Oxidative Addition, Carbonyl Insertion, and *O*-Demethylation Reactions of Rhodium Complexes with Tertiary 2-Methoxyphenylphosphines †

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The complex *trans*-$[\mathrm{RhCl(CO)}\{\mathrm{PMe_2(2\text{-}MeOC_6H_4)}\}_2]$ undergoes rapid oxidative addition with HCl, MeCl, MeI, CCl_4, Cl_2, and PhCOCl (R–X) to give rhodium(III) adducts of the normal type, *i.e.* $[\mathrm{RhClXR(CO)L_2}]$. Addition of HCl is readily reversed. Allyl chloride (R–X) also adds reversibly in benzene solution but in polar solvents the adduct rapidly isomerizes to the acyl complex $[\mathrm{RhCl_2(COCH_2CH{:}CH_2)L_2}]$. Analogous acyl complexes were prepared from $\mathrm{CH_2{:}C(Me)CH_2Cl}$, $\mathrm{MeCH{:}CHCH_2Cl}$, and $\mathrm{MeCHClCH{:}CH_2}$. The complex *trans*-$[\mathrm{RhCl(CO)}\{\mathrm{PBu^t_2(2\text{-}MeOC_6H_4)}\}_2]$ resists oxidative addition reactions but in boiling propan-2-ol demethylation of one ligand occurs to give the chelate $[\overline{\mathrm{Rh(CO)(PBu^t_2C_6H_4O}})\{\mathrm{PBu^t_2(2\text{-}MeOC_6H_4)}\}]$. $\mathrm{RhCl_3{,}3H_2O}$ reacts with $\mathrm{PMe_2(2\text{-}MeOC_6H_4)}$ to give ultimately $[\overline{\mathrm{Rh(PMe_2C_6H_4O}})_3]$ and with $\mathrm{PBu^t_2(2\text{-}MeOC_6H_4)}$ to give the intensely blue rhodium(II) species $[\overline{\mathrm{Rh(PBu^t_2C_6H_4O}})_2]$, accompanied by small amounts of what appear to be carbonyl or hydrido-species.

2-METHOXYPHENYLPHOSPHINES have been shown to have interesting properties as ligands. Thus with iridium(I) the oxygen atom will interact directly with the metal and greatly increase the rates of some oxidative addition reactions[1] (the effect is analogous to the so-called anchimeric effect in organic chemistry). We have also shown that platinum(II) can either *O*-metallate or *C*-metallate a methoxy-group of a 2-methoxyphenylphosphine ligand.[2] Particular interest in 2-methoxyphenylphosphine ligands has been aroused by the work of Knowles and his co-workers[3] on the synthesis of L-amino-acids, including L-3,4-dihydroxyphenylalanine, by catalytic asymmetric hydrogenation. These workers found the highest stereospecificity (at least 90%) with rhodium complexed to the asymmetric ligand cyclohexyl-(2-methoxyphenyl)propylphosphine. The rhodium catalyst was prepared *in situ* and although its nature is not known it was suggested that an important factor in the high stereoselectivity was a direct interaction between the oxygen atom of the 2-methoxy-group and the substrate.

We report here a study of the products of the reactions of $\mathrm{PMe_2(2\text{-}MeOC_6H_4)}$ or the very bulky $\mathrm{PBu^t_2(2\text{-}MeOC_6H_4)}$ with (*a*) $[\mathrm{Rh_2Cl_2(CO)_4}]$ and (*b*) $\mathrm{RhCl_3{,}3H_2O}$. The complex $[\mathrm{Rh_2Cl_2(CO)_4}]$ reacted smoothly with $\mathrm{PMe_2(2\text{-}MeO_6H_4)}$ (L) to give *trans*-$[\mathrm{RhCl(CO)L_2}]$. We have studied some oxidative addition reactions of this product, anticipating that there might be some unusual effects due to the 2-methoxyphenyl groups.

