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Five-Coordinate Complexes $[RuHCl(CO)(PBu^t_2R)_2]$ (R = Me or Et) Formed from Ruthenium Trichloride and the Tertiary Phosphine in 2-Methoxyethanol†

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$RuCl_3$ and PBu^t_2R (R = Me or Et) react in boiling 2-methoxyethanol to give five-coordinate complexes of type $[RuHCl(CO)(PBu^t_2R)_2]$, which are light- and air-sensitive. $RuHCl(CO)(PBu^t_2Me)_2$ reacts with carbon monoxide to give $RuHCl(CO)_2(PBu^t_2Me)_2$, configuration (VI). $RuHCl(CO)(PBu^t_2Et)_2$ reacts similarly with carbon monoxide and also reacts with methyl isocyanide to give a single product $[RuHCl(CO)(MeNC)(PBu^t_2Et)_2]$, probably having configuration (VII). With hydrogen chloride $[RuHCl(CO)(PBu^t_2Me)_2]$ gives an unidentified red product which with pyridine gives $[RuCl_2(CO)(py)_2(PBu^t_2Me)]$ (X). ^1H n.m.r. and i.r. data {ν(Ru–H), ν(Ru–Cl), ν(C=O), ν(C≡N)} are given and discussed.

Introduction

Bulky tertiary phosphine ligands (L) such as PBu^t_3, PBu^t_2R and $P(C_6H_{11})_3$ promote unusual chemical and physical properties in metal complexes [1]. For instance, they promote hydride formation and stabilize the resultant hydride *e.g.* for hydrides of the types *trans*-$[PtHClL_2]$ and *trans*-$[PtH_2L_2]$ [2]; they stabilize coordinatively unsaturated species, *e.g.* PdL_2, PtL_2, [3–5], $IrHCl_2L_2$ [6], $RhHCl_2L_2$ [7]: and they also promote carbonyl abstraction reactions from primary alcohols *e.g.* the formation of *trans*-$[IrCl(CO)(PBu^t_2Ph)_2]$ from $IrCl_3$ and PBu^t_2Ph in 2-methoxyethanol [8]. We have shown that the ligands PBu^t_2(aryl) where aryl = phenyl or *p*-tolyl react with ruthenium(II) carbonyl chlorides in alcohol solvents to give binuclear ruthenium(I) complexes of the type $[Ru_2Cl_2(CO)_4(PBu^t_2aryl)_2]$ containing a ruthenium–ruthenium bond [9, 10]. Similar treatment of ruthenium(II) carbonyl chlorides with the purely aliphatic phosphines, PBu^t_2R, R = Et, Pr^n or Bu^n, gives coordinatively saturated ruthenium(II) complexes of the type $[RuCl_2(CO)_2(PBu^t_2R)_2]$ (two isomers). We now describe the results of a study of the action of PBu^t_2Me and PBu^t_2Et on ruthenium trichloride in 2-methoxyethanol.

Experimental

The general techniques and instruments used are the sames as those described previously [11].

Carbonylchlorohydridobis(methyldi-t-butylphosphine)ruthenium(II)

Methyldi-t-butylphosphine (6.4 g, 40 mmol) was added to a solution of ruthenium trichloride trihydrate (2.0 g, 8.0 mmol) in 2-methoxyethanol (50 cm^3) and the mixture heated under reflux for 72 h. The mixture was then cooled to –20 °C to give the *product* (2.24 g) as orange prisms.

Carbonylchlorobis(ethyldi-t-butylphosphine)hydridoruthenium(II)

This was obtained similarly as orange prisms.

Dicarbonylchlorohydridobis(methyldi-t-butylphosphine)ruthenium(II)

Carbon monoxide was passed through a boiling solution of carbonylchlorohydridobis(methyldi-t-butylphosphine)ruthenium(II) (0.81 g) in benzene (10 cm^3) for 2½ h. The solution was evaporated to give the required product as *colourless prisms* (0.68 g) from methanol.

