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Reaction of mer-$RuCl_3(PMe_2Ph)_3$ with $NaBH_4$ in ethanol at 25 °C gives mer-$RuH(\eta^2\text{-}BH_4)(PMe_2Ph)_3$. In the presence of chloride ion, this reacts with $NaBH_4$/ethanol at reflux to give a 1:1 mixture of cis,mer-$RuH_2CO(PMe_2Ph)_3$, 1a, and mer-$RuHClCO(PMe_2Ph)_3$, 1b, identified by decoupling in the ^1H and ^{31}P NMR, IR, and, for 1a, X-ray crystallography. In the absence of chloride ion, pure $RuH(BH_4)(PMe_2Ph)_3$ in refluxing ethanol still converts to $RuH_2CO(PMe_2Ph)_3$, 1a, which represents unusually mild conditions for decarbonylation of ethanol. Crystallographic data for $RuH_2CO(PMe_2Ph)_3$: triclinic, $P\bar{1}$ with (−160 °C): $a = 12.752(4)$ Å, $b = 11.759(4)$, $c = 9.487(3)$, $\alpha = 75.96(2)°$, $\beta = 107.13(2)$, $\gamma = 102.25(2)$ and $Z = 2$.

Introduction

We have been seeking thermal synthetic routes to polyhydride complexes of the first and second transition series. In order to extend our photochemical studies of $OsH_4(PMe_2Ph)_3$ to ruthenium, we have studied the borohydride reduction of *mer*-$RuCl_3(PMe_2Ph)_3$ [1]. This is the required starting material based on the analogous osmium chemistry as well as an empirical principle of polyhydride phosphine synthetic chemistry: in the reaction of a chlorophosphine complex with BH_4^-, the number of phosphine ligands remains constant. We considered $RuH_4(PMe_2Ph)_3$ a reasonable target; the analogous $RuH_4(PPh_3)_3$ [2, 3] is known, but stable only under a H_2 atmosphere. We hoped the smaller, more basic PMe_2Ph ligand would lessen the tendency toward reductive elimination, particularly in view of the reported thermal stability of other Ru(IV) polyhydrides such as $(C_5Me_5)Ru(PPh_3)H_3$ [4] and $RuH_5(PPh_3)_2^-K^+$ [5]. Herein we report the outcome of our pursuit of $RuH_4(PMe_2Ph)_3$, which does indeed yield a tris-phosphine complex, but with some surprising twists.

Experimental

General

All manipulations were carried out with the exclusion of air and moisture using standard Schlenk techniques under an atmosphere of pre-purified N_2. Solid transfers were effected in a Vacuum Atmospheres Corporation dry box. Absolute ethanol was degassed *in vacuo* prior to use. Benzene and toluene (Aldrich) were distilled from sodium under N_2 and stored over molecular sieves under N_2. Carbon tetrachloride (Aldrich) was dried over molecular sieves and degassed *in vacuo*. Sodium borohydride (Aldrich) was used as received.

Proton NMR spectra were recorded on a Nicolet NT-360 (FT, 360 MHz) instrument. Phosphorus NMR spectra were determined on a Varian XL-100 spectrometer (FT, phosphorus at 40.5 MHz). Phosphine chemical shifts are relative to external 85% H_3PO_4, with positive values downfield. Heteronuclear decoupling experiments were performed on the Nicolet NT-360; phosphorus decoupling was accomplished with an external frequency generator designed locally. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer.

X-ray Crystallography

A yellow-orange crystal was cleaved to obtain a nearly equidimensional cube of maximum dimension 0.10 mm. After affixing the crystal to a glass fiber using silicone grease, the sample was transferred to the goniostat where it was cooled to −160 °C. A systematic search of a limited hemisphere of reciprocal space revealed no symmetry or systematic extinctions, leading to the choice of P1 or $P\bar{1}$ for the proper space group. Subsequent statistical tests and solution and refinement of the structure proved the centrosymmetric choice ($P\bar{1}$) to be correct. Data collection techniques ($6° \leqslant 2\theta \leqslant 45°$) have been described [6]. Characteristics of the data collected appear in Table I. The structure was solved by means of a three-dimensional Patterson function and Fourier techniques. All atoms, including hydrogens, were located and refined, although

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TABLE I. Crystal Data for *cis, mer*-$RuH_2CO(PMe_2Ph)_3$.

