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^{13}C NMR studies of silyl and germyl complexes of rhodium and iridium containing carbonyl ligands

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Abstract

Oxidative additions of simple silanes and germanes of the type $\text{MH}_{4-n}\text{X}_n$, in which $\text{M} = \text{Si}, \text{Ge}$; $\text{X} = \text{halogen}$, to complexes of the type $\text{M}(\text{CO})\text{X}(\text{PEt}_3)_2$, where $\text{M} = \text{Rh}, \text{Ir}$; $\text{X} = \text{halogen}$ had previously been thought frequently to proceed in a *trans* fashion to give species with hydride *trans* to silyl or germyl. By using material enriched with ^{13}C in the carbonyl position and studying the couplings between carbonyl and hydride by ^{13}C NMR spectroscopy, we have found, in all the cases examined, that hydride is in fact situated *cis* to silyl or germyl and not *trans*. The same was found to be the case for the reaction of SiH_2F_2 with $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$, which had not previously been investigated.

That silanes and germanes oxidatively add to Vaska's compound has been known for many years [1,2] but the insolubility of the products and the difficulty of crystallizing them has hampered their investigation. Most of the evidence for their structures has come from IR spectroscopy, which is not a reliable technique for this purpose [3], but studies involving use of optically active silanes $\text{R}_3\text{Si}^*\text{H}$ showed that Vaska's complex promotes $\text{Si}^*\text{H}/\text{Si}^*\text{D}$ exchange with complete retention of configuration of Si, and this was interpreted as evidence for a *cis* concerted addition of the silane to Vaska's compound [2].

Other workers have also found that oxidative addition of silanes to iridium substrates gives rise to products in which the hydride is *cis* to the silyl ligand; for example, silane addition to IrClL_3 ($\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{AsPh}_3$) to give $\text{IrHCl}(\text{SiR}_3)\text{L}_n$, where $n = 2$ or 3 [4], and addition of silane to $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ to give $\text{IrH}_2(\text{CO})(\text{SiR}_3)(\text{PPh}_3)_2$ [5].

Much less is known about silyl or germyl complexes of rhodium. Their tendency to dissociate at or below room temperature and the consequent difficulty of isolating them has hindered their characterization [6]. NMR spectroscopy is the

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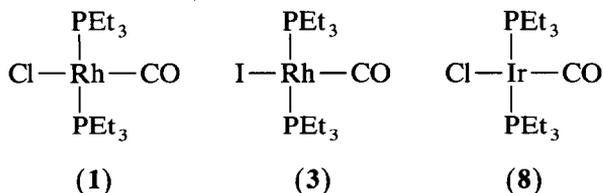
most useful technique in this case, the magnitudes of the various coupling constants giving information about the relative positions of the ligands [7].

It has been shown previously that in the NMR spectra of transition metal complexes, *cis* $^2J(CX)$ ($X = P, H$) couplings tend to be small and *trans* ones large [8,9]. The same effect is well known for $^2J(PX)$ ($X = P, H$) couplings [10,11] and, particularly in platinum metal systems, is a reliable guide to molecular geometry. In the course of research at the University of Edinburgh, a range of silyl and germyl complexes of rhodium and iridium have been prepared and their structures determined by 1H and ^{31}P NMR spectroscopy. In the case of the silyl complexes, it had been believed that in the majority of cases, the hydride lay *trans* to the silyl group. This assignment was made because the magnitude of the coupling $^3J(HMSiH)$ (typically 2–5 Hz) was greater than that in the corresponding germyl complexes in which the coupling, if resolved, was often less than 1 Hz. These values were therefore assumed to represent *trans* and *cis* couplings, respectively [3,7]. Three-bond couplings, however, depend on the rotational angle and are much less reliable than two-bond couplings as guides to geometry.

The aim of this study was to use the carbonyl-to-hydride coupling to determine the position of the carbonyl group relative to the hydride and hence relative to the silyl or germyl group. The reactions were carried out under the same conditions of temperature and solvent as used by the original workers but with ^{13}C -enriched starting materials. The original 1H and ^{31}P NMR data for the compounds may be found in the references given and is not repeated here.

