Some Complexes of Rhodium(I), Rhodium(II), and Rhodium(III) containing Tertiary t-Butylphosphines as Ligands

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Paramagnetic rhodium(II) complexes of the type trans-$[RhCl_2(PBu^t_2R)_2]$ (R = Me, Et, or Pr^n) are formed rapidly by treating ethanolic rhodium(III) chloride trihydrate with the tertiary phosphine at 25 °C. The complexes have low magnetic moments in the solid state (<1·4 B.M.) but in solution trans-$[RhCl_2(PBu^t_2Me)_2]$ has the expected moment of ca. 2·12 B.M. Treatment of rhodium trichloride trihydrate with some t-butylphosphines (L = PBu^{t}Pr$^n_2$, PBu$^t_2$Me, PBu$^t_2$Et, or PBu$^t_2$Pr^n) in refluxing propan-2-ol gives square pyramidal hydridorhodium(III) complexes $[RhHCl_2L_2]$. $[RhHCl_2(PBu^tPr^n_2)_2]$ reacts with some ligands Q [Q = MeNC, MeCN, pyridine, or P(OMe)$_3$] to give complexes of type $[RhHCl_2(PBu^tPr^n_2)_2Q]$. $[RhHCl_2(PBu^t_2Me)_2]$ reacts with hydrogen gas to give $[RhH_2Cl-(PBu^t_2Me)_2]$, and trans-$[RhCl_2(PBu^t_2Me)_2]$ with hydrogen gas gives a ca. 1:1 mixture of $[RhHCl_2(PBu^t_2Me)_2]$ and $[Rh_2Cl(PBu^t_2Me)_2]$. Treatment of rhodium chloride in propan-2-ol with tri-t-butylphosphine gives the five-co-ordinate dihydride $[RhH_2Cl(PBu^t_3)_2]$. $[RhH_2Cl(PBu^tMePh)_3]$ was formed similarly as a mixture of enanti-omers. Prolonged (7 days) treatment of hydrated rhodium trichloride in ethanol at 20 °C with di-t-butylalkyl-phosphines gives rhodium(I) carbonyl complexes trans-$[RhCl(CO)(PBu^t_2R)_2]$ (R = Me, Et, or Pr^n) in ca. 75% yield. Addition of a strong base (e.g., NaOMe) to solutions of complexes of the type $[RhHCl_2L_2]$ in ethanol or methanol gives trans-$[RhCl(CO)L_2]$ within a few seconds. Ethanolic rhodium trichloride reacts with PHBu$^t_2$ to give $[RhCl(PHBu^t_2)_3]$. ^{1}H and ^{31}P N.m.r., i.r., and electronic absorption spectral data are reported and discussed as are magnetic susceptibility data for the rhodium(II) complexes.

WE have reported briefly that the very bulky tertiary t-butylphosphines are unusual ligands for the platinum metals. Thus they promote internal transition metal–carbon bond formation in platinum(II) or palladium(II) complexes,[1,2] and give unusual products with chloro-iridous acid [3] or rhodium trichloride trihydrate.[4] We

† No reprints available.

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[2] A. J. Cheney and B. L. Shaw, unpublished results.

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[4] C. Masters, W. S. McDonald, G. Raper, and B. L. Shaw, *Chem. Comm.*, 1971, 210.

6 I

here report, in more detail, on the products obtained from the reaction of secondary or tertiary t-butylphosphines with rhodium trichloride trihydrate in an alcoholic or ketonic solvent.

Rhodium(II) *Complexes.*—Hydrated rhodium(III) chloride in ethanol at room temperature (*ca.* 18 °C) reacts rapidly (*ca.* 5 min) with di-t-butyl(alkyl)phosphines (R = Me, Et, or Pr^n) (greater than four mole per

chlorine stretching vibrations possibly split by a solid-state interaction. The palladium(II) complexes *trans*-$[PdCl_2(PBu^t_2R)_2]$ with R = Me or Pr^n show only one band due to a palladium–chlorine stretching vibration [5] but with R = Et two bands at 342s and 354 cm⁻¹ are obtained. These bands are absent from the spectra of the corresponding bromides. We therefore suggest a square planar *trans*-stereochemistry for our complexes.

TABLE 1

Tertiary t-butylphosphine complexes of rhodium

$[RhX_2L_2]$ configuration (I)

L	X	Colour [e]	M.p. (t/°C) [d]	Yield (%)	C (%)	H (%)	Halogen (%)	M [a,b]	ν(Rh–Cl) [e]/ cm⁻¹	ν(Rh–H) [e]/ cm⁻¹
PBu^tPr^n	Cl	r	122—125	90	45·7 (46·0)	8·8 (8·9)	13·7 (13·6)		340s	1945w
$PBu^tPr^n_2$	Br	dr	161—171	69	39·9 (39·2)	7·9 (7·7)	26·3 (26·1)	570 (612)		1946w (1946)
PBu^t_2Me	Cl	r	170—190	86	43·8 (43·7)	8·7 (8·8)	14·4 (14·3)	428 (495)	340s	1938s (1942)
PBu^t_2Me	Br	dr	150—170	78	37·8 (37·0)	7·9 (7·4)	28·9 (27·4)			1938m (1942)
PBu^t_2Et	Cl	r	157—162	66	45·4 (45·9)	8·9 (9·1)	13·4 (13·6)		341s, 355sh	1940m (1940)
$PBu^t_2Pr^n$	Cl	k	175—190	63	48·2 (47·9)	9·2 (9·3)	13·0 (12·9)	541 (551)	344s	1936m (1938)

trans-$[RhCl_2L_2]$

L	X	Colour [e]	M.p. (t/°C) [d]	Yield (%)	C (%)	H (%)	Halogen (%)	M [a,b]	ν(Rh–Cl) [e]/ cm⁻¹	ν(Rh–H) [e]/ cm⁻¹
PBu^t_2Me		p	170—200	75	44·0 (43·7)	8·7 (8·6)	14·1 (14·4)	465 (494)	348s, 352sh	
PBu^t_2Et		g	165—175	67	45·7 (46·0)	8·9 (8·9)	13·6 (13·6)		344s, 360s	
$PBu^t_2Pr^n$		g	175—195	76	47·7 (47·9)	9·2 (9·3)	12·9 (12·9)	542 (550)	344sh, 352s	

trans-$[PdCl_2L_2]$

L	X	Colour [e]	M.p. (t/°C) [d]	Yield (%)	C (%)	H (%)	Halogen (%)	M [a,b]	ν(Rh–Cl) [e]/ cm⁻¹	ν(Rh–H) [e]/ cm⁻¹
[g] PBu^t_2Me									344s	
[h] PBu^t_2Et									342s, 354m	
[g] $PBu^t_2Pr^n$									347s	

