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Reactions of phosphine–boron trihalide adducts with carbonylbis(triethylphosphine)rhodium(I) halides

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Abstract

The complex *trans*-[$Rh(CO)X(PEt_3)_2$] (**1**) (X = Br, I) reacts with PH_3BY_3 (Y = Cl, Br) in dichloromethane at 183 K to give [$Rh(CO)XH(PH_2BY_3)(PEt_3)_2$] (**2**). When X = NCS, Y = Br, [$Rh(CO)H(PH_2BBr_3)_2(PEt_3)_2$] results When X = Y = Cl, only known, PH_3-containing species result, no $-PH_2BY_3$ groups are formed. When X = I, Y = F, there is very little oxidative addition, reaction occurring between **1** and free phosphine. Some simple reactions of **2** were examined. Enrichment with ^{13}C in the carbonyl positions enabled the use of ^{13}C NMR spectroscopy to investigate these reactions and the parameters of eight rhodium complexes observed in this work are given.

Key words Rhodium complexes; Phosphine complexes; Boron complexes

Introduction

The reactions of PH_3 with [$IrX(CO)(PEt_3)_2$] (X = Cl, Br) in methylene chloride and toluene have been well described [1, 2].

These give rise to various species containing PH_3 and PH_2 ligands, the latter being formed by oxidative addition. More recently, the reactions of PH_3 with [$RhX(CO)(PEt_3)_2$] (**1**) (X = NCS, Cl, Br, I) and with [$Rh(CO)Cl_2H(PEt_3)_2$] have been investigated and found to give products with PH_3 groups but not PH_2 groups [3].

In compounds containing terminal PX_2 groups (X = H or halogen), the lone pair on the phosphorus should, in principle, still be available for donation to Lewis acids such as boron halides and B_2H_6. Ligands of the type $-PX_2BY_3$ (X and Y = H or halogen) should therefore be possible.

Reports of such ligands are rare. The terminal PCl_2 group in [$IrCl_2(CO)(PEt_3)_2(PCl_2)$] reacts with B_2H_6 and BCl_3 to give $-PCl_2BH_3$ and $-PCl_2BCl_3$ moieties. On warming, the $-PCl_2BH_3$ group converts to $-PH_2BCl_3$ and $-PH_2BHCl_2$ moieties [4]. The compound [$IrH(CO)(PH_2)(PH_3)(PEt_3)_2$]$^+$, formed in the reaction of PH_3 with [$IrCl(CO)(PEt_3)_2$] also reacts with BCl_3 and B_2H_6 giving rise to compounds with two $-PH_2BY_3$ (Y = H, Cl) groups [2].

It was behaviour such as this, taken with the electronic analogy between SiH_3Y and PH_3BY_3, that suggested the possibility that the adducts of PH_3 with boron halides might undergo oxidative addition reactions with transition metal substrates to produce such moieties directly. This paper describes the reactions of PH_3BY_3 (Y = F, Cl, Br) with [$RhX(CO)(PEt_3)_2$] (**1**) (X = NCS, Cl, Br, I) in which such moieties were formed. One such compound was isolated and some reactions of this are described. Enrichment with ^{13}C in the carbonyl position was used to facilitate ^{13}C NMR studies.

The large number of spin-1/2 nuclei (^{13}C, ^{1}H, ^{31}P, ^{103}Rh) and the presence of ^{11}B ($I = 3/2$) in these systems, together with the convenience of handling such air and moisture sensitive materials in NMR tubes made NMR the obvious technique for structure elucidation Relative positions of ligands were assigned using well-established relationships involving coupling constants and chemical shifts. For example, *trans* couplings tend to be much larger than *cis* ones [5, 6] and hydrides *trans* to chloride resonate at around −13 to −17 ppm whereas those *trans* to carbonyl or phosphorus resonate at around −7 to −11 ppm [7]. Heteronuclear selective decoupling experiments (selectively irradiating resonances in the ^{31}P NMR spectrum whilst observing the ^{1}H NMR spectrum) were used to relate resonances to each other.