Empirical Formula	$C_{25}H_{35}OP_3Ru$
Color	Orange
Crystal Dimensions (mm)	0.09 × 0.09 × 0.10
Space Group	$P\bar{1}$
Cell Dimensions	
(at −160 °C; 42 reflections)	
a	12.752(4) Å
b	11.759(4)
c	9.487(3)
α	75.96(2)°
β	107.13(2)
γ	102.25(2)
Molecules/cell	2
Volume ($Å^3$)	1303.48
Calculated Density (gm/cm^3)	1.39
Wavelength	0.71069
Molecular Weight	545.54
Linear Absorption Coefficient (cm^{-1})	7.85
Number of Unique Intensities Collected	3407
Number with F > 2.33 σ(F)	2894
Final Residuals	
R(F)	0.0540
R_w(F)	0.0561
Goodness of Fit for the Last Cycle	1.28
Maximum Δ/σ for Last Cycle	0.05

TABLE II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $RuH_2CO(PMe_2Ph)_3$.

	10^4x	10^4y	10^4z	$10B_{iso}$
Ru(1)	2489.5(5)	2737(1)	3840(1)	20
P(2)	1324(1)	1570(2)	2135(2)	20
P(3)	1206(2)	3504(2)	4451(2)	27
P(4)	4148(2)	2679(3)	3405(3)	49
C(5)	704(7)	2290(8)	229(9)	32
C(6)	85(6)	684(7)	2704(9)	29
C(7)	1880(5)	360(6)	1818(8)	21
C(8)	2085(6)	−607(7)	2979(9)	28
C(9)	2445(7)	−1568(7)	2794(10)	34
C(10)	2641(6)	−1574(8)	1441(11)	36
C(11)	2479(6)	−604(8)	289(10)	32
C(12)	2100(6)	351(7)	471(8)	24
C(13)	995(7)	2887(11)	6326(10)	48
C(14)	1602(8)	5064(9)	4543(14)	55
C(15)	−229(6)	3518(6)	3282(8)	23
C(16)	−1104(6)	2711(7)	3708(9)	29
C(17)	−2179(6)	2721(7)	2760(11)	33
C(18)	−2391(7)	3513(8)	1426(10)	36
C(19)	−1523(7)	4297(8)	1008(10)	35
C(20)	−457(7)	4291(7)	1934(10)	32
C(21)	5262(9)	3658(16)	4079(16)	105
C(22)	4756(10)	1281(14)	4553(16)	86
C(23)	4279(6)	2589(7)	1582(9)	31
C(24)	3857(8)	3455(13)	402(12)	75
C(25)	4740(8)	1730(11)	1342(17)	77
C(26)	4792(10)	1770(17)	−275(21)	102
C(27)	4321(10)	2722(16)	−1224(16)	90
C(28)	3930(10)	3642(15)	−998(15)	90
C(29)	2597(7)	1421(8)	5472(10)	42
O(30)	2652(7)	635(6)	6444(7)	61
H(1)	331(6)	359(6)	487(8)	66(16)
H(2)	266(6)	459(6)	219(8)	31(16)

[a] Hydrogen coordinates are ×10^3. [b] Isotropic values for those atoms refined anisotropically are calculated using the fomula given by W. C. Hamilton, *Acta Cryst.*, *12*, 609 (1959).

TABLE III. Selected Bond Distances (Å) and Angles (deg.) for *cis,mer*-$RuH_2Co(PMe_2Ph)_3$.

Ru	P(2)	2.3459(20) Å
Ru	P(3)	2.2952(21)
Ru	P(4)	2.2882(24)
Ru	C(29)	1.902(10)
Ru	H(1)	1.59(7)
Ru	H(2)	2.39(7)
C(29)	O(30)	1.133(10)

P(2)	Ru	P(3)	100.81(7)°
P(2)	Ru	P(4)	98.54(8)
P(2)	Ru	C(29)	92.51(26)
P(2)	Ru	H(2)	99.6(17)
P(3)	Ru	P(4)	157.44(9)
P(3)	Ru	C(29)	95.71(27)
P(3)	Ru	H(2)	83.7(17)
P(4)	Ru	C(29)	94.9(3)
P(4)	Ru	H(2)	81.7(16)
C(29)	Ru	H(2)	167.8(17)
P(2)	Ru	H(1)	175.8(25)
P(3)	Ru	H(1)	81.3(25)
P(4)	Ru	H(1)	78.7(25)
C(29)	Ru	H(1)	90.9(25)
H(1)	Ru	H(2)	77.0(3)
Ru	C(29)	O(30)	179.7(9)

those hydrogens involved with the P(4) phosphine were poorly defined.

