Reactions of Phosphine with Carbonylbis(triethylphosphine)-rhodium(I) Halides and Derivatives

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The complex *trans*-[Rh(CO)X(PEt$_3$)$_2$] **1** (X = Cl, Br, I or NCS) reacts with PH$_3$ in dichloromethane at 183 K to give [Rh(CO)(PH$_3$)$_2$(PEt$_3$)$_2$]$^+$ **2** which in turn reacts with CO in dichloromethane at 213 K to give [Rh(CO)$_2$(PH$_3$)(PEt$_3$)$_2$]$^+$. The complex [Rh(CO)Cl$_2$H(PEt$_3$)$_2$], formed by reaction of **1** and HCl, reacts with PH$_3$ in dichloromethane at 219 K to give [Rh(CO)Cl(H)(PH$_3$)(PEt$_3$)$_2$]$^+$; on warming, further displacement reactions with PH$_3$ give first [RhCl(H)(PH$_3$)$_2$(PEt$_3$)$_2$]$^+$ and then the tris(phosphine) species [RhH(PH$_3$)$_3$(PEt$_3$)$_2$]$^{2+}$. Enrichment with ^{13}C in the carbonyl positions enabled the use of ^{13}C NMR spectroscopy to investigate these reactions and the parameters of eleven rhodium complexes observed in this work are given.

Complexes of transition metals and in particular platinum metals with tertiary phosphines are well known. In contrast, the behaviour of PH$_3$ towards transition-metal complexes has received little attention. Its complexes of Mo^0 and W^0 have been known for some years[1,2] and it displaces chloride from [PtCl(H)(PEt$_3$)$_2$] in a reversible reaction.[3] It can also react with [Ir(dppe)$_2$]$^+$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) in an open vessel to give a five-co-ordinate iridium(I) species containing a PH$_3$ ligand or, in a sealed tube, to give a PH$_2$ complex of Ir^{III} by oxidative addition.[4]

More relevantly, the reactions of PH$_3$ with [IrX(CO)(PEt$_3$)$_2$] (X = Cl or Br) have been well investigated.[5,6] In toluene, a 1:1 ratio of PH$_3$ and [IrX(CO)(PEt$_3$)$_2$] gives the oxidative-addition product [Ir(CO)X(H)(PH$_2$)(PEt$_3$)$_2$] with H *cis* to PH$_2$ and CO. Hydrogen chloride can protonate the PH$_2$ ligand, giving rise to a PH$_3$ ligand. In dichloromethane, the five-co-ordinate species [Ir(CO)(PH$_3$)$_2$(PEt$_3$)$_2$]$^+$ (axial PEt$_3$ groups) results. On warming, this reacts with more of the starting material to form the PH$_2$ species above. In the presence of 2 equivalents of PH$_3$ in dichloromethane the five-co-ordinate species is again formed; when warmed, it undergoes an internal oxidative addition to give [Ir(CO)H(PH$_2$)(PH$_3$)(PEt$_3$)$_2$]$^+$ with H *trans* to PH$_3$ and *cis* to PH$_2$ and CO. This complex could be protonated with HCl to give a bis(PH$_3$) species or deprotonated with NMe$_3$ to give a bis(PH$_2$) species. Further reaction with HCl displaced PH$_3$ giving first the mono(PH$_3$) compound [Ir(CO)Cl(H)(PH$_3$)(PEt$_3$)$_2$]$^+$ (H *trans* to PH$_3$) and finally the dichloro species [Ir(CO)Cl$_2$H(PEt$_3$)$_2$].

In this work the reactions of PH$_3$ with [RhX(CO)(PEt$_3$)$_2$] **1** (X = Cl, Br, I or NCS) and of PH$_3$ with the oxidative-addition product of **1** and HCl, [Rh(CO)Cl$_2$H(PEt$_3$)$_2$], in dichloromethane are described.

