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THE PREPARATION, PROPERTIES AND SOME CATALYTIC REACTIONS OF *mer*-HYDRIDO(TETRAHYDROBORATO)TRIS(METHYLDIPHENYLPHOSPHINE)RUTHENIUM(II) AND SOME RELATED COMPLEXES

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Summary

The complexes $[Ru_2Cl_3L_6]Cl$ react with $Ag[BF_4]$ in organic nitriles to give *fac*-$[Ru(RCN)_3L_3][BF_4]_2$ (L = PMe_2Ph, R = Me, Et, n-Pr, $MeOC(O)CH_2$; L = $PMePh_2$, R = Me, Et, n-Pr, Ph, $MeOC(O)CH_2$). *fac*-$[Ru(MeCN)_3(PMePh_2)_3][BF_4]_2$ reacts with $Na[BH_4]$ to give *mer*-$[RuH(BH_4)(PMePh_2)_3]$ (IV), which in turn, reacts with carboxylic acids to give $[Ru(O_2CR)_2(PMePh_2)_3]$ (R = Me or CMe_3), or with triethylamine in the presence of ligand L′ to give the known $[RuH_2L'(PMePh_2)_3]$ (L′ = $PMePh_2$ or CO). IV is catalytically active for olefin hydrogenation; this activity is greater in the presence of NEt_3. Isopropanol is preferred as a reducing agent over ethanol when metal carbonyl formation is to be avoided, $[Ru_2Cl_3(PMePh_2)_6]Cl$ and KOH give *cis*-$[RuH_2(PMePh_2)_4]$ in i-PrOH but $[RuH_2(CO)(PMePh_2)_3]$ in EtOH.

Introduction

The complex $[RuCl_2(PPh_3)_3]$ [1] is a convenient and widely used starting material for the preparation of a variety of other ruthenium complexes [2,3]. In contrast, the corresponding triply chloro-bridged dimers [4] containing diarylalkyl- or aryldialkyl-phosphines, have been less exploited as starting materials. Complexes which have been prepared from these dimers by treatment with the appropriate ligand L, include *cis*-$[RuCl_2L_2]$ (L = ditertiary phosphine) [4], and *cis*-$[RuCl_2(PEt_2Ph)_2L]$ (L = 1,1′-bipyridyl or 1,10-phenanthroline) [4]. Reactions with ethanol [5], allyl alcohol [5a] or butyraldehyde [6] have led to hydridocarbonyl- and di- or mono-carbonyl complexes, respectively. The dihy-

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drido complex, *cis*-$[RuH_2(PMePh_2)_4]$ has been prepared using hydrazine or dihydrogen as reducing agent [7].

Our own work has been aimed at increasing the synthetic utility of the triply chloro-bridged dimers and so extending the range of ruthenium complexes containing phosphine ligands other than triphenylphosphine.

Results and discussion

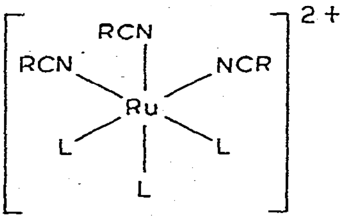
Preparation of some ruthenium-nitrile complexes

On heating the suspensions of the complexes $[Ru_2Cl_3L_6]Cl$ [4], and slightly more than four equivalents of $Ag[BF_4]$ in organic nitriles as solvents, AgCl is precipitated and pale yellow solutions are formed. Addition of ether to the filtered solutions gives the complexes $[Ru(RCN)_3L_3][BF_4]_2$ (I: L = PMe_2Ph, Ia, R = Me; Ib, R = Et; Ic, R = n-Pr; Ie, R = $MeOCOCH_2$. II: L = $PMePh_2$, IIa, R = Me; IIb, R = Et; IIc, R = n-Pr; IId, R = Ph; IIe, R = $MeOCOCH_2$) as pale-cream or white crystalline solids (eq. 1). Acetone was useful as a cosolvent for the reaction since isolation of the products was easier, but in one case this procedure resulted in a different product (IIc) from that obtained using nitrile alone (III). Similarly, IIb was only obtained pure if the reaction times were quite short (<3/4 h), otherwise a second complex was also formed, probably $[Ru(EtCN)_4(PMePh_2)_2][BF_4]_2$, but this product could not be separated from IIb, nor isolated in a pure state.