Results

Starting materials



Reaction of $RhCl(CO)(PEt_3)_2$ (1) with SiH_3Cl

This reaction, carried out in toluene at 203 K, was believed to give product 2 [7]. The chemical shift of the hydride was -8.9 ppm, consistent with hydride *trans* to CO or silyl but not to chloride [12]. The ligand *trans* to hydride was identified as SiH_2Cl from the relatively large value (5.5 Hz) of $^3J(HH')$.

The reaction was repeated using 1 *ca.* 70% enriched with ^{13}C in the carbonyl position. The ^{31}P and 1H NMR spectra confirmed that the expected product had been generated. The hydride resonance in the proton spectrum was broad and unresolved. The carbonyl region of the ^{13}C - $\{^1H\}$ spectrum showed a doublet of triplets at $+175.7$ ppm. On retention of proton coupling, this became a doublet of doublets of triplets; the new doublet coupling was large (53 Hz), indicating that the CO group was *trans* to the hydride. The silyl group must therefore be *trans* to halide and not (as previously proposed) to hydride; the $^3J(HH')$ coupling of 5.5 Hz is actually a *cis* coupling.

Reaction of $RhI(CO)(PEt_3)_2$ (**3**) with GeH_3I

This reaction, in toluene at 203 K, had been found to give two products, which were assigned the structures **4** and **5** [7]. The chemical shifts of the hydride protons were -10.0 ppm for compound **4** and -12.1 ppm for compound **5**. The value for **5** is consistent with H *trans* to I, while that for **4** is consistent with H *trans* to CO or Ge but not to I. The $^3J(HH')$ couplings seemed to bear this out. For **4**, the coupling was 6.0 Hz, but no such coupling was resolved for **5**.

Repetition of the reaction using ^{13}C -enriched **3** gave the same two products, as confirmed by their ^{31}P and 1H NMR spectra. The hydride signals in the 1H spectrum were broad and poorly resolved, but that from compound **4** at -10 ppm clearly showed a large doublet coupling, suggesting a *trans* CO ligand.

The carbonyl region of the $^{13}C\{-^1H\}$ spectrum consisted of two doublets of triplets, as would be expected for the two isomers **4** and **5**. On retention of proton coupling these each showed very different additional couplings. The higher frequency resonance, due to **5**, became a doublet of doublets of triplets, the new doublet splitting being 55 Hz, indicating a *trans* hydride. The other resonance became a doublet of multiplets too complex to be accounted for if the only new splitting was a doublet. Presumably coupling to the protons in the germyl group was also resolved. It was not possible to measure the coupling to hydride accurately, but it was less than 10 Hz and therefore a *cis* coupling.

The previously assigned structure of **5**, with hydride *cis* to CO and *trans* to I, is probably correct. The structure of **4** is wrong. From the magnitude of $^3J(CH)$, the hydride must be *trans* to CO, and therefore *cis* to Ge and iodide.

The reaction of **3** with SiH_4

The reaction of **3** with silane in toluene at 203 K gave one product, believed to be either **6** or **7** [7]. The chemical shift of the hydride (-9.4 ppm) was consistent with either structure, but $^3J(HH')$, such as might be expected for structure **6**, was not observed.

Repetition of the reaction but with ^{13}C -enriched **3** gave the same product, as confirmed by ^{31}P and 1H NMR. Again, the resonances in the proton spectrum were poorly resolved but the hydride showed what appeared to be a large (*ca.* 50 Hz) coupling. The $^{13}C\{-^1H\}$ NMR spectrum showed the expected doublet of triplets in the carbonyl region; on retention of proton coupling, this became a doublet of doublets of triplets of narrow quartets. The new doublet coupling was *ca.* 51 Hz, showing that the hydride was *trans* to CO as in structure **7**. The quartet coupling (*ca.* 3 Hz) presumably represents coupling to the protons bound to silicon.