Results

Table 1 summarises the appearance of the ^{1}H, ^{31}P and ^{13}C NMR spectra of the various species observed. Heteronuclear selective-decoupling experiments (selectively irradiating resonances in the ^{31}P NMR spectrum whilst observing the ^{1}H NMR spectrum or *vice versa*) and a two-dimensional P–P correlation spectroscopy (COSY)[7] experiment were used to relate resonances to each other.

Table 1 The ^{31}P, ^{1}H and ^{13}C NMR peaks of the compounds described

Complex	PEt$_3$	PH$_3$	H	PH_3	CO
1	d				dt
2[a]	dt [1] (2nd)	dt [1]		2nd[b]	dtt (dtt)
3	d		dt		dt (dtd)
4	dd [2]	dt [1] (qdtd)	ddt	dt	ddt (ddt)
5	dd [2]	dt [1] (qddt)	ddt	dm	ddt (ddtd)
6	dt [2]	dt [2] (2nd)	m	2nd[b]	
7	dd [2]	dt [1] (qdt)		dt	ddt (ddt)
8	dtd [2]	P′: dtd [2] (2nd) P″: m [1] (qdm)	dm	H′ and H″: dm[c]	

2nd = Second order, d = doublet, t = triplet, q = quartet, m = multiplet too complex to be readily interpreted, dt = doublet of triplets, ddt = doublet of doublet of triplets, *etc.*; proton-coupled ^{31}P resonances in parentheses, integral ratios of ^{31}P resonances in square brackets. The ^{31}P and ^{1}H NMR spectra are of non-^{13}C-enriched materials.

[a] Phosphorus resonances broaden (reversibly) on warming. [b] Analysed as due to spin system (AX$_3$)$_2$. [c] Partially obscured by overlap with other resonances.

The relative positions of the ligands were assigned using well known relationships involving coupling constants and chemical shifts. For example, *trans* couplings tend to be large and *cis* ones small,[8,9] and hydrides *trans* to chloride resonate at around δ −13 to −17 whereas those *trans* to carbonyl or phosphorus resonate at around δ −7 to −11.[10] Labelling with ^{13}C in the carbonyl position was used to gather additional information and served to confirm the structures assigned on the basis of their ^{1}H and ^{31}P NMR spectra.

The NMR parameters are listed in Tables 2 and 3 and structural formulae are shown in Scheme 1.

Reaction of [Rh(CO)Cl(PEt$_3$)$_2$] **1** *with* PH$_3$.—Equimolar quantities of complex **1** and PH$_3$ reacted at 183 K in

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Table 2 The ^{31}P and ^{1}H NMR parameters of the compounds described

	δ				^1J		
Complex	P	P′	H	H′	PRh	P′Rh	HRh
2	+30.7	−165.1		+3.6	77.5	124.4	
4	+21.3	−108.4	−14.0	+4.5	73.4	94.7	15.2
5	+27.5	−143.6	−7.4	+4.0	74.3	67.4	10.3
6	+17.0	−109.8	−16.7	+4.3	78.3	101.9	15.1
7	+34.6	−174.8		+3.6	74.7	114.7	
8	+17.0	−118.4	−9.6	+4.7	71.8	92.4	*ca.* 10
	^1J(H′P′)	^2J(PP′)	^2J(P′P′)	^2J(HP)	^2J(HP′)	^3J(PH′)	^3J(P′H′)
2	314.5	47.0	94.8			6.3	11.9
4	397.0	41.8		10.0	19.6	7.8	
5	349.4	24.2		8.3	220.2	*ca.* 3	
6	377.0	39.9	392.4	11.7	17.3	7.2	5.6
7	320.4	42.1				5.3	
8	n.d.	36.6	n.d.	*ca.* 8	*ca.* 12	n.d.	n.d.

