Inorganica Chimica Acta, 198-200 (1992) 111-118 111

An investigation of the reaction of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ with some tertiary phosphines, and $PPh(OMe)_2$, and the X-ray structure of $[Rh(COMe)I_2(Ph_2PCH_2PPh_2)]$

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Abstract

The reactions between $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ and tertiary phosphines, and $PPh(OMe)_2$, have been studied by ^{13}C and ^{31}P NMR spectroscopy. The stereochemistry of the products was determined using ^{13}C enrichment. Reaction intermediates containing both one and two phosphorus ligands were identified. When $Ph_2P(CH_2)_nPPh_2$ ($n=1$, 2) is used, carbon monoxide is lost to yield the five-coordinate compound, $[Rh(COMe)I_2\{Ph_2P(CH_2P(CH_2)_nPPh_2\}]$; the X-ray structure was determined when $n=1$. The reaction of these five-coordinate compounds with other ligands was also investigated.

Introduction

Continuing our investigation of the chemistry of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ [1], we have studied its reactions with a selection of phosphorus compounds, in order to extend our studies of its reactions with pyridine, carbon monoxide and methanol [2]. Phosphorus compounds have the advantage of being able to use ^{31}P NMR spectroscopy to monitor the reactions and coupling between ^{31}P and other nuclei to define the stereochemistry of the products.

There have been no earlier reports of similar studies, but a number of related acetyl rhodium(III) complexes with tertiary phosphines have been reported previously [3]. These have generally been formed by the oxidative addition of RCOCl to a Rh^I species, such as $[RhCl(PPh_3)_3]$, or MeI to a $Rh^I(CO)$ species, such as $[RhCl(CO)(PR_3)_2]$, followed by migration of the methyl group to the carbonyl. The structures of a number of these species have been determined. They are generally square pyramidal [3a, 3c, 3e, 31], with the acyl in the axial site, although six-coordinate species, $[Rh(COMe)(CO)(NC_5H_5)I_3]^-$ [2], $[Rh_2Cl_3(COMe)_2(PMe_2Ph)_4]^+$ [4] and $[Rh_2(CO)_2(COMe)_2I_6]^{2-}$ [5] have also been characterised by X-ray crystallography.

Experimental

The NMR spectra were recorded on JEOL PFT-100, Bruker WP80-SY and Bruker WH 400 instruments. IR spectra were recorded on a Perkin-Elmer 257 spectrometer.

$[Rh_2(CO)_4Cl_2]$ and $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ were prepared according to literature methods [6, 7]. 90% Enriched ^{13}CO was purchased from Amersham International, and the preparation of the ^{13}C enriched compounds has been previously reported [2].

Tetraphenylarsonium fac-acetylcarbonyl-(dimethylphenylphosphine)triiodorhodium(III), $[AsPh_4][Rh(COMe)I_3(CO)(PMe_2Ph)]$

Dimethylphenylphosphine (15.6 μl, 0.11 mmol) in dichloromethane (1 ml) was added dropwise to a solution of $[AsPh_4]_2[Rh_2(COMe)_2I_6(CO)_2]$ (100 mg, 0.06 mmol) in dichloromethane (2 ml) at −80 °C with a slow passage of pre-cooled dinitrogen gas to mix the solutions. The solution was then allowed to warm to room temperature over *c.* 1 h. Sufficient diethyl ether was then added (*c.* 1 ml) to the solution to just cause a cloudiness. Crystallization at −20 °C yielded very dark maroon microcrystals of $[AsPh_4][Rh(COMe)I_3(CO)(PMe_2Ph)]$ (31 mg, 0.03 mmol, 25%) which were collected by filtration and dried *in vacuo*, m.p. 124–127 °C, decomposition. *Anal.* Found: C, 38.75; H, 3.21; I, 35.47. Calc.: C, 38.96; H, 3.15; I, 35.34%. IR: $\nu(CO)=2068$ cm^{-1}, $\nu(COMe)$ 1671 cm^{-1}. ^1H NMR spectrum in CD_2Cl_2: δ 3.00 (s, COMe), δ 2.46, 2.16 ((d, PMe_2, $^2J(^{31}P-^1H)=12$ Hz).

Acetyl{bis(diphenylphosphino)methane}diiodorhodium-(III), $[Rh(COMe)I_2(Ph_2PCH_2PPh_2)]$

$[AsPh_4]_2[Rh_2(COMe)_2I_6(CO)_2]$ (0.32 g, 0.17 mmol) in dichloromethane (4.0 ml) was added to bis-diphenyl-

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0020-1693/92/$5.00

TABLE 1. Atomic positional parameters with e.s.d.s. for [Rh(COMe)I_2(dppm)]