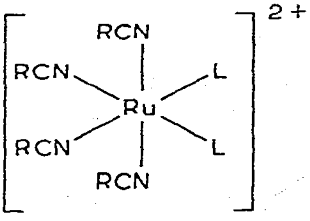
$$[Ru_2Cl_3L_6]^+ \xrightarrow{Ag^+/RCN} \underset{(I,\ II)}{[Ru(RCN)_3L_3]^{2+}} \xrightarrow{PrCN} \underset{(III)}{[Ru(n\text{-}PrCN)_4(PMePh_2)_2]^{2+}} \qquad (1)$$

The complexes I—III are all air-stable and behave as 2/1 electrolytes in ca. 10^{-3} *M* acetone solutions (Table 1).

The complexes I, II have a band in the IR spectrum assigned to ν(CN) at 2280—2320 cm^{-1} (Table 1). Ia and IIa show an additional weak band at 2320 cm^{-1}. As expected [8] for *N*-bonded nitriles, these bands occur at higher frequencies than in the free ligands. The ^{1}H NMR resonances for the PMe groups in complexes I, II exhibit a complex multiplet pattern, a broad central peak and two partially resolved side resonances, due to virtual coupling of intermediate strength between these groups and characteristic [9] of a facial arrangement of the tertiary phosphine ligands. On the basis of these spectral data, the complexes I, II are assigned structure A.



(A)



(B)

The IR spectrum of complex III shows only one ν(CN) band, whereas the ^{1}H NMR spectrum shows a PMe pattern characteristic of *cis*-phosphine ligands [7]. The two overlapping triplets for the $CH_3CH_2CH_2CN$ protons of the nitrile ligands suggest two different nitrile environments in the complex (Table 1). Complex III, therefore, is assigned structure B.

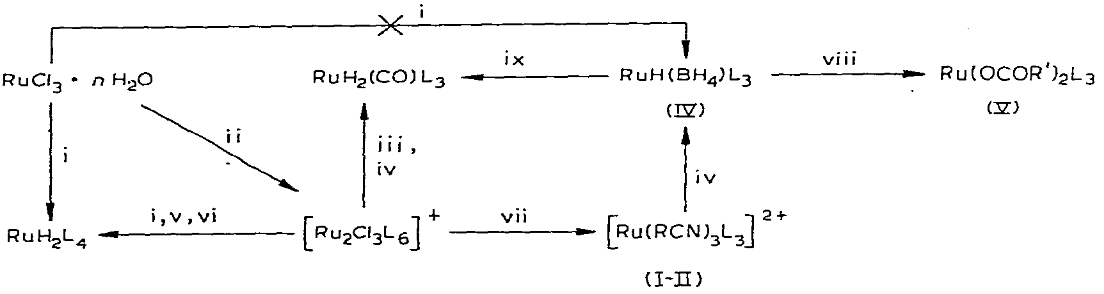
Some analogous complexes $[RuL_2(CH_3CN)_4][PF_6]_2$ (L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OMe)_2Ph$, or $P(OMe)_3$) have recently been prepared [10] from the dimer $[(cod)RuCl_2]_2$ (cod = 1,5 cyclooctadiene) via the complex $[(cod)Ru(CH_3CN)_4][PF_6]_2$, but structural assignments were not given.

Preparation and reactions of a ruthenium tetrahydroborato complex and some catalytic studies

The complex IIa reacts rapidly in methanol with $Na[BH_4]$ to give the yellow, air-sensitive tetrahydroborato complex $[RuH(BH_4)(PMePh_2)_3]$ (IV) (Scheme 1). Complex Ia also reacts rapidly with $Na[BH_4]$ in methanol to give a yellow solution but no pure solid products could be isolated.

