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NMR studies of some carbonyl complexes of iridium(I) and (III)

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Abstract

The trigonal bipyramidal species $[Ir(CO)_3(PEt_3)_2]BF_4$ reacts with PH_3 to form $[Ir(CO)_2(PH_3)(PEt_3)_2]BF_4$. Both of these undergo oxidative addition reactions with HX (X = Cl, Br, I) with loss of CO, except in the case of X = I when the phosphine complex eliminates PH_3 instead. SiH_3Br reacts to give a simple oxidative addition product in each case but when PH_3 is present the solvent and anion both affect the outcome of the reaction. Enrichment with ^{13}C in the carbonyl positions allowed the use of ^{13}C NMR spectroscopy to identify the products.

Introduction

Trigonal bipyramidal compounds of the type $[Ir(CO)_3L_2]^+$, where L = various alkyl phosphine and arsine ligands in axial positions, were first prepared by Church *et al.* [1]. They were found to undergo oxidative addition with hydrogen to give species of the type $[Ir(CO)_2H_2L_2]^+$. Only when L = $PMePh_2$ was the reaction with hydrogen halide investigated. This was found to produce the known compound $Ir(CO)Cl_2HL_2$ [2]. Reactions with phenylacetylene [3], N_2O_4 [4], $LiBHEt_3$ [5] and xenon difluoride [6] have also been studied.

In this paper, the reactions of $[Ir(CO)_3(PEt_3)_2]BF_4$ (**1**) with HX (X = Cl, Br, I), PH_3 and SiH_3Br are described. Both displacement and oxidative addition reactions were observed. A compound containing a PH_3 group was isolated and some reactions of this are also described.

As a by-product of some other unrelated work, a supply of **1** enriched with ^{13}C at the carbonyl positions was available. This presented a unique opportunity to investigate the system by ^{13}C NMR spectroscopy. The presence of so many spin-1/2 nuclei (^{13}C, ^{31}P, ^1H, ^{29}Si and ^{19}F) made NMR the obvious technique for determining the structures of the products. Furthermore, the handling of such air-sensitive materials as PH_3, SiH_3Br and their transition metal derivatives is most easily carried out in sealed tubes. NMR tubes are ideally suited for this purpose as they can be sealed under vacuum and stored in liquid nitrogen. Previous workers in this department have also found NMR rather than IR to be much the preferred method for studying such systems [7, 8].

Compared to ^{31}P and ^1H, ^{13}C NMR parameters are relatively scarce in the literature on iridium carbonyl complexes. The ^{13}C NMR parameters of thirteen such complexes given here are a significant addition.

Results

NMR chemical shifts are given in Table 1, NMR coupling constants in Table 2.

Reactions of 1 with PH_3

Equimolar proportions of **1** and PH_3 in CD_2Cl_2 were monitored by $^{31}P\{^1H\}$ NMR from 183 K to room temperature. Reaction commenced at 233 K and was complete by 253 K leaving no unreacted **1** or PH_3. Only one product was observed which, at room temperature, gave rise to a doublet at −6.5 ppm and a triplet at −204.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum, each with $^2J(PP)$ coupling of 31 Hz. On retention of proton coupling the resonance at −204.4 ppm was split into a quartet of triplets with $^1J(PH) = 354$ Hz, typical of four-coordinate phosphorus [9], showing that a coordinated PH_3 group was responsible for this resonance. There were no additional splittings, suggesting the absence of any hydride, which was confirmed by the proton NMR spectrum: this showed a doublet of triplets at +3.5 ppm with $^1J(HP) = 354$ Hz and $^2J(HP) = 5.8$ Hz but no hydride resonance.