Results

Tables 1 and 2 list the NMR chemical shifts and coupling constants, respectively, of the various species observed.

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TABLE 1. NMR chemical shifts (ppm) of the compounds described

Complex	X	Y	δ					
			P	P′	H	H′	^{11}B	C
2	Br	Cl	+16.1	−67.4	−13.5	+4.0	+4	nd
2	Br	Br	+15.7	−56.2	−13.4	+4.5	−14	+185.4
2	I	Br	+12.3	−61.8	−11.6	+4.7	−13	+185.7
2	I	Cl	+12.7	−74	−11.8	+4.2	+4	nd
3	Cl		+21.3	−108.4	−14.0	+4.5		+184.0
3	Br		+19.2	−108.8	−13.0	+4.7		+183.4
3	I		+15.8	−116.0	−11.3	+5.0		+183.7
4	Cl		+27.5	−143.6	−7.4	+4.0		+181.2
4	Br		+24.7	−149.7	−7.6	+4.1		+180.1
4	I		nd	−158	−7.8	nd		+176.6
5		Br	+16.0	−99	−8.4	+4.6	nd	nd
6	Br	Br	+8.7	−74.7		+4.7		nd
7	Br		+13.0	−101.6		+5.1		+180.4
8	Br		+10.7					+179.4

Solvent = CD_2Cl_2, temperature = 213 K, chemical shifts positive to high frequency of $SiMe_4$ (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P) and $B(OMe)_3$ (^{11}B), nd = not determined. Other parameters for **5** are δP″ = −77 ppm and δH″ = +4.3 ppm

Reaction of [RhX(CO)(PEt$_3$)$_2$] (1) with PH$_3$BY$_3$ (X = Br, I; Y = Br, Cl)

The reaction of **1** with PH_3BY_3 in equimolar proportions in methylene chloride at 183 K gave rise to one product identified by its ^{31}P, ^{1}H, ^{11}B and ^{13}C NMR spectra as [RhX(CO)H(P′H′$_2$BY$_3$)(PEt$_3$)$_2$] (**2**). When X = Y = Br, P′ was observed in the ^{31}P{^{1}H} NMR spectrum as a broad resonance at −56 ppm. On retention of proton coupling this became a broad triplet with ^1J(P′H′) of a magnitude (347 Hz) typical of four-coordinate phosphorus [8]. The ^{11}B{^{1}H} NMR spectrum showed a very broad peak at −14 ppm. This and the broad ^{31}P resonance undergo a dramatic change in chemical shift (to +4 and to −67.4 ppm, respectively) when Y = Cl, while the other NMR parameters are only slightly affected. The microanalysis data when X = Y = Br (see 'Experimental') is consistent with a total of four bromine atoms in the whole molecule. This evidence, together with the fact that couplings between P′ and the other ligands are well resolved, even at room temperature, indicates that the BY_3 group has remained bound to phosphorus and that the breadth of the P′ resonance (which is also unaffected by temperature) is due to scalar relaxation by boron rather than to an exchange process.

^{13}C NMR of an enriched sample of **1** confirmed the presence of a carbonyl ligand, its large ^2J(CP′) coupling (110 Hz) showing it to be *trans* to the $-PH_2BY_3$ ligand.

Reaction of [RhX(CO)(PEt$_3$)$_2$] (1) with PH$_3$BBr$_3$ and HBr

When **1**, with X = Br, was reacted with equimolar PH_3BBr_3 and HBr simultaneously at 193 K, the yield of **2** was much diminished and three new compounds were observed. Two of these were identified by their ^{31}P, ^{1}H and ^{13}C NMR spectra as isomers of [RhBrH(CO)(PH$_3$)(PEt$_3$)$_2$]$^+$ with hydride *trans* to halide (compound **3**) and hydride *trans* to PH_3 (compound **4**), the former predominating over the latter. Chloride analogues of both of these have been described from the reaction of PH_3 with [Rh(CO)HCl$_2$(PEt$_3$)$_2$] [3], the spectra being very similar with only slight changes in chemical shifts and coupling constants on changing the halogen.