Chemical shifts in ppm, positive to high frequency of $SiMe_4$ (^{1}H) and 85% H_3PO_4 (^{31}P), coupling constants in Hz. Solvent = CD_2Cl_2, temperature = 213 K, n.d. = not determined. Other parameters for complex **8**: δ(P″) = −150, ^1J(H″P″) = *ca.* 350, ^2J(P″P′) = 30.3, ^2J(PP″) = 25.5, ^2J(HP″) = 166 Hz.

Table 3 Carbon-13 NMR parameters of the compounds described

Complex	X	δ(C)	^1J(CRh)	^2J(CP)	^2J(CP′)	^2J(CH)
1	Cl	+187.6	76.2	15.8		
	Br	+187.2	78.5	15.5		
	I	+185.7	79.6	15.1		
	NCS	+190.8	70.8	15.7		
2		+196.2	74.5	15.7	48.4	
3	Cl	+183.2	68.1	11.4		3.9
	Br	+182.7	64.5	10.4		2.6
	I	+180.1	63.8	10.0		0.8
4	Cl	+184.0	54.3	11.9	134.6	n.o.
5	Cl	+181.2	61.0	9.7	9.6	4.4
7		+190.7	68.3	14.7	28.9	

Chemical shifts in ppm and positive to high frequency of $SiMe_4$, coupling constants in Hz; n.o. = not observed. Solvent = CD_2Cl_2, temperature = 213 K, except for complex **1** for which solvent = $CDCl_3$ and temperature = 223 K. The parameters for **1** are the same at 298 K except that couplings are lost when X = Cl or NCS.

dichloromethane to give a species **2** identified by its NMR spectra as having the structure shown, and also some unreacted **1**. The magnitudes of ^2J(P′P′) and ^2J(CP′) (94.8 and 48.4 Hz respectively) were intermediate between those expected of *cis* or *trans* couplings but were appropriate for coupling between equatorial ligands in a trigonal-bipyramidal complex.[11]

Repetition of the reaction using a PH_3:**1** ratio of 2:1 gave complex **2** as the sole product with no remaining unreacted **1**. Reaction of a 4:1 PH_3:**1** ratio again gave **2** together with unreacted PH_3. Addition of equimolar BCl_3 to the reaction mixture gave rise to BCl_4^- (observed in the ^{11}B NMR spectrum) consistent with the presence of free chloride ion. Repeating the reaction using Br, I and NCS analogues of **1** gave **2** as the sole product in each case. The NMR parameters showed no dependence on the nature of the halogen or pseudohalogen which is therefore thought to be ionised and not bound to Rh.

Reactions of [Rh(CO)Cl_2H(PEt_3)$_2$] **3** *with* PH_3.—The compound HX (X = Cl, Br or I) reacts with [RhX(CO)(PPh_3)$_2$] forming compounds of the type **3**.[12–14] Ojeda[15] repeated the reactions using **1** and obtained directly analogous products. In the cases of X = Br or I the products are readily isolated at room temperature. When X = Cl the reaction is a reversible equilibrium at room temperature, the ^{31}P NMR spectrum revealing the presence of both **1** and **3** in dichloromethane solution. Complex **3** is the sole compound detectable by ^{31}P NMR spectroscopy only when HCl is present in a three-fold excess or more.