Dicarbonylchlorobis(ethyldi-t-butylphosphine)hydridoruthenium(II)

This was prepared in a similar manner to give the product as colourless prisms from dichloromethane–methanol.

Carbonylchlorohydrido(methyl isocyanide)bis(methyldi-t-butylphosphine)ruthenium(II)

Methyl isocyanide (55 μl, 0.99 mmol) was added to a solution of carbonylchlorohydridobis(methyldi-t-butylphosphine)ruthenium(II) (0.42 g, 0.82 mmol) in

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benzene (10 cm^3) and the mixture put aside for 30 min. Evaporation gave the product as colourless *plates* (0.19 g) from methanol.

The action of Hydrogen Chloride on Dicarbonylchlorohydridobis(methyldi-t-butylphosphine)ruthenium(II)

A solution of hydrogen chloride (0.19 mmol) in diethyl ether (0.04 cm^3) was added to a solution of the hydrido complex (0.09 g, 0.17 mmol) in benzene (3 cm^3). Evaporation gave dicarbonyldichlorobis-(methyldi-t-butylphosphine)ruthenium(II) (0.09 g) identified by comparison of its i.r. spectrum with that of an authentic sample.

The Action of Hydrogen Chloride on Carbonylchlorohydridobis(methyldi-t-butylphosphine)ruthenium(II)

A solution of hydrogen chloride (15.0 mmol) in diethyl ether (5 cm^3) was added to a solution of the hydrido-complex (0.74 g, 1.5 mmol) in chloroform (10 cm^3). Dihydrogen was evolved and a red solution formed. Evaporation gave *product A* as orange-red prisms (0.58 g) from dichloromethane–methanol. This material could not be identified (see Discussion). The mother liquors when treated with a large excess of sodium tetraphenylboron in methanol gave a precipitate of hydridomethyldi-t-butylphosphonium tetraphenylboron (0.36 g). Found: C, 83.4; H, 8.95%. Calc. for $C_{33}H_{42}BP$: C, 82.5; H, 8.8%. Molar conductivity in acetone at 296 K = 93 ohm^{-1} cm^2 mol^{-1}.

The Action of Pyridine on Product A

Pyridine (160 μl) was added to a suspension of product A (0.32 g) (see above) in benzene (15 cm^3). The mixture was boiled for 4 mins giving a clear orange-yellow solution. Isolation gave carbonyldichlorobis(pyridine)(methyldi-t-butylphosphine)ruthenium(II) (0.28 g) as orange prisms (0.28 g) from methanol.

Results and Discussion

Initially we investigated the action of mono-t-butyl-phosphines, PBu^tR_2, on ruthenium trichloride in 2-methoxyethanol, but only dark solids of unknown and variable compositions, or dark oils were obtained. However, we find that when a solution of $RuCl_3{\cdot}3H_2O$ in 2-methoxyethanol is heated under reflux with PBu^t_2Me (5 mol equivalent) the initially dark solution gradually lightens and after 3 days a red solution has formed which when cooled deposits the five-coordinate carbonyl hydride $RuHCl(CO)(PBu^t_2Me)_2$ as orange prisms. This complex is both air- and light-sensitive either of which cause darkening. The formulation follows from the microanalytical data (Table I) and the i.r. (Table II) and ^1H n.m.r. (Table III) data. The i.r. spectrum shows a weak band at 2108 cm^{-1} due to ν(Ru–H), a very strong band at 1902 cm^{-1} due to ν(C≡O) and a strong band due to ν(Ru–Cl), at 284 cm^{-1}. The ^1H n.m.r. spectrum shows a triplet pattern due to the methyl group and two overlapping triplets due to the t-butyls. Thus $^2J(PP)$ is large and the phosphines are mutually *trans* or nearly so [12]. Two t-butyl triplets are observed because there is no plane of symmetry along an Ru–P bond and hence the t-butyls on a single phosphorus atom are non-equivalent. The hydride resonance at $\delta = -24.9$ indicates coupling to two equivalent phosphorus nuclei. We are unable to determine from these data whether the complex is trigonal bipyramidal (I) or square pyramidal (II), (III), or (IV). The five-coordinate complex $[RuHCl(PPh_3)_3]$ has been shown by X-ray diffraction to have a distorted trigonal bipyramidal structure with the hydride ligand in an equatorial position [13]. If our compound is square pyramidal then (II) seems more likely than (III) or (IV) since in (II) the ligand with the strongest *trans*-influence is *trans* to a vacant coordination site, and the least sterically demanding ligand (the hydride) is in the most crowded (the

TABLE I. Analytical[a], Melting Point, Molecular Weight[a,b] Data, Colours and % Yields.