SCHEME 1

Some reactions of $[Ru_2Cl_3L_6]^+$. Reagents: (i) $NaBH_4$, L, EtOH; (ii) L, EtOH [4]; (iii) KOH, EtOH; (iv) $NaBH_4$, EtOH; (v) KOH, L, EtOH or i-PrOH; (vi) KOH, i-PrOH; (vii) $AgBF_4$, RCN; (viii) $R'CO_2H$ (R' = Me or t-Bu); (ix) NEt_3, CO. (L = $PMePh_2$. All reactions at reflux temperature except iv, viii and ix (25°C)).



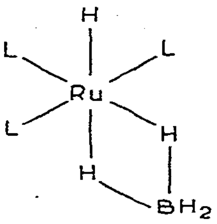
The organic products in the reduction of IIa by $Na[BH_4]$ were ethylamine (1 mol) and acetonitrile (2 mol). The acetonitrile ligand is therefore greatly activated toward $Na[BH_4]$ reduction by coordination to the cationic ruthenium centre. Once the first nitrile has been reduced, a coordination site on the metal is exposed and subsequent $Na[BH_4]$ attack is at the metal.

Only four other tetrahydroborato complexes of ruthenium have been reported to date: $[Ru(BH_4)(\eta\text{-}C_5H_5)(PPh_3)_2]$ [11], $[RuH(BH_4)(CO)(PPh_3)_3]$ [12], $[RuH(BH_4)(CO)_2(PCy_3)_2]$ [12], and $[RuH(BH_4)(PPh_3)_3]$ [1].

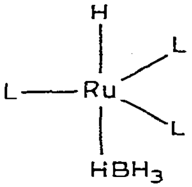
The infrared spectrum of complex IV shows bands which shift in the deuterio analogue as expected for B—H(D) vibrations, at frequencies which are consistent with bidentate coordination of the tetrahydroborato group [13]. The Ru—H unit was not detected by IR, possibly due to it being obscured by the BH_4 absorption in that region. The ^{1}H NMR spectrum (Table 1) consists of (i) a doublet and a triplet in the ratio 1/2 for the PMe resonances, consistent with a meridional arrangement of the phosphine ligands [7], (ii) a fairly broad overlapping doublet of triplets at δ −14.09 ppm assigned to the Ru—H hydride, arising from coupling to the two sets of phosphine ligands and some additional coupling with the BH_4

unit, and (iii) two very broad bands centred at δ −5.1 and −9.1 ppm assigned to the RuH_2B hydrogens. No resonance was detected for the terminal BH_2 hydrogens, but this behaviour has precedents [14].

On the basis of these spectroscopic data, structure C is proposed for complex IV. This contrasts with the proposed structure for the analogous complex $[RuH(BH_4)(PPh_3)_3]$ [12] which was thought to adopt a distorted trigonal bipyramidal structure, D, containing a monodentate tetrahydroborato ligand; indeed, there are considerable differences in the ^1H NMR and IR spectra of the two complexes consistent with the idea that the two complexes have different structures. Possibly, the greater size of the PPh_3 ligand favours structure D, in which these groups are less crowded than they would be in structure C. If this is so, then this constitutes an interesting example of a steric effect causing an 18- to 16-electron rearrangement at the metal centre.



(C)



(D)

The tetrahydroborato complex IV reacts with carboxylic acids to give the bis-carboxylato complexes Va and Vb (Scheme 1).

The complexes V have bands in the infrared spectrum corresponding to both monodentate and bidentate carboxylato groups [15] although the band corresponding to the symmetrical $\nu(CO)_2$ stretching mode of a monodentate acetato group in complex Va could not be unequivocally assigned (Table 1). The ^1H NMR spectra of both complexes have a broad PMe resonance consistent with a facial arrangement of the phosphine ligands [9], and a singlet for the carboxylato-methyl groups. This suggested that the carboxylato groups are fluxional and the presence of two resonances at −60°C in the spectrum of Vb confirmed this idea.