$[RhHCl_2Q(PBu^tPr^n_2)_2]$ configuration (II)

Q	X	Colour [e]	M.p. (t/°C) [d]	Yield (%)	C (%)	H (%)	Halogen (%)	M [a,b]	ν(Rh–Cl) [e]/ cm⁻¹	ν(Rh–H) [e]/ cm⁻¹
MeNC [i,j]		o	124—131	73	47·0 (46·8)	8·9 (8·9)	12·8 (12·6)	554 (564) [k]	326s	2083m
MeCN [l,m]		o	99—105	60	46·9 (46·8)	9·0 (8·9)	13·0 (12·6)		327s	[n]
py [o]		o	122—126	78	49·9 (49·8)	8·7 (8·7)	12·5 (11·8)	570 (602) [k]	327s	2188m (2155)
$P(OMe)_3$		o	85—100	58	42·6 (42·9)	8·8 (8·2)	11·2 (11·0)		334s	2088m

$[RhH_2ClL_2]$

L	X	Colour [e]	M.p. (t/°C) [d]	Yield (%)	C (%)	H (%)	Halogen (%)	M [a,b]	ν(Rh–Cl) [e]/ cm⁻¹	ν(Rh–H) [e]/ cm⁻¹
PBu^t_3		dr	178—182	51	52·8 (52·9)	10·0 (10·4)	6·2 (6·5)	570 (545)	264s	2220m, 2200w (2222)
PBu^t_2Me		o	160—176		47·2 (46·9)	9·3 (9·6)				2212w, 2137m) (2179, 2132)
$[RhH_2Cl(PBu^t-MePh)_3]$		c	103—111	74	58·3 (58·2)	7·9 (7·8)	5·4 (5·2)		244m, 227s	2101m 2066m (2101, 2075)
$[RhCl(PBu^t_2H)_2]$ [p]		o	150—160	49	50·1 (50·0)	9·9 (10·0)	6·1 (6·2)		290s, 229m	

[a] Required values in parentheses. [b] Measured in benzene. [e] r = Red, k = khaki, p = purple, g = green, dr = deep red, o = orange, c = colourless. [d] With decomposition. [e] Measured in Nujol. [f] Value in parentheses measured in benzene solution. [g] Data from R. M. Slade, Thesis, The University, Leeds, 1970. [h] M. Cole and B. L. Shaw, unpublished results. [i] N % 2·7 (2·5). [j] ν(N–C) 2193s cm⁻¹ (Nujol), 2203 cm⁻¹ (benzene.) [k] Measured in chloroform. [l] N % 2·3 (2·5). [m] ν(C–N) 2198w cm⁻¹ (Nujol). [n] ν(Rh–H) not detected, possibly coincident with ν(C–N) at 2198 cm⁻¹. [o] N % 2·3 (2·5). [p] ν(P–H) 2313m, 2285m, 2273m,sh cm⁻¹ (Nujol); 2322, 2290 cm⁻¹ (benzene).

Rh atom) to give rhodium(II) complexes (Table 1) of type $[RhCl_2(PBu^t_2R)_2]$ as stable purple (R = Me) or green (R = Et or Pr^n) prisms; these are soluble in many organic solvents giving dark red-brown solutions.

Their i.r. spectra (4000—650 cm⁻¹) are virtually identical with those of palladium(II) complexes of the type *trans*-$[PdCl_2(PBu^t_2R)_2]$;[5] in particular they show no band attributable to ν(Rh–H) or ν(CO). The two complexes $[RhCl_2(PBu^t_2R)_2]$ with R = Me or Pr^n each show a strong i.r. absorption band with a shoulder at *ca.* 350 cm⁻¹ whilst $[RhCl_2(PBu^t_2Et)_2]$ shows two bands in this region (Table 1). We assign these bands to rhodium–

A similar bivalent rhodium complex, *trans*-$[RhCl_2\{P(o\text{-}tolyl)_3\}_2]$, has been obtained by the reaction of an excess of tri-o-tolylphosphine with rhodium trichloride trihydrate in ethanol at room temperature.[6]

Our rhodium(II) complexes *trans*-$[RhCl_2(PBu^t_2R)_2]$ show two maxima in their electronic absorption spectra in the visible region, *e.g.*, with R = Me, $\lambda_{max.}$ 446 nm (ε = 481), $\lambda_{max.}$ 559 (ε = 125) and with R = Pr^n, $\lambda_{max.}$ 484 (ε = 110), $\lambda_{max.}$ 583 (ε = 147). The complexes are paramagnetic but the magnetic moments, measured at room temperature, are much lower than the 'spin only' values being 1·04—1·38 ± 0·03 B.M. (R = Me, on

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different samples), 0.92 ± 0.02 B.M. (R = Et), and 0.30—0.53 ± 0.02 B.M. (R = Pr^n, on different samples). T.l.c. suggests that the complexes are not mixtures.

Dr. A. Earnshaw at Leeds University has measured the magnetic susceptibility of trans-[RhCl$_2$(PBu$^t_2$Me)$_2$] over the temperature range 82—300 K. The results are in Table 2. A plot of $1/\chi_A$ against T shows a slight downward curvature at higher temperatures, indicative of a contribution from temperature-independent paramagnetism (t.i.p.).[7] This is estimated at 335×10^{-6} c.g.s.u. from a plot of χ_A against $1/T$ (value at $1/T = 0$), giving a value for the corrected magnetic moment of 0.72 ± 0.02 B.M. (The t.i.p. contribution estimated for the complex trans-[RhCl$_2${P(o-tolyl)$_3$}$_2$] is 400×10^{-6} c.g.s.u. giving 2.07 ± 0.02 B.M. for the corrected magnetic moment.[6]) A plot of $1/\chi_A^1$ ($\chi_A^1 = \chi_A - 335 \times 10^{-6}$ c.g.s.u.) against T is linear passing through the origin.