The third new species was identified by its ^{31}P and ^{1}H NMR spectra as the bis($-PH_2BBr_3$) species **5**. It was formed in much higher yield in the reaction of

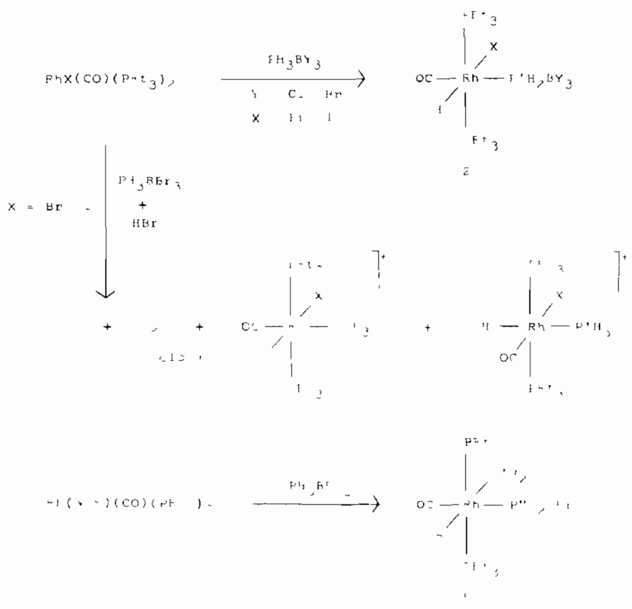


TABLE 2 NMR coupling constants (Hz) of the compounds described

Complex	X	Y	^1J					^2J(CH)
			PRh	P'Rh	P'H'	HRh	CRh	
2	Br	Cl	76.8	nd	342.6	nd	nd	nd
2	Br	Br	77.4	nd	346.9	*c.* 18	52.1	*c.* 2
2	I	Br	76.6	nd	348.6	nd	nd	nd
2	I	Cl	76.6	nd	345	nd	51.3	no
3	Cl		73.4	94.7	397.0	15.2	54.3	no
3	Br		72.2	94.9	396.5	18.0	54	no
3	I		72.7	93.3	396.0	18.3	53.7	no
4	Cl		74.3	67.4	349.4	10.3	61.0	4.4
4	Br		75.7	70.7	348	8.9	61.5	nd
4	I			*c.* 70			61.1	*c.* 3
5		Br	73.6	nd	345.5	*c.* 12.4	nd	nd
6	Br	Br	69	nd	348.1		nd	nd
7	Br		66.7	88	406.7		49.4	
8	Br		72.1				56.6	
			^2J					^3J(H'P)
			PP'	HP	HP'	CP	CP'	
2	Br	Cl	35.2	nd	nd	nd	nd	11.0
2	Br	Br	34.9	11	*c.* 22	12.9	110.0	10.8
2	I	Br	33.6	nd	nd	nd	nd	10.8
2	I	Cl	34.0	nd	nd	12.4	108.8	11
3	Cl		41.8	10.0	19.6	11.9	134.6	7.8
3	Br		40.5	9.4	18.8	12.3	134	7.8
3	I		40.6	9.3	18.0	12.0	135.2	7.9
4	Cl		24.2	8.3	220.2	9.7	9.6	*c.* 3
4	Br		24.1	8.9	216.7	9.3	8.9	*c.* 4
4	I				*c.* 200	9.1	9.3	
5		Br		*c.* 12	132.7	nd	nd	nd
6	Br	Br	28			nd	nd	10.0
7	Br		36.8			11.0	167.9	7.0
8	Br					9.2		

Solvent = CD_2Cl_2, temperature = 213 K, nd = not determined, no = not observed. For compounds with $-PH_2BY_3$ groups, ^1J(P'Rh) could not be determined due to the broad nature of the resonance. In the case of complex **2**, couplings to hydride could not be accurately determined due to the complexity of the resonance. Other parameters for **5** are ^1J(H''P'') = 348, ^2J(HP'') = *c.* 12.4, ^3J(H''P) = *c.* 10, ^3J(H''P') = 4.5 Hz. Couplings between H' and P or P'' not determined due to overlap with other resonances. ^2J(PP') and ^2J(PP'') were 18.3 and 30.5 Hz but it was not possible to determine which was which.