By freezing the tube's contents with liquid nitrogen and opening it on a vacuum line a non-condensible

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TABLE 1. NMR chemical shifts of the compounds described

Species	Halogen	δP	δP′	δH	δH′	δC′	δC″
1		−1.6				+170.4	
2		−6.5	−204.4		+3.5	+178.1	
4	Cl	−1.5		−16.9		+162.4	
4	Br	−9.3		−16.0		+162.1	
4	I	−21.5		−14.6		+160.0	
5	Cl	−5.1		−16.2		+165.6	
5	Br	−8.8		−15.1		+164.8	
5	I	−14.4		−13.5		+163.7	
6	Cl	−1.4		−9.9		+155.4	+164.2
6	Br	−6.3		−10.4		+153.9	+162.3
6	I	−13.8		−11.3		+149.9	+159.7
7		−10.4		−11.2	+4.4	+161.8	+168.0
11		−8.6		−9.2	+4.4	+176.1	
12		−5.1		−8.7	+6.4	n.d.	

Units: ppm, positive to high frequency of $SiMe_4$ (for ^{1}H, ^{13}C), H_3PO_4 (for ^{31}P). Solvent $CDCl_3$, temperature 298 K, n.d. = not determined. For **12**, δF = −105.8 ppm (CCl_3F standard). C″ is *trans* to hydride.

TABLE 2. NMR coupling constants of the compounds described

Species	Halogen	^{2}J(HP)	^{2}J(HC′)	^{2}J(HC″)	^{2}J(C′P)	^{2}J(C″P)	^{2}J(C′C″)
1					11.6		
2					12.9		
4	Cl	11.4	6.0		8.0		
4	Br	11.2	5.1		7.7		
4	I	11.0	4.0		7.6		
5	Cl	9.6	5.0		10.1		
5	Br	9.9	5.0		10.0		
5	I	10.2	4.8		9.9		
6	Cl	12.5	6.7	58.6	6.8	5.8	n.o.
6	Br	12.5	6.5	57.1	6.7	5.8	n.o.
6	I	12.6	6.2	54.8	6.8	5.8	n.o.
7		13.0	*ca*4.4	37.4	8.4	6.7	1.9
11		15.0	40.8		7.6		
12		15.2	n.d.		n.d.		

Other parameters: Species **2**: ^{1}J(H′P′) = 354.0, ^{2}J(CP′) = 27.1, ^{2}J(PP′) = 30.9, ^{3}J(H′P) = 5.8, ^{3}J(C′H′) n.o. Species **7**: ^{1}J(H′Si) = 223, ^{2}J(H′P) = 9.8, ^{3}J(HH′) = 3.4, ^{3}J(C′H′) = *c.* 4.1. Species **11**: ^{1}J(H′^{29}Si) = 212, ^{3}J(H′P) = 8.0, ^{3}J(HH′) = 3.6, ^{3}J(CH′) n.o. Species **12**: ^{1}J(F^{29}Si) = 334.3, ^{1}J(H′^{29}Si) = *c.* 248, ^{2}J(FH′) = 68.9, ^{3}J(FH) = 7.9, ^{3}J(FP) = 3.9, ^{3}J(H′P) = 4.4, ^{3}J(HH′) = 4.5. Units = Hz, n.o. = not observed, n.d. = not determined, solvent = $CDCl_3$, temperature = 298 K.

gas was detected and identified as carbon monoxide from its IR spectrum.

The reaction was repeated using **1** with approximately 60% enrichment with ^{13}C at the carbonyl positions. The ^{13}C{^{1}H} NMR spectrum of the product showed a doublet of triplets at +178.1 ppm in the region associated with carbonyl bound to a metal. The triplet coupling to the two PEt_3 groups was 13 Hz, the doublet coupling to the PH_3 group was 27 Hz. This doublet coupling is intermediate between typical *cis* and *trans* ^{2}J(CP) couplings [10].

The PEt_3 region of the ^{31}P{^{1}H} NMR spectrum showed a pattern which could be interpreted as a prominent doublet (molecules with no ^{13}C) overlapping a doublet of doublets (molecules with one ^{13}C) overlapping a weaker doublet of triplets (molecules with two ^{13}C atoms), the central peaks of the triplets lying under the main doublet. The PH_3 resonance was more complex and less well resolved but also exhibited a pattern too complex to be accounted for if only one carbonyl ligand was present.