Reaction of $IrCl(CO)(PEt_3)_2$ (**8**) with GeH_4

The reaction of germane with **8** in benzene at room temperature was reported to give two products, **9** and **10** [3]. The hydride in **10** (the dominant product) resonates at -16.3 ppm in the proton spectrum, suggesting that it was *trans* to chloride. The hydride in **9** resonates at -10.5 ppm, a value typical of hydride *trans* to either CO or Ge. The $^3J(HH')$ couplings were 0.5 Hz for **10** and 2.6 Hz for **9**. Since the latter was much larger than the former, it was concluded that the larger coupling was a *trans* and the smaller one a *cis* coupling. Hydride was therefore judged to be *trans* to Ge in **9** and *cis* to Ge in **10**.

The same two products were obtained when the reaction was repeated using **8**, 99% enriched with ^{13}C in the carbonyl position. In the proton spectrum, the hydride resonance due to **10** was a triplet of doublets; the doublet coupling ($^2J(\text{HC})$) was small (4 Hz), showing that the hydride was *cis* to carbonyl, as expected. The $^3J(\text{HH}')$ coupling could be resolved only by using a very narrow spectral width.

The hydride resonance due to **9** showed a wide doublet coupling (45 Hz), showing that the hydride was *trans* to CO and not *cis* as previously supposed. The $^3J(\text{HH}')$ coupling (2.6 Hz) for this compound must therefore be a *cis* coupling.

The $^{13}\text{C}\{-^1\text{H}\}$ spectrum, in the CO region, showed two triplets. On retention of proton coupling, the high frequency resonance became a doublet of triplets of quartets. The doublet splitting was 44.8 Hz, suggesting a *trans* hydride. The quartet splitting $^3J(\text{C IrGeH})$, was 2.4 Hz. The other resonance, which was also the dominant one (and so presumably due to **10**), became a multiplet too complex to be readily interpreted. It would be expected to contain doublet, triplet and quartet splittings.

The $^2J(\text{CH})$ couplings observed in the ^{13}C and ^1H spectra confirm that in **10**, the hydride is *cis* to CO but show that in **9** the hydride is actually *trans* to CO. In both cases $^3J(\text{CH}')$ is observed even though the carbonyl group is *trans* to germanium in only one of the compounds.

Reaction of $\text{IrX}(\text{CO})(\text{PEt}_3)_2$ with SiH_3Y

Reaction of $\text{IrX}(\text{CO})(\text{PEt}_3)_2$ ($\text{X} = \text{Cl, I}$) with SiH_3Y ($\text{Y} = \text{H, Cl, Br, I}$) in toluene was previously thought to give rise to a series of compounds of the type **11** in which hydride was believed to be *cis* to halide (on account of the chemical shift values) and *trans* to Si on account of the magnitude of $^3J(\text{HH}')$ (typically around 3–4 Hz) [3].

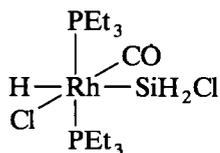
Two of these reactions ($\text{X} = \text{Y} = \text{Cl}$; $\text{X} = \text{I}$ and $\text{Y} = \text{Br}$) were repeated using starting material 99% enriched with ^{13}C in the carbonyl position. Each gave the expected product (confirmed by ^1H and ^{31}P NMR), and in each case the hydride resonance in the ^1H spectrum showed an additional doublet coupling of around 40 Hz, revealing that the carbonyl group was *trans* to hydride and not *cis* as previously supposed.

The ^{13}C NMR spectra confirmed these findings. When proton decoupled, the CO group in each compound gave rise to a triplet. On retention of ^1H coupling, doublets of triplets resulted, with $^2J(\text{CH}) = ca. 40$ Hz.

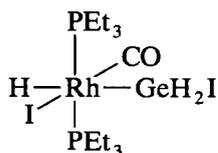
*The reaction of **8** with SiH_2F_2*

This reaction was originally carried out by one of the authors (S.M.) using unenriched materials and found to give two products **12** and **13**. Because this reaction has not been reported before, it is necessary to describe the original spectra obtained using non-enriched **8**. The reaction of **8** with an equimolar amount of SiH_2F_2 was carried out at room temperature in CDCl_3 in a sealed NMR tube. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum showed that two products were present; the dominant one, **12**, gave rise to a triplet (coupling to two F nuclei) at -1.4 ppm and the other to a quartet (coupling to three equivalent fluorines) at -1.2 ppm.