[Rh(NCS)(CO)$(PEt_3)_2$] with PH_3BBr_3 where it is described in more detail.

When X = I, analogous reaction products were observed but the iodide analogue of **4** was present in such small amounts it was not possible to obtain complete NMR parameters for it.

Reaction of [Rh(NCS)(CO)$(PEt_3)_2$] with PH_3BBr_3

The main product of this reaction at 193 K was compound **5**. It gave rise to two broad resonances at −77 and −99 ppm in the $^{31}P\{^1H\}$ NMR spectrum which became broad triplets (^1J(H'P') = 348 and 346 Hz, respectively) on retention of proton coupling. Heteronuclear selective decoupling related these and a doublet of doublets of doublets at +16 ppm to a hydride resonance at −8.4 ppm in the ^1H NMR spectrum. The parameters remained the same whether this compound was generated in the iodide, bromide or thiocyanate systems as would be expected if no halogen was bound to rhodium. In a simple vacuum line experiment, no free carbon monoxide gas was detected in the NMR tube in contrast to other rhodium–phosphine systems in which CO is displaced and readily detected [3], so this ligand has remained bound to Rh.

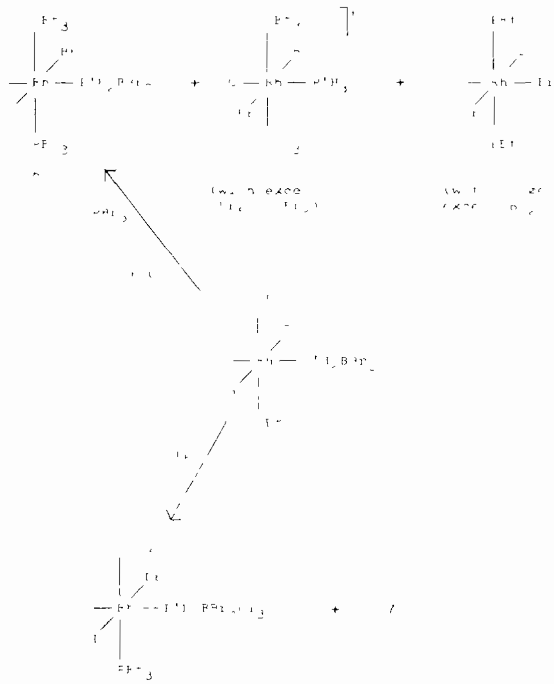
Two weak, broad resonances at −60 and −85 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a weak hydride resonance at −7.1 ppm in the ^1H NMR spectrum remained unidentified. Three doublets with chemical shifts of 30.0, 26.9 and 25.5 ppm and ^1J(PRh) couplings of 74, 75 and 75 Hz, respectively, probably corresponded to three hydride resonances (each doublets of triplets) at −11.1, −12.3 and −14.1 ppm (not respectively).

These may represent various isomers formed by oxidative addition of HBr to the starting material with hydride *trans* to CO, NCS or Br. Reaction of HBr with $[Rh(CO)(NCS)(PEt_3)_2]$ was found to give three species with the same ^{31}P and ^{1}H NMR parameters, albeit in different proportions. No attempt was made to characterise these further. Repeating the reaction with two equivalents of PH_3BBr_3 did not increase the yield of **5** but led to the formation of a small amount of **3**.