Psi scans of five reflections near χ = 90° were nearly flat, indicating no absorption correction was necessary. The results of the structure determination appear in Tables II and III and Figs. 3 and 4. Additional details (anisotropic thermal parameters, intraligand distances and angles, hydrogen positional and thermal parameters, and observed and calculated Fs) are available as Molecular Structure Center Report 83099 from the Chemistry Library, Indiana University.

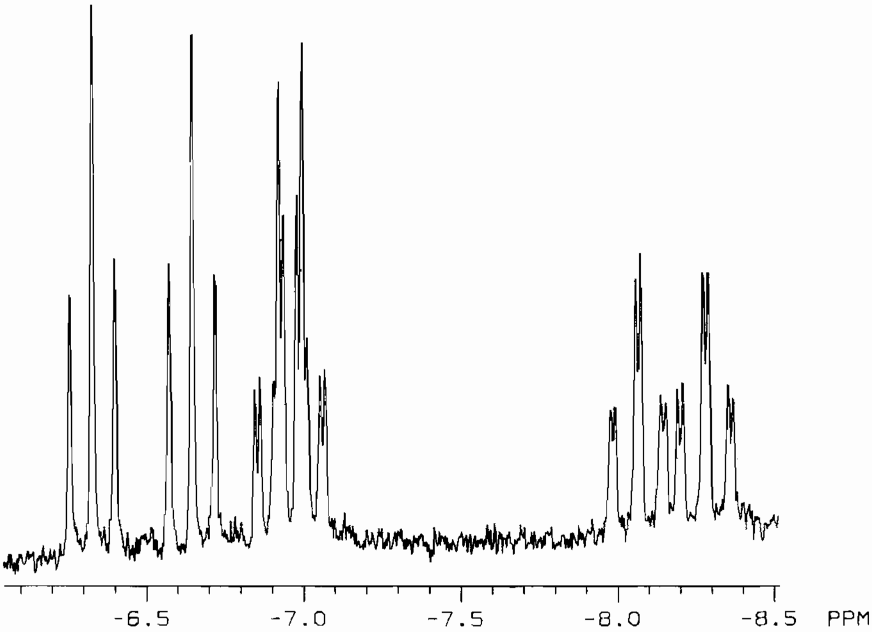


Fig. 1. 360 MHz ^1H NMR spectrum (Ru–H region) of **1**.

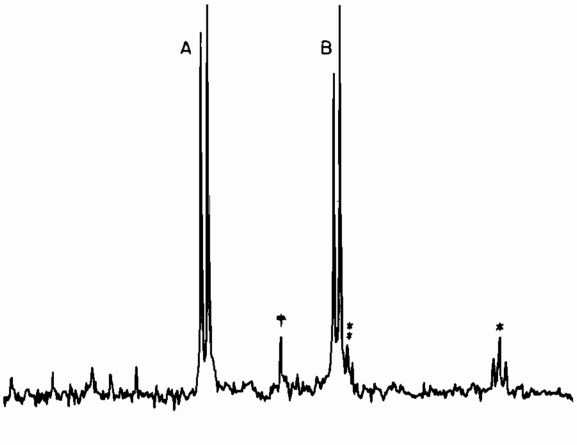


Fig. 2. 40.5 MHz $^{31}P\{^1H\}$ NMR spectrum of **1**. A: 14.7 ppm (J = 23.4 Hz); B: 3.3 ppm (J = 21.0 Hz). ‡: impurity. *: see text.

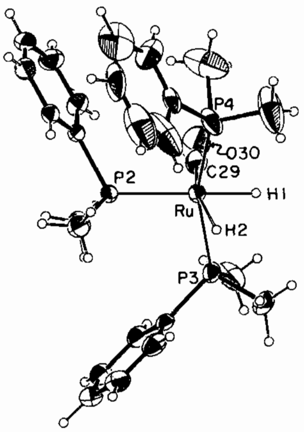


Fig. 3. ORTEP drawing of the molecular structure of **1a**, *cis, mer*-$RuH_2CO(PMe_2Ph)_3$, showing atom labelling.