Oxidative addition reactions of rhodium(I) complexes of the types *trans*-$[\mathrm{RhCl(CO)(PR_3)_2}]$ and -$[\mathrm{RhCl(CO)(AsR_3)_2}]$ to give rhodium(III) complexes have been studied extensively.[4-11] Our complex, *trans*-$[\mathrm{RhCl(CO)L_2}]$, reacted rapidly with HCl, MeCl, MeI, CCl_4, Cl_2, and PhCOCl (R–X) to give rhodium(III) adducts of the normal type, *e.g.* with the same stereochemistry (1) as the product formed by *trans*-$[\mathrm{RhCl(CO)(PMe_2Ph)_2}]$.[10] Qualitatively (*e.g.* from colour changes) we observed that *trans*-$[\mathrm{RhCl(CO)}\{\mathrm{PMe_2(2\text{-}MeOC_6H_4)}\}_2]$ undergoes oxidative addition faster than *trans*-$[\mathrm{RhCl(CO)(PMe_2Ph)_2}]$ (as did the iridium analogue).[1] With the exception of the HCl adduct all were stable in solution and showed no indication of losing the addenda: the HCl addition was readily reversed in solution and *trans*-$[\mathrm{RhCl(CO)L_2}]$ could be recovered. The configuration (1) for these adducts follows from the ^1H n.m.r. and i.r. data (Tables) and since they are of the normal type they will not be discussed further (see Experimental section for details of preparation *etc.*). The behaviour towards allylic chlorides shows some unusual features, however. When a yellow solution of *trans*-$[\mathrm{RhCl(CO)L_2}]$ in allyl chloride was refluxed for 1 min it became colourless and $[\mathrm{RhCl_2(\sigma\text{-}CH_2CH{:}CH_2)(CO)}\{\mathrm{PMe_2(2\text{-}MeOC_6H_4)}\}_2]$, configuration (1) ($R = \mathrm{CH_2CH{:}CH_2}$, $X = \mathrm{Cl}$), was produced. The configuration follows from the spectroscopic data (Table 2). This adduct, when recrystallized from benzene, underwent partial loss of allyl chloride and reverted to *trans*-$[\mathrm{RhCl(CO)L_2}]$. In this it is similar to the allyl chloride adducts of *trans*-$[\mathrm{RhCl(CO)(PPh_3)_2}]$ and *trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]$,[5] and contrasts with the allyl chloride adduct of *trans*-$[\mathrm{RhCl(CO)(PMe_2Ph)_2}]$ which is recovered unchanged from hot benzene.[10] The tendency of $[\mathrm{RhCl_2(\sigma\text{-}CH_2CH{:}CH_2)(CO)}\{\mathrm{PMe_2(2\text{-}MeOC_6H_4)}\}_2]$ to revert to *trans*-$[\mathrm{RhCl(CO)}\{\mathrm{PMe(2\text{-}MeOC_6H_4)}\}_2]$ may in part be promoted by steric crowding of the 2-methoxy-groups in the six-co-ordinate complex and in part by interaction of the oxygen atoms of the methoxy-groups with the rhodium in *trans*-

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† No reprints available.

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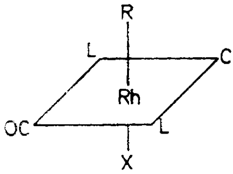
TABLE 1

Yields, colours, m.p.s, microanalyses (%; calc. values in parentheses), molecular weights, and i.r. (cm^{-1}) data for rhodium complexes prepared