The tetrahydroborato complex IV also reacts with triethylamine in benzene to give a red solution from which only *cis*-$[RuH_2(PMePh_2)_4]$ [7] could be isolated in low yield. Reaction of complex IV with NEt_3 in the presence of excess phosphine, however, gives high yields of the dihydrido complex (eq. 2).

$$\underset{(IV)}{[RuH(BH_4)(PMePh_2)_3]} + NEt_3 + PMePh_2 \rightarrow cis\text{-}[RuH_2(PMePh_2)_4] \qquad (2)$$

Bubbling carbon monoxide through solutions of IV and NEt_3 in benzene results in the formation of the known [7] hydridocarbonyl complex $[RuH_2(CO)(PMePh_2)_3]$ (Scheme 1).

It seems likely that the role of the triethylamine in these reactions is to remove BH_3 in the form of $[Et_3NBH_3]$, from IV, giving the 16-electron complex $[RuH_2(PMePh_2)_3]$, thus creating an active site for the attachment of the added ligand, $PMePh_2$ or CO.

Preliminary studies have shown that the tetrahydroborato complex IV catalyses the hydrogenation of hexene-1 under ambient conditions in benzene, but the reaction is very slow, and isomerisation is a serious competitor. The analogous complex, [$RuH(BH_4)(PPh_3)_3$] also catalyses the hydrogenation of hexene-1, but isomerisation was not reported [16]. Under the same conditions, complex IV did not hydrogenate hexene-2 or cyclohexene.

In the presence of triethylamine, the hydrogenation of hexene-1 was much faster (ca. 200 mol/mol Ru in 1 h) and only ca. 5% isomerisation products were produced; hexene-2 and cyclohexene were also slowly hydrogenated.

The catalytic species are probably different in the two cases above, as suggested by the different colours of the solutions: yellow in the absence of NEt_3 and red in the presence of NEt_3. In the absence of NEt_3, the dissociation of tertiary phosphine may be required, as suggested in the case of the PPh_3 analogue [16]. In the presence of NEt_3, the 16-electron intermediate [$RuH_2(PMePh_2)_3$] is probably formed, as discussed above, and this complex is also probably the active catalyst. Removal of BH_3 with NEt_3 constitutes a novel way of creating an active site at a metal centre.

Some further reactions of [$Ru_2Cl_3(PMePh_2)_6$]Cl

Attempts to prepare the tetrahydroborato complex IV by other routes, for example, by treatment of [$Ru_2Cl_6(PMePh_2)_6$]Cl with Na[BH_4] in ethanol, were unsuccessful. Reaction took place only on heating at reflux to give either *cis*-[$RuH_2(PMePh_2)_4$] (when excess phosphine was present) or [$RuH_2(CO)(PMePh_2)_3$] (with absence of excess phosphine). Treatment of $RuCl_3 \cdot n\text{-}H_2O$ with Na[BH_4] and $PMePh_2$ in ethanol at room temperature also gives *cis*-[$RuH_2(PMePh_2)_4$], in contrast with the analogous triphenylphosphine series, where [$RuH(BH_4)(PPh_3)_3$] can be prepared from both $RuCl_3 \cdot n\text{-}H_2O$ and [$RuCl_2(PPh_3)_3$] by treatment with Na[BH_4] and PPh_3 in ethanol [12].