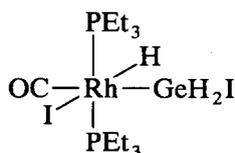
Structures as originally assigned



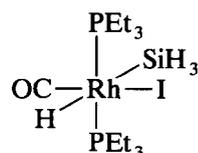
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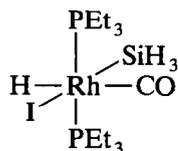
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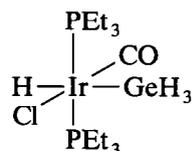
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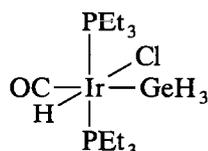
(6)



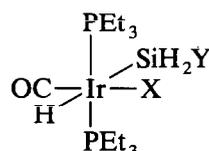
(7)



(9)



(10)



(11)

The proton spectrum showed two hydride resonances. The stronger one, at -8.1 ppm, was a triplet of triplets of doublets, as would be expected for a hydride coupling to two equivalent PEt_3 groups, two equivalent fluorines, and the hydrogen bound to silicon. The other hydride resonance, at -8.5 ppm, was a triplet of quartets. This would be expected for a hydride coupling to two equivalent PEt_3 groups and to the three equivalent fluorines in a $-\text{SiF}_3$ group, and is consistent with the quartet splitting seen in the ^{31}P spectrum.

There was also a triplet of quartets at $+6.4$ ppm with ^{29}Si satellites. The triplet coupling was 69 Hz. Irradiation of the hydride resonance at -8.1 ppm turned the quartets into triplets, showing that they were actually overlapping doublets of triplets. There were no other SiH resonances in this region of the ^1H spectrum, and so this resonance is assigned to the SiH proton of **12**.

The ^{31}P and ^1H spectra therefore indicated the presence of two compounds, each with a hydride, one with a $-\text{SiHF}_2$ group, the other with a $-\text{SiF}_3$ group. The chemical shifts of the hydrides were consistent with their being *trans* to either CO or Si but not Cl.

The ^{19}F NMR spectra were consistent with these findings. The $^{19}\text{F}\{-^1\text{H}\}$ spectrum showed two narrow triplets with ^{29}Si satellites. On retention of proton coupling these became a doublet of triplets (compound **12**) and a doublet of doublets of triplets (compound **13**), the latter having a large doublet coupling of 69 Hz.

The tendency for fluorosilanes to disproportionate when reacting with platinum metals and to give mixtures of products has been noted before [13].

The reaction was repeated using **8** with 99% ^{13}C in the carbonyl position. The resonances in the ^{31}P , ^1H and ^{19}F spectra all (with the exception of the SiH resonance in the ^1H spectrum) showed an extra doublet coupling. The hydride resonances in the proton spectrum each showed a new doublet coupling of *ca.* 40 Hz, showing that the hydrides were *trans* to carbonyl. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum showed two resonances in the carbonyl region: a triplet of quartets, as would be expected for **13**, and a triplet of triplets, as would be expected for **12**. On retention of proton coupling, these each acquired a large (*ca.* 40 Hz) doublet coupling.

Table 1

¹H, ³¹P and ¹⁹F NMR parameters for compounds **12** and **13**^a

Compound	$\delta(\text{P})$	$\delta(\text{H})$	$\delta(\text{H}')$	$\delta(\text{F})$
12	-1.4	-8.1	+6.4	-106.5
13	-1.2	-8.5		-92.4
	$^2J(\text{PH})$	$^3J(\text{PH}')$	$^3J(\text{PF})$	$^2J(\text{H}'\text{F})$
12	15.4	8.1	3.9	68.9
13	14.8		1.9	
	$^3J(\text{HH}')$	$^3J(\text{HF})$	$^1J(\text{H}'\text{Si})$	$^1J(\text{FSi})$
12	4.1	7.7	245.3	331
13		8.6		336

^a Chemical shifts in ppm, positive to high frequency of SiMe₄ (for ¹H), H₃PO₄ (for ³¹P), CCl₃F (for ¹⁹F). Coupling constants in Hz. Solvent = CDCl₃, temperature = 298 K.