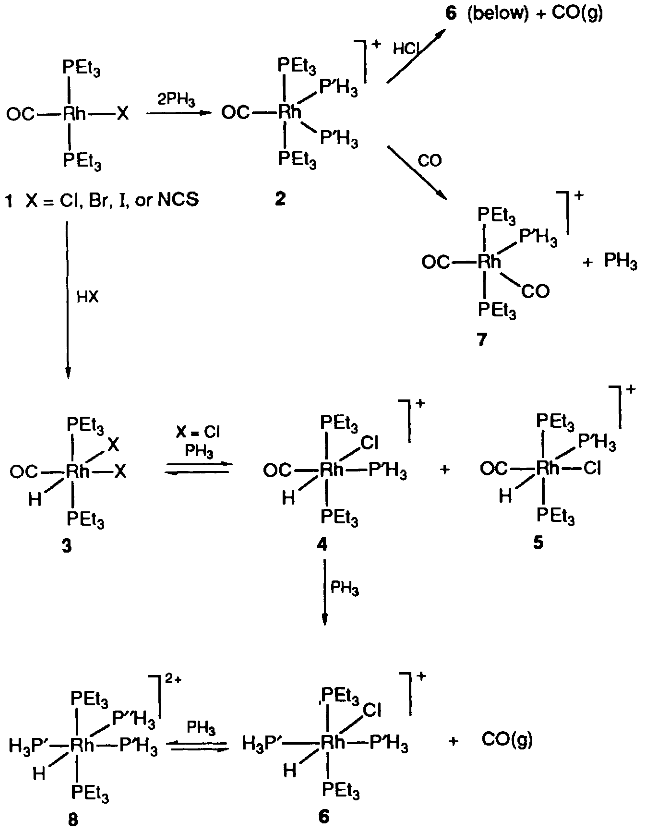
In the following reactions complex **1** and HCl were allowed to react to form **3** and PH_3 was then added to the mixture before sealing the tube and following the reaction by NMR spectroscopy. In the bromide and iodide systems no reaction with PH_3 was observed.

Complex **1** *with* HCl *and* PH_3 *in the ratio* 1:3:1. Complex **1** was treated with 3 equivalents of HCl in dichloromethane to ensure complete reaction and formation of **3**. After completion of the reaction the mixture was frozen and 1 equivalent of PH_3 added. The ^{31}P-{^{1}H} NMR spectrum was studied from 183 K to room temperature. At 183 K, **3**, PH_3 and a small amount of a new species **4** were present. On warming, **4** increased rapidly while **3** and PH_3 diminished. At 219 K the only species observed were **4** and a minor amount of another new species **5**.

The bromide and iodide analogues of complexes **4** and **5** are formed in reactions of BX_3·PH_3 (X = Cl or Br) with [RhX(CO)(PEt_3)$_2$] (X = Br or I)[16] and have almost identical NMR spectra but with slightly different chemical shifts indicating the presence of halide bound to Rh.

On warming the reaction mixture further a new species **6** began to appear at 250 K. At the same time **3** reappeared and **4** diminished. At room temperature **3** and **6** were the main products in roughly equal proportions, the level of **5** was unchanged and **4** had completely disappeared. The reaction did not reverse on cooling.

The two magnetically inequivalent PH_3 groups in complex **6** gave rise to a second-order pattern in the proton-coupled ^{31}P NMR spectrum. As further confirmation of the proposed structure of **6** a spectral simulation of this resonance was carried out, but with the hydride selectively decoupled (to avoid



Scheme 1

exceeding the memory capacity of the computer). Using the data calculated from the proton spectrum [which contained a second-order pattern analysed as being due to the $(AX_3)_2$ spin system] together with those from the first-order spectra, the simulated spectrum compared very well with that observed when the simulation was carried out on the basis of there being three hydrogens on each phosphorus.

In a simple vacuum-line experiment, a non-condensible gas was found to be present in this tube and was identified by its IR spectrum as carbon monoxide.

The first reaction observed in this system is the displacement of chloride from complex **3** by PH_3 to give **4** (with minor amounts of its isomer **5**) according to Scheme 1. Further reaction of PH_3 with **4** displaces the CO *trans* to PH_3 to give **6**. Complex **5** seems to be unreactive in this regard. Because all the PH_3 was used up in the formation of **4** the only source of PH_3 for the formation of **6** is from the reverse of the first step. Hence the reappearance of **3** when **6** is formed. When the reaction was repeated using 2 equivalents of PH_3 the same reaction sequence occurred but without the reappearance of **3**.