This evidence indicates a species **2** with the structure shown formed by the displacement of one CO group by PH_3.

Reaction of **1** with two equivalents of PH_3 gave **2** as the main product. A small amount of the known species $[Ir(CO)H(PH_2)(PH_3)(PEt_3)_2]^+$ (**3**) was also formed as identified by its ^{31}P and ^{1}H NMR spectra [8]. This could be formed by oxidative addition of PH_3 to **2** with displacement of CO.

Reactions of 1 with HX (X=Cl, Br, I) (Scheme 1)

Reaction with HCl

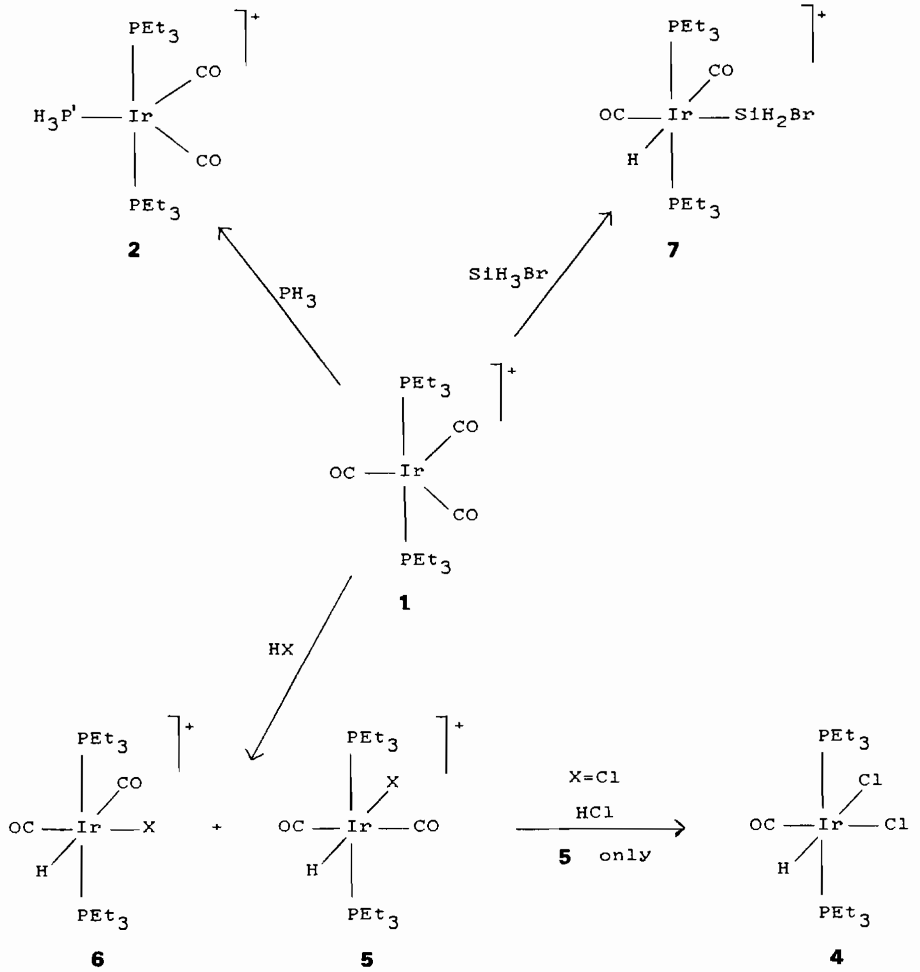
Equimolar proportions of **1** and HCl react in $CDCl_3$ at room temperature evolving a gas identified by its IR spectrum as carbon monoxide. The $^{31}P\{^1H\}$ NMR spectrum of the solution consisted of three singlets, at −5.1, −1.4 and −1.5 ppm, the last of these being very weak. The proton NMR spectrum contained three hydride resonances, a weak one at −16.9 ppm and stronger ones at −16.2 and −9.9 ppm, all triplets. The weak resonances at −1.5 and −16.9 ppm in the $^{31}P\{^1H\}$ and ^1H NMR spectra, respectively, correspond to the known compound $Ir(CO)Cl_2H(PEt_3)_2$ (**4**) prepared by reaction of HCl with $Ir(CO)Cl(PEt_3)_2$. The other two were assigned to the isomers **5** and **6**.