Atom	*x/a*	*y/b*	*z/c*
I(1)	0.10152(14)	0.15067(11)	0.20587(13)
I(2)	−0.08935(15)	0.15915(11)	0.39671(13)
Rh(1)	−0.08625(15)	0.22437(10)	0.20814(14)
P(1)	−0.1258(5)	0.2630(4)	0.0354(5)
P(2)	−0.2624(5)	0.2632(4)	0.1682(5)
O(1)	−0.0908(15)	0.3865(9)	0.2067(14)
C(1)	0.0539(18)	0.3338(15)	0.3401(20)
C(2)	−0.0451(20)	0.3329(14)	0.2478(17)
C(3)	−0.2603(17)	0.3048(15)	0.0386(17)
C(4)	−0.0434(20)	0.3374(14)	−0.0107(17)
C(5)	0.0651(17)	0.3279(15)	0.0130(20)
C(6)	0.1271(17)	0.3868(15)	−0.0248(20)
C(7)	0.0733(24)	0.4395(15)	−0.0976(20)
C(8)	−0.0344(21)	0.4466(15)	−0.1219(18)
C(9)	−0.0955(18)	0.3945(14)	−0.0788(19)
C(10)	−0.1481(20)	0.1890(15)	−0.0674(19)
C(11)	−0.1613(19)	0.1139(14)	−0.0392(19)
C(12)	−0.1850(20)	0.0548(14)	−0.1175(23)
C(13)	−0.1885(22)	0.0764(16)	−0.2197(21)
C(14)	−0.1702(21)	0.1470(17)	−0.2487(19)
C(15)	−0.1482(23)	0.2087(16)	−0.1726(20)
C(16)	−0.3606(18)	0.1877(14)	0.1478(16)
C(17)	−0.3316(20)	0.1097(12)	0.1480(18)
C(18)	−0.4085(25)	0.0523(13)	0.1336(19)
C(19)	−0.5199(25)	0.0735(19)	0.1072(22)
C(20)	−0.5492(22)	0.1475(15)	0.1038(22)
C(21)	−0.4727(18)	0.2058(13)	0.1287(18)
C(22)	−0.3150(17)	0.3345(14)	0.2411(17)
C(23)	−0.3644(18)	0.4004(15)	0.2013(18)
C(24)	−0.4080(24)	0.4538(13)	0.2570(23)
C(25)	−0.4037(20)	0.4388(16)	0.3617(21)
C(26)	−0.3575(22)	0.3740(19)	0.4062(22)
C(27)	−0.3109(22)	0.3207(16)	0.3488(24)

phosphinomethane (0.13 g, 0.336 mmol) in dichloromethane (4.0 ml) with stirring. After stirring for 15 min, sufficient petroleum ether (*c.* 3 ml, b.p. 40–60 °C) was added to cause cloudiness of the solution, and the solution allowed to crystallise at −20 °C to yield the product as dark orange crystals (0.185 g, 0.24 mmol, 69%) which were collected and washed with petroleum ether (b.p. 40–60 °C); m.p. 179–184 °C, decomposes. IR: ν(CO) (CH_2Cl_2) 1709 cm^{-1}. ^{1}H in CD_2Cl_2: δ 1.78 (s, 2H, CH_2), δ 3.10 (s, 3H, $COCH_3$), δ 7.70 (m, 20H, PPh_2). ^{13}C in CD_2Cl_2: δ 213.08 (COMe). ^{31}P in CD_2Cl_2: δ −35.62, $^1J(^{103}Rh, ^{31}P) = 120$ Hz. *Anal.* Found: C, 41.39; H, 3.26; I, 31.98. Calc.: C, 41.33; H, 3.19; I, 32.40%. Mass spectrum, expected 784, observed 614 (*M*−COMeI).

Acetyl{bis-1,2-(diphenylphosphino)ethane}diiodorhodium(III), [Rh(COMe)I$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]

Bis-1,2-(diphenylphosphino)ethane (43 mg, 0.11 mmol) in dichloromethane (1 ml) was added dropwise to a solution of $[AsPh_4][Rh_2(COMe)_2I_6(CO)_2]$ (100 mg, 0.06 mmol) in dichloromethane (2 ml) at −80 °C with a slow passage of pre-cooled nitrogen to promote mixing. The solution was allowed to warm to room temperature over *c.* 1 h. Petroleum ether (b.p. 40–60 °C) was then added to the solution to cause a slight clouding. Cooling to −20 °C caused the precipitation of $[AsPh_4]I$. After filtration, more petroleum ether was added to cause cloudiness, when the product crystallised at −20 °C as bright orange crystals (26 mg, 0.03 mmol, 25%), which were collected by decanting: m.p. 140–145 °C, decomposes IR: ν(COMe) (CH_2Cl_2): 1713 cm^{-1}. Mass spectrum, expected 798, found 628 (*M*−COMeI). ^{1}H in CD_2Cl_2: δ 1.55 (s, 4H, PCH_2CH_2P), δ 2.73 (s, 3H, $COCH_3$), δ 7.3–7.9 (m, 20H, Ph_2P). ^{31}P in CD_2Cl_2: δ 70.14, $^1J(^{103}Rh–^{31}P) = 139$ Hz. *Anal.* Found: (C, 41.78; H, 3.48; I, 30.60. Calc.: C, 42.11; H, 3.38; I, 31.83%.