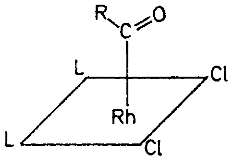
				Analyses				ν(C=O)			Other
Complex [a]	Yield (%)	Colour	M.p. (°C)	C	H	Cl	*M*	CHCl$_3$	Nujol	ν(Rh–Cl) (Nujol)	bands (Nujol)
$[\mathrm{RhCl(CO)L_2}]$	82	Yellow	145—150 [b]	45·45 (45·4)	5·40 (5·2)	7·25 (7·05)	501 (503)	1969 [d]	1967 1920sh	299	
$[\mathrm{RhCl_2(Me)(CO)L_2}]$	75	White	185—192 [b]	45·45 (42·20)	5·4 (5·4)	12·85 (13·1)		2050	298 2060sh	298 248	
$[\mathrm{RhCl(I)(Me)(CO)L_2}]$	91	Cream	160—162 [b]	37·55 (37·25)	4·4 (4·55)	5·6 (5·5) [c]		2049	2055 2010sh	298	
$[\mathrm{RhCl_3(CO)L_2}]$	56	Yellow	190—195	39·6 (39·8)	4·6 (4·6)	18·3 (18·55)		2095	2094 2020	296 315 [e]	
$[\mathrm{RhCl(CCl_3)(CO)L_2}]$	49	Cream	157—170 [b]	36·8 (36·6)	4·0 (4·0)	26·05 (26·2)	651 (656)	2088	2090 2040	287 318 249	
$[\mathrm{RhCl_2(H)(CO)L_2}]$	81	White	132—145 [b]	42·2 (42·35)	5·05 (5·05)	13·55 (13·15)		2060	2060 2070 2075	304 314sh 244	ν(Rh–H) [f] 2090
$[\mathrm{RhCl_2(COC_6H_5)(CO)L_2}]$	83	White	149—155 [b]	48·7 (48·55)	4·9 (4·85)	11·25 (11·05)		2083 2066sh	2070 2055sh 2025sh	304 246	ν(C=O)acyl 1612
$[\mathrm{RhCl_2(CH_2C{:}CH_2)(CO)L_2}]$	83	Cream	78—125	45·55 (45·6)	5·45 (5·25)	12·45 (12·25)			2050	298 246	ν(C=C) 1615
$[\mathrm{RhCl_2(COCH_2C{:}CH_2)L_2}]$	83	Cream	137—140	45·7 (45·6)	5·45 (5·25)	11·9 (12·25)	590 (279)			*g*	ν(C=O)acyl 1650
$[\mathrm{RhCl_2\{COCH_2C(Me){:}CH_2\}L_2}]$	66	Cream	137—140	46·4 (46·6)	5·6 (5·6)	11·9 (11·95)				*g*	1658
$[\mathrm{RhCl_2\{COCH_2C{:}CH(Me)\}L_2}]$	80	Cream	154—160	46·85 (46·6)	5·7 (5·6)	12·4 (11·95)				*g*	1655
$[\overline{\mathrm{Rh\{PMe_2(C_6H_4O}})\}_3]$	40	White	>325	50·9 (51·25)	5·4 (5·4)	0 (0)					
$[\mathrm{RhCl(CO)Q_2}]$	91	Yellow	155—157	55·0 (55·5)	7·45 (7·5)				1938	289	
$[\overline{\mathrm{Rh(CO)\{PBu_2^t(C_6H_5O}})\}\mathrm{Q}]$	53	Yellow	210—214	57·4 (58·1)	7·55 (7·65)		626 (621)		1932		
trans-$[\overline{\mathrm{Rh\{PBu_2^t(C_6H_4O}})\}_2]$	20—50	Dark blue	>350 [b]	57·5 (58·2)	7·65 (7·65)		583 (576)				

[a] L = 2-Methoxyphenyl(dimethyl)phosphine, Q = 2-methoxyphenyl(di-t-butyl)phosphine. [b] With decomposition. [c] I, 19·65 (19·68). [d] In benzene. [e] Also ν(Rh–Cl) (*trans*-Cl). [f] In chloroform. [g] Very broad peak.

$[\mathrm{RhCl(CO)\{PMe_2(2\text{-}MeOC_6H_4)\}_2}]$ [which would therefore be stabilized relative to the rhodium(III) adduct], *i.e.* although *trans*-$[\mathrm{RhCl(CO)\{PMe_2(2\text{-}MeOC_6H_4)\}_2}]$ reacts faster than *trans*-$[\mathrm{RhCl(CO)(PMe_2Ph)_2}]$ with allyl chloride, conversion at equilibrium is less complete.



(1)



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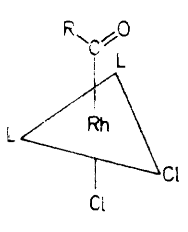

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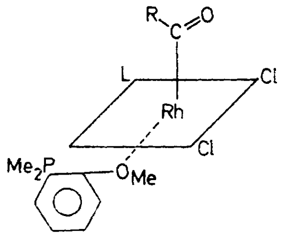


(4)

When dissolved in hot methanol or hot chloroform the σ-allyl complex $[\mathrm{RhCl_2(C_3H_5)(CO)L_2}]$ was isomerized rapidly (in less than 1 min) to the white acyl complex $[\mathrm{RhCl_2(COCH_2CH{:}CH_2)(CO)L_2}]$. The formulation of the latter is based on analytical and molecular weight data (Table 1) and the i.r. absorption spectrum, which showed the absence of terminal C≡O but the presence of an acyl C=O. The isomerization of the σ-allyl to the σ-but-3-enoyl complex was followed by i.r. spectroscopy: the disappearance of the peak at 2050 cm^{-1} was accompanied by the appearance of an acyl peak at 1665 cm^{-1}. The ^{31}P n.m.r. spectrum shows that both phosphines are equivalent [δ +17·7 p.p.m. from H_3PO_4; ^1J(Rh,P) 146·5 Hz] and the ^{1}H n.m.r. spectrum (Table 2) shows two well separated doublets for non-equivalent methyl groups, thus these must be equivalent phosphines in mutually *cis*-positions with no plane of symmetry through either phosphorus–rhodium bond.