$[RhCl(^{13}CO)(PEt_3)_2]$ *with* HCl *and* PH_3 *in the ratio* 1:3:1. The above reaction was repeated using complex **1** with *ca.* 60–70% ^{13}C in the carbonyl position, and monitored by ^{13}C-$\{^1H\}$ NMR spectroscopy. Initially the only resonance visible in the carbonyl region was due to **3**. On warming this diminished and **4** and the minor product **5** appeared.

On further warming (to *ca.* 260 K) the quantity of complex **4** was suddenly much reduced and **3** much increased; **5** was unchanged. There were no new resonances in the ^{13}C NMR spectrum. In the ^{31}P-$\{^1H\}$ NMR spectrum at this point the dominant products were **4** and **6** with some **3** and minor **5**. All but **6** showed ^{13}C 'satellites' confirming the absence of CO in **6**.

Complex **1** *with* HCl *and* PH_3 *in the ratios* 1:1:1 *and* 1:1:2. In the reaction of PH_3 with complex **3** made from equimolar proportions of **1** and HCl the same reaction sequences were observed. However large amounts of **2** were also formed (presumably from **1** + PH_3) together with small amounts of a new species **7**. The latter was prepared in much larger yield by the reaction of carbon monoxide with **2** and details are given there.

Complex **1** *with* HCl *and* PH_3 *in the ratio* 1:1:5. Complex **1** was treated with 1 equivalent of HCl then with 5 equivalents of PH_3. The expected sequence **3** then **4** then **6** was observed, but much **2**, some **7** and a little **5** were also present. At 216 K a new species **8** became dominant, accompanied by **2**, **7** and **6** with minor **4** and a trace of **5**.

Because of overlapping with many other resonances in the PH_3 region of the proton spectrum it was not possible to determine all the NMR parameters of complex **8** but enough data were available from this and the ^{31}P NMR spectrum (with and without proton coupling) to enable determination of the structure shown.

Complex **1** *with* HCl *and* PH_3 *in the ratio* 1:3:5. This reaction gave the same products as before but with much less **2**. Complexes **6** and **8** were the major and second major products respectively. Complex **8** is probably formed by the displacement of chloride from **6** (Scheme 1). Adding more HCl to the mixture may give a cleaner reaction but it must also increase the amount of chloride ions and so may push this equilibrium to the left. This would account for the greater proportion of **6** observed in this experiment.

Reactions of Complex **2**.—*With carbon monoxide.* Approximately 0.1 mmol CO was introduced into an NMR tube containing a frozen solution of complex **2**. The tube was sealed and the ^{31}P and ^{13}C NMR spectra obtained at 213 K. The major product was **7** with the structure shown, a little **2** and much free PH_3. Repetition of the reaction using $[Rh(CO)I(PEt_3)_2]$ as initial starting material gave the same product with identical NMR parameters, confirming the absence of halide. The complex is formed by the displacement of one PH_3 ligand from **2** by CO.

With 1 *equivalent of* HX (X = Cl, Br *or* I). From 183 to 213 K, **2** with minor **3** were the only species observed in the ^{31}P-$\{^1H\}$ NMR spectrum when X = Cl. At 223 K, **6** and **7** appeared together with $[PEt_3H]^+$ and more **3**. On further warming **6** became the dominant product. No **4** was observed at any stage. This shows that **6** can be formed directly from **2** by oxidative addition of the HCl and displacement of CO. (Free CO was detected in this tube by a simple vacuum-line experiment.) The compounds HBr and HI only gave the bromide and iodide analogues of **3** when used in this reaction. However, small amounts of the bromide analogue of **4** were observed briefly at 193 K.

Discussion

The displacement of halide from complex **1** to form **2** is directly analogous to the corresponding reaction in the iridium system.[6] The sequence of reactions with PH_3 displacing ligands from **3** has no parallel in the iridium system. The iridium analogue of **3** was found to be unreactive towards PH_3. Again, in contrast to the iridium systems, no oxidative-addition reactions of PH_3 forming PH_2 groups were observed.