Reaction of $[RhI(CO)(PEt_3)_2]$ with PH_3BF_3

1, with X = I, reacted with PH_3BF_3 in much the same way as it does with free PH_3, giving the known compound $[Rh(CO)(PH_3)_2(PEt_3)_2]^+$ as the main product [3], but also very minor **3**. The $^{31}P\{^1H\}$ NMR spectrum contained a weak, broad resonance at −89 ppm and a complex, overlapping resonance at +15 ppm. The proton spectrum revealed several hydride resonances at −11 to −12 ppm overlapping with each other making it impossible to derive structural information from them.

The $^{19}F\{^1H\}$ NMR spectrum revealed a doublet ($^2J(FP') = 207$ Hz) of 1:1 1:1 quartets ($^1J(FB) = 55$ Hz) at −132 ppm. This is consistent with a $-PH_2BF_3$ group. It was found that the ^{19}F NMR spectrum of a 1:1 mixture of BF_3 and PH_3 in methylene chloride gives rise to a singlet at −121 ppm at 191 K. The adduct $Me_2PH \cdot BF_3$ is more stable in solution and has $^2J(P'F) = 275$ Hz and $^1J(BF) = 54$ Hz [9]. There is therefore some evidence that oxidative addition has occurred to give a $-PH_2BF_3$ group but it has not been possible to fully characterise what was a very minor product of the reaction.



Reaction of $[RhX(CO)(PEt_3)_2]$ (1) (X = Cl, NCS) with PH_3BCl_3

This gave only known compounds: the five-coordinate species $[Rh(CO)(PH_3)_2(PEt_3)_2]^+$ and $[Rh(CO)_2(PH_3)(PEt_3)_2]^+$ and the six-coordinate $[RhClH(PH_3)_2(PEt_3)_2]^+$ [3] there being no evidence for any $-PH_2BCl_3$ moieties. These compounds are formed in the reaction of **1** with PH_3 and HCl, in this case the HCl may have been a contaminant of the BCl_3 although it did not cause any analogous reactions when other halogens were present in **1** instead of chloride.

Reactions of 2

2, with X = Y = Br, was isolated and its reactions with a few simple molecules investigated.

Reactions with HX (X = Cl, Br)

2 was found not to react with equimolar HBr or HCl, even at room temperature. Only with a large excess (*c.* eight-fold) of HBr was the formation of a small amount of **3** observed. No reaction was observed between **2** and a mixture of HBr and BBr_3 (which should generate $H^+[BBr_4^-]$).

Reaction with PBr_5

Reaction commenced at 213 K giving a species identified by its ^{31}P and ^{1}H NMR spectra as **6**. With an excess of PBr_5 small amounts of **7** were formed.

Reaction with Br_2

As might be expected, this gave the same products as were observed in the reaction of **2** and PBr_5, **7** being formed when excess Br_2 was used. With a large (*c.* four-fold) excess of Br_2 **8** was formed. Compounds of this type are well-known from the oxidative addition of halogens with the four-coordinate starting material **1** [10].

Reaction with PCl_5

Some **7** was observed in this system but the main reaction, at 213 K, was a halogen exchange between the BBr_3 group on **2** and PCl_5. The dominant product was **2** with all the bromine bound to boron replaced by chlorine atoms. Some unchlorinated **2** remained. The $^{31}P\{^1H\}$ NMR resonances of the $-PH_2BY_3$ group in this and its chlorinated analogue merged into one another as might be expected if partially chlorinated intermediates were also present. As confirmation of this, the $-PH_2BY_3$ region of the proton spectrum showed four sets of very similar doublets of triplets with chemical shifts of +4.53, +4.35, +4.16 and +4.00 ppm. These represent compounds with 0, 1, 2 and 3 chlorine atoms on the boron, respectively. If these chemical shifts are plotted against the number of chlorine atoms the result is a straight line. It has been observed before that the proton chemical shift in PH_3BY_3 adducts moves to lower frequency as the halogens on the boron get lighter [9].

A singlet at +228 ppm in the ^{31}P spectrum showed that PBr_3 was present.