The resonance of the CH_2 group bonded to the carbonyl consists of a doublet at τ 5·38. Irradiation of this signal causes collapse of the multiplet at τ 4·06 to a double doublet and a sharpening of both the doublet at τ 4·71 and the singlet at τ 4·96 (Table 2): these effects are consistent with the assigned structure. Since the τ values of the vinyl protons in $[\mathrm{RhCl_2(COCH_2CH{:}CH_2)L_2}]$ are very similar to those of allyl chloride it is unlikely that there is any π-bonding interaction between the rhodium and the C=C bond. Either configuration (2) or (3) (R = allyl) is in agreement with these results.

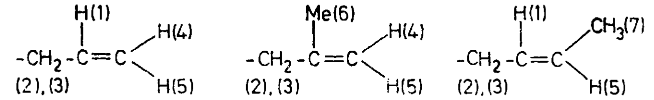
The far i.r. spectrum (400—200 cm^{-1}) shows very broad, poorly resolved peaks and we could not identify ν(Rh–Cl). An alternative structure (4) in which a methoxy-group takes up the sixth position is also possible. If this structure is correct there must be a rapid movement of the rhodium from one methoxy-group to the other in order to explain the equivalence of the phosphines on the ^{1}H and ^{31}P n.m.r. time scales. A methoxy–rhodium interaction has been shown to occur in $[RhCl_3\{AsMe_2(2\text{-}MeOC_6H_4)\}_2]$ by *X*-ray diffraction,[12] *i.e.* this complex is six-co-ordinate. However, since the triphenylphosphine complex $[RhClI(COMe)(PPh_3)_2]$ [11] is probably five-co-ordinate we favour a five-co-ordinate formulation such as (2) or (3) for our complex. The but-3-enoxyl complex $[RhCl_2(COCH_2CH{:}CH_2)L_2]$ was also made directly from *trans*-$[RhCl(CO)L_2]$ by adding allyl chloride in hot methanol solution. Whereas addition of allyl chloride (neat) to *trans*-$[RhCl(CO)L_2]$ gives the σ-allyl complex, similar treatment with 3-chloro-2-methylpropene gave a mixture which its i.r. spectrum showed to consist of the σ-2-methylallyl complex and its acyl isomer. The ^{1}H n.m.r. spectrum of this mixture in deuteriochloroform was complex but it changed over several hours to that of $[RhCl_2(COCH_2CMe{:}CH_2)L_2]$. This acyl complex was more readily prepared by treating *trans*-$[RhCl(CO)L_2]$ with 3-chloro-2-methylpropene in methanol and was characterized by microanalysis and by i.r. and n.m.r. spectroscopy (Tables). Treatment of *trans*-$[RhCl(CO)L_2]$ with either 1-chlorobut-2-ene or 3-chlorobut-1-ene gave the acyl complex $[RhCl_2\{COCH_2CH{:}CHMe\}L_2]$. This formulation follows from the physical and analytical data (Tables); in particular a CH_2 resonance pattern at τ 5·51 in the ^{1}H n.m.r. spectrum is very similar to that of $[RhCl_2(COCH_2CH{:}CH_2)L_2]$. In the complex $[C_5H_5RhCl\{COCH_2CH{:}CHMe\}PPh_3]$ the $CH_2CH{:}CHCH_3$ double bond was tentatively assigned a *trans*-stereochemistry from i.r. data.[13] We also tentatively assign

TABLE 2

^{1}H N.m.r. data for the rhodium complexes prepared; solutions in deuteriochloroform at 34° and 60 MHz unless stated otherwise; τ values ±0·02 p.p.m.; *J* values ±0·2 Hz; s = singlet, d = doublet, m = multiplet, br = broad, t = 1 : 2 : 1 triplet