The complex $[Rh(CO)X_2H(PEt_3)_2]$ is much more labile when X = Cl than Br or I as shown by the fact that the bromide and iodide compounds are readily isolable whereas the chloride is not. This is reflected in the ^{31}P and ^{13}C NMR spectra which show that, when X = Cl, **1** and **3** exist in an equilibrium. The greater lability of the chloride system would account for its reactivity towards PH_3 which is in contrast to the lack of reaction observed in the bromide and iodide systems even after several days at room temperature.

Rhodium has a greater affinity for heavier halogens (heavier halogens displace lighter ones) and in complexes of the type *trans*-$[RhX(CO)L_2]$ electron density on the rhodium increases with a decrease in the electronegativity of X,[17] this being accompanied by a decrease in bond lengths of the other ligands to Rh. These trends, if true of the six-co-ordinate species of type **3**, may explain the differences in behaviour between chloride and heavier halide systems, the ligands in the bromide and iodide complexes being more tightly bound to rhodium.

Although some empirical relationships do exist, phosphorus chemical shifts are known to be very difficult to predict by electronic theories.[18] However, chemical shifts for PR_3 in species of type **1** do show a tendency to move to lower frequency as the halogen becomes heavier, perhaps because of the less electron-withdrawing and so less deshielding nature of the heavier halogens.[19] The same trend occurs with Vaska's compound $[IrX(CO)(PPh_3)_2]$ (X = Cl, Br or I).[20]

The ^{13}C chemical shifts observed here show similar patterns but literature data are sparse and inconclusive. For $[RhX(CO)(PPh_3)_2]$ there is no clear trend and for $[RhX(CO)_2(PPh_3)_2]$ the trend is in the reverse direction (X = Cl, Br or I).[21] In the case of *trans*-$[PtX(CO)(PPh_3)_2]^+$ (X = Cl, Br or I) there is again no trend in ^{13}C chemical shifts.[22]

The $^1J(CRh)$ couplings tend to be greater (70–80 Hz) for the rhodium-(I) than the -(III) complexes (54–68 Hz). This has been observed before[23] and is to be expected as the 5s orbital of the rhodium is distributed amongst four or five bonds in Rh^I and six bonds in Rh^{III} so the degree of s character of each bond diminishes as the co-ordination number increases.

The $^2J(CX)$ (X = H or P) couplings tend to be small when *cis* and large when *trans*,[8,9] the same being true of $^2J(PX)$.[24,25] This tendency is pronounced here; for example, $^2J(CP)$ values of 10–16 and 135 Hz were assigned to *cis* and *trans* couplings respectively. The five-co-ordinate systems had intermediate values (29 and 48 Hz). These were consistent with structure assignments made on the basis of ^1H and ^{31}P NMR spectroscopy and the structures of the four-co-ordinate species are known on independent grounds (IR and crystal structures) to have carbonyl *cis* to two mutually *trans* PEt_3 groups. The self-consistency of the NMR data and the fact that two-bond couplings tend to fall into such distinct groups indicates that this method of determining *cis*/*trans* relationships is probably quite reliable.

Experimental

Conventional vacuum and Schlenk-line techniques were used to handle volatile compounds and air-sensitive materials. The NMR spectra were recorded using Bruker WH360 (^1H, ^{31}P, ^{13}C), WP200 (^{31}P, ^{13}C) and WP80 (^1H) spectrometers. Rhodium starting materials were made by the method of Chatt and Shaw,[26] ^{13}C labelling being achieved by shaking an acetone solution of the product for several hours in an atmosphere of ^{13}CO.[23] Reactions were conducted in sealed NMR tubes using standard procedures.[5] Attempts at isolating products of reactions with PH_3 by removal of solvent invariably resulted in decomposition.

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