Complexes	% Yield	Colour	M.P. °C	C	H	Cl	Mol. Wt.
$RuHCl(CO)(PBu^t_2Me)_2$	58	Orange	150–160[c]	46.9(46.95)	8.8(8.9)		
$RuHCl(CO)(PBu^t_2Et)_2$	69	Orange	130–140[c]	48.25(49.05)	8.85(9.2)		
$RuHCl(CO)_2(PBu^t_2Me)_2$	79	White	130–192[c]	46.8(46.75)	8.25(8.45)		525(514)
$RuHCl(CO)_2(PBu^t_2Et)_2$	72	White	155–170[c]	48.3(48.75)	8.8(8.75)	6.65(6.55)	
$RuHCl(CO)(CNMe)(PBu^t_2Et)_2$[e]	42	White	167–173[c]	50.0(49.75)	9.2(9.1)	6.5(6.4)	
$RuCl_2(CO)(py)_2(PBu^t_2Me)$[f]		Yellow	199–210[c,d]	46.4(46.35)	6.05(6.05)	13.8(13.7)	505(518)

[a]Calculated values in parentheses. [b]Measured in chloroform solution osmometrically. [c]With decomposition. [d]Gas evolved. [e]N = 2.7(2.5)%. [f]N = 5.35(5.4)%.

TABLE II. I.r. Data (±3 cm^{-1}).

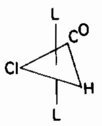
Complexes	ν(C≡O)		ν(Ru–H)		ν(Ru–Cl) Nujol
	Nujol	Chloroform	Nujol	Chloroform	
$RuHCl(CO)(PBu^t_2Me)_2$	1902vs	1906vs[a]	2188w	2105w[a]	184vs
$RuHCl(CO)(PBu^t_2Et)_2$	1902vs	1908vs	2108w	2114w	284vs
$RuHCl(CO)_2(PBu^t_2Me)_2$	2042vs 1923vs	2043vs 1930vs	1967s	1957m	229s
$RuHCl(CO)_2(PBu^t_2Et)_2$	2045vs 1922vs	2045vs 1927vs	1971m	1969m	284s
$RuHCl(CO)(CNMe)(PBu^t_2Et)_2$ [b]	1912vs	1908vs	1990m	1980w	292s
$RuCl_2(CO)(py_2)(PBu^t_2Me)$	1937vs 1920vs	1960vs			324vs

[a] In benzene. [b] ν(N≡C) 2170s (Nujol), 2163s (Chloroform).

TABLE III. [1]H N.m.r. Data[a].

Complexes	δ(Bu^t)	$^3J(PH) + {}^5J(PH)$	δ(Me)	$^2J(PH) + {}^4J(PH)$	δ(Ru*H*)	$^2J(PH)$
$RuHCl(CO)(PBu^t_2Me)_2$	1.2t 1.22t	12.7 12.7	1.42t	5.8	−24.9t	19.4
$RuHCl(CO)(PBu^t_2Et)_2$	1.41t 1.43	12.4 12.4			−24.9t	18.2
$RuHCl(CO)_2(PBu^t_2Me)_2$	1.40t 1.43t	13.7 14.1	1.64	6.4	−5.67	19.7
$RuHCl(CO)_2(PBu^t_2Et)_2$	1.45t 1.47t	12.5 12.6			−5.48t	19.2
$RuHCl(CO)(MeNC)(PBu^t_2Et)_2$ [b]	1.43t 1.49t	12.0 12.3	2.5 [c]		−7.01t	20.3
$RuCl_2(CO)(Py)_2(PBu^t_2Me)$ [d]	1.30d	12.7e				