The X-ray data were collected on a Nicolet R3m four circle automatic diffractometer using molybdenum Kα X-radiation. The crystals system was monoclinic with space group $P2_1/n$ (non-standard setting of $P2_1/c$). The final *R* factor was 0.0518 based on 1669 reflections with $3.5 < 2\theta < 50°$ for which $I > 3.0\sigma(I)$. There are four molecules per unit cell and the unit cell dimensions are $a = 12.617(11)$, $b = 17.436(20)$, $c = 12.901(10)$ Å, $\beta = 103.72(6)°$. The final atomic positional parameters are collected in Table 1.

Results and discussion

The reactions between $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ (**1**) and tertiary phosphines and $P(OMe)_3$ have been monitored by ^{13}C and ^{31}P NMR spectroscopy. When $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ (**1**) is treated with PMe_2Ph in CD_2Cl_2 at −80 °C, two new species are immediately formed: one a doublet at $\delta(^{31}P)$ −38.99, $^1J(^{103}Rh, ^{31}P) = 69$ Hz and the other an AMX pattern, X = ^{103}Rh, at $\delta(^{31}P)$ −43.63, $^1J(^{103}Rh, ^{31}P) = 64$ Hz, $^2J(^{31}P, ^{31}P) = 30$ Hz, and at $\delta(^{31}P)$ −17.12, $^1J(^{103}Rh, ^{31}P) = 100$ Hz. This latter species is favoured by using an excess of PMe_2Ph. On warming to −10 °C, a new species appears at $\delta(^{31}P)$ −16.11, but the signal is broad. Cooling to −60 °C results in this signal sharpening to reveal $^1J(^{103}Rh, ^{31}P) = 104$ Hz. Warming to room temperature produces two new species. The major one is at $\delta(^{31}P)$ 5.06, with $^1J(^{103}Rh, ^{31}P) = 124$ Hz, and the minor one is at $\delta(^{31}P)$ −10.84, with $^1J(^{103}Rh, ^{31}P) = 84$ Hz. Although it is possible to guess structures compatible with these data, the nature of most of these species was established using ^{13}C labelling.

Treatment of $[Rh_2(^{13}COMe)_2I_6(^{13}CO)_2]^{2-}$ with PMe_2Ph at −80 °C gives the major species with a ^{31}P NMR signal at δ −38.97 showing not only ^{103}Rh coupling, but coupling to two different carbon nuclei, with $^1J(^{31}P–^{13}C) = 135$ and 10Hz. Examination of the ^{13}C

NMR spectrum shows that the 135 Hz coupling is to the ^{13}COMe signal at δ 230.40 and the 10 Hz coupling is to the ^{13}CO signal at δ 179.72, see Fig. 1. It is well established that for Rh(III), *trans* coupling constants are large, while *cis* coupling constants are small [8]. This clearly establishes that the PMe_2Ph group is *trans* to the acyl group, structure **2**. A close examination of Fig. 1 shows that the ^{31}P coupling pattern is not centrosymmetric as might be expected. The loss of symmetry arises from a two-bond secondary isotope effect from the 30% of the molecules containing a ^{12}COMe group not having the same chemical shift as the molecules containing the ^{13}COMe group. This effect is only detected for the *trans* group. The *cis* ^{12}CO group produces a signal in the middle of the ^{13}CO coupled doublet.

The second low temperature species can be similarly identified, see Fig. 2. The ^{31}P NMR signal at δ -43.63 is further coupled to two ^{13}C nuclei to give $^2J(^{31}P-^{13}C) = 112.5$ and 9 Hz, while the signal at $\delta(^{31}P)$ -17.12 shows coupling $^2J(^{31}P, ^{13}C) = 155$ and 7 Hz. These couplings are also shown in the ^{13}C NMR spectrum showing that the PMe_2Ph at $\delta(^{31}P)$ -43.63 is *trans* to COMe while that at $\delta(^{31}P)$ -17.12 is *trans* to CO, structure **3**. The remaining data are summarised in Table 2.