Brown crystalline *mer*-$RuCl_3(PMe_2Ph)_3$ was prepared according to the method of Chatt [1].

mer-*$RuH(\eta^2\text{-}BH_4)(PMe_2Ph)_3$ (3)*

To a slurry of 0.32 g (8 mmol) $NaBH_4$ in 40 ml ethanol was added 0.5 g (0.8 mmol) *mer*-$RuCl_3(PMe_2Ph)_3$. The brown color was discharged rapidly, giving way to an orange color. After stirring 10 minutes at 25 °C, the solution was stripped to dryness *in vacuo*. The residue was extracted with 25 ml benzene and the resulting filterered solution was stripped, giving an orange oil. The oil was dissolved in ethanol and refrigerated, yielding an orange precipitate. ^1H NMR (C_6D_6): 7.72(m), 7.14(m) (P–Ph); 5.45 (br, BH_2), 1.62 (6H) and 1.52 (6H), virtual triplets (P–Me); 0.84 (d J_{PH} = 8 Hz, P-Me_2); –5.91 (broad singlet, Ru–H–B); –9.08 (broad multiplet, Ru–H–B); –14.84 (d of t, J = 32 Hz, 22 Hz, Ru–H). $^{31}P\{^1H\}$ (C_6D_6): 29.29 ppm (d, J_{PP} = 33 Hz); 16.50 (t, J_{PP} = 33 Hz). Infrared (KBr): 2402(s), 2395(sh), 2312 cm^{-1} (m), η^2-BH_4; 1928 m (Ru–H). *Anal.* for $C_{24}H_{37}P_3BRu$: C, 54.29, H, 7.02. Found: C, 54.69, H, 7.33.

Reaction of mer-*$RuCl_3(PMe_2Ph)_3$ with $NaBH_4$*

To 20 ml of ethanol was added 0.4 g (0.8 mmol) *mer*-$RuCl_3(PMe_2Ph)_3$ and 0.38 g (9.3 mmol) $NaBH_4$

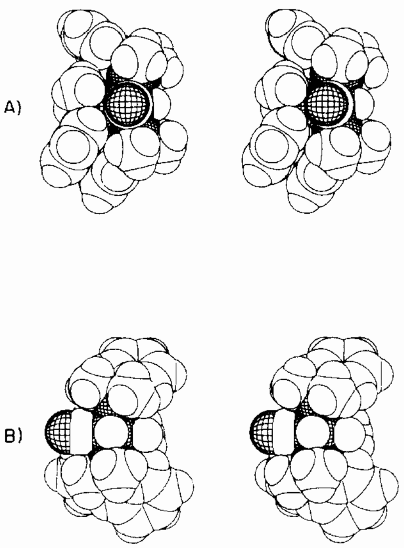


Fig. 4. Stereo space-filling drawings of 1a viewed A) down the CO bond and B) down the Ru–H1 bond. Methyl/phenyl contacts between P2 and P3 and P4 are especially evident in A).

(12:1 B:Ru); gas evolution and loss of brown color resulted. The solution was refluxed under nitrogen for one hour, and the solvent removed *in vacuo*. The solid was extracted with benzene, the benzene removed *in vacuo*, and the resulting orange oil dissolved in ethanol. Cooling led to precipitation of a beige solid which proved to be mixture 1 as discussed in the text. Spectral data are cited there.

Thermolysis of $RuH(BH_4)(PMe_2Ph)_3$

Compound 1a could be obtained in pure form as follows: 0.50 g (1.0 mmol) of $RuH(BH_4)(PMe_2Ph)_3$ (3) was dissolved in 40 ml ethanol and 0.25 g (3.5 mmol) $NaBH_4$ added; $NaBH_4$ was subsequently found to be unnecessary in this thermolysis. The solution was refluxed for one hour, then stripped to dryness. The residue was extracted with 40 ml C_6H_6 and the C_6H_6 removed *in vacuo*, leaving an oily solid. Slow cooling of an ethanol solution resulted in beige crystals of *cis,mer*-$RuH_2CO(PMe_2Ph)_3$. $^{31}P\{^1H\}$ NMR (C_6D_6): 14.75 ppm (d) and 2.7 ppm (t), J_{PP} = 23 Hz. ^1H NMR (C_6D_6): 7.7, 7.1 ppm (broad multiplets, P-Ph); 1.648 and 1.630 ppm, overlapping virtual triplets (P-Me); 1.035 (d, J = 6 Hz, P-Me); –6.96 (d of t of d, J = 18, 20, 5 Hz, hydride *trans* to CO); –8.17 (d of t of d, J = 78, 29, 5 Hz, hydride *trans* to P). Infrared (KBr): 1910 (vs, br, CO) and 1838 cm^{-1} (vs, br, Ru–H). In benzene these bands shift to 1920 and 1860 cm^{-1}.