	PMe		OMe	Other resonances		
Complex	τ	$\lvert{}^2J(P,H) + {}^4J(P,H)\rvert$	τ	τ	*J*	Assignment [d]
L = $PMe_2(2\text{-}MeOC_6H_4)$						
$[RhCl(CO)L_2]$ [a]	8·15t		6·58s			
$[RhCl_2(Me)(CO)L_2]$	7·89t	7·6	6·16s	9·40dt	$^3J(P,H)$ 5·1	Rh–Me
	8·03t	8·5			$^2J(Rh,H)$ 2·0	
$[RhCl(I)Me(CO)L_2]$	7·55t	7·3	6·08s	9·14dt	$^3J(P,H)$ 5·5	Rh–Me
	7·90t	8·3			$^2J(Rh,H)$ 2·1	
$[RhCl_3(CO)L_2]$	7·90t	8·60	6·13s			
$[RhCl_2(CCl_3)(CO)L_2]$	7·66t	8·0	5·98s			
	7·96t	9·6				
$[RhCl_2(H)(CO)L_2]$	7·93t	8·0	6·08s	23·51dt	$^2J(P,H)$ 11·5	Rh–H
					$J(Rh,H)$ 16·1	
$[RhCl_2(COC_6H_5)(CO)L_2]$	7·81t	9·0	6·31s			
	7·95t	8·6				
$[RhCl_2(CH_2CH{:}CH_2)(CO)L_2]$ [a]	7·90t	8·5	6·65s	4·10m		H(1)
	8·08t	9·3		5·50m		H(4), H(5)
				8·23 [b]		H(2), H(3)
$[RhCl_2\{COCH_2CH{:}CH_2\}L_2]$ [c]	7·98d	10·0	6·72s	4·06m		H(1)
	8·30d	10·2		4·71d	$J(1,5)$ 8·2	H(5)
				4·96s		H(4)
				5·38d	$J[2(3),1]$ 8·0	H(2), H(3)
$[RhCl_2\{COCH_2C(Me){:}CH_2\}L_2]$ [c]	8·00d	10·0	6·80s	5·14br, s (5·1)	$J(4,5)$ 2·2	H(5)
	8·33d	10·0		5·20br, s (5·1)		H(4)
				5·46s		H(2), H(3)
				8·18s		H(6)
$[RhCl_2\{COCH_2CH{:}CH(Me)\}L_2]$ [c]	8·01d	10·20	6·80s	4·42m		H(1), H(5)
	8·31d	9·30		5·51d	$J[2(3),1]$ 4	H(2), H(3)
				8·36 [b]		H(7)
	PBu^t	$\lvert{}^3J(P,H) + {}^5J(P,H)\rvert$				
Q = $PBu^t_2(2\text{-}MeOC_6H_4)$						
$[RhCl(CO)Q_2]$	8·35t	13·5	6·1s			
$[\overline{Rh(CO)\{PBu^t_2(C_6H_4O}\}Q]$	8·50t	14·0	6·1s	1·3	See text	
	8·53t			3·0	Aromatic protons	

[a] In benzene. [b] Overlapping phosphine signal. [c] At 90 MHz. [d] Labelling scheme shown below.



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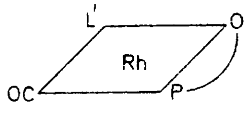
a *trans*-stereochemistry to the $CH_2CH{:}CHCH_3$ double bond because of the presence of a shoulder at 1668 cm^{-1} in the i.r. spectrum.[14]

We have attempted some reactions of these five-co-ordinate acylrhodium complexes. Attempts to isomerize the C:C bond of $[RhCl_2\{COCH_2C(Me){:}CH_2\}L_2]$ into conjugation with the carbonyl group failed. Thus treatment of the complex in chloroform–methanol with concentrated hydrochloric acid (2% v/v) for 5 days at room temperature or with sodium hydroxide (2% v/v, 2M) for 5 days gave back unchanged starting material with no evidence of isomerization. Surprisingly the complex $[RhCl_2\{COCH_2C(Me){:}CH_2\}L_2]$ failed to take up either CO or PMe_2Ph into its sixth position, *e.g.* even after passing carbon monoxide through a chloroform–methanol solution for 16 h no peaks corresponding to CO co-ordinated to rhodium were detected in the i.r. spectrum of the solution and $[RhCl_2\{COCH_2C(Me){:}CH_2\}L_2]$ was recovered unchanged. Similar treatment of a solution of $[RhI_2(COMe)(PPh_3)_2]$ with CO gave material showing absorption bands at 2075 and 1680 cm^{-1}, presumably due to $[RhI_2(COMe)(CO)(PPh_3)_2]$;[11] in the same way $[RhBr_2Me(CO)(PMe_2Ph)_2]$ was converted into $[RhBr_2(COMe)(CO)(PMe_2Ph)_2]$[10] and $[RhIClMe(CO)(PBu^n_3)_2]$ into $[RhICl(COMe)(CO)(PBu^n_3)_2]$ by CO.[5] It is possible that in our compound steric interference by the methoxy-groups prevents attack by CO.