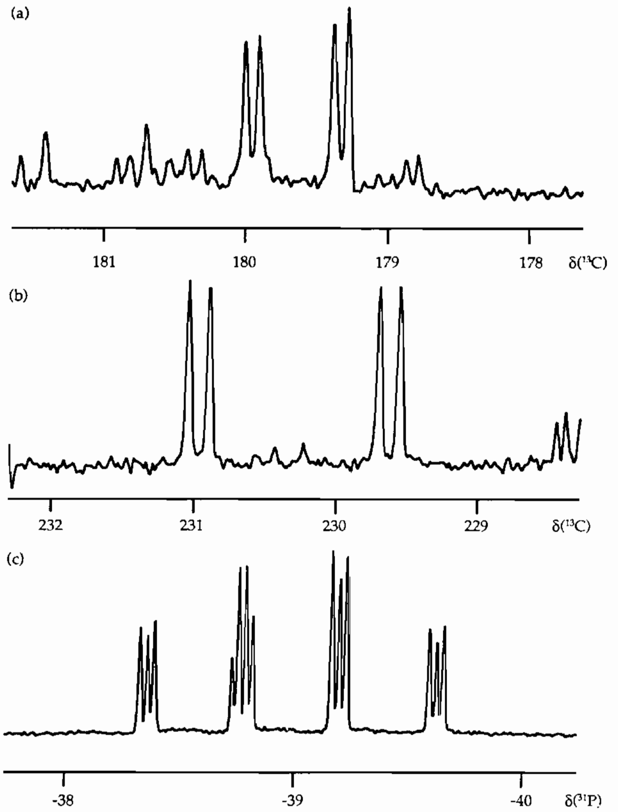


Fig. 1. Partial 100.62 MHz ^{13}C and 162.0 MHz ^{31}P NMR spectra of *mer*-$[Rh(^{13}COMe)(^{13}CO)(PMe_2Ph)I_3]^-$ in CD_2Cl_2 at -80 °C. (a) ^{13}CO NMR signal, (b) ^{13}COMe NMR signal, (c) ^{31}P NMR signal.

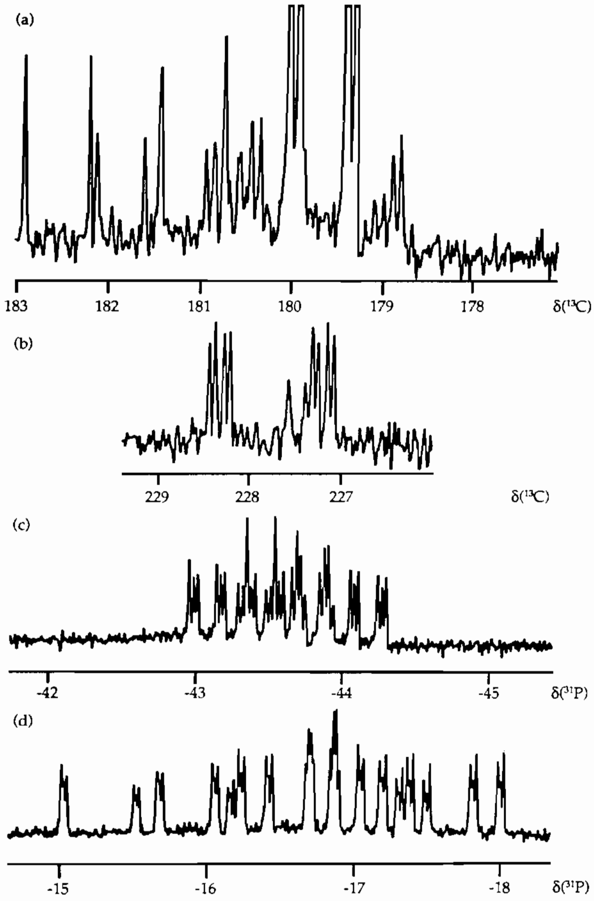


Fig. 2. Partial 100.62 MHz ^{13}C and 162.0 MHz ^{31}P NMR spectra of $[Rh(^{13}COMe)(^{13}CO)(PMe_2Ph)_2I_2]$ in CD_2Cl_2 at -80 °C. (a) ^{13}CO NMR signal, (b) ^{13}COMe NMR signal, (c) and (d) ^{31}P NMR signal. There are additional signals due to other compounds, see text.

The species formed at -10 °C shows additional coupling to two ^{13}C nuclei with $^2J(^{31}P, ^{13}C) = 167$ and 6 Hz, with the large coupling being shown by the ^{13}CO signal in the ^{13}C NMR spectrum. The broadness of the signal at 10 °C indicates that a dynamic process is occurring. This could be PMe_2Ph dissociation, but it is more likely to be I^- dissociation, due to the large *trans* influence of the COMe group. On this basis, this species, is believed to be the six-coordinate species, **4**, with the PMe_2Ph *trans* to CO.

Little additional coupling is observed for the two species formed at room temperature. The species with $\delta(^{31}P)$ 5.06 shows no additional coupling. Hence the PMe_2Ph is *trans* to I, suggesting a *mer* ligand arrangement, **5**. The species at $\delta(^{31}P)$ -10.84 shows coupling to one ^{13}C with $^2J(^{31}P-^{13}C) = 10$ Hz, while in the ^{13}C NMR spectrum, a carbonyl group is a triplet with $^2J(^{31}P-^{13}C) = 9$ Hz. It is therefore postulated that this compound contains *trans*-$(PMe_2Ph)_2$ (**6**). This stereo-

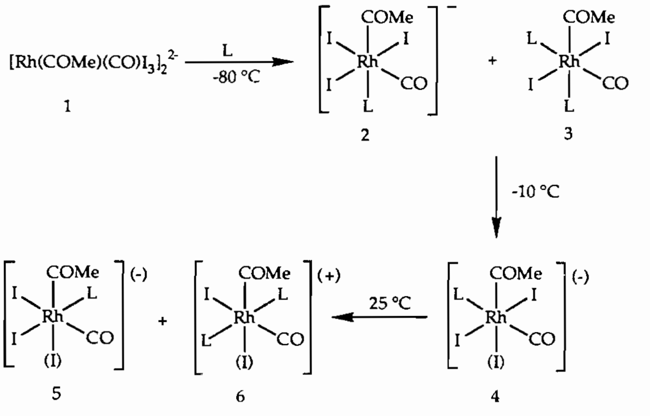
TABLE 2. ^{13}C and ^{31}P NMR data for the products of the reaction of $[Rh(^{13}COMe)I_3(^{13}CO)]_2^{2-}$ with PMe_2Ph in CD_2Cl_2

