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Synthesis and Reactions of $[M(CO)_4(Ph_2PSiMe_3)X]$ Complexes (M = Mn, Re; X = Halogen)

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Abstract

The silylphosphine ligand Ph_2PSiMe_3 reacts readily with a slurry of $[Re(CO)_5X]$ (X = Cl, Br) in polar and in non-polar solvents to yield soluble *cis*-$[Re(CO)_4(Ph_2PSiMe_3)X]$ (**Ia**, X = Cl; **Ib**, X = Br) via CO substitution. Compound **I** is readily hydrolyzed by water or silica gel to *cis*-$[Re(CO)_4(Ph_2PH)X]$. Compound **Ib** reacts with $[Re(CO)_5Br]$ to yield $[Re_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**II**), and with $[Mn(CO)_5Br]$ to yield $[MnRe(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**III**).

The reaction of Ph_2PSiMe_3 with $[Mn(CO)_5X]$ (X = Cl, Br, I) is highly dependent upon reaction conditions. In polar and in non-polar solvents, an excess of ligand gives mainly *cis*-$[Mn(CO)_4(Ph_2PSiMe_3)X]$ (**IVa**, X = Cl; **IVb**, X = Br; **IVc**, X = I). With ligand: $[Mn(CO)_5X]$ reacting ratios in the range 0.5–1.0:1, the products from the three respective halomanganese complexes in THF were: (a) mainly $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (**Va**); (b) both $[Mn(CO)_4(Ph_2PSiMe_3)Br]$ and $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**Vb**); and (c) exclusively $[Mn(CO)_4(Ph_2PSiMe_3)I]$. The compounds **IVa–c** are stable in solution at ambient temperatures and are readily hydrolyzed by water or methanol to $[Mn(CO)_4(Ph_2PH)X]$. Compound **IVb** reacts at room temperature with $[Mn(CO)_5Cl]$ to yield only $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**Vb**); compound **IVc** reacts in hot toluene with $[Mn(CO)_5Cl]$ to yield mainly $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}I)]$ (**Vc**), together with a small amount of the chloro-bridged analog.

The dinuclear species **II**, **III** and **Va–c** appear to be formed mainly via an intermolecular elimination of Me_3SiX from the appropriate $[M(CO)_4(Ph_2PSiMe_3)X]$ and metalpentacarbonylhalide (chloride or bromide) complexes.

Introduction

The potential utility of phosphido-bridged polynuclear species as possible multi-site catalysts is an area of substantial current interest [1]. On the one hand, bridging ligands may inhibit cluster fragmentation [1c, 1e–h], or, alternatively, ligand lability may provide routes to active site formation [1a, g, i, j] and to the formation of novel dynamic polynuclear systems [1b].

Several procedures for the synthesis of phosphido-bridged complexes have been described [1j, 2]. In this paper, we report our studies of the reactions of Ph_2PSiMe_3 with $[M(CO)_5X]$ (M = Mn, Re; X = halogen), and the general properties of the new complexes $[M(CO)_4(Ph_2PSiMe_3)X]$, $[M_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}X)]$ and $[MnRe(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$.

Discussion

The reaction of Ph_2PSiMe_3 with $[M(CO)_5X]$ (M = Mn, Re; X = halogen) in refluxing dimethoxyethane (DME) was reported to yield $[M(CO)_4PPh_2]_2$ (M = Mn, Re) and $[Mn(CO)_3PPh_2]_3$ [3a]. None of the possible intermediates – $[Mn(CO)_4(Ph_2PSiMe_3)X]$, $[M(CO)_{4,5}(PPh_2)]$, or $[(X)(CO)_4M(\mu\text{-}PPh_2)M(CO)_4(Ph_2PSiMe_3)]$ – were detected by the earlier workers. Thus, the details of the reaction pathway(s) leading to the claimed phosphido-bridged products have remained a mystery. Reactions between $P(EMe_3)_3$ (E = Ge, Sn) and $[Mn(CO)_5X]$ have also been reported to yield dinuclear $[Mn(CO)_4P(EMe_3)_2]_2$ [3b].