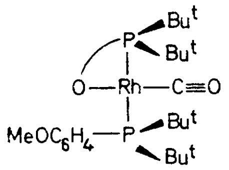
We have also prepared the very sterically hindered complex *trans*-$[RhCl(CO)\{PBu^t_2(2\text{-}MeOC_6H_4)\}_2]$ by adding $PBu^t_2(2\text{-}MeOC_6H_4)$ to $[Rh_2Cl_2(CO)_4]$. Not surprisingly this complex would not undergo oxidative addition reactions with molecules such as MeI *etc.* We have shown that sterically hindered 2-methoxyphosphine ligands can be demethylated by platinum metals and now find that on heating a solution of *trans*-$[RhCl(CO)\{PBu^t_2(2\text{-}MeOC_6H_4)\}_2]$ in propan-2-ol for 4·5 h one ligand is demethylated to give the chelate $[\overline{Rh(CO)PBu^t_2(C_6H_4O)}\{PBu^t_2(2\text{-}MeOC_6H_4)\}]$ (5). This complex showed no i.r. absorption due to ν(Rh–Cl) and the bands at 1250 and 800 cm^{-1} associated with the MeO group in the starting chloro-complex were much less intense.

The ^1H and ^{31}P n.m.r. spectra of $[\overline{Rh(CO)PBu^t_2(C_6H_4O)}\{PBu^t_2(2\text{-}MeOC_6H_4)\}]$ (5) showed a complex behaviour with temperature which we cannot fully explain. The ^{31}P n.m.r. spectrum at 233 K ($CDCl_3$ solution) showed a single ABX pattern with $\delta_{P(A)}$ +85·0, $\delta_{P(B)}$ +76·4 p.p.m., $^2J(P_A,P_B)$ 273, $^1J(Rh,P_A)$ 131, and $^1J(Rh,P_B)$ 139 Hz. At 298 K, however, the pattern consists of two doublets, each with a $^{31}P,^{103}Rh$ coupling of 134 Hz, at 86·5 and 79 p.p.m. with relative intensities 1 : 10. We tentatively suggest that at 298 K two rotamers such as (6a and b) are present but that at 233 K one rotamer is preferred and gives rise to the expected ABX pattern. We cannot explain the apparent absence of phosphorus–phosphorus coupling in the 298 K spectrum unless the two P nuclei in each rotamer have the same chemical shift.

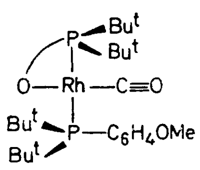
The ^1H n.m.r. spectrum of this complex at 300 K in $CDCl_3$ showed two second-order triplet resonances for the t-butyl groups. The central peak of each triplet was much broader than the outer two peaks. The two resonances were separated by *ca.* 2 Hz at 60 MHz and by *ca.* 3 Hz at 90 MHz, and may therefore be assigned to non-equivalent t-butyl groups. At lower temperatures the central peak of each triplet first collapses (288 to 258 K) and subsequently broadening of the outer peaks occurs to give, at 218 K, an eight-line second-order spectrum. The t-butyl groups in this complex are part of an $X_{18}AMBY_{18}$ spin system. Since rhodium–t-butyl coupling is not observed such a system can be compared with those discussed by Verkade and his co-workers,[15] where different phosphines were complexed to a metal. For such complexes, if $^2J(A,B)$ is much larger than $\nu_A - \nu_B$ a 1 : 2 : 1 triplet results, but if $J(A,B)$ and $\nu_A - \nu_B$ are comparable in magnitude the central peak is broader and not as high as the outer peaks. Similar conclusions have also been drawn from calculations of the $[AM_3S_3]_2BX$ spin system as applied to complexes of the type *mer*-$[MoOX_2(Me_2PhP)_3]$ and *mer*-$[OsX_2L(Me_2PhP)_3]$.[16]



(5)



(6a)



(6b)

We suggest that the complex changes which occur in the ^1H n.m.r. patterns with temperature are due in part to the complexity of the spin system and in part to the presence of conformers.

Another feature of the ^1H n.m.r. spectrum of this compound is a one-proton resonance at τ 1·3. At high temperatures (333 to 313 K) the resonance appears as a 1 : 3 : 3 : 1 quartet (J *ca.* 6 Hz); at lower temperatures (313 to 263 K) it is broad and unresolved ($W_{\frac{1}{2}}$ *ca.* 24 Hz); and below 263 K it appears as a double doublet with coupling constants of *ca.* 7 and *ca.* 11 Hz. The resonance has also been observed in a similar iridium complex,[17] and is tentatively ascribed to one aromatic proton.

We have also studied the products formed from the

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[16] R. M. Lynden-Bell, G. G. Mather, and A. Pidcock, *J.C.S. Dalton*, 1973, 715.