We also find that the dimer [$Ru_2Cl_3(PMePh_2)_6$]Cl reacts with isopropanol in the presence of KOH and $PMePh_2$ to give high yields of the dihydrido complex *cis*-[$RuH_2(PMePh_2)_4$]. Performing the reaction in the absence of added phosphine greatly lowers the yield of the dihydrido complex but no other solid products could be isolated. The same *cis*-dihydrido complex is also found if a mixture of the dimer, KOH and $PMePh_2$ in ethanol is heated under reflux, but in the absence of excess phosphine the known [7] dihydridocarbonyl complex [$RuH_2(CO)(PMePh_2)_3$] is formed, in contrast to the analogous reaction involving [$Ru_2Cl_3(PEt_2Ph)_6$]Cl, which yields the complex [$RuHCl(CO)(PEt_2Ph)_3$] [5a].

Metal carbonyl formation, due to decarbonylation of the organic carbonyl compound formed in alcohol reductions, can therefore be prevented either (i) by use of an excess of phosphine, which apparently excludes the acetaldehyde from the metal, or (ii) by the use of isopropanol, whose oxidation product, acetone, is stable to decarbonylation. These reactions are summarised in Scheme 1.

Experimental

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated.

(continued on p. 342)

TABLE 1

YIELDS, ANALYSES AND PHYSICAL DATA FOR THE NEW COMPLEXES

Complex [a]		Yield (%)	Conductivity [b] (S cm^2 mol^{-1})	Analysis: (found (calcd.) (%))			IR [c] (cm^{-1})	PMR data [d] δ (ppm)
				C	H	N		
$[Ru(MeCN)_3(PMe_2Ph)_3][BF_4]_2 \cdot MeCN$	(Ia)	87	182	45.0 (45.0)	5.3 (5.3)	6.5 (6.5)	2250, 2295 2325w	1.8, m(8.4), PMe; 1.94 and 2.15, s, MeCN (free and coordinated)
$[Ru(EtCN)_3(PMe_2Ph)_3][BF_4]_2$	(Ib)	71	197	46.4 (46.4)	5.7 (5.7)	5.0 (4.9)	2285	1.1, t and 2.5, q(7.2), Et; 1.8; m(8.7), PMe
$[Ru(n\text{-}PrCN)_3(PMe_2Ph)_3][BF_4]_2$	(Ic)	74	196	48.2 (48.2)	6.0 (6.1)	4.7 (4.7)	2285	0.9, 1.46 and 2.5, c, n-Pr; 1.8, m(8.7), PMe
$[Ru(RCN)_3(PMe_2Ph)_3][BF_4]_2$	(Ie)	80	185	43.8 (43.8)	4.9 (4.9)	4.2 (4.3)	2300w 1755s(br) [e]	1.9, m, PMe; 3.78, s, Ac; 4.0, s, CH_2 [f]
$[Ru(MeCN)_3(PMePh_2)_3][BF_4]_2$	(IIa)	77	168	54.1 (54.1)	5.0 (4.9)	4.3 (4.2)	2285mw 2320w	2.1, c, Me
$[Ru(EtCN)_3(PMePh_2)_3][BF_4]_2$	(IIb)	73	179	55.5 (55.4)	5.3 (5.2)	3.8 (4.0)	2290	1.0, t and 2.6, q(7.2), Et; 2.1, m(6.9), PMe
$[Ru(n\text{-}PrCN)_3(PMePh_2)_3][BF_4]_2$	(IIc)	83	183	56.3 (56.6)	5.4 (5.6)	4.1 (3.9)	2285	0.9, 1.4 and 2.5, c, n-Pr; 2.1, m(6.9), PMe