In our studies of the reaction of Ph_2PSiMe_3 with slurries of $[Re(CO)_5X]$ (X = Cl, Br) in hexane, benzene, toluene, THF and DME at ambient temperatures, we observed the formation of *cis*-$[Re(CO)_4(PPh_2SiMe_3)X]$ (**Ia**, X = Cl; **Ib**, X = Br). The free ligand and compounds **Ia,b** are extremely sensitive to moisture, so that the pale yellow solid products obtained upon removal of solvent were invariably contaminated with $[Re(CO)_4(Ph_2PH)X]$ [4]. When **Ia** and **Ib** were chromatographed on silica gel, with benzene as the eluant, the latter secondary phosphine complexes were obtained in high yield. Compounds **Ia,b** were characterized by IR, ^1H and ^{31}P NMR spectroscopy (see 'Experimental'). Compounds **Ia,b** are stable in solution at ambient temperatures but, at elevated temperatures, highly insoluble products were formed. These products showed infrared bands in the

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ν(CO) region that have been ascribed in the literature to the dimer $[Re(CO)_4PPh_2]_2$ [3a]; on the basis of later evidence, it appears that this product may consist of an equilibrium mixture of polynuclear species [5].

When combined with $[Re(CO)_5Br]$ and with $[Mn(CO)_5Br]$, $[Re(CO)_4(Ph_2PSiMe_3)Br]$ gave the dinuclear species $[Re_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**II**) and $[MnRe(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**III**), respectively. Compounds **II** and **III** were characterized by IR, ^{31}P and mass spectroscopy. The IR spectra of compound **II** and the related $[Re_2(CO)_8(\mu\text{-}P(CF_3)_2(\mu\text{-}X)]$ [6] compounds show five major strong ν(CO) bands, in a pattern indicative of their structural similarities, *viz.*, equivalent C_1 '$M(CO)_4$', units linked by halogen and phosphido bridges. The mixed metal complex $[MnRe(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**III**), containing inequivalent '$M(CO)_4$' units, showed only six resolvable ν(CO) bands. The IR spectra of $[Re(CO)_8X_2]$ (X = Cl, Br, I) [7], and $[Re_2(CO)_8(PPh_2)_2]$ [3a] show four major bands. The ^{31}P chemical shifts of **II** and **III** are typical for phosphido-bridged structures that do not contain a metal–metal bond [8].

The reactions of Ph_2PSiMe_3 with $[Mn(CO)_5X]$ (X = Cl, Br, I) were monitored by IR (ν(CO) region) and NMR (^1H and ^{31}P) spectroscopy, using various ligand-to-complex molar ratios in the solvents hexane, d_6-benzene, toluene, THF and DME. In polar solvents, rapid evolution of gas bubbles was observed and deep red solutions were formed. The toluene solutions reacted more slowly and showed variable induction periods before CO evolution was apparent. The hexane solutions reacted even more slowly at room temperature, being substantially incomplete even after two days. Under comparable conditions in hexane solution, it was found that the reaction of Ph_2PSiMe_3 with $[Mn(CO)_5Cl]$ was much slower than the reaction of Ph_3P. The more rapid reaction of Ph_2PSiMe_3 with $[Mn(CO)_5X]$ in polar solvents is noteworthy and is in contrast to reports that tertiary phosphines in general react more rapidly in non-polar media [5, 9]. In addition, the rates of substitution of CO by Ph_2PSiMe_3 vary in the order $Cl > Br > I$ in polar solvents, similar to relative rates of substitution by tertiary phosphines [9].

As noted above, the complete removal of Ph_2PH from Ph_2PSiMe_3 was difficult to achieve (but usually less than 5%, based on ^{31}P NMR signal integrals). It was found, however, that the secondary phosphine reacted more rapidly in hexane with $[Mn(CO)_5X]$ than Ph_2PSiMe_3, yielding $[Mn(CO)_4(Ph_2PH)X]$ [4, 10] and, occasionally, $[Mn(CO)_3(Ph_2PH)_2X]$ [10].