Species	Temperature (°C)	^{13}C NMR data				^{31}P NMR data			
		δ (ppm)	^1J (RhC)	*cis*-J(CRhP)	*trans*-J(CRhP)	δ (ppm)	$^{12}C/^{13}C$ isotope shift	^1J(RhP)	^2J(PRhP)
2	−80	179.72[a]	62	10		−38.99	0.016	69	
		230.40[b]	15		135				
3	−80	179.87[a]	50	9	155	−43.63[c]	0.016	64	30
		227.84[b]	17	6	113	−17.12[d]	0.028	100	
4	−80	182.88[a]	52		168	−16.11	0.025	104	
		222.05[b]	20	6					
5	20	177.44[a]	70			5.06		124	
		225.72[b]	24						
6	20	179.54[a]	66	9(t)		−10.84		84	
		215.80[b]	18						

[a]Carbonyl. [b]Acetyl. [c]*trans* to acetyl. [d]*trans* to carbonyl.

chemistry was confirmed by carrying out the reaction using a 1:1 mixture of PMe_2Ph and PEt_3. Among the species formed in addition to those formed when only PMe_2Ph or PEt_3 are used, is a species with δ −15.11 and 7.60, with $^2J(^{31}P, ^{31}P) = 486$ Hz, confirming the mutually *trans* arrangement of the tertiary phosphine. These reactions are summarized in Scheme 1. Attempts to isolate the final product failed, probably due to the slow loss of acetyl iodide, following the analogous reaction postulated by Forster [7] for the dicarbonyl analogue. Once again, it is not known if the I^- *trans* to acetyl is coordinated.

These results establish a *trans* influence order MeCO > PMe_2Ph > CO > I, and permit the identification of other related compounds based on $^1J(^{103}Rh-^{31}P)$ data. This is a rather unusual *trans* influence order. Usually, CO is a stronger *trans* influence ligand than a tertiary phosphine. This order probably is attributable to the reluctance of rhodium(III) to π-bond to carbon monoxide. The observation of a broad ^{31}P NMR signal for 4 at −10 °C can be attributed to intermolecular iodide or tertiary phosphine exchange, with $\Delta G^{\dagger} = c.$ 12 kcal mol^{-1}.



Scheme 1. The reaction sequence for the reaction of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ with a phosphorus ligand.

The reaction with $PMePh_2$ follows a very similar course, Table 3, with the exception that 3, L = $PMePh_2$, gives a very broad signal due to the $PMePh_2$ *trans* to CO, and is not sharp until −120 °C. This facile intermolecular ligand exchange is analogous to that observed for 4, L = PMe_2Ph, but with the process made more facile by the greater inter-ligand repulsions resulting from the larger $PMePh_2$ group as judged by the Tolman cone angle [6]. On further cooling to −140 °C, the signal broadens again, and this behaviour is attributed to restricted rotation about the Rh–COMe bond, analogous to that already reported for $[Rh(COMe)(CO)_2I_3]^-$ [4], but could be due to restricted rotation about the Rh–P bond, analogous to that reported for *trans*-$MCl(CO)(PBu^t{}_2R)_2$ [9] (M = Rh, Ir) and $[Pt(\eta^3\text{-}C_3H_5)\{P(cyclohexyl)_3\}_2]^+$ [10].

Reaction with PEt_3, $PEtPh_2$ and $PPh(OMe)_2$ follows a very similar course to that reported above for PMe_2Ph and the results are collected in Table 3. The major exception is that species 3 was not detected when L = $PEtPh_2$ or $PPh(OMe)_2$. In the case of L = $PEtPh_2$, the reason is probably steric. $PPh(OMe)_2$ is a much smaller ligand, so the reason is presumably electronic.

The reaction between $[Rh_2(COMe)_2I_6(CO)_2]^{2-}$ and $Ph_2PCH_2PPh_2$ proceeds rather differently. At −70 °C, the expected compound 2, L = monodentate $Ph_2PCH_2PPh_2$, is formed. It might be expected that 3 would be formed easily with a chelating ligand, but it is not formed until the solution is warmed to −10 °C. At room temperature, a new species is formed, with a ^{31}P chemical shift of −25.65, $^1J(^{103}Rh-^{31}P) = 120$ Hz. When the reaction is monitored by ^{13}C and ^{31}P NMR spectroscopy, using ^{13}C enriched starting complex, then the additional information on the new species is obtained, see Table 3. Of particular interest is that on warming to room temperature, no coordinated carbonyl

TABLE 3. ^{31}P NMR spectra of the products of the reaction of tertiary phosphines and $PPh(OMe)_2$ with $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ in CD_2Cl_2