The proton resonance at −16.2 ppm is in the region associated with hydride *trans* to halide [11] and so was assigned to **5**; the proton resonance at −9.9 ppm is in the region expected for a hydride *trans* to carbonyl and so was assigned to **6**.

The reaction was repeated using **1** with approximately 10% ^{13}C in the carbonyl positions. The $^{31}P\{^1H\}$ and ^1H NMR spectra confirmed the presence of the same products. In the former, the ^{13}C satellites were poorly resolved, but in the proton spectrum the hydride resonance at −9.9 ppm showed two distinct pairs of satellites with $^2J(HC)$ couplings of 7 and 59 Hz. These were interpreted as being due to *cis* and *trans* carbonyls, respectively, in **6**. The $^{13}C\{^1H\}$ NMR spectrum revealed triplets at +166, +164 and +155 ppm. On retention of proton coupling the +166 ppm resonance became a triplet of doublets with $^2J(CH)=5$ Hz, attributed to the *cis* hydride in **5**. The +164 and +155 ppm resonances became doublets of triplets with $^2J(CH)=59$ and 7 Hz, respectively, corresponding to the couplings observed in the ^1H spectrum. Resonances due to **4** were not observed in the ^{13}C spectra due to its low concentration.

Reaction with excess HCl

1 with *c.* 10% ^{13}CO ligands was reacted with HCl in the ratio 1:3. The $^{31}P\{^1H\}$ and ^1H NMR spectra revealed the same three products but in very different proportions to those previously observed: **6** and **4** were the dominant products and **5** was almost absent. The $^{13}C\{^1H\}$ NMR spectrum revealed a new triplet at +162.4



Scheme 1. Reactions of **1**.

ppm due to **4** (confirmed by ^{13}C NMR of a pure sample). The triplet at +166 ppm due to **5** was much reduced as was the singlet at −5.1 ppm in the ^{31}P{^{1}H} spectrum which was therefore also attributed to **5**.

Reactions with HBr and HI

The reactions of **1** with HBr and HI in $CDCl_3$ at room temperature were found to give analogous products with similar spectra to those described in the chloride system, the chemical shifts changing slightly as the halide changed. In each case the dihalide product of type **4** was very minor. The product of type **6** was dominant, whereas in the chloride system **5** and **6** were formed in approximately equal amounts as indicated by the relative intensities of their resonances in the ^{31}P and ^{1}H NMR spectra.

Reaction with SiH_3Br

SiH_3Y is known to react with $Ir(CO)X(PEt_3)_2$ to form $Ir(CO)XH(SiH_2Y)(PEt_3)_2$ (Y = H, Cl, Br, I; X = Cl, I) [7]. Hydride was originally believed to lie *trans* to Si but recent ^{13}C NMR work has shown it to be *cis* to Si and *trans* to CO [12]. SiH_3Br was found to react with **1** in CD_3Cl to give a similar product **7** but with an extra CO ligand in place of the halide.

Effervescence was observed and the gas identified by IR spectroscopy as carbon monoxide. The ^{31}P{^{1}H} NMR spectrum showed only a singlet at −10.4 ppm. The ^{1}H spectrum revealed a triplet of triplets at −11.2 ppm due to a hydride and a triplet of doublets at +4.4 ppm with ^{29}Si satellites, the doublet coupling of 3.3 Hz being the same as the smaller triplet coupling in the hydride resonance. This is to be expected of a $^3J(H\text{SiIr}H)$ coupling [7]. This evidence indicates a species with a hydride and a $-SiH_2Br$ group.