The products in solution resulting from the silylphosphine–$[Mn(CO)_5X]$ reactions were identified as *cis*-$[Mn(CO)_4(Ph_2PSiMe_3)X]$ (**IVa**, X = Cl; **IVb**, X = Br; **IVc**, X = I), $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}X)]$ (**Va**, X = Cl; **Vb**, X = Br; the iodo analog **Vc** was not observed) and traces of $[Mn_2(CO)_8(\mu\text{-}H)(\mu\text{-}PPh_2)]$ [2p, 11]. Compounds **IVa–c** were identified in solution by IR and NMR (^1H and ^{31}P) spectroscopy and by their essentially quantitative hydrolysis to $[Mn(CO)_4(Ph_2PH)X]$ [4, 10]. Compound **Vc**, $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}I)]$, was prepared in a separate experiment, via the reaction of **IVc** with $[Mn(CO)_5Cl]$. The complexes **Va–c** were characterized by IR, NMR and mass spectroscopy. Their IR spectra (ν(CO) region) showed a weak high energy band and four other strong bands, in a pattern very similar to those of $[Mn_2(CO)_8(\mu\text{-}P(CF_3)_2(\mu\text{-}X)]$ [12] and the (μ-X)(μ-phosphido)–dirhenium analogs. The relative proportions of **IV** and **V** were found to vary, depending on nature of solvent, relative amount of ligand present, nature of halogen 'X' and time of reaction. In all cases, dark brown components which could not be eluted from silica gel chromatographic columns were also obtained.

The reaction of $[Mn(CO)_5Cl]$ with excess ligand gave mainly compound **IVa** in polar and in nonpolar solvents, whereas a deficiency of ligand gave rise to appreciable quantities of **Va** as well as **IVa**; the latter apparently reacts with $[Mn(CO)_5Cl]$ to yield **Va**. The formation of **Va** was favored in polar solvents.

The reaction of $[Mn(CO)_5Br]$ with equivalent and with excess amounts of Ph_2PSiMe_3 in hexane gave mainly compound **IVb**. In polar solvents, however, both **IVb** and **Vb** were observed in the early stages of the reaction, regardless of the molar ratios of reactants employed. In a separate study, it was shown that **IVb** reacts very slowly with $[Mn(CO)_5Br]$, indicating that there is another pathway to compound **Vb** in the early stages of the reaction involving Ph_2PSiMe_3. Compound **Vb** was also prepared by the reaction of $LiPPh_2$ with $[Mn(CO)_5Br]$ (1:2 molar ratio). The iodo system was different yet again, in that $[Mn(CO)_5I]$ gave only **IVc**, regardless of solvent type or reactant ratios.

In one experiment, the photolytic preparation of $[Mn(CO)_4(Ph_2PSiMe_3)Cl]$ from $Mn(CO)_5Cl$ and Ph_2PSiMe_3 was attempted. The reaction was complex, however, giving a variety of products, including short-lived paramagnetic species. The photolytic studies were therefore discontinued.

The possible role of the $[Mn(CO)_{4,3}(Ph_2PH)_{1,2}X]$ impurities as intermediates in reaction sequences leading to phosphido-bridged species was examined. In separate studies, it was found that the above complexes do not thermally eliminate HX in solution, nor do they react significantly with $[Mn(CO)_5X]$ or $[Mn(CO)_4(Ph_2PSiMe_3)X]$. For comparison, it is reported that complexes of the type $[M(CO)_n(Ph_2PH)]$ (M = Fe, Ni) undergo dehydrohalogenation with various metal halide complexes, in the presence of diethylamine, to yield mono-μ-phosphido derivatives [13], while several $[M(CO)_n(Ph_2PH)_m]$ complexes polymerize via dehydrogenation [14, 15].