$a = 8.00 \pm 0.03, b = 12.40 \pm 0.05, c = 11.35 \pm 0.04$ Å, $\beta = 110.9° \pm 0.2°$.

Preliminary results show that the minimum Rh–Rh distance is not less than 4 Å. Molecular models show that in complexes of the type trans-[RhCl$_2$(PBu$^t_2$R)$_2$] t-butyl groups lie above and below the plane of the complex and block the two octahedral sites. We suggest that these complexes owe their apparent stability to a kinetic effect, i.e., the blocking by the t-butyl groups of the vacant co-ordination sites from attack. Similar explanations have been put forward for the apparent stability of ortho-substituted aryl derivatives of nickel-(II),[11] cobalt(II),[12] and iron(II) [12] and for complexes of type [RhBr$_2$(1-naphthyl)(PR$_3$)$_2$].[13] It was suggested that steric factors helped stabilize trans-[RhCl$_2${P(o-tolyl)$_3$}$_2$] although it was further suggested that the low solubility of this complex was an important factor and

TABLE 2

Variation of atomic susceptibility, χ_A, and effective magnetic moment, μ_{eff}, of trans-[RhCl$_2$(PBu$^t_2$Me)$_2$] with temperature

T/K	$10^6\chi_A$ ^{a}/c.g.s.u.	$1/\chi_A$	μ_{eff}/B.M. ± 0.02	$1/\chi_{A'}$ ^{b}	μ_{eff}/B.M. ^{c} ± 0.02
300.0	550.1	1818	1.15	4649	0.72
270.3	573.1	1745	1.11	4200	0.72
240.1	600.9	1664	1.08	3761	0.72
202.3	650.1	1538	1.03	3174	0.72
167.2	718.1	1393	0.98	2610	0.72
132.0	819.8	1220	0.93	2062	0.72
102.0	967.6	1033	0.89	1581	0.72
82.8	1107.4	904	0.86	1294	0.72

^{a} Including a diamagnetic correction of 344×10^{-6} c.g.s.u.; this is composed of an estimated value of 20×10^{-6} c.g.s.u. for Rh^{II}, 20.1×10^{-6} c.g.s.u. for Cl (ref. 5, p. 403), and 142×10^{-6} c.g.s.u. for PBu$^t_2$Me estimated for Pascal's constants (ref. 7, p. 6). ^{b} $\chi_{A'} = \chi_A - 335 \times 10^{-6}$ c.g.s.u. (t.i.p. contribution, see text). ^{c} Magnetic moment corrected for t.i.p.

One would expect the paramagnetic moment of rhodium-(II) to be ca. 2 B.M.[6,8-10] and therefore our results suggest that in the solid state [RhCl$_2$(PBu$^t_2$Me)$_2$] is composed of ca. 10% of paramagnetic Rh^{II} and ca. 90% of diamagnetic species. We have therefore measured the magnetic susceptibility of [RhCl$_2$(PBu$^t_2$Me)$_2$] in dichloromethane solution and obtained a value of 2.30 ± 0.05 B.M. for the magnetic moment (2.12 ± 0.05, corrected for t.i.p. contribution) which compares well with the magnetic moment found for trans-[RhCl$_2${P(o-tolyl)$_3$}$_2$].[6] We conclude that for complexes of the type trans-[RhCl$_2$-(PBu$^t_2$R)] (R = Me, Et, or Pr^n) in the solid state there is an intermolecular interaction which causes a decrease in the magnetic moment. A similar type of interaction may be responsible for the low magnetic moment (0.8—1.1 B.M. on different samples) obtained for the complex [RhCl$_2${PPh(o-tolyl)$_2$}$_2$].[6]

Drs. W. S. McDonald and G. Raper at Leeds University are investigating the structure of trans-[RhCl$_2$(PBu$^t_2$-Me)$_2$] by single-crystal X-ray diffraction. Preliminary data show the crystals to be monoclinic, space-group $P2_1/c$ with two molecules in a unit cell of dimensions

enabled it to be isolated. Our results show that low solubility is not necessarily an important factor since our rhodium(II) complexes are quite soluble and their solutions in solvents such as benzene stable for days. We find no evidence for rhodium(II) complex formation when rhodium trichloride reacts with less bulky tertiary phosphines such as PEt$_3$, PMe$_2$Ph, PEt$_2$Ph, PPr$^n_2$Ph, PBu$^n_2$Ph, PBu$^n_3$, or PBu^{t}Pr$^n_2$.

Hydrido-rhodium(III) Complexes.—When hydrated rhodium trichloride is heated with an excess of some t-butyl-tertiary phosphines in alcohols or ethyl methyl ketone, well defined crystals of diamagnetic five-co-ordinate rhodium(III) hydrides [RhHCl$_2$L$_2$] (L = PBu^t-Pr$^n_2$, PBu$^t_2$Me, PBu$^t_2$Et, or PBu$^t_2$Pr^n) are formed. Analytical compositions, m.p.s, colour, molecular weights, and yields for these complexes are in Table 1. The complexes are stable and readily soluble in many organic solvents. They are monomeric in benzene. The complex [RhHCl$_2$(PBu$^t_2$Me)$_2$] has ν(Rh–H) 1938s cm^{-1} and some weak bands in the range 620—570 cm^{-1}; the rest of the i.r. spectrum (over the range 4000—400 cm^{-1}) is virtually identical with that of trans-[PdCl$_2$(PBu$^t_2$Me)$_2$] or trans-[RhCl$_2$(PBu$^t_2$Me)$_2$]. The hydride resonance at