Species	Ligand	Temperature (°C)	δ (ppm)	^{31}P NMR data	
				$^1J(^{103}Rh,^{31}P)$ (Hz)	$^2J(^{31}P,^{31}P)$ (Hz)
2	PMe_2Ph	−80	−38.99	69	
2	$PMePh_2$	−80	−34.75	66	
2	PEt_3	−80	−27.39	69	
2	$PEtPh_2$	−70	−20.60	64	
2	$PPh_2CH_2CH_2PPh_2$	−70	−24.00[a]	63	28
			−15.06[b]		28
8	$PPh_2CH_2CH_2PPh_2$	−70	−18.45	64	
2	$PPh(OMe)_2$	−70	126.56	95	
3	PMe_2Ph	−80	−43.63[c]	64	30
			−17.12[d]	100	30
3	$PMePh_2$	−80	−37.84[c]	59	34
			−11[d]		
3	PEt_3	−80	−31.28[c]	61	31
			0.35[d]	99	31
3	$PPh_2CH_2CH_2PPh_2$	−10	5.76[c]	63	18
			11.94[d]	101	18
4	PMe_2Ph	−70	−16.11	104	
4	$PMePh_2$	−10	−5.24	111	
4	PEt_3	0	0.81	108	
4	$PEtPh_2$	−20	9.02	110	
4	$PPh(OMe)_2$	10	120.86	124	
5	PMe_2Ph	25	5.06	124	
5	$PMePh_2$	20	8.16	131	
5	PEt_3	25	28.19	124	
5	$PEtPh_2$	35	22.25	131	
5	$PPh(OMe)_2$	25	136.50	187	
6	PMe_2Ph	25	−10.84	84	
6	$PMePh_2$	−10	−0.02	87	
6	PEt_3	0	2.84	82	
6	$PEtPh_2$	−10	13.26	86	
6	$PPh(OMe)_2$	−50	125.19	112	
6	PMe_2Ph[e]	0	−15.11	82	486
	PEt_3[e]	0	7.60	85	486
7	$PPh_2CH_2PPh_2$	25	−25.65	120	
7	$PPh_2CH_2CH_2PPh_2$	25	70.14	139	

[a] Coordinated. [b] Uncoordinated. [c] *trans* to COMe. [d] *trans* to CO. [e] Mixed ligand complex.

signal is observed, and a singlet at δ 184.0 due to free CO appears. This compound was isolated from the solution and the crystal structure determined as **7**.

The structure of $[Rh(COMe)I_2(dppm)]$ is given in Fig. 3, and shows the molecule as a distorted square base pyramid with an apical acetyl group and *cis*-basal iodides. The apical acetyl group is expected in view of its high *trans* influence. Selected bond lengths and angles are given in Table 4. The Rh–C(O)Me and Rh–P bond lengths and Rh–C–O bond angle are comparable with those published, see Table 5.

It is evident from C(2)–Rh(1)–I(1) = 106° and C(2)–Rh(1)–I(2) = 103°, compared with C(2)–Rh(1)–P(1) = 87° and C(2)–Rh(1)–P(2) = 88°, that the acetyl group is inclined from the true apical position such that it is further away from the iodide ligands. This is probably a steric effect. Figure 3 shows the orientation of the acetyl group with respect to the basal plane. The torsion angle of 45.9° clearly shows that the position of the acetyl group is such that steric interactions are minimised.

The reaction between $[Rh_2(COMe)_2I_6(CO)_2]^{2-}$ and $Ph_2PCH_2CH_2PPh_2$ follows a similar course to that of $Ph_2PCH_2PPh_2$, but on the initial addition of ligand, two species are observed with $^1J(^{103}Rh–^{31}P) = 63$ or 64 Hz. This coupling constant is characteristic of a tertiary phosphine *trans* to the acetyl group. The two resonances differ in that one shows a coupling of 28 Hz to a phosphorus at δ −15.06, i.e. with a chemical shift similar to that of the free ligand at δ −11.3. This species then is **2**, L = monodentate $Ph_2PCH_2CH_2PPh_2$, and the other species is probably that with the ligand