Reaction with Cl_2

This reaction, in equimolar proportions, gave **6** and minor **7** together with much unreacted **2**. The ^{31}P chemical shifts of the $-PH_2BY_3$ groups in **2** and **6** were shifted very slightly (by 3.2 and 1.1 ppm, respectively) and appeared slightly broader than normal. There may have been some replacement of Br by Cl in the $-PH_2BY_3$ group in these compounds This would act as a source for the extra Br on the rhodium. One would not expect to observe Cl bound to rhodium in such a system due to rhodium's greater affinity for heavier halogens (heavier halogens displace lighter ones).

Other reactions

It had been hoped that it would be possible to remove the BBr_3 group from **2** leaving a terminal $-PH_2$ group. The bases pyridine and methyl, dimethyl and trimethylamine were all tried unsuccessfully. **2** with BCl_3 in place of BBr_3 was also reacted with Me_3N in the hope that the weaker P–B bond would be easier to break but the reaction gave rise to numerous, broad and unresolved resonances in the $^{31}P\{^1H\}$ NMR spectrum and characterisation of the products was not possible

There was no reaction with PH_3BBr_3 which had been attempted in the hope of generating **5**

Discussion

Boron halides form more stable adducts with Lewis bases the heavier the halogen on the boron, the order of acceptor strength for BY_3 being $BI_3 > BBr_3 > BCl_3 > BF_3$ [11, 12]. The bond between BF_3 and PH_3 is particularly weak. The only resonance in the ^{31}P NMR spectrum of a methylene chloride solution of an equimolar mixture at 185 K is due to PH_3 However, its chemical shift is slightly to higher frequency (−228.7 ppm) than that expected (−236 ppm) and $^1J(PH)$ is 204 Hz, rather than the expected 182 Hz [13], suggesting that there may be a small concentration (< 10%) of an adduct in dynamic equilibrium with PH_3. PH_3BBr_3, in contrast, is only about 2% dissociated in methylene chloride solution at 298 K [14]. PH_3BCl_3 in CD_2Cl_2 is intermediate in its behaviour It is present as the adduct at 183 K but dissociates reversibly on warming so that coupling between ^{11}B and ^{31}P is lost above 243 K [13]

In view of the largely dissociated nature of PH_3BF_3, it is not surprising that this adduct behaved like free PH_3 when reacted with **1**. Even so, there was some evidence that oxidative addition may have occurred, albeit only as a minor reaction, to give a $-PH_2BF_3$ group.

As anticipated, PH_3BY_3 (Y = Cl, Br) adducts can indeed undergo oxidative addition reactions to give ligands of the type $-PH_2BY_3$ In the systems described here this is usually in a simple *cis* fashion to give a single $-PH_2BY_3$ moiety. With $[Rh(NCS)(CO)(PEt_3)_2]$ the reaction is more complex giving rise to a product with two such moieties. A similar compound is known in the iridium system in which PH_3 reacts with $[Ir(CO)Cl(PEt_3)_2]$ giving $[Ir(CO)(PH_3)_2(PEt_3)_2]^+$ which then converts to $[Ir(CO)H(PH_2)(PH_3)(PEt_3)_2]^+$, this latter species can be reacted with BCl_3 to give a bis($-PH_2BCl_3$) compound [2].

The mechanism by which the bis($-PH_2BY_3$) species **5** is formed with rhodium substrates is less clear. $[Rh(CO)(PH_3)_2(PEt_3)_2]^+$ is known from studies of the reactions of **1** with phosphine [3] but it does not react with BCl_3 and there is no evidence that it gives rise to a species analogous to $[Ir(CO)H(PH_2)(PH_3)(PEt_3)_2]^+$, nor does this mechanism explain why the thiocyanate starting material should behave so differently to the others. Although observed in minor amounts in bromide and iodide systems, **5** is the predominant product only in the thiocyanate system. One can postulate an initial reaction giving rise to $[RhH(CO)(NCS)(PH_2BBr_3)(PEt_3)_2]$, analogous to compound **2**. The greater lability of the NCS ligand compared to Br or I (which readily displace NCS but not vice versa) may facilitate subsequent reaction with more PH_3BBr_3 to give the bis($-PH_2BBr_3$) species **5** and HNCS HNCS may exchange with the BBr_3 to give HBr which would explain the apparent presence of oxidative addition products of HBr and the starting material in this reaction.