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τ 41·4 consists of a doublet of triplets, J(Rh–H) 31·6 Hz and J(P–H) 13 Hz. The t-butyl ^{1}H n.m.r. pattern is a
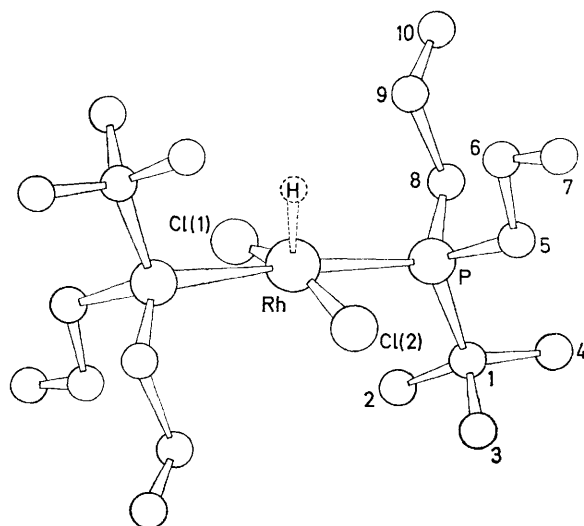

FIGURE 1 Structure of [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$] determined by X-ray diffraction. The probable position of the hydride hydrogen is shown

well defined triplet showing that $|J$(P–P)$|$ is large and that the two PBu$^t_2$Me ligands are probably mutually

mutually *trans*-chlorines. Similar data are found for the other complexes of type [RhHCl$_2$L$_2$] suggesting they have the square-pyramidal structure (I).

Drs. W. S. McDonald and G. Raper at Leeds University have determined the structure of [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$] by single-crystal X-ray diffraction. Crystals are monoclinic, space-group $P2_1/c$, with two molecules in the unit cell. The rhodium atom is therefore required to occupy a position of crystallographic symmetry $\bar{1}$. Refinement with anisotropic temperature factors for Rh, P, and Cl showed large vibrations normal to the co-ordination plane. This suggested that the square-pyramidal molecules with the hydrogen in the apical position were randomly arranged in two orientations so as to produce effective centrosymmetry. Refinement of such a disordered model converged satisfactorily to $R = 8.5\%$ based on 2434 reflections. The resulting structure is shown in Figure 1. The Rh–P length is 2·31 Å, and Rh–Cl is 2·33 Å. The angles P–Rh–P and Cl–Rh–Cl are 174 and 163°, respectively. The hydrogen atom was not located, and its postulated position is shown in Figure 1. ^{1}H N.m.r. data are in Table 3. The hydride resonances for these complexes occur at exceptionally high τ-values (*ca.* 41) for tertiary phosphine hydrido-complexes of rhodium(III). Previously hydride resonances for hydridorhodium(III) complexes have been re-

TABLE 3

^{1}H and ^{31}P N.m.r. data for some tertiary t-butylphosphine hydridorhodium(III) complexes measured in dichloromethane. τ values are accurate to ± 0.02, J values to ± 0.2 Hz, and δ_p values to ± 0.2 p.p.m.

			t-Butyl resonance		Hydride resonance			
[RhHX$_2$L$_2$] configuration (I)		τ (Bu^t)	$\lvert ^3J$(P–H) + ^5J(P–H)$\rvert$	τ	^1J(Rh–H)	J(P–H)	δ_p ^{a}/p.p.m.	$^1J(^{103}$Rh–^{31}P)
L	X							
PBu^{t}Pr$^n_2$	Cl	8·70	13·0	41·37	34·0	13·0	105·1	96·4
PBu^{t}Pr$^n_2$	Br	8·69	13·0	41·10	30·0	14·3	107·9	94·9
PBu^{t}Pr$^n_2$	I	8·71	13·0	40·40	26·0	14·3	109·6	93·4
PBu$^t_2$Me	Cl	8·62	13·0	41·40	31·6	13·0	105·5	97 $\pm$ 1
PBu$^t_2$Me	Br	8·60	13·1	41·10	28·5	12·9	—	—
PBu$^t_2$Et	Cl	8·53	12·3	41·10	31·3	11·8	89·1	96·9
PBu$^t_2$Pr^n	Cl	8·57	12·3	41·15	32·6	12·4	91·9	96·7
[RhHCl$_2$Q(PBu^{t}Pr$^n_2$)$_2$] configuration (II)								
Q								
^{b} MeNC		8·72	12·9	20·86	c	c	103·7	92·6
^{d} MeCN		8·72	13·1	33·60	15·6	12·0	109·5	96·6
py		8·77	13·0	28·90	5·0	12·5	115·4	95·4
[RhH$_2$ClL$_2$]								
L								
PBu$^t_3$		8·42	11·9	35·50	26·2	14·9	53·5	110·3
^{e,f} PBu$^t_2$Me		8·62	12·9	32·30	26·7	14·7		

^{a} ^{31}P chemical shifts are measured relative to P(OMe)$_3$ as external standard. ^{b} Methyl resonance at τ 7·63, both methyl resonance and hydride resonance broad (see text). ^{c} Coupling unresolved. ^{d} Methyl resonance at τ 7·85, hydride resonance slightly broadened. ^{e} Methyl resonance at τ 8·35, $\lvert ^2J$(P–H) + ^4J(P–H) $\rvert$ = 5·0 Hz and ^3J(Rh–H) = 1·0 Hz. ^{f} Measured in benzene.

trans.[14-16] The far-i.r. spectrum shows only one rhodium–chlorine stretching frequency (340 cm^{-1}) indicating

ported in the range τ 17—30, *e.g.*, [RhHCl$_2$(PPh$_3$)$_2$], 0·5CH$_2$Cl$_2$] at τ 26·1; [RhClH$_2$(PPh$_3$)$_2$] at τ 28·2, 21·5, and 18·8;[17,18] and [RhClH$_2$(PEtPh$_2$)$_3$] at τ 27·7, 20·8, and 18·0.[19] The high τ-values for a transition-metal hydride