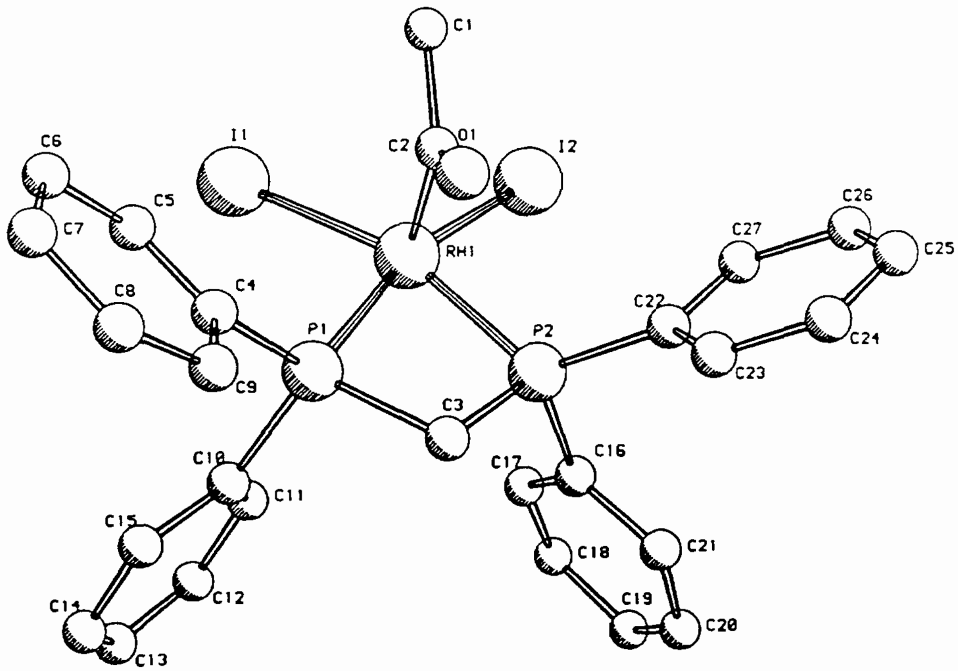


Fig. 3. View of [Rh(COMe)(dppm)I_2].

TABLE 4. Selected bond lengths and angles in [Rh(COMe)I_2(dppm)] with e.s.d.s. in parentheses

Bond lengths (Å)		Bond angles (°)	
Rh(1)–C(2)	2.00(2)	I(1)–Rh(1)–P(2)	163.0(2)
Rh(1)–I(1)	2.702(4)	I(2)–Rh(1)–P(1)	165.0(2)
Rh(1)–I(2)	2.694(4)	I(1)–Rh(1)–I(2)	90.55(10)
Rh(1)–P(1)	2.267(6)	P(1)–Rh(1)–P(2)	73.3(2)
Rh(1)–P(2)	2.262(7)	C(2)–Rh(1)–I(1)	106.2(7)
C(2)–O(1)	1.16(3)	C(2)–Rh(1)–I(2)	103.1(7)
C(2)–C(1)	1.51(3)	C(2)–Rh(1)–P(1)	87.4(7)
P(1)–C(3)	1.86(2)	C(2)–Rh(1)–P(2)	87.5(7)
P(2)–C(3)	1.83(2)	O(1)–C(2)–Rh(1)	125(2)
P(1)–C(4)	1.85(2)	C(1)–C(2)–Rh(1)	109(2)
P(1)–C(10)	1.82(3)	O(1)–C(2)–C(1)	126(2)
P(2)–C(16)	1.78(2)	P(1)–C(3)–P(2)	94(1)
P(2)–C(22)	1.78(2)		

bridging two metals, as in **8**. On warming, the reaction follows the same course as that observed for when $Ph_2PCH_2PPh_2$ is used, and the data are collected in Table 3. The final product, [Rh(COMe)I_2(dppe)] has been reported previously [12].

The formation of [Rh(COMe)I_2\{$Ph_2P(CH_2)_nPPh_2$\}] ($n=1$, 2) with the elimination of CO was unexpected. It is known that acetylrhodium(III) complexes tend to form square pyramidal complexes, with the acetyl group axial, but the loss of CO rather than iodide was surprising. The complex was observed in solution in the presence of CO. Consequently, the interaction between this five-coordinate complex and other ligands was investigated. As the preparation of the $Ph_2PCH_2PPh_2$ complex could be carried out more easily, it was this compound that was studied.

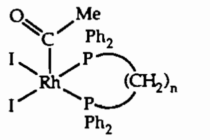
Methyl isonitrile is very similar to carbon monoxide and was therefore tried as a ligand. Addition of MeNC at −80 °C in CD_2Cl_2 caused the ^{31}P NMR signal of the complex to move from δ −25.65 to −33.97, and $^1J(^{103}Rh\text{–}^{31}P)$ decreased from 120 to 115 Hz. The product is then **9**, L = MeNC. The NMR tube was then warmed to room temperature, and placed back in the probe at −80 °C. The spectrum had changed completely to an ABX spectrum, with signals at δ −49.91, $^1J(^{103}Rh\text{–}^{31}P) = 92$ Hz, $^2J(^{31}P\text{–}^{31}P) = 60$ Hz, and δ −27.07, $^1J(^{103}Rh\text{–}^{31}P) = 106$ Hz. In view of the magnitude of both $^1J(^{103}Rh, ^{31}P)$, neither end of the chelate is *trans* to COMe, as in **10**, L = MeNC. It is not known whether the iodide *trans* to acetyl is bound. The MeNC is not strongly bound, as all attempts to isolate the product have yielded the starting material, [Rh(COMe)I_2($Ph_2PCH_2PPh_2$)].