mer-*RuHCl(CO)(PMe₂Ph)₃ (1b)*

The presence of this compound in the synthetic mixture 1 was verified by comparison of its spectral data to that in the literature [7]. $^{31}P\{^1H\}$ (C_6D_6): 3.20 (d) and –10.7 ppm (t), J_{PP} = 20 Hz. ^1H NMR (C_6D_6): 7.7, 7.1 ppm (broad multiplets, P-Ph); 1.702 and 1.698 (overlapping virtual triplets, P-Me); 1.111 (d, J_{PH} = 6 Hz, P-Me); –6.50 (d of t, J = 114, 26 Hz, Ru–H).

mer-*RuCl₂(CO)(PMe₂Ph)₃ (2) [7]*

This was prepared in high purity by reaction of mixture 1 with excess $CHCl_3$ or CCl_4 in C_6D_6 solvent. $^{31}P\{^1H\}$ (C_6D_6): 17.13 (t) and –1.51 ppm (d), J_{PP} = 27 Hz. ^1H NMR (C_6D_6): 6.7–7.6 ppm (broad, P-Ph); 1.885 and 1.853 (virtual triplets, P-Me); 1.044 (d, J_{PH} = 10 Hz, P-Me).

Results and Discussion

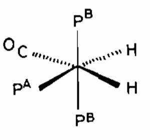
Reaction of excess $NaBH_4$ with *mer*-$RuCl_3(PMe_2Ph)_3$ (12:1 B:Ru) in refluxing ethanol proceeds with gas evolution to give an orange solution. Removal of solvent, followed by extraction of the resulting solid with benzene gives an orange benzene solution. Concentrating this solution resulted in the precipitation of a yellow-orange oily solid 1, which yielded beige micro-crystals on recrystallization from ethanol solution.

While 1 has solubility properties qualitatively compatible with the desired $RuH_4(PMe_2Ph)_3$, and it also shows hydride ^1H NMR signals, the pattern in the hydride region (Fig. 1) is far too complex for the desired compound. The $^{31}P\{^1H\}$ spectrum (Fig. 2) is also too complex for $RuH_4(PMe_2Ph)_3$. The complex pattern is mirrored in the P-Me region of the ^1H NMR spectrum which shows six chemical shifts, two doublets and four virtual triplets, in integer intensity ratios. Since these NMR patterns, and their intensities, were independent of reaction time (1–3 h) and persisted through recrystallization from an ethanol solution, we began to consider that 1 was actually a polyhydride dimer $Ru_2H_m(PMe_2Ph)_n$. The dimer $Ru_2H_4(PMe_3)_6$ has been reported to have a complex hydride resonance pattern inconsistent with its solid state structure [8]. A key feature of the hydride region ^1H NMR spectrum of 1 is the 1:1:1 intensity ratio of the multiplets centered at –6.50, –6.96, and –8.17 ppm. The small (5 Hz) couplings common to the latter two multiplets were confirmed to be H···H couplings by homonuclear decoupling experiments. Thus, homonuclear decoupling at –6.96 ppm converts the –8.17 ppm resonance to a doublet of triplets (concluded to be due to a $P^AP^B{}_2$ spin system). Homonuclear proton decoupling at –8.17 ppm converts the –6.96 ppm resonance to an overlapping doublet of triplets (again consistent with a $P^AP^B{}_2$ spin system). Although the –6.50 ppm multiplet was unaffected by the two decoupling frequencies already described, its doublet of triplet structure is also consistent with a $P^AP^{B_2}$ phosphorus spin system in the molecule. Wholly consistent with our working hypothesis was the indication of a trisphosphine stoichiometry.