Table 2

¹³C NMR parameters for the compounds described^a

Compound	δC	$^1J(\text{CRh})$	$^2J(\text{CP})$	$^2J(\text{CH})$	$^3J(\text{CH}')$	$^3J(\text{CF})$
2	+175.7	49.1	10.5	53.1	n.o.	
4	+190.6	48.2	10.5	55.1	n.o.	
5	+185.4	51.5	11.0	n.d.	n.o.	
7	+190.8	48.9	10.8	ca. 51	ca. 3	
9	+178.6		7.2	44.8	2.4	
10	+173.3		8.6	3.7	3.6	
11 ^b	+176.1		7.4	41.6	0.5	
11 ^c	+174.7		7.9	39.6	n.o.	
12	+176.4		7.4	41.5	n.o.	3.8
13	+175.4		7.3	43.1		2.2

^a Chemical shifts in ppm, positive to high frequency of SiMe₄. Coupling constants in Hz. n.o., not observed; n.d., not determined (but < 10 Hz). Solvent, C₇D₈ except for **12** and **13** for which solvent was CDCl₃. Temperature, 203 K for **2**–**7**, 298 K for **9**–**13** inclusive. ^b X = Y = Cl; ^c X = I, Y = Br.

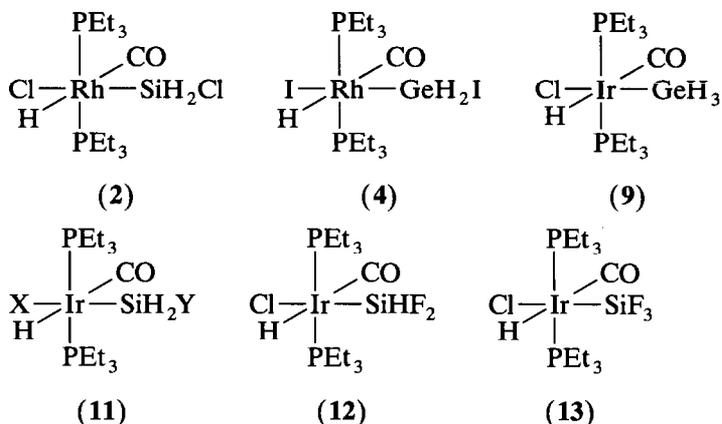
It was therefore concluded that in each case, the hydride was located *trans* to the carbonyl. The ³¹P, ¹H and ¹⁹F NMR parameters of **12** and **13** are listed in Table 1. The ¹³C NMR parameters of all the products described in this paper are listed in Table 2.

Discussion

In all the silyl and germyl systems studied, the hydride was found to be *trans* to either carbonyl or halide. In no case could it be demonstrated that it lay *trans* to Si or Ge. In most cases the hydride is *trans* to the carbonyl as shown by the large size of the coupling (typically *ca.* 40–50 Hz). In just two cases, it was found to be *cis* to carbonyl. In one of these $^2J(\text{CH})$ was 3.7 Hz; in the other it could not be determined but was certainly < 10 Hz. The *cis* $^2J(\text{CH})$ couplings in 22 other Rh and Ir complexes were previously shown to have values ranging from 0 to 6.7 Hz [14]. In many of these, it was known from independent evidence (³¹P and ¹H

NMR) that the carbonyl ligands were *cis* to hydride. In view of the fact that the two groups of $^2J(\text{CH})$ values are very distinct from each other, this method of determining the *cis/trans* relationships of hydride and CO ligands has great potential, and has been used previously for related systems. In three isomers of $\text{IrBr}(^{13}\text{CO})\text{H}(\text{SiR}_3)(\text{DPPE})$, where $\text{R} = \text{OEt}$, hydride was always *cis* to Si but could be either *cis* or *trans* to ^{13}CO . Two *cis* $^2J(\text{CH})$ couplings of 4.6 Hz and a *trans* $^2J(\text{CH})$ coupling of 42.8 Hz were observed [15].