When $P(OMe)_3$ was used as the ligand, the reaction followed the same course, with **9**, L = $P(OMe)_3$, having a ^{31}P NMR spectrum with δ −36.97, $^1J(^{103}Rh\text{–}^{31}P) = 117$ Hz, $^2J(^{31}P, ^{31}P) = 33$ Hz, due to $Ph_2PCH_2PPh_2$, and δ 101.47, $^1J(^{103}Rh, ^{31}P) = 115$ Hz, due to $P(OMe)_3$. At room temperature, **10**, L = $P(OMe)_3$, is formed with signals at δ −62.23, $^1J(^{103}Rh\text{–}^{31}P) = 86$ Hz, $^2J(^{31}P\text{–}^{31}P) = 47$ and 685 Hz, δ −23.66, $^1J(^{103}Rh\text{–}^{31}P) = 126$ Hz, $^2J(^{31}P\text{–}^{31}P) = 4$ and 47 Hz, due to $Ph_2PCH_2PPh_2$, and δ 109.30, $^1J(^{103}Rh\text{–}^{31}P) = 182$ Hz, $^2J(^{31}P\text{–}^{31}P) = 4$ and 684 Hz, due to $P(OMe)_3$. The large $^2J(^{31}P\text{–}^{31}P)$ clearly demonstrates that $P(OMe)_3$ is *trans*

TABLE 5. Selected bond lengths and bond angles for some Rh^{III}–acyl compounds

	Rh–C(O)Me	Rh–P	Rh–C–O	P–Rh–C
$[Rh(COMe)I_2(dppm)]$[a]	2.00(2)	2.267(6) 2.262(7)	125(2)	87.47(7) 87.5(7)
trans-$[Rh(COCH_2CH_2Ph)Cl_2(PPh_3)_2]$ [10]	1.93(7)	2.36(2) 2.36(2)		91(3) 95(3)
trans-$[Rh(COEt)Cl_2(PPh_3)_2]$ [11]	1.953(10)	2.320(3) 2.311(3)	126.3(8)	91.5(3) 93.0(3)
$[Rh(COEt)(maleonitriledithiolate)(PEt_3)_2]$ [1d]	1.971(5)			
$[Rh(COPr^n)(maleonitriledithiolate)(PEt_3)_2]$ [1b, c]	2.002(7)	2.349(5) 2.346(5)	125.1(4)	92.09(22) 92.31(21)
cis-$[Rh(COPh)Cl_2(dppp)]$ [1e, 11]	1.992(3)	2.290(1) 2.274(1)		89.15(10) 91.26(9)
$[Rh(COPh)(etio\text{-}1)]$ [1f][b]	1.963(7)			
$[RhCl_2(COMe)(PPh_3)]$ [10]	1.93(7)			
$[RhCl(COMe)(PMe_2Ph)_3]$ [1a]	1.971(5)	2.388(1) 2.285(1) 2.384(1)	125.5(4)	97.0(2) 91.3(2) 90.1(2)
$[Rh_2Cl_3(COMe)_2(PMe_2Ph)_4]^+$ [j]	1.995(5) 2.010(5)	2.278(1) 2.296(1) 2.302(2) 2.267(1)	124.6(5) 125.1(4)	86.0(2) 92.1(2)
$[Rh_2(CO)_2(COMe)_2I_6]^{2-}$ [5]	2.062(23)			

[a] This work. [b] etio-1 is 2,7,12,17-tetraethyl-3,8,13,18-tetramethyl-21*H*,23*H*-porphine.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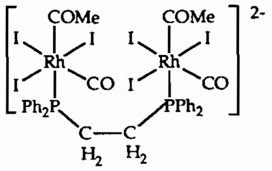
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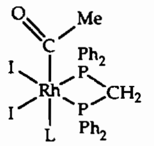
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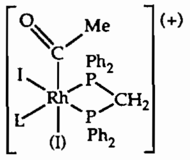
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to one of the $Ph_2PCH_2PPh_2$ phosphorus atoms. All attempts at isolating the product have yielded a mixture of starting material and product.

When $PMePh_2$ was used, then the species **9** was not detected, but **10** $L = PMePh_2$, was formed even at −80 °C, with signals at δ −46.89, $^1J(^{103}Rh\text{–}^{31}P) = 87$ Hz, $^2J(^{31}P\text{–}^{31}P) = 54$ and 413 Hz, $\delta = -32.89$, $^1J(^{103}Rh\text{–}^{31}P) = 135$ Hz, $^2J(^{31}P\text{–}^{31}P) = 54$ Hz, due to $Ph_2PCH_2PPh_2$, and δ −2.55, $^1J(^{103}Rh\text{–}^{31}P) = 105$ Hz, $^2J(^{31}P\text{–}^{31}P) = 413$ Hz, due to $PMePh_2$.

The reaction with pyridine caused a change in both the ^{31}P chemical shift to δ −33.23, and $^1J(^{103}Rh, {}^{31}P)$ to 123 Hz, consistent with structure **9**, L = pyridine, but no isomerization to **10**, was detected, and no product was isolated.

Acknowledgements

We wish to thank B. P. Chemicals, the S.E.R.C. and the Royal Society for financial support, the S.E.R.C. for access to the Bruker WH 400 and Johnson Matthey for the loan of $RhCl_3(H_2O)_3$.

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