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ligand have been attributed to paramagnetic shielding [20,21] by valence d-electrons of the metal and according to this theory one would expect the shielding to increase (1) as the separation between the ground and electronically excited states decreases, and (2) as the metal–hydrogen distance decreases. Our five-co-ordinate rhodium(III) hydrides show electronic absorption maxima at very low frequencies for hydrides, e.g., in benzene solution trans-[RhHCl$_2$(PBu$^t_2$Me)$_2$] has $\lambda_{max.}$ 458 nm (ε = 318) and trans-[RhHCl$_2$(PBu$^t_2$Pr^n)$_2$] has $\lambda_{max.}$ 474 nm (ε = 236). There could thus be an unusual amount of ' mixing in ' of excited states under the influence of a magnetic field. This could be the major contributor to the high τ-values. A short rhodium–hydrogen distance, which might be expected from the absence of a trans-ligand, could also contribute towards a high τ-value. We have observed similar effects in analogous hydrido-complexes of iridium-(III) for which the τ-values are >60.[3] Complexes of the type [RhHX$_2$L$_2$], configuration (I), are co-ordinately unsaturated. We find that [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$] will react with some neutral ligands Q {Q = MeCN, MeNC, py, or P(OMe)$_3$} to give orange complexes [RhHCl$_2$(PBu^t-Pr$^n_2$)$_2$Q] of configuration (II). Analytical compositions, m.p.s., molecular weights, i.r. data, and yields are in Table 1, and ^{1}H n.m.r. data in Table 3. With Q = MeCN, MeNC, or C$_5$H$_5$N the complex [RhHCl$_2$(PBu^t-Pr$^n_2$)$_2$Q] of configuration (II) forms readily and is un-dissociated in dichloromethane solution at ca. 30 °C, whereas [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2${P(OMe)$_3$}], although it forms readily, is partially dissociated at ca. 28 °C as shown by ^{31}P and ^{1}H n.m.r. measurements. Addition of dimethylphenylphosphine (1 mol per rhodium g-atom) to a dichloromethane–propan-2-ol solution of [RhHCl$_2$-(PBu^{t}Pr$^n_2$)$_2$], configuration (I), caused the colour of the solution to change from red to orange but only [RhHCl$_2$-(PBu^{t}Pr$^n_2$)$_2$] could be isolated from the solution. The very sterically hindered 2,6-dimethylpyridine did not appear to co-ordinate at all to [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$]. Thus potential ligands with low steric requirements can co-ordinate to the vacant co-ordination site of this five-co-ordinate hydride but more bulky ligands co-ordinate less strongly or not at all. The hydride chemical shifts for these six-co-ordinated complexes [RhHCl$_2$(PBu^t-Pr$^n_2$)$_2$Q] are lower than the hydride chemical shift of [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$] (see Table 3). The hydride resonance of [RhHCl$_2$(PBu^{t}Pr$^n_2$)(MeCN)], configuration (II) (Q = MeCN), is broad {line-width at half-height ca. 4 Hz compared with 1·5 Hz for [RhHCl$_2$(PBu^{t}Pr$^n_2$)], configuration (I)} and the coupling to phosphines or rhodium in the broad hydride resonance of [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$-(MeNC)], configuration (II) (Q = MeNC), is not resolved. Quadrupole broadening to the ^{14}N is probably responsible for these effects. Broadening is also observed in the ^{1}H n.m.r. hydride spectra of complexes of the type trans-[PtHX(PEt$_3$)$_2$] (X = NCS or NCO) [22] and in the ^{31}P

n.m.r. spectra of complexes of the type trans-[PtX-{(PhO)$_2$PO}(PBu$^n_3$)] (X = NCO or NCS).[23] The ^{1}H n.m.r. (hydride) spectra of [RhHCl$_2$(PBu^{t}Pr$^n_2$)(Py)], configuration (II) (Q = Py), shows two sharp well re-solved triplets. The absence of ^{14}N broadening in this complex is probably due to very rapid quadrupole re-laxation of the ^{14}N nucleus. Quadrupole relaxation of ^{14}N has been suggested as an explanation for the sharp ^{31}P and ^{1}H n.m.r. spectra obtained for the complexes trans-[PtX{(PhO)$_2$PO}(PBu$^n_3$)$_2$] (X = N$_3$ or NO$_2$).[23] We were unable to obtain n.m.r. parameters for the complex [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2${P(OMe)$_3$}] configuration (II) {Q = P(OMe)$_3$} since the complex was highly dis-sociated in dichloromethane solution. Complexes of type [RhHCl$_2$L$_2$], configuration (I) (X = Cl; L = PBu^{t}Pr$^n_2$ or PBu$^t_2$Me), react rapidly with LiBr in solu-tion to give [RhHBr$_2$L$_2$], configuration (I) (X = Br; L = PBu^{t}Pr$^n_2$ or PBu$^t_2$Me), in good (69 and 78%) yield. When a solution of sodium iodide in aqueous propan-2-ol is added to a solution of [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$], configura-tion (I), in a dichloromethane–propan-2-ol mixture the colour of the solution changes rapidly (ca. 1 min) from red to black. ^{1}H N.m.r. and i.r. data (Tables 1 and 3) suggest that [RhHI$_2$(PBu^{t}Pr$^n_2$)$_2$], configuration (I), is formed. However the product did not analyse satis-factorily. Addition of a solution of sodium iodide in aqueous propan-2-ol to a solution of [RhHCl$_2$(PBu$^t_2$-Me)$_2$], configuration (I), in dichloromethane–propan-2-ol caused rapid decomposition with deposition of rhodium metal. Possibly iodides of type [RhHI$_2$(PBu$^t_2$R)$_2$] are much less stable than the chlorides because the greater size of the iodide ligand causes too much steric interac-tion with the very bulky tertiary phosphine ligand.