On the basis of the above studies, it is evident that Ph_2PSiMe_3 reacts with $[Re(CO)_5X]$ to produce $[Re(CO)_4(Ph_2PSiMe_3)X]$ in high yields, via displacement of carbon monoxide (eqn. (1)).

$$Ph_2PSiMe_3 + M(CO)_5X \longrightarrow M(CO)_4(Ph_2PSiMe_3)X + CO \qquad (1)$$

The reactions of Ph_2PSiMe_3 with $[Mn(CO)_5X]$ are more complex than those of the rhenium analogues. The dominant primary process again appears to be displacement of CO, leading to $[Mn(CO)_4(Ph_2PSiMe_3)X]$ (**IVa–c**) via eqn. (1). Because of the greater reactivity of the manganese derivatives, condensation products are readily formed. It appears that one route to such dinuclear species involves an initial nucleophilic attack by halide (chloride and bromide, but not iodide) at the silicon center of a coordinated trimethylsilyldiphenylphosphine ligand (eqn. (2)). Evidence supporting this conclusion

$$M(CO)_4(Ph_2PSiMe_3)X + M'(CO)_5X' \longrightarrow MM'(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}X) + \text{others} \qquad (2)$$

includes: (i) The reactions of $[Mn(CO)_5Cl]$ with $[Mn(CO)_4(Ph_2PSiMe_3)X]$ ($X = Br$, **IVb**; $X = I$, **IVc**) to yield $Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}X)$ ($X = Br$, **Vb**; $X = I$, **Vc**), via the elimination of Me_3SiCl. (ii) The reactions of $[Re(CO)_4(Ph_2PSiMe_3)Br]$ (**Ib**) with $[Re(CO)_5Br]$ and with $[Mn(CO)_5Br]$, at ambient temperature, to yield $Re_2CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)$ (**II**) and $MnRe(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)$ (**III**), respectively. (iii) Attempts to trap the possible '$Re(CO)_4PPh_2$' intermediate [3a] as a saturated complex $[Re(CO)_4(L)(PPh_2)]$, by carrying out reactions in the presence of an excess of various ligands L, were unsuccessful. (iv) Hydrolysis of the coordinated Ph_2PSiMe_3 ligand occurs readily, giving complexes of Ph_2PH. In addition, the compounds $[M(CO)_4(Ph_2PSiMe_3)X]$ are relatively stable in solution at ambient temperature, indicating that the intramolecular elimination of Me_3SiX is not a favourable reaction pathway.

Contrasting with the mechanism proposed above, it is suggested in the literature [6] that the reaction of $[M(CO)_5X]$ ($M = Mn$, Re; $X =$ halogen) with $P_2(CF_3)_4$ or $As_2(CF_3)_4$ proceeds first via metal–halogen bond cleavage rather than CO substitution, giving a terminal phosphido or arsenido complex $[M(CO)_5E(CF_3)_2]$ ($E = P$, As). The latter then reacts further with $[M(CO)_5X]$ to generate $[M_2(CO)_8(\mu\text{-}E(CF_3)_2(\mu\text{-}X)]$ species. The participation of $[Mn(CO)_5PPh_2]$ in the formation of dinuclear species, in competition with halide attack at silicon (eqn. (2)), cannot be ruled out completely in our work. Such terminal phosphido species are known to dimerize or polymerize readily, unless the basic center is modified by the presence of highly electronegative substituents [16].

Experimental

Reactions were carried out under a purified nitrogen atmosphere, using conventional Schlenk and vacuum equipment and a Vacuum Atmospheres Model HE493 drybox, as appropriate. Solvents were dried and distilled under nitrogen before use. The halocomplexes $[M(CO)_5X]$ ($M = Mn$, Re; $X = Cl$, Br, I) were prepared from $[Mn_2(CO)_{10}]$ or $[Re_2(CO)_{10}]$ by reaction with halogen, according to published procedures [17, 18]. The ligand Ph_2PSiMe_3 was prepared as described in the literature [19] but, despite careful distillation, some Ph_2PH impurity was invariably present. The purity was checked by ^{31}P NMR spectroscopy.