Structures determined in the light of ^{13}C NMR data



Compounds 5, 7 and 10 remain unchanged; 2, 4, 9 and 11 have been revised and 6 eliminated.

As with the examples given in the introduction, the oxidative addition reactions of silyl or germyl compounds studied in this paper all seem to proceed in a *cis* fashion. This is consistent with the now generally accepted view that such reactions proceed via a concerted *cis* mechanism, the silane approach to the metal centre being nucleophilic and the reaction stereoselective [15].

In the silyl and germyl complexes described here, coupling between the carbonyl ligand and the hydrogens on the silicon or germanium was sometimes observed. Values ranged from 0 to 4.1 Hz and, although examples were few, observation of this coupling did not appear to be dependent on whether the carbonyl was *cis* or *trans* to the silyl or germyl group.

The $^3J(\text{HH}')$ values reported in the literature for these compounds vary greatly ranging from 0 to 6 Hz. The larger ones were assumed to arise from *trans* couplings but from the work described here it is now known that even 6 Hz is a possible value for a *cis* $^3J(\text{HH}')$ coupling. In the absence of any data for $^3J(\text{HH}')$ for cases in which it is known that hydride is *trans* to Si or Ge, the magnitude of this coupling does not seem to be a reliable guide to molecular geometry, and many structure assignments made on the basis of this parameter may have to be revised.

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. Iridium starting materials were prepared from the complex $[\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4]$ by treatment with CO and PEt_3 in acetone [17]. ^{13}C may be used instead of normal CO [14]. Rhodium starting materials were made as described by Chatt and Shaw [18], ^{13}C -labelling being achieved by shaking an acetone solution of the product for several hours under an atmosphere of ^{13}C CO [14]. Reactions were conducted in sealed NMR tubes by standard procedures [19].

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References

- 1 A.J. Chalk, *Chem. Commun.* (1969) 1207.
- 2 L.H. Sommer, J.E. Lyons and H. Fujimoto, *J. Am. Chem. Soc.*, 91 (1969) 7051.
- 3 E.A.V. Ebsworth and T.E. Fraser, *J. Chem. Soc. Dalton Trans.*, (1979) 1960.
- 4 M.A. Bennett, R. Charles and P.J. Fraser, *Aust. J. Chem.*, 30 (1977) 1201.
- 5 J.P. Fawcett and J.F. Harrod, *J. Organomet. Chem.*, 113 (1976) 245.
- 6 F. de Chartenay, J.A. Osborne and G. Wilkinson, *J. Chem. Soc. A* (1968) 787.
- 7 E.A.V. Ebsworth, M.R. Ojeda and D.W.H. Rankin, *J. Chem. Soc., Dalton Trans.*, (1982) 1513.
- 8 A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, 83 (1961) 525.
- 9 B.E. Mann, *Adv. Organomet. Chem.*, 12 (1974) 135.
- 10 F.B. Ogilvie, J.M. Jenkins and J.G. Verkade, *J. Am. Chem. Soc.*, 92 (1970) 1916.
- 11 J.M. Jenkins and B.L. Shaw, *J. Chem. Soc. A*, (1966) 1407.
- 12 J. Chatt, N.P. Johnson and B.L. Shaw, *J. Chem. Soc.*, (1964) 1625.
- 13 S.G.D. Henderson, M.Phil. Thesis, University of Edinburgh, 1980.
- 14 S. Moreton, Ph.D. Thesis, University of Edinburgh, 1989.
- 15 C.E. Johnson and R. Eisenberg, *J. Am. Chem. Soc.*, 107 (1985) 6531.
- 16 G.W. Parshall, *Inorg. Synth.*, 15 (1974) 19.
- 17 T.E. Fraser, Ph.D. Thesis, University of Edinburgh, 1977.
- 18 J. Chatt and B.L. Shaw, *J. Chem. Soc. A*, (1966) 1437.
- 19 E.A.V. Ebsworth, R.O. Gould, R.A. Mayo and M. Walkinshaw, *J. Chem. Soc., Dalton Trans.*, (1987) 2831.