Using **1** with *c.* 60% ^{13}C in the CO ligands the ^{31}P{^{1}H} spectrum showed a singlet with two sets of ^{13}C 'satellites', which was to be expected if two CO groups were present. The ^{13}C{^{1}H} spectrum revealed two triplets of equal intensity at +162 and +168 ppm. Using a narrower width ^2J(CC) = 1.9 Hz was resolved. On retention of ^{1}H coupling the +168 ppm resonance became a doublet of triplets with ^2J(CH) = 37 Hz indicating a *trans* hydride. The other resonance became a complex multiplet which could be explained if the original triplet with ^2J(CP) = *c.* 8 Hz had acquired a *cis* ^2J(CH) coupling of *c.* 4 Hz and a ^3J(CH′) coupling also of *c.* 4 Hz.

The reaction was the same irrespective of whether BF_4^- or BPh_4^- counterions were used.

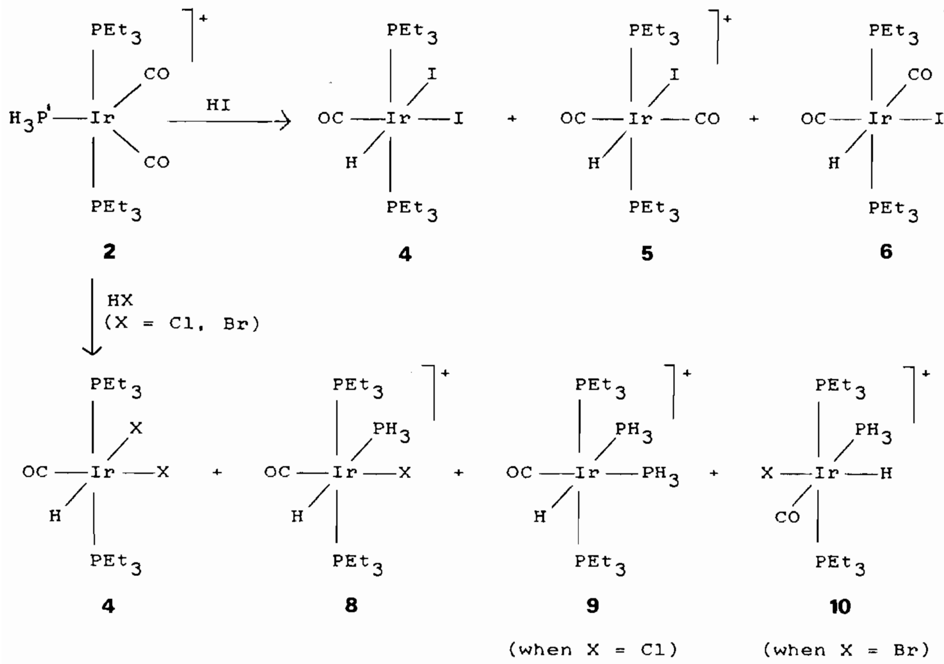
Reactions of 2 (Scheme 2)