Spectra were obtained using the Perkin-Elmer 983 infrared spectrometer, the Hewlett Packard 5985 mass spectrometer and the Brüker WM400 and Varian EM360 NMR spectrometers. The phosphorus coordination chemical shift $\Delta(\delta^{31}P)$ was evaluated as $\delta^{31}P$ (free ligand–$\delta^{31}P$ (complex). In a few cases, evolved carbon monoxide was measured by means of a Sprengle pump and its purity checked by gas chromatography.

Unless otherwise noted, reactions were performed on 0.3–0.6 mmol scales. The following selected descriptions are typical of the procedures used.

(a) $[Re(CO)_5X] + Ph_2PSiMe_3$ in Toluene and Benzene

(i) A mixture (1:1 molar ratio) of $[Re(CO)_5X]$ ($X = Cl$, Br) and Ph_2PSiMe_3 was heated until CO evolution was complete, giving a pale yellow solution. An IR spectrum of the solution showed $\nu(CO)$ bands attributable to *cis*-$[Re(CO)_4(Ph_2PSiMe_3)X]$ (**Ia**, $X = Cl$; **Ib**, $X = Br$). The solvent was removed, giving compounds **Ia**,**b** as a pale yellow solid in high yield, contaminated with *cis*-$[Re(CO)_4(Ph_2PH)X]$.

(ii) Reactions were also carried out in C_6D_6, in order to obtain ^1H and ^{31}P NMR spectra.

(iii) A mixture (2:1 molar ratio) of $[Re(CO)_5Br]$ and Ph_2PSiMe_3 in toluene was heated to reflux for 3 h. The IR spectrum showed that all of the $[Re(CO)_5Br]$ had been consumed. The solvent was removed under vacuum and the residue was dissolved in $CDCl_3$. The ^{31}P NMR spectrum showed only two phosphorus-containing compounds, $[Re(CO)_4(Ph_2PH)Br]$ and $[Re_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**II**) (50–60%). These products were separated and purified by TLC.

(b) $[Re(CO)_5Br] + Ph_2PSiMe_3$ in 1,2-dimethoxyethane (DME)

In this experiment, a reaction vessel consisting of two compartments separated by 'Rotaflow' valves was used so that evolved carbon monoxide could be measured. A solution of Ph_2PSiMe_3 in toluene was placed in one compartment and solid $[Re(CO)_5Br]$

(1 molar equivalent) was placed in the other compartment. The apparatus was evacuated and degassed. The reagents were mixed and allowed to react for several hours. The vessel was cooled in liquid N_2, and the evolved carbon monoxide was collected by means of a Sprengle pump. 96% of the expected amount was obtained. Its purity was checked by gas chromatography. The initial IR spectrum of the DME solution was essentially similar to that of $[Re(CO)_4(Ph_2PSiMe_3)Br]$ (**Ib**) in benzene. After several hours, changes in the IR spectrum were noted and a white precipitate, identified by IR and mass spectroscopy as $[Re(CO)_4PPh_2]_2$ [3a], was obtained.

(c) Conversion of cis-[Re(CO)$_4$(Ph$_2$PSiMe$_3$)Br] (Ib) into cis-[Re(CO)$_4$(Ph$_2$PH)Br]

A benzene solution of compound **Ib** was placed on a silica gel column and eluted with benzene. The solvent was removed under vacuum and the residue, *cis*-$[Re(CO)_4(Ph_2PH)Br]$, was recrystallized from hexane. Yield, 85%, based on $[Re(CO)_5Br]$ taken.