$[Ru(PhCN)_3(PMePh_2)_3]$- $[BF_4]_2 \cdot Me_2CO$	(IId)	64	214	60.5 (60.9)	4.9 (4.9)	3.5 (3.4)	2270s 1712s [e]	2.1, s, Me_2CO; 2.3, m, PMe
$[Ru(RCN)_3(PMePh_2)_3]$- $[BF_4]_2$	(IIe)	82	174	52.1 (52.2)	4.6 (4.7)	4.0 (3.6)	2310w 1760vs(br) [e]	2.1, m, PMe; 3.7, s, Ac; 3.8, s, CH_2
$[Ru(n\text{-}PrCN)_4(PMePh_2)_2]$- $[BF_4]_2$	(III)	78	193	52.8 (53.0)	5.7 (5.7)	5.7 (5.9)	2295	0.9, 1.6 and 2.7, c, n-Pr; 1.9, m(8.7), PMe
$[Ru(H)(BH_4)(PMePh_2)_3]$	(IV)	74	[g]	64.9 (65.3)	6.2 (6.2)		[h]	−14.1, dt(22 and 29), RuH; −5.1 and −9.1, br, RuH_2B; 1.3, d(8.2) and 1.9, t(5.3), PMe [j]
$[Ru(OCOMe)_2(PMePh_2)_3]$ $\cdot 2\ H_2O$	(Va)	50	[k]	59.9 (60.3)	5.5 (5.8)		[l]	1.6, c, PMe; 2.0, s, Ac [j]
$[Ru(OCOCMe_3)_2(PMePh_2)_3]$	(Vb)	56	[k]	64.8 (65.1)	6.3 (6.4)		[m]	0.9, s, Me_3C; 1.7, c, PMe [n]

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[a] All complexes were white in colour except IIa, IIb and IIe (cream), IIc (pale green) and IV and V (yellow). R = $MeOCOCH_2$. [b] At 20°C and 10^{-3} *M* in acetone, except where stated. [c] In Nujol mull. ν(CN) vibrations of medium intensity unless stated. s, strong; w, weak; (br), broad, (sh), shoulder. [d] In CD_2Cl_2 at 35°C, except where stated. Resonances reported as follows: position (δ, ppm), multiplicity (coupling constant (Hz)), assignment. All spectra had a complex resonance at δ 7.0—7.9 ppm assigned to the aromatic protons. Satisfactory integrals were obtained. s, singlet; d, doublet; t, triplet; q, quartet; c, complex resonance, (br), broad; m, complex multiplet consisting of a broad central peak and two partially resolved outer peaks (separation (Hz) of outer peaks in brackets). Ac = CH_3CO. [e] ν(CO). [f] In $(CD_3)_2CO$ solution. The PMe resonances were partially obscured. [g] A non-conductor in benzene. [h] 2395s, 2375(sh), 2315s, ν(BH terminal); 1945s, 1370s(br), ν(BH bridging); 1180s, δ(BH). The deuterio-analogue had the following peaks: 1795m, 1760w(br), 1710s, 1405m, 1032s(br), (sixth band presumably obscured). [j] In C_6D_6 solution. [k] A non-conductor in CH_2Cl_2 solution. [l] In Nujol and hexachlorobutadiene mulls: 1600s(br), ν(CO_2 *asym* monodentate); 1520m, ν(CO_2 *asym* bidentate); 1478s, ν(CO_2 *sym*); 3665m, 3380m(br), 3215w, ν(OH). [m] 1618s, ν(CO_2 *asym* monodentate); 1515m, ν(CO_2 *asym* bidentate); 1488s, ν(CO_2 sym bidentate); 1325s, ν(CO_2 *sym* monodentate). [n] In $CDCl_3$.

^{1}H NMR spectra were recorded on a Perkin—Elmer R12A or Bruker H-90 FT spectrometer. IR spectra were recorded on a Perkin—Elmer 257 spectrophometer. Conductivity measurements were performed using a Phillips PW9504/00 conductivity meter and a PW9510 conductivity cell. Analyses were performed by the Service de Microanalyse, C.N.R.S., Gif-sur-Yvette.

fac-Tris(methyldiphenylphosphine)tris(methyl cyanide) ruthenium (II) bistetrafluoroborate. To a mixture of $[Ru_2Cl_3(PMePh_2)_6]Cl \cdot 3\ H_2O$ [4] (0.5 g) and $Ag[BF_4]$ (0.25 g, 4.1 mol/mol complex) was added MeCN (10 cm^3) and the mixture heated under reflux for 2 h. The resulting mixture was allowed to cool, filtered to remove AgCl and the pale-yellow solution reduced to about half-volume in vacuo. Addition of ether gave cream crystals which were filtered off, washed with ether and dried (yield 0.48 g, 77%).