[a] Recorded at 35 °C in $CDCl_3$ unless stated otherwise. δ-values ± 0.02, J-values ± 0.5 Hz; t = triplet, d = doublet. [b] In benzene. [c] Methyl group of methyl isocyanide ligand. [d] Signals for pyridine ligands at *ca.* δ 8.7 and 9.6. [e] $^3J(PH)$.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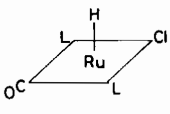
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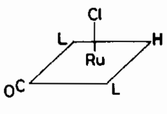
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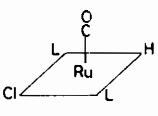
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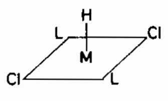
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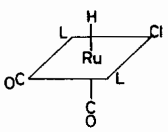
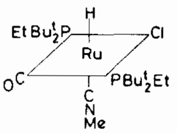

(VI)

apical site. Structure (IV) seems unlikely because ν(Ru–Cl) is high (284 cm^{-1}) and one would expect a much lower value *trans* to hydrogen. We have shown that the five coordinate hydride, $RhHCl_2(PBu^tPr^n_2)_2$ has the square pyramidal structure (V) (M = Rh; L = $PBu^tPr^n_2$) [14]. Other hydrides of this type [$MHCl_2$-L_2] (M = Rh or Ir; L = PBu^tR_2 or PBu^t_2R) also probably have stereochemistry (V) [6, 7].

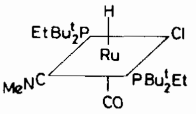
When carbon monoxide is bubbled through a boiling benzene solution of [$RuHCl(CO)(PBu^t_2Me)_2$], the solution rapidly changes from red to colourless. The white product was identified as [$RuHCl(CO)_2$-$(PBu^t_2Me)_2$] of stereochemistry (VI) since it shows two very strong bands at 2043 and 1923 cm^{-1} due to ν(C≡O), a strong band at 1967 cm^{-1} assigned to ν(Ru–H) and a strong band at 279 cm^{-1} which is typical of ν(Ru–Cl) with chlorine *trans* to carbonyl [15]. The [1]H n.m.r. spectrum shows two t-butyl triplet and one methyl triplet pattern showing mutually *trans* phosphines and a hydride triplet at δ = −5.67. These data indicate configuration (VI). It is interesting that the hydride resonance of the six-coordinate complex $[RuHCl(CO)_2(PBu^t_2Me)_2]$ (VI) occurs at much lower field {$\delta = -5.67$} than in the five-coordinate complex {$\delta = -24.9$} {configurations (I) or (II)}. A large change in δ-value (becoming more positive) occurs when carbon monoxide is added to five-coordinate complexes of the type $[MHCl_2L_2]$ (V) M = Rh or Ir; L = PBu^t_2alkyl [6, 7, 16].

Treatment of ruthenium trichloride with PBu^t_2Et in refluxing 2-methoxyethanol gives $[RuHCl(CO)(PBu^t_2Et)_2]$. This material could not be obtained pure and in addition to i.r. absorption bands at 2108 cm^{-1} assigned to ν(Ru–H) and one at 1902 cm^{-1} {ν(C≡O)} it showed a strong band at 1935 cm^{-1} and a weak band at 2035 cm^{-1}. These two bands are similar in frequency to those obtained when $[RuHCl(CO)(PBu^t_2Me)_2]$ decomposes in air (2035 and 1932 cm^{-1}) hence it is possible that some decomposition of the PBu^t_2Et occurs on isolation. The far i.r. spectrum of $[RuHCl(CO)(PBu^t_2Et)_2]$ shows ν(Ru–Cl) at 284 cm^{-1}. The ^1H n.m.r. spectrum showed only one hydride resonance pattern (triplet at –24.9) and two t-butyl triplets as expected (Table III).