Reaction with HCl

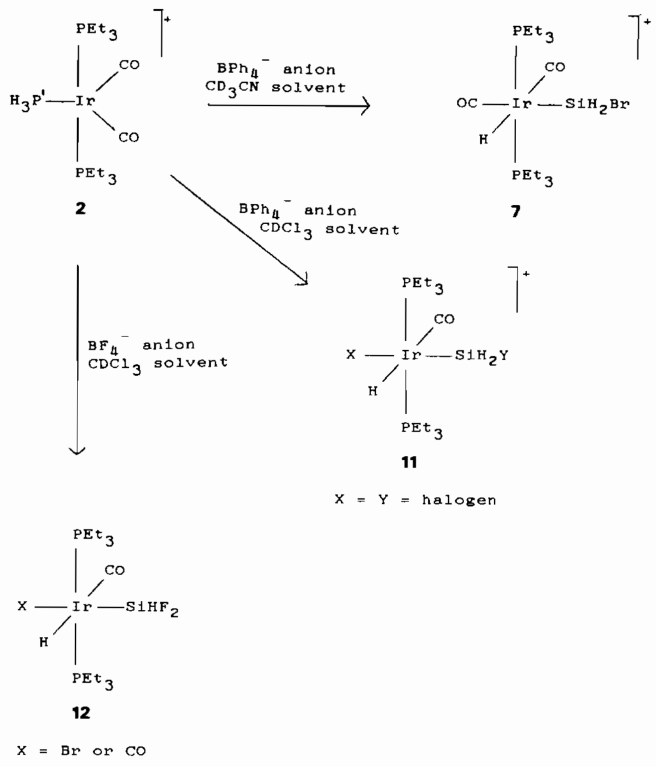
Reaction of **2** with HCl in a 1:1 molar ratio gave rise to **4**, the two known PH_3-containing species **8** and **9** [8], and a little free phosphine as shown by their ^{31}P and ^{1}H NMR spectra. Free CO was also present.

Reaction with HBr

The main product of the reaction of **2** with HBr was the dibromo analogue of **4**. PH_3, the bromide analogue of **8** and its known isomer **10** [13] were also observed.



Scheme 2. Reactions of **2** with HX.



Scheme 3. Reactions of 2 with SiH_3Br.

Reaction with HI

The reaction of **2** with HI differed from those with HCl and HBr in that no PH_3-containing species were observed. The iodide analogue of **5** was the dominant product with minor amounts of the diiodide analogue of **4** and only traces of the iodide analogue of **6**. Much free PH_3 was also present.

Reactions with SiH_3Br (Scheme 3)

The reactions of **2** with SiH_3Br were found to be influenced by the nature of the counterion and the solvent. Using BPh_4^- as anion and CD_3CN as solvent, **7** is produced cleanly and PH_3 displaced. Using BPh_4^- and $CDCl_3$ solvent, compound **11** is formed with ^{31}P and ^{1}H parameters very similar to species of the type shown where X and Y are various halides [7]. By means of ^{13}C labelling and NMR, **11** was found to contain only one CO ligand with a large (therefore *trans*) ^{2}J(CH) coupling (41 Hz), which is consistent with a structure of the type shown but the nature of the halogens present could not be determined. Some $Ir(CO)Br_2H(PEt_3)_2$, **7** and free PH_3 were also present.

When BF_4^- anion was used in $CDCl_3$ solvent, fluorination of the silyl group occurred giving rise to a species **12** whose ^{1}H, ^{31}P and ^{19}F NMR spectra were almost indistinguishable from the species $Ir(CO)ClH(SiHF_2)(PEt_3)_2$, with H *trans* to CO, formed in the reaction of $IrCl(CO)(PEt_3)_2$ with SiH_2F_2 [12] but with slightly different chemical shifts. Some **7** and **11** were also formed. **12** was also made by reacting PH_3 with the BF_4^- salt of **7** in $CDCl_3$; it is probably analogous to $Ir(CO)ClH(SiHF_2)(PEt_3)_2$ but with either Br or CO in place of Cl.

Discussion

1 is highly reactive towards those simple molecules that were examined. Except with PH_3, which simply displaced a CO ligand, oxidative addition with loss of CO was the norm. With HX, both *cis* and *trans* isomers result. Reaction with excess HCl shows that **5** is susceptible to displacement of CO by chloride to form **4**. This would agree with Church *et al.* [1] who postulated bis-carbonyl species as intermediates in the formation of $Ir(CO)HCl_2(PMePh_2)_2$ from the $PMePh_2$ analogue of **1** and HCl.