[17] H. D. Empsall, E. M. Miller, and B. L. Shaw, unpublished observation.

reactions of hydrated rhodium trichloride with $\mathrm{PMe_2(2\text{-}MeOC_6H_4)}$ and $\mathrm{PBu^t_2(2\text{-}MeOC_6H_4)}$. On adding $\mathrm{PMe_2(2\text{-}MeOC_6H_4)}$ to $\mathrm{RhCl_3,3H_2O}$ in ethanol a deep red solution was formed. We were unable to isolate crystalline products from this mixture even after heating it for a few hours (contrast with the behaviour towards $\mathrm{PMe_2Ph}$ and other simple phosphines[18]). After prolonged (24 h) boiling, however, a white precipitate had been formed. This was formulated as tris{2-(dimethylphosphino)phenoxy}rhodium(III) on the basis of analytical data (Table 1) and the i.r. spectrum, which shows no bands at 1250 and 800 cm^{-1} corresponding to C–O–CH$_3$ stretching and bending deformation, respectively, and always observed with complexes of the methoxy-ligand. The complex was too insoluble for n.m.r. studies and we could not determine whether the P ligand atoms are *fac* or *mer*. The intermediate red solutions presumably contained a complex mixture including partially demethylated species.

When $\mathrm{RhCl_3,3H_2O}$ was heated under reflux in propan-2-ol with $\mathrm{PBu^t_2(2\text{-}MeOC_6H_4)}$ for *ca.* 2 h it gave an intensely inky-blue solution and a blue-black crystalline solid. The complex was paramagnetic as shown by the extreme broadness of peaks in the ^{1}H n.m.r. spectrum. The i.r. absorption spectrum was virtually identical with that of *trans*-[$\mathrm{\overline{Pt\{PBu^t_2(C_6H_4O}})\}_2$], showing no peaks corresponding to ν(C–O–CH$_3$), δ(C–O–CH$_3$), or ν(Rh–Cl), and there were no methoxy-signals in the ^{1}H n.m.r. spectrum. These results, coupled with the microanalytical data, lead us to formulate this intensely blue species as the rhodium(II) complex *trans*-[$\mathrm{\overline{Rh\{PBu^t_2(C_6H_4O}})\}_2$]. It showed electronic absorption maxima in CHCl$_3$ at λ 586 (ε 4540), 330 (5530), 300 (9620), and 290 nm (11,200). The complex was very frequently contaminated by small amounts of impurities which were very difficult to remove by crystallization. These were characterized by weak i.r. absorption peaks at 1962 and 1935 cm^{-1}, possibly due to the presence of a rhodium(I) carbonyl species and a rhodium hydride species. The rhodium(II) species *trans*-[$\mathrm{RhCl_2(PBu^t_2R)_2}$] (R = Me, Et, or Pr^n) have been shown previously to be converted readily into carbonyl or hydrido-species.[19]

EXPERIMENTAL

All operations involving free tertiary phosphines were carried out in an atmosphere of argon. M.p.s were determined on a Kofler hot-stage apparatus and are corrected. I.r. spectra were determined on a Perkin-Elmer 457 spectrometer (4000—250 cm^{-1}) or Grubb–Parsons spectrometer (500—200 cm^{-1}). ^{1}H N.m.r. spectra were measured at 60 MHz on a Perkin-Elmer R12 spectrometer and at 90 MHz on a Bruker HX-90 spectrometer. ^{31}P N.m.r. spectra were recorded at 36·43 MHz in CDCl$_3$ on a Bruker HX-90 spectrometer with broad band proton decoupling. ^{31}P Chemical shifts were recorded with an external reference of 10% P(OMe)$_3$ in CDCl$_3$ which absorbs at 141 p.p.m. to low field of 85% H$_3$PO$_4$. Shifts to low field are positive.

trans-*Carbonyl(chloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium*(I).— 2-Methoxyphenyl(dimethyl)phosphine (0·455 g, 8·66 mmol) was added to a methanolic solution of tetracarbonyldi-μ-chloro-rhodium (0·765 g, 3·94 mg atom Rh; 30 ml) at 65°. The *product* separated as yellow prisms (1·62 g, 3·23 mmol, 82%).

trans-*Carbonyl(chloro)bis{(2-methoxyphenyl)-di-t-butylphosphine}rhodium*(I) was similarly prepared as yellow prisms (91%).

Carbonyl(chloro)(iodo)bis{(2-methoxyphenyl)dimethylphosphine}methylrhodium(III).—Methyl iodide (0·56 ml, 9 mmol) was added to a solution of carbonyl(chloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(I) (0·20 g, 0·40 mmol) in benzene (2 ml). The solution was heated to boiling for 1 min and then cooled. The *product* formed as cream prisms (0·234 g, 0·364 mmol, 91%).

Benzoyl(carbonyl)(dichloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(III) was prepared similarly (5 min reflux) as yellow prisms (79%).