To confirm the P–H coupling deduced above, heteronuclear decoupling experiments were carried out. Decoupling at 14.75 ppm in the ^{31}P spectrum caused the hydride signal at –6.96 ppm to collapse from the doublet of triplets of doublets to a doublet of doublets with J_{PH} = 18 Hz and J_{HH} = 5 Hz. Simultaneously, the signal at –8.17 ppm likewise reduced to a doublet of doublets with J_{PH} = 78 Hz and J_{HH} = 5 Hz. During this experiment the downfield hydride signal at –6.50 ppm remained unaffected as a doublet of triplets. When the ^{31}P signal at 3.3 ppm was irradiated, the hydride signal at –6.50 ppm collapsed to a doublet with J_{PH} = 114 Hz. The remaining hydride signals were converted from doublets of triplets of doublets to triplets of doublets with J_{PH} = 20 Hz (–6.96 ppm) and 26 Hz (–8.17 ppm) and J_{HH} = 5 Hz at both sites. From these studies it appeared that the upfield hydride signals (–6.96 and –8.17 ppm) were related and coupled to the phosphorus signal at 14.75 ppm. However, all three hydrides appeared to couple to the phosphorus doublet at 3.3 ppm, a seeming inconsistency. Finally, the infrared spectrum of **1** (Nujol mull and C_6D_6 solution) showed broad and fairly strong absorptions at 1910 and 1838 cm^{-1}.

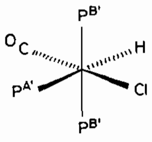
It was hoped that X-ray crystallography would reveal the origin of our paradoxical spectral data by detailing the geometry of the anticipated dimer, or perhaps by revealing an even higher degree of aggregation. To that end, single crystals were obtained by slow cooling of a saturated ethanol solution.

In a surprising way the resulting diffraction study did lead to a complete understanding of the spectral data. This technique revealed that the crystal selected for study contained essentially (*vide infra*) exclusively *cis,mer*-$RuH_2(CO)(PMe_2Ph)_3$ (**1a**, Fig. 3) [9]. This compound, with two inequivalent hydride ligands, accounts for two-thirds of the hydride resonance in the ^1H NMR spectrum [9b]. It also accounts for three P-Me chemical shifts, a doublet and two virtual triplets, since the *trans* phosphine methyl groups are diastereotopic. The infrared band (1910 cm^{-1}) which we had attributed to a terminal Ru–H stretch is in fact due to a C≡O stretch. It is also clear we had ignored a crucial (if low amplitude) feature of the $^{31}P\{^1H\}$ NMR spectrum: *cis, mer*-$RuH_2(CO)(PMe_2Ph)_3$ must have an AB_2 pattern in the phosphorus NMR, and the required A triplet is in fact present (see double asterisk in Fig. 2). The previous neglect of this triplet was made easier since the lines of the triplet are broadened relative to those of the doublet, an effect we attribute to exchange broadening of the phosphine *trans* to hydride. Moreover, this triplet lies close to and nearly under (at 40 MHz) a larger doublet (3.3 ppm), the origin of which is discussed below.



1a

Having established the presence of the unanticipated carbonyl ligand, it was a simple matter to assign the other hydride and P-Me ^1H NMR resonances in **1** to the following isomers of *mer*-$RuHCl(CO)(PMe_2Ph)_3$ (**1b**) [7]. The crucial accident in our samples of **1** is that all samples we had produced from $RuCl_3(PMe_2Ph)_3$ are an equimolar mixture of **1a** and **1b**.



1b

The hydride resonance at –6.50 ppm is the expected doublet of triplets of **1b**, with the larger (doublet) splitting due to coupling to the *trans* $P^{A'}$. This molecule (**1b**) introduces three P-Me chemical shifts into all ^1H NMR spectra. It also adds a second, equally abundant AB_2 pattern to the $^{31}P\{^1H\}$ NMR spectrum, the doublet of which (3.3 ppm) nearly obliterates the triplet due to **1a**. Hence, in the previously described heteronuclear decoupling experiments, when the decoupler was centered at 3.3 ppm in the ^{31}P region, decoupling was effected at *both* the P^A triplet due to $RuH_2(CO)P_3$ (**1a**) and the $P^{B'}$ doublet due to the mutually *trans* phosphines of **1b**. The result of the latter was collapse of the hydride signal (–6.50 ppm) to a doublet, derived from coupling to the unique phosphine *trans* to hydride. The magnitude of this coupling (114 Hz) is also consistent with a *trans* P–H coupling. The $P^{A'}$ resonance of **1b** is the triplet denoted by the single asterisk (–10.6 ppm) in Fig. 2.