The complexes I, II and III were prepared similarly using the appropriate ruthenium dimer and either the nitrile or an acetone/nitrile (10 cm^3/1 cm^3) mixture as solvent (see Scheme 1). Yields and analytical data are presented in Table 1.

Hydrido(tetrahydroborato)-mer-tris(methyldiphenylphosphine)ruthenium (II). $Na[BH_4]$ (0.07 g) was added, with stirring, to a suspension of $[Ru(MeCN)_3(PMePh_2)_3][BF_4]_2$ (IIa) (0.3 g) in methanol (10 cm^3). A yellow solid, immediately precipitated. The mixture was stirred for 10 min and then the solid was filtered off, washed with a water/methanol (1/1) mixture (3 × 10 cm^3) then with ether (5 cm^3) and was dried in vacuo (yield 0.16 g, 74%).

The organic products were distilled in vacuo and determined by GC. In addition, the ethylamine was isolated as the hydrochloride (yield 80%) and identified by its IR spectrum.

The complex $[RuD(BD_4)(PMePh_2)_3]$ was similarly prepared using $Na[BD_4]$ and MeOD.

Bis(carboxylato)-fac-tris(methyldiphenylphosphine)ruthenium(II) dihydrate. Acetic acid (0.2 cm^3) was added to $[RuH(BH_4)(PMePh_2)_3]$ (0.1 g) in benzene (10 cm^3) and the mixture stirred for 18 h. The resulting yellow solution was filtered, reduced to half-volume in vacuo, and methanol (10 cm^3) was added. After several weeks at —40° C yellow crystals were deposited. These were filtered off, washed with cold methanol (5 cm^3) and dried in vacuo (yield 0.06 g, 50%). The bis(trimethylacetato) complex was prepared similarly and isolated with ether (yield 0.07 g, 56%).

Reaction of $[RuH(BH_4)(PMePh_2)_3]$ with triethylamine and methyldiphenylphosphine or carbon monoxide. To a solution of $[RuH(BH_4)(PMePh_2)_3]$ (0.2 g) in benzene (10 cm^3) was added NEt_3 (0.04 cm^3) and $PMePh_2$ (0.05 cm^3) and the mixture stirred for 18 h. The resulting yellow solution was filtered and concentrated in vacuo and methanol (10 cm^3) added. Further slow concentration of the solution led to the deposition of *cis*-$[RuH_2(PMePh_2)_4]$ as a cream microcrystalline solid (yield 0.2 g, 79%), identified by its IR and ^{1}H NMR spectra [7]. (Found: C, 69.4; H, 6.2. $C_{52}H_{54}P_4Ru$ calcd.: C, 69.1; H, 6.0%). When a stream of CO (2 ml/min, 60 min) was substituted for the $PMePh_2$ in the above preparation, *cis-mer*-$[RuH_2(CO)(PMePh_2)_3]$ was isolated in the same way as a cream microcrystalline solid (yield 0.15 g, 64%). It was identified by its IR and NMR spectra [7]. (Found: C, 65.3; H, 5.7. $C_{40}H_{41}P_4ORu$ calcd.: C, 65.6; H, 5.7%).

Interaction of [RuH(BH$_4$)(PMePh$_2$)$_3$] with triethylamine. NEt$_3$ (0.05 cm^3) was added to a solution of [RuH(BH$_4$)(PMePh$_2$)$_3$] (0.21 g) in benzene (10 cm^3) and the mixture stirred for 18 h. The resulting red solution was filtered, concentrated, and hexane added to precipitate a small amount (0.05 g) of a pale brown solid, identified as *cis*-[RuH$_2$(PMePh$_2$)$_4$] by its IR spectrum [7]. No other solid product could be obtained.