Alternatively a disproportionation reaction such as

$$2[RhH(CO)(NCS)(PH_2BBr_3)(PEt_3)_2] \longrightarrow [RhH(CO)(NCS)_2(PEt_3)_2] + \underset{\mathbf{5}}{[RhH(CO)(PH_2BBr_3)_2(PEt_3)_2]}$$

may give the same result. Scrambling of the NCS ligands in $[RhH(CO)(NCS)_2(PEt_3)_2]$ with the bromine in **5** may then occur to give the species interpreted as oxidative addition products of HBr and the four-coordinate starting material. In the absence of a complete characterisation of these other products, which was beyond the scope of this study, it is not possible to determine which, if either, of the above mechanisms is correct.

When **1** contained Br or I, oxidative addition was the norm giving the expected $-PH_2BY_3$ moiety whereas no such reaction occurred in the analogous chloride system. The heavier halides appear to make the metal centre more likely to undergo oxidative addition reactions. This is to be expected. An increase in electron density on the metal centre favours oxidative addition and it is known that in complexes of the type *trans*-$[RhX(CO)L_2]$, electron density on the rhodium increases with a decrease in the electronegativity of X [15].

In the case of $[Rh(NCS)(CO)(PEt_3)_2]$, no oxidative addition of PH_3BCl_3 occurred but it did with PH_3BBr_3. In the latter case it could be argued that the NCS complex was converted to the bromide complex first (the bromide coming from the BBr_3) and that oxidative addition then occurred with the resultant bromide complex, although this would mitigate against the subsequent production of **5** according to the mechanisms suggested above for its formation. It was not possible to prove the existence of any analogue of **2** with NCS bound to rhodium.

In the case of compound **2**, with the reagents that were examined, reaction at hydride seemed to occur more readily than at the $-PH_2BBr_3$ group. The latter is not entirely inert as shown by its reaction with excess bromide and its halogen exchange with PCl_5

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, ^{11}B) and WP80 (^1H) spectrometers. Rhodium starting materials were made by the method of Chatt and Shaw [16], ^{13}C labelling being achieved by shaking an acetone solution of the product for several hours in an atmosphere of ^{13}CO [17]. Reactions were conducted in sealed NMR tubes using standard procedures [1].

Isolation of $[RhBrH(CO)(PEt_3)_2(PH_2BBr_3)]$ (2)

Methylene chloride (*c.* 2 ml) followed by phosphine and boron tribromide (0.4 mmol each) were condensed into a Schlenk tube attached to the vacuum line. The mixture was warmed to room temperature to allow formation of the adduct and then frozen to 77 K. $[RhBr(CO)(PEt_3)_2]$ (**1**) (0.4 mmol) was then added under nitrogen, the tube evacuated and the mixture allowed to warm to room temperature After 10 min, the solvent was removed under vacuum leaving a pale yellow gum. Diethyl ether (*c.* 10 ml) was then condensed in and the tube left for 10 to 20 min. The gum gradually crystallised. Trituration with more ether resulted in a pale cream powder, soluble in methylene chloride, chloroform, THF and toluene; insoluble in diethyl ether and petroleum ether. Yield 80–90%. It is important that all solvents used are rigorously dried beforehand. The material is best handled under nitrogen and is stable for only 2–3 days at room temperature.

Crystals suitable for X-ray work could not be obtained and attempts at FAB mass spectrometry resulted in spectra too complex to be readily interpreted. *Anal.* Calc.: C, 21.34; H, 4.55; Br, 43.69. Found: C, 21.0; H, 4.45; Br, 43.8%. Main IR bands (cm^{-1}, KBr disc): 2076(vs), 2060(vs), 1454, 1031, 828, 762(vs), 733(vs), 709, 591(vs), 513(vs).

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