Carbonyl(trichloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(III) was similarly prepared, by using an excess of chlorine in carbon tetrachloride (no heating), as yellow prisms (55%).

Carbonyl(dichloro)bis{(2-methoxyphenyl)dimethylphosphine}methylrhodium(III).—Methyl chloride (*ca.* 2 ml) was condensed into a mixture of benzene (2 ml) and the rhodium(I) compound (0·20 g, 0·40 mmol) at −68°. The mixture was sealed off and after 2 weeks at 20° the *product* was isolated by evaporation and addition of methanol (yield 0·166 g, 0·307 mmol, 77%).

Carbonyl(dichloro)bis{(2-methoxyphenyl)dimethylphosphine}trichloromethylrhodium(III).—Carbon tetrachloride (0·2 ml, 2·00 mmol) was added to a solution of carbonyl (chloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(I) (0·20 g, 0·40 mmol) in benzene (2 ml). The solution was cooled to 0° giving the *product* as cream prisms (0·129 g, 0·197 mmol, 49%).

Carbonyl(dichloro)(hydrido)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(III).—A solution of hydrogen chloride (1·4 mmol) in diethyl ether (1 ml) was added to a solution of the rhodium(I) complex (0·20 g, 0·40 mmol) in benzene (2 ml). The *product* crystallized out as white prisms (0·174 g, 0·323 mmol, 81%).

σ-Allyl(carbonyl)(dichloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(III).—A solution of carbonyl(chloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(I) (0·200 g, 0·40 mmol) in allyl chloride (1 ml, 12·1 mmol) was heated to boiling for 1 min. Diethyl ether (1 ml) was added and the *product* crystallized as cream prisms (0·192 g, 0·331 mmol, 83%).

But-3-enoyl(dichloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(III).—*Method* (1). Allyl chloride (1 ml, 12·1 mmol) was added to a solution of carbonyl(chloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium(I) (0·400 g, 0·80 mmol) in methanol (2 ml). The solution was heated to boiling for 1 min and cooled to 0° to give the *product* as cream prisms (0·372 g, 0·644 mmol, 81%).

Method (2). *Isomerization of (σ-allylcarbonyl)(dichloro)bis{(2-methoxyphenyl)dimethylphosphine}rhodium*(III). The σ-allyl complex (0·065 g, 0·11 mmol) was dissolved in warm methanol (1 ml). The solution was cooled to 0° and the product crystallized out (0·04 g, 0·07 mmol, 63%).

Dichlorobis{(2-methoxyphenyl)dimethylphosphine}(3-methylbut-3-enoyl)rhodium(III).—This complex was prepared

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[18] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.

[19] C. Masters and B. L. Shaw, *J. Chem. Soc. (A)*, 1971, 3679.

by method (1) from 3-chloro-2-methylpropene as cream *prisms* (68%).

Dichlorobis{(2-*methoxyphenyl*)*dimethylphosphine*}*pent*-3-*enoyl*)*rhodium*(III).—This complex was prepared by method (1) from 3-chlorobut-1-ene to give the *product* as cream prisms (85%), or from 1-chlorobut-2-ene (67%).

Tris{2-(*dimethylphosphino*)*phenoxy*}*rhodium*(III).— (2-Methoxyphenyl)dimethylphosphine (1·21 g, 7·25 mmol) was added to a solution of rhodium trichloride hydrate (0·55 g, 2·2 mmol) in ethanol (20 ml) and the resultant red solution was refluxed for 24 h. A white precipitate was formed. The suspension was cooled to 0° and filtered to give the *product* as white prisms (0·50 g, 0·86 mmol, 40%).

Carbonyl{2-(*di-t-butylphosphino*)*phenoxy*}{(2-*methoxyphenyl*)*di-t-butylphosphine*}*rhodium*(I).—A solution of *trans*-carbonyl(chloro)bis{(2-methoxyphenyl)di-t-butylphosphine}rhodium(I) (0·204 g, 0·304 mmol) in propan-2-ol (25 ml) was heated under reflux for 4·5 h. The solution was then cooled to −20° giving the *product* as yellow prisms (0·10 g, 0·162 mmol, 53%).

trans-*Bis*{2-(*di-t-butylphosphino*)*phenoxy*}*rhodium*(II).— A solution of hydrated rhodium trichloride (0·304 g, 1·2 mmol) and (2-methoxyphenyl)di-t-butylphosphine (1·445 g, 5·74 mmol) in propan-2-ol (30 ml) was heated under reflux for 1 h. The dark blue solution was then cooled at −20° for 24 h giving the *product* as dark blue prisms (0·150 g, 0·26 mmol, 21%).

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