Characterization of Rhenium Complexes

$[Re(CO)_4(Ph_2PH)Br]$, ν(CO) in hexane, 2108 m, 2023 s, 2012 vs, 1944 m; δ ^{31}P (in $CDCl_3$), −11.7d, J(PH) = 383 Hz; $\Delta(\delta\ ^{31}P) = -28$ ppm; lit. [4], δ ^1H (PH), 7.1 ppm, J(PH) = 382 Hz. The mass spectrum showed the parent ion multiplet at m/e 562, 564 and 566 and stepwise loss of four CO groups. Melting point 127.5–129 °C, lit. [4] 128 °C. *Anal.* calc. for $C_{16}H_{11}BrO_4PRe$: C, 34.04; H, 1.95. Found: C, 34.2; H, 1.95%. $[Re(CO)_4(Ph_2PSiMe_3)Br]$, **Ib**, ν(CO) in hexane, 2107 s, 2010 s, 2002 m, 1946 s; δ ^1H ($PSiMe_3$), 0.24 d, J(PH) = 5.7 Hz; δ ^{31}P, −56.3; Δ (δ ^{31}P) = 0.4 ppm $[Re_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**II**), ν(CO) in hexane, 2111 w, 2095 m, 2018 vs, 2010 m, 2003 s, 1951 s; δ ^{31}P (in $CDCl_3$), −93.3.

(d) [Mn(CO)$_5$Cl] + Ph$_2$PSiMe$_3$ in Benzene

In an NMR tube, a slurry of $[Mn(CO)_5Cl]$ in C_6D_6 and Ph_2PSiMe_3 was photolyzed for 7 min, giving an orange solution. The evolved gas pressure was released. The first ^1H NMR spectra showed no fine structure, due to the presence of paramagnetic species. After several minutes, the ^1H NMR spectrum showed a strong methyl singlet (due to Me_3SiCl) and two weaker doublets (due to free Ph_2PSiMe_3 and $[Mn(CO)_4(Ph_2PSiMe_3)Cl]$ (**IVa**). The solution was allowed to stand for several days. The products were separated by silica gel TLC, giving many bands from which $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (**Va**) and $[Mn_2(CO)_8(\mu\text{-}H)(\mu\text{-}PPh_2)]$ (trace) were isolated.

(e) [Mn(CO)$_5$Cl] + Ph$_2$PSiMe$_3$ in THF

(i) The ligand Ph_2PSiMe_3 (0.68 mmol) was syringed through a rubber septum into a solution of $[Mn(CO)_5Cl]$ (0.68 mmol) in THF in a 10 mm NMR tube. Almost immediately, carbon monoxide was evolved and the solution turned red. Excess pressure was released via the septum. After ≈45 min, the $^{31}P\{H\}$ NMR spectrum was observed. Many signals were present, the main ones being due to $[Mn(CO)_4(Ph_2PSiMe_3)Cl]$ (**IVa**) (relative intensity = 1); $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (**Va**) (intensity ≈1.7); $[Mn(CO)_4(Ph_2PH)Cl]$ (intensity ≈2); and $[Mn(CO)_3(Ph_2PH)_2Cl]$ (intensity ≈1.7). Upon exposure to air, the signal due to **IVa** was lost. Chromatograpic separation (using 4:1 hexane/chloroform eluant) yielded **Va** (0.05 mmol) and $[Mn(CO)_3(Ph_2PH)_2Cl]$.

(ii) The above reaction was repeated, using a 2:1 molar ratio of ligand to manganese complex. The ^{31}P NMR spectrum showed the presence of $[Mn(CO)_4(Ph_2PSiMe_3)Cl]$ (**IVa**) and *fac*-$[Mn(CO)_3)(Ph_2PH)_2Cl]$, but only trace amounts of $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (**Va**) and $[Mn(CO)_4(Ph_2PH)Cl]$. The secondary phosphine Ph_2PH was also present. The solution was stored under anhydrous conditions for 4 weeks. The only major change in the ^{31}P NMR spectrum was a decrease in the intensity of the signal due to *fac*-$[Mn(CO)_3(Ph_2PH)_2Cl]$, coupled with the appearance of signals due to other complexes of Ph_2PH. The *fac*- to *mer-trans*-isomerization of $[