We have investigated the effect of hydrogen gas on the complexes [RhHCl$_2$(PBu$^t_2$Me)$_2$], configuration (I), and trans-[RhCl$_2$(PBu$^t_2$Me)$_2$]. We find that in the presence of triethylamine a benzene solution of RhHCl$_2$(PBu$^t_2$Me)$_2$, configuration (I), absorbs one mol of hydrogen gas per mol of rhodium during 22 h to give RhH$_2$Cl(PBu$^t_2$Me)$_2$. This complex has ν(Rh–H) at 2212w and 2137m cm^{-1}. The hydride resonance at τ 32·30 consists of a doublet of triplets, J(Rh–H) 26·7 Hz and J(P–H) 14·7 Hz. The t-butyl ^{1}H n.m.r. pattern is a well defined triplet showing that $|J$(P–P)$|$ is large and that the two PBu$^t_2$Me ligands are probably mutually trans.[14–16] The ^{31}P n.m.r. spec-trum with decoupling of the methyl and t-butyl protons is a doublet of triplets owing to coupling with two equiva-lent hydridic hydrogens and the ^{103}Rh (Table 3). On shaking a solution of [RhHCl$_2$(PBu$_2$Me)$_2$] in hydrogen in the absence of triethylamine we obtained a ca. 1:1 mixture of [RhHCl$_2$(PBu$^t_2$Me)$_2$], configuration (I), and [RhH$_2$Cl(PBu$^t_2$Me)$_2$] during 30 min. Dihydrorhodium-(III) species of the type [RhH$_2$X(PPh$_3$)$_2$] (X = Cl, Br, I) have been suggested as intermediates in the homogeneous catalytic reaction with [RhCl(PPh$_3$)$_3$] as catalyst.[18] However in contrast with our complex this complex has

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[21] P. W. Atkins, J. C. Green, and M. L. H. Green, J. Chem. Soc. (A), 1968, 2275.

[22] J. Powell and B. L. Shaw, J. Chem. Soc., 1965, 3879.
[23] F. H. Allen, A. Pidcock, and C. R. Waterhouse, J. Chem. Soc. (A), 1970, 2087.

been shown to contain *cis*-triphenylphosphine ligands.[18] Hydrogen gas will also react with *trans*-[RhCl$_2$(PBu$^t_2$Me)$_2$] in dichloromethane solution to give a *ca.* 1 : 1 mixture of [RhHCl$_2$(PBu$^t_2$Me)$_2$], configuration (I), and [RhH$_2$Cl(PBu$^t_2$Me)$_2$]; the resultant solution is acidic.

On adding 1 mol of a base (*e.g.*, NaOMe) per rhodium g-atom to [RhHCl$_2$L$_2$] in ethanol or methanol the solution becomes orange and then rapidly yellow and complexes of the type *trans*-[RhCl(CO)L$_2$] are formed in high (>80%) yield (L = a tertiary t-butylphosphine). However, in propan-2-ol plus sodium isopropoxide, abstraction of carbon monoxide from the solvent occurs only very slowly and [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$] in propan-2-ol containing sodium isopropoxide (2 mol per Rh g-atom) gives a very active hydrogenation catalyst for olefins or

cm^{-1} and ν(Rh–Cl) 263 cm^{-1}. This dihydro-complex is a highly active hydrogenation catalyst for olefins and the presence of a base is not necessary for activity.

Drs. W. S. McDonald and G. Raper at Leeds are investigating the structure of this complex by single-crystal X-ray diffraction.

When hydrated rhodium trichloride is treated with t-butylmethylphenylphosphine in propan-2-ol a mixture of isomers [RhH$_2$Cl(PBu^{t}MePh)$_3$] of configuration (III) is formed in *ca.* 75% yield. Because of the asymmetric centre at the phosphorus atom of this ligand there are four enantiomeric mixtures possible for [RhH$_2$Cl-(PBu^{t}MePh)$_3$] of configuration (III). The t-butyl ^{1}H n.m.r. resonance pattern consists of a 1 : 2 : 1 triplet at τ 8.87 $|^3J$(P–H) + ^5J(P–H)$|$ = 14 Hz and a doublet at
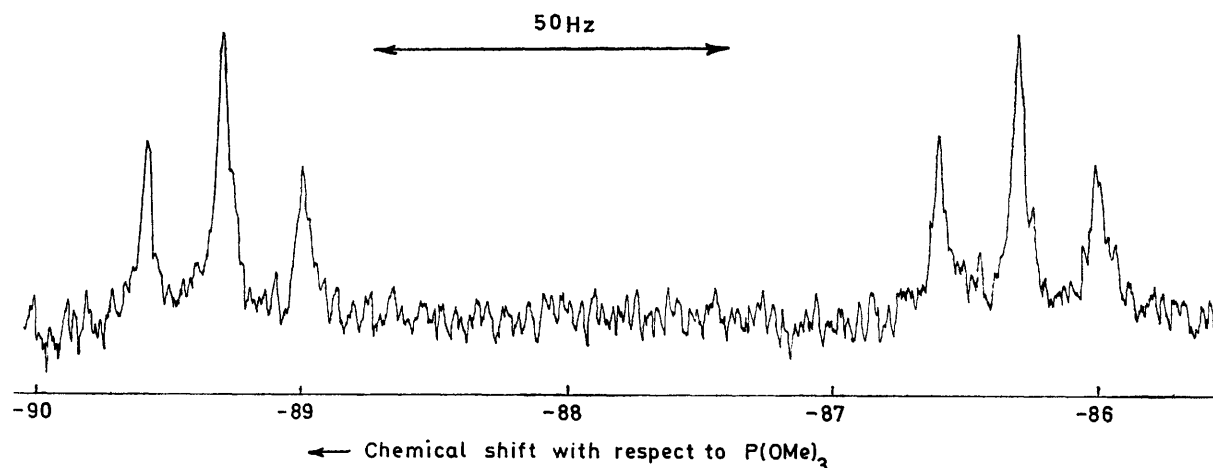

FIGURE 2 The ^{31}P n.m.r. spectrum of [RhH$_2$Cl(PBu$^t_3$)$_2$] with decoupling of the t-butyl protons

acetylenes at 1 atm and 20 °C. As a catalyst for the hydrogenation of hex-1-ene it is as active as [RhCl-(PPh$_3$)$_3$].[19] Other complexes of type [RhHCl$_2$L$_2$] are also active catalysts in the presence of base but less so than [RhHCl$_2$(PBu^{t}Pr$^n_2$)$_2$]. We are presently studying the use of these complexes as homogeneous hydrogenation catalysts. On treating a refluxing propan-2-ol solution of hydrated rhodium trichloride with an excess of this tri-t-butylphosphine a very dark red complex of formula [RhH$_2$Cl(PBu$^t_3$)$_2$] is obtained. The complex is monomeric in benzene solution. In the ^{1}H n.m.r. spectrum the hydridic hydrogens are equivalent, $\tau_{\rm H}$ 35.5, J(P–H) 14.9 Hz, J(Rh–H) 26.2 Hz, and the t-butyl hydrogens form a 'virtually coupled' 1 : 2 : 1 triplet pattern, indicative of *trans*-tertiary phosphine ligands. The presence of *two* equivalent hydridic hydrogens is shown by ^{1}H and ^{31}P n.m.r. spectroscopy. Integration of the ^{1}H n.m.r. spectrum of a dichloromethane solution of the complex which gives areas for the resonances in the ratio 53.5 : 2 for t-butyl : H (expected 54 : 2). The ^{31}P n.m.r. spectrum with decoupling of the t-butyl protons is a very well defined doublet of triplets (Figure 2) owing to coupling with two equivalent hydridic hydrogens and ^{103}Rh.