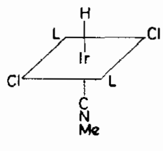
Treatment of $[RuHCl(CO)(PBu^t_2Et)_2]$ with carbon monoxide gives a six-coordinate hydrocarbonyl complex $[RuHCl(CO)_2(PBu^t_2Et)_2]$ which was readily purified, analysed correctly for C, H and Cl (Table I) and showed the expected i.r. and n.m.r. values (Tables II and III). Treatment of $[RuHCl(CO)(PBu^t_2Et)_2]$ with methyl isocyanide gave $[RuHCl(CO)(MeNC)(PBu^t_2Et)_2]$. The i.r. spectrum (Table II) shows a strong band due to ν(C≡O) at 1912 cm^{-1}, a strong band at 2170 cm^{-1} assigned to ν(C≡N) and a moderately intense band at 1990 cm^{-1} due to ν(Ru–H). The hydride resonance is a broadened 1:2:1 triplet at $\delta = -7.01$. We have observed previously that with complexes of the type $[IrHCl_2(MeNC)(L_2)]$ of



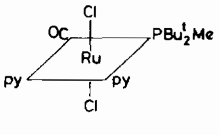
(VII)



(VIII)



(IX)



(X)

configuration (IX) L = PBu^t_2Me, PBu^t_2Et or $PBu^t_2Pr^n$ the hydride resonance occurs at somewhat higher field that with the corresponding hydridocarbonyl and is broadened, probably because of coupling to the quadrupolar ^{14}N-nucleus in *trans*-position [7]. We therefore slightly favour (VII) as the configuration of $[RuHCl(CO)(MeNC)(PBu^t_2Et)_2]$ rather than (VIII).

We also studied the action of hydrogen chloride on $[RuHCl(CO)(PBu^t_2Me)_2]$ in ether–benzene. A vigorous evolution of hydrogen occurred and a deep red complex, which we shall call *product A*, was formed. Addition of sodium tetraphenylboron to the mother liquor gave $[PBu^t_2MeH]BPh_4$, in an amount corresponding to the loss of one PBu^t_2Me per P ruthenium atom from the original complex. Product A showed a very strong band at 1949 cm^{-1} due to ν(C≡O) and a weak band at 2383 cm^{-1} probably due to ν(P–H). The far i.r. spectrum showed bands at 323vs, 279m, and 234s cm^{-1}. The ^1H n.m.r. spectrum was very complex and we could not draw definite conclusions from it. Molecular weight determinations in chloroform gave values of 882 and 886. We were unable to purify or identify product A. However, when a suspension of product A in benzene was treated with pyridine an orange crystalline complex $[RuCl_2(CO)(py)_2(PBu^t_2Me)]$ formed readily. The i.r. spectrum shows one band due to ν(C≡O) (at 1960 cm^{-1}) and only one band due to ν(Ru–Cl) (at 324vs cm^{-1}). This suggests a *trans*-Cl–Ru–Cl moiety. The t-butyl resonance was a doublet at $\delta = 1.30$ showing that there is a plane of symmetry along the Ru–P bond. Two sets of resonances due to the pyridine protons were observed showing the presence of non-equivalent pyridine ligands. The data show that the complex has configuration (X).

Moers and Langhout [17] showed that when ruthenium trichloride was treated with tricyclohexylphosphine the 5-coordinate $RuHCl(CO)\{P(C_6H_{11})_3\}_2$ was formed. They did not report n.m.r. data and their values for ν(Ru–H) (2030w cm^{-1}) and ν(Ru–Cl) (337s cm^{-1}) are quite different from ours. Possibly their bis-tricyclohexylphosphine complex has a different stereochemistry from our di-t-butyl(alkyl)-phosphine complexes. Interestingly it was reported that $RuHCl(CO)\{P(C_6H_{11})_3\}_2$ darkens in air and a new band appears at 1935 cm^{-1} due to an unidentified product. As reported above, our compounds are also changed on exposure to air and a new band at *ca.* 1935 cm^{-1} appears.

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