2 was similarly reactive towards the same reagents. With HX, either CO or PH_3 could be displaced giving rise to mixtures of products. The counterion and solvent made no difference in these reactions (some of which were repeated with BPh_4^- in place of BF_4^-) but were important in the reaction with SiH_3Br. It is conjectured that PH_3 may interact with BF_4^- encouraging formation of BF_3 and F^-, either BF_3 or F^- being responsible for the fluorination of **7**. BF_3 is known to react with $[Ir(CO)HI(PEt_3)_2(SiH_2)]_2O$ giving a species with an $-SiHF_2$ group [14].

The rhodium analogue of **2** is a known species, being formed in the reaction of the trigonal bipyramidal species $[Rh(CO)(PH_3)_2(PEt_3)_2]^+$ with CO [12]. This and **2** both exhibit sharp resonances with clearly resolved couplings in their ^{31}P and ^{13}C NMR spectra at room temperature in contrast to $[Rh(CO)(PH_3)_2(PEt_3)_2]^+$. The ^{31}P and ^{13}C NMR resonances of this latter species broaden reversibly on warming to room temperature, the chemical shifts remaining constant but all couplings being lost showing it to be a much more fluxional species on the NMR timescale than either of the mono-phosphine compounds. $[Ir(CO)(PH_3)_2(PEt_3)_2]^+$ is also known to exist [8] but is stable only up to 220 K at which temperature its resonances are still sharp.

The trends in ^{1}H NMR parameters confirm previous observations. Thus hydride chemical shifts move to high frequency as the *trans* halide gets heavier or to low frequency if the halide is *cis* to hydride, the latter effect being much weaker than the former [7]. The ^{13}C chemical shifts moved to lower frequency with heavier halogens. Literature data is sparse on this topic but Sanger [15] reported the reverse trend for ^{13}C chemical shifts in $RhX(CO)_2(PPh_3)_2$ and no clear trend for $RhX(CO)(PPh_3)_2$, (X = Cl, Br, I). Similar results were reported for $[trans\text{-}PtX(CO)(PPh_3)_2]^+$ [16]. The factors affecting ^{13}C chemical shifts in transition metal complexes are known to be complex and poorly understood [10].

The observation that *cis* $^2J(CX)$ ($X = P, H$) couplings tend to be small and *trans* ones large [17, 18], is well borne out by the data here. $^2J(CH)$ couplings fall into two very distinct groups, 4.0–6.7 and 37.4–58.6 Hz, these being interpreted as *cis* and *trans* couplings, respectively. These assignments agreed with assignments of ligands (halide or CO) *trans* to hydride made on the basis of the hydride chemical shift, making this parameter a useful method for determining structural geometry.

Experimental

Conventional vacuum and Schlenk line techniques were used to handle volatile compounds and air-sensitive materials. NMR spectra were recorded using Bruker WP200 (^{31}P, ^{13}C) and Bruker WP80 (^1H, ^{19}F) spectrometers. Reactions were conducted in sealed NMR tubes using standard procedures [13]. A total of 0.1 mmol of **1** or **2** was placed in an NMR tube and attached to the vacuum line. After evacuation, solvent was condensed in, the starting material dissolved and the solution frozen with liquid nitrogen. The appropriate quantity of gaseous reactant (PH_3, HX or SiH_3Br) was then condensed in and the tube sealed. **1** was prepared by the method of Church *et al.* [1], ^{13}C labelling being achieved by using labelled carbon monoxide in place of normal CO. **2** was isolated as a white powder by removing the solvent from the reaction mixture and triturating the residue with diethyl ether [12]. *Anal.* Calc.: C, 27.8%, H, 5.5; N, 0. Found: C, 27.5; H, 5.6; N, 0%. Main IR bands (cm^{-1}, nujol mull): 2020(w), 2000(m), 1970–1900(broad), 1180–900(v. broad), 757(m), 570(w). An attempt at FAB mass spectroscopy gave a spectrum too complex to be readily interpreted.

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