The i.r. spectrum (Nujol) has ν(Rh–H) 2242 and 2227

τ 9.3 $|^3J$(P–H) + ^5J(P–H)$|$ = 12.2 Hz. Complex hydride resonances are found at τ 21.55 and 29.0, and suggest the presence of two of the possible isomers for [RhH$_2$Cl-(PBu^{t}MePh)$_3$] of configuration (III). The ^{31}P n.m.r.
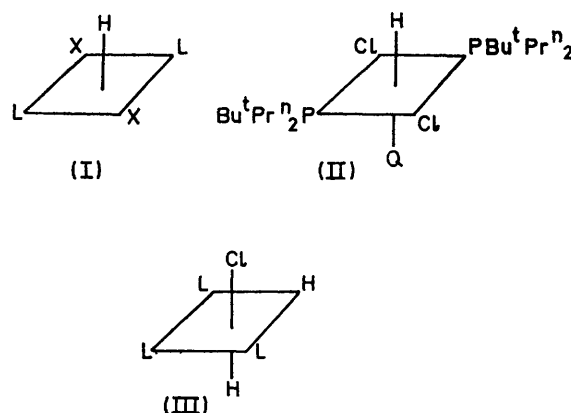
spectrum with random noise decoupling of the aliphatic hydrogens show four doublets of approximately equal intensity, due to the mutually *trans*-phosphines, and suggests that the mixture is composed of two of the possible enantiomeric mixtures present in approximately

equal amounts. The mixture shows bands due to ν(Rh–H) and ν(Rh–Cl) (Table 1).

It has been suggested that the stability of hydrido-complexes of rhodium(III) is very sensitive to small changes in the σ-donor and π-acceptor properties of the tertiary phosphine ligands.[24] Our results suggest that steric factors are very important in determining the nature of the hydride formed.

Rhodium(I) *Species.*—As described above treatment of rhodium trichloride trihydrate in ethanol with a di-t-butylalkylphosphine (R = Me, Et, or Pr^n) gives initially *trans*-[RhCl$_2$(PBu$^t_2$R)$_2$] and then [RhHCl$_2$(PBu^{t}R)$_2$]. We find that prolonged (7 days) treatment at room temperature gives high (*ca.* 75%) yields of rhodium(I) complexes *trans*-[RhCl(CO)(PBu$^t_2$R)$_2$] presumably by carbonyl abstraction from the solvent. As described above, the conversion of [RhCl$_2$L$_2$] into [RhCl(CO)L$_2$] (L = PBu^{t}Pr$^n_2$) is extremely rapid in methanol in the presence of sodium methoxide.

When rhodium trichloride trihydrate is treated with di-t-butylphosphine the rhodium(I) complex [RhCl(PHBu$^t_2$)$_3$] is formed. This complex appears to dissociate in benzene solution since attempts to determine its molecular weight osmometrically gave very erratic results. The ^{1}H n.m.r. spectrum in benzene solution showed a very broad barely resolved doublet at *ca.* τ 8·5. Although the complex appears to be formally analogous to the very active hydrogenation catalyst [RhCl(PPh$_3$)$_3$] we find it to be inactive for the hydrogenation of hex-1-ene.

EXPERIMENTAL

Preparations involving free tertiary phosphine and di-t-butylphosphine were carried out in a nitrogen or argon atmosphere. M.p.s were determined on a Kofler hot-stage apparatus and are corrected.

I.r. spectra were recorded on a Grubb–Parsons G.S.4 spectrometer (4000—450 cm^{-1}) and a Grubb–Parsons D.B.3/D.N.2 spectrometer (400—200 cm^{-1}). All the complexes showed bands due to the tertiary phosphine ligands and only additional bands are listed. Molecular weights were determined on a Hitachi–Perkin-Elmer 115 apparatus for solutions in chloroform at 30 °C or benzene at 37 °C. Electronic absorption spectra were recorded on a Unicam SP 500 instrument in benzene at ambient temperature. ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R.12 spectrometer at 34 °C and 60 MHz in dichloromethane or benzene with tetramethylsilane as internal standard. ^{31}P N.m.r. spectra were recorded on a Bruker Spectrospin HFX spectrometer at *ca.* 28 °C and 36·43 MHz. Approximately 0·1M solutions of the complexes in dichloromethane containing 10% of hexafluorobenzene to provide ^{19}F field-frequency lock, were used. Shifts are quoted with respect to 10% trimethyl phosphite in dichloromethane containing 10% hexafluorobenzene. All coupling of the protons was removed by a random-noise generator.

Magnetic susceptibilities were measured at room temperature on powdered samples by the Gouy method, following the procedure given by Figgis and Lewis.[25] The Gouy tube

was calibrated with [Ni(en)$_3$]S$_2$O$_3$ ($\chi_g = 11·04 \times 10^{-6}$ c.g.s.u. at 20 °C [26]). A field strength of 5817 Oe was used. The variation with temperature of the magnetic susceptibility of *trans*-[RhCl$_2$(PBu$^t_2$Me)$_2$] was studied on powdered samples by use of a Newport Instruments variable-temperature Gouy balance. Field strengths of 6407 and 6960 Oe were used.