The X-ray study of the crystals isolated from **1** permitted refinement of electron density corresponding to two hydride ligands. The hydride *trans* to PMe_2Ph, H1, refined to a quite typical Ru–H distance of 1.59(7) Å. The electron density *trans* to CO (H2) refined to an excessively long distance, 2.39(7) Å, even though the standard deviation is not anomalously large. This distance of 2.39 Å is, however, quite reasonable for a Ru–Cl distance when chloride is *trans* to CO [10]. Consequently, we suggest that the crystal selected here had on the order of 1/18th mol fraction of $RuHCl(CO)(PMe_2Ph)_3$ (**1b**) impurity ($Z_{Cl} = 18\ Z_H$) in primarily **1a**. The affected coordination site is of course exactly that occupied by Cl in spectroscopically detected $RuHCl(CO)(PMe_2Ph)_3$, **1b**. In effect, then, we have determined the structure of 94% pure material (**1a**), but, at one coordination site we have refined the location of the heavy impurity atom. The other (fully occupied) ligand positions are those of $RuH_2(CO)(PMe_2Ph)_3$ (**1a**), however.

The structure shows distortions from a regular octahedron (Table III) typical of compounds with two very small (*e.g.* hydride) ligands in the presence of larger ligands (PMe_2Ph). Such distortions are smaller for the OC–Ru–P angles (92.5°–95.7°) than for the P–Ru–P angles (98.5° and 100.8°). The methyl/phenyl contacts responsible for this distortion are evident in Fig. 4. The Ru-P distances in this molecule show evidence of a *trans* lengthening, by H1 on P2, of 0.054 Å or 22 σ. The Ru–CO distance, at 1.902 Å, is longer than a typical value [11] (1.798 Å) for CO *trans* to chloride; a *trans* influence of H2 on the carbonyl in $RuH_2(CO)(PMe_2Ph)_3$ is thus also evident.

The identification of **1b** as $RuHCl(CO)(PMe_2Ph)_3$ is further supported by chemical methods. Halocarbons are known to convert M–H to M–Cl units [12]. Thus, treatment of the mixture **1** with a ten fold excess of CCl_4 in C_6D_6 led to immediate conversion to a single product, *cis,mer*-$RuCl_2(CO)(PMe_2Ph)_3$ (**2**) [7]. The latter exhibits an AB_2 pattern in the $^{31}P\{^1H\}$ NMR spectrum (17.13 ppm, t; –1.51 ppm, d; J_{PP} = 27 Hz). It also shows three P-Me resonances, a doublet (1.044 ppm) for the unique PMe_2 moiety (J_{PH} = 10 Hz) and a pair of virtual triplets (1.885, 1.853 ppm) for the diastereotopic methyls of the *trans* phosphines. Employing the more selective reagent $CHCl_3$ in a similar manner, one can observe the sequence illustrated in eqns. 1 and 2. Here, the $RuH_2(CO)(PMe_2Ph)_3$ (**1a**) present

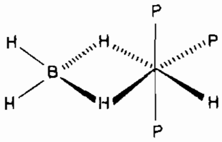
$$\underset{\mathbf{1a}}{RuH_2(CO)P_3} + CHCl_3 \longrightarrow \underset{\mathbf{1b}}{RuHCl(CO)P_3} \qquad (1)$$

$$\underset{\mathbf{1b}}{RuHCl(CO)P_3} + CHCl_3 \longrightarrow \underset{\mathbf{2}}{RuCl_2(CO)P_3} \qquad (2)$$

reacts with $CHCl_3$ to form more $RuHCl(CO)(PMe_2Ph)_3$ (**1b**); the latter reacts more slowly to give *mer*-$RuCl_2(CO)(PMe_2Ph)_3$ (**2**).

Conversion in the opposite direction (*i.e.*: RuHCl → RuH_2) is both more useful and more relevant to the question of why isolated **1** is a mixture. To address this question, the 1:1 mixture which comprises solid **1** was dissolved in pure ethanol and a 15-fold excess of $NaBH_4$ was added. The solution was refluxed for one hour, at which time $^{31}P\{^1H\}$ NMR indicated complete conversion of $RuHCl(CO)P_3$ to $RuH_2(CO)P_3$. While this result was not unanticipated, it seems to contradict the fact that (at comparable reaction time and B:Ru mol ratio) the one-pot synthetic reaction beginning with $RuCl_3P_3$ always yields the mixture of **1a** and **1b**. In an attempt to explain this, we chose to follow the reaction as it occurred at *room temperature*.