Some reactions of [Ru$_2$Cl$_3$(PMePh$_2$)$_6$]Cl · 3 H$_2$O. (a) With Na[BH$_4$] and PMePh$_2$ in ethanol. A mixture of the dimer (0.2 g), Na[BH$_4$] (0.1 g) and PMePh$_2$ (0.26 cm^3) in ethanol (10 cm^3) was heated under reflux for 4 h during which time a pale cream solid and pale yellow solution were produced. The solid was filtered off, washed with ethanol (5 cm^3), water (5 cm^3) and ethanol (5 cm^3), dried in vacuo and identified as *cis*-[RuH$_2$(PMePh$_2$)$_4$] by its IR and NMR spectra [7] (yield 0.18 g, 80%). (Found: C, 69.3; H, 6.1. $C_{52}H_{54}P_4Ru$ calcd.: C, 69.1; H, 6.0%).

(b) With Na[BH$_4$] in ethanol. When PMePh$_2$ was omitted from the preparation above, a cream solid was isolated and shown to be [RuH$_2$(CO)(PMePh$_2$)$_3$] (IR and NMR) [7]. (Yield 0.12 g, 66%.) (Found: C, 65.4; H, 5.6. $C_{40}H_{41}P_4ORu$ calcd.: C, 65.5; H, 5.7%).

(c) With isopropanol in the presence of KOH and PMePh$_2$. A mixture of the dimer (0.4 g), KOH (0.4 g) and PMePh$_2$ (0.4 cm^3) in isopropanol (10 cm^3) was heated under reflux for 2 h. The cream *cis*-[RuH$_2$(PMePh$_2$)$_4$] (IR and NMR) was filtered off, washed with ethanol, water and ethanol and dried in vacuo (0.4 g, 88%). (Found: C, 68.9; H, 6.0. $C_{52}H_{54}P_4Ru$ calcd.: C, 69.1; H, 6.0%).

If the reaction is carried out in the absence of added phosphine, a low yield (ca. 30%) of the dihydride results and no other solid products could be isolated from the remaining red solution.

(d) With ethanol in the presence of KOH. A mixture of the dimer (0.4 g and KOH (0.4 g) in ethanol (10 cm^3) was heated under reflux for 2 h. The resulting white solid was isolated and shown to be [RuH$_2$(CO)(PMePh$_2$)$_3$] (IR and NMR) [7] (yield) 0.28 g, 77%) (Found: C, 65.4; H, 5.7. $C_{40}H_{41}P_4ORu$ calcd.: C, 65.6; H, 5.7%).

(e) With ethanol in the presence of KOH and PMePh$_2$. When PMePh$_2$ (0.5 cm^3) was included in the reaction mixture above, a cream solid was isolated after reflux and shown to be *cis*-[RuH$_2$(PMePh$_2$)$_4$] (IR and NMR) [7] (yield 0.37 g, 82%). (Found: C, 69.3; H, 6.2. $C_{52}H_{54}P_4Ru$ calcd.: C, 69.1; H, 6.0%).

Reaction of RuCl$_3$ · n-H$_2$O with Na[BH$_4$] and PMePh$_2$. To a solution of RuCl$_3$ · n-H$_2$O (0.21 g) and PMePh$_2$ (0.87 cm^3) in ethanol (10 cm^3) was added dropwise Na[BH$_4$] (0.33 g) in ethanol (5 cm^3) and the mixture stirred vigorously. A pale red brown solid began to deposit from solution after 15 min. The stirring was continued for 3 h and the solid was isolated (yield 0.48 g, 66%) and identified as *cis*-[RuH$_2$(PMePh$_2$)$_4$] (IR and NMR) [7].

Catalytic studies

Our apparatus and methods have been described [17]. Conditions: catalyst, 50 m*M*; substrate, 1 *M*; NEt$_3$, 0.1 *M*; $p(H_2)$, 60 cmHg; 25°C; solvent benzene, 15 cm^3.

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