The solution susceptibility was measured on a 0·168M solution of *trans*-[RhCl$_2$(PBu$^t_2$Me)$_2$] in dichloromethane at a field strength of 14,228 Oe.

trans-Dichlorobis(di-t-butylmethylphosphine)rhodium(II).—A mixture of hydrated rhodium(III) chloride (0·49 g, 2·03 mmol) and di-t-butylmethylphosphine (1·639 g, 10·25 mmol) in degassed ethanol (50 ml) was shaken (4 h, 20 °C). The *product* (0·525 g, 1·06 mmol) separated as prisms. *trans-Dichlorobis(di-t-butylethylphosphine)rhodium*(II) *and trans-dichlorobis(di-t-butyl-n-propylphosphine)rhodium*(II) were similarly prepared.

Hydrodichlorobis(di-n-propyl-t-butylphosphine)rhodium-(III), *Configuration* (I) (X = Cl; L = PBu^{t}Pr$^n_2$).—Hydrated rhodium(III) chloride (1·535 g, 6·14 mmol) and di-n-propyl-t-butylphosphine (4·376 g, 25·2 mmol) in water (6 ml)–propan-2-ol (35 ml) was heated under reflux (2¼ h). On cooling the *product* (2·877 g, 5·5 mmole) separated as prisms. *Hydrodichlorobis(di-t-butylmethylphosphine)rhodium*(III), *hydrodichlorobis(di-t-butylethylphosphine)rhodium*(III), and *hydrodichlorobis(di-t-butyl-n-propylphosphine)rhodium*(III), all of configuration (I) (X = Cl; L = PBu$^t_2$Me, PBu$^t_2$Et, or PBu$^t_2$Pr^n) were similarly prepared.

Hydrodibromobis(di-n-propyl-t-butylphosphine)rhodium-(III), *Configuration* (I) (X = Br; L = PBu^{t}Pr$^n_2$).—Lithium bromide (0·416 g, 4·8 mmol) in water (2 ml)–propan-2-ol (5 ml) was added to hydrodichlorobis(di-n-propyl-t-butyl-phosphine)rhodium(III) of configuration (I) (X = Cl; L = PBu^{t}Pr$^n_2$) (0·500 g, 0·955 mmol) in dichloromethane (5 ml)–propan-2-ol (10 ml) mixture. The mixture was set aside in the dark (29½ h). The *product* (0·404 g, 0·66 mmol) separated as prisms. *Hydrodibromobis(di-t-butylmethyl-phosphine)rhodium*(III), configuration (I) (X = Br; L = PBu$^t_2$Me) and *hydrodi-iodobis(di-n-propyl-t-butylphosphine)-rhodium*(III), configuration (I) (X = I; L = PBu^{t}Pr$^n_2$) were similarly prepared.

Hydrodichloro(methyl isocyanide)bis(di-n-propyl-t-butyl-phosphine)rhodium(III), *Configuration* (II) (Q = MeNC).—Methyl isocyanide (46 μl, 0·85 mmol) was added to hydrodichlorobis(di-n-propyl-t-butylphosphine)rhodium(III) of configuration (I) (X = Cl; L = PBu^{t}Pr$^n_2$) (0·400 g, 0·764 mmol) in dichloromethane (4 ml)–propan-2-ol (10 ml). The mixture turned from deep red to orange in *ca.* 1 min. After 10 min the volume of solvent was reduced to *ca.* 3 ml under reduced pressure whereupon the *product* (0·262 g, 0·465 mmol) separated as prisms. *Hydrodichloro(methyl cyanide)-bis(di-n-propyl-t-butylphosphine)rhodium*(III), *hydrodichloro-(pyridine)bis(di-n-propyl-t-butylphosphine)rhodium*(III), and *hydrodichloro(trimethylphosphite)bis(di-n-propyl-t-butylphos-phine)rhodium*(III), all of configuration (II) [Q = MeCN, Py, or P(OMe)$_3$], were similarly prepared.

Dihydrochlorobis(tri-t-butylphosphine)rhodium(III).— A mixture of tri-t-butylphosphine (1·537 g, 7·61 mmol) and hydrated rhodium trichloride (0·367 g, 1·52 mmol) in water (2 ml)–propan-2-ol (25 ml) was heated under reflux (3 h).

[24] A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc.* (*A*), 1966, 1670.

[25] B. N. Figgis and J. Lewis, in 'Modern Co-ordination Chemistry,' ed. J. Lewis and R. G. Wilkins, Interscience Publishers Inc., New York, 1960, ch. 6, p. 416.

[26] N. F. Curtis, *J. Chem. Soc.*, 1961, 3147.

After cooling the volume of the solvent was reduced to *ca.* 5 ml under reduced pressure whereupon the *product* (0·321 g, 0·586 mmol) separated as plates.

Dihydrochlorobis(di-t-butylmethylphosphine)rhodium(III).— A mixture of hydrodichlorobis(di-t-butylmethylphosphine)-rhodium(III) of configuration (I) (X = Cl; L = PBu^t_2Me) (2·268 g, 0·542 mmol) and triethylamine (83 μl, 0·597 mmol) in benzene (5 ml) was stirred in an atmosphere of hydrogen gas for 22½ h. 11·5 ml (0·515 mmol, corrected to s.t.p.) of hydrogen gas was absorbed. ^{31}P and ^{1}H N.m.r. measurements on the reaction mixture showed the di-hydrido-species to be the only product. Removal of the solvent under reduced pressure gave the *product* (0·124 g, 0·269 mmol) as microprisms.

Hydrodichlorotris(t-butylmethylphenylphosphine)rhodium-(III).—A mixture of t-butylmethylphenylphosphine (1·098 g, 1 mmol) and hydrated rhodium trichloride (0·358 g, 1·49 mmol) in water (1 ml)–propan-2-ol (30 ml) was heated under reflux (43 h). After cooling the volume of the solvent was reduced to *ca.* 5 ml whereupon the *product* (0·740 g, 1·085 mmol) separated as prisms.

Chlorotris(di-t-butylphosphine)rhodium(III).—A mixture of di-t-butylphosphine (500 μl, 2·84 mmol) and hydrated rhodium trichloride (0·137 g, 0·568 mmol) in water (0·5 ml)–ethanol (6 ml) mixture was shaken (44 min) at room temperature (20 °C). The *product* (0·133 g, 0·205 mmol) separated as prisms.