When ten equivalents of $NaBH_4$ were added to a slurry of dark brown *mer*-$RuCl_3(PMe_2Ph)_3$ in ethanol, immediate gas evolution resulted. After a few minutes the now homogeneous solution exhibited a pale orange color. Upon work-up, a new orange compound was isolated which we have characterized as *mer*-$RuH(\eta^2\text{-}BH_4)(PMe_2Ph)_3$ (**3**) [13]. This compound exhibits a three band pattern in the infrared typical of $\eta^2\text{-}BH_4$ [14], as well as a Ru–H stretch at 1928 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum shows the expected AB_2 pattern. In addition to P-Me signals, the ^1H NMR shows resonances for terminal B–H (5.4 ppm, very broad singlet), Ru–H–B at –5.91 (broad singlet) and –9.08 ppm (broad multiplet), and Ru – H at –14.84 ppm (doublet of triplets J_{PH} = 32 and 22 Hz). Thus, this product is formed according to eqn. 3.



3

$$RuCl_3P_3 + 3NaBH_4 \longrightarrow RuH(BH_4)P_3 + 3NaCl + \ldots \qquad (3)$$

The dark brown color of *mer*-$RuCl_3P_3$ is wholly discharged, the $^{31}P\{^1H\}$ NMR spectrum shows no evidence of other phosphorus containing species, and the isolated yield of $RuH(BH_4)P_3$ (**3**) is high. Conversely, if this compound is not isolated but the reaction mixture from eqn. 3 is refluxed for one hour, the result is the product *mixture* **1**. Hence, **3** is undoubtedly the precursor to both **1a** and **1b**, and the obvious source of the chloride ligand in **1b** is the by-product NaCl (eqn. 3) resulting from formation of **3**. Indeed, if *isolated* **3** is refluxed in pure ethanol, either with or without added $NaBH_4$, the result is pure $RuH_2(CO)P_3$ (**1a**). Thus, the chloride ligand in **1b** results from return of free chloride to the coordination sphere.

The particularly surprising aspect of the conversion of **3** to **1a** and **1b** is the emergence of the carbonyl ligand; this can only be derived from ethanol. While extraction of CO from ethanol is well established [15], this is promoted by basic conditions which initiate the reaction via coordinated ethoxide. The base promoter can be KOH, but even a basic phosphine will suffice. Nevertheless, our reaction conditions involve pre-formed $RuCl_3(PMe_2Ph)_3$, with no free phosphine available, and thus represent unusually mild conditions for decarbonylation of ethanol. Even in the absence of excess BH_4^-, $HRu(BH_4)(PMe_2Ph)_3$ (**3**) is able to effect decarbonylation. Although the mechanism of this process is obscure, it probably involves reaction of ethanol with the intact ruthenium borohydride linkage (**3**) or with a boron hydride derived therefrom. Further, the sequence must include a species able to react with NaCl to generate **1b**, although the timing of this relative to decarbonylation is also unknown.

In summary, the present work has established that metal borohydride formation occurs readily at room temperature. However, thermolysis of these ruthenium compounds leads to extremely facile ethanol decarbonylation rather than polyhydride phosphine production. This contrasts with the analogous osmium chemistry. There, treatment of *mer*-$OsCl_3(PMe_2Ph)_3$ with $NaBH_4$ in ethanol at 25 °C leads to gas evolution and immediate loss of the bright red color of $OsCl_3(PMe_2Ph)_3$. However, subsequent thermolysis leads to $OsH_4(PMe_2Ph)_3$ with no trace of carbonyl products, even though large excesses of $NaBH_4$ are used. The difference may reflect a reluctance of ruthenium to assume the +4 oxidation state (compared to osmium); all products discussed here involve Ru(II). Finally, treatment of $RuH(BH_4)(PMe_2Ph)_3$ with NEt_3 [13a] under H_2 pressure failed to yield $RuH_4(PMe_2Ph)_3$. The course of this reaction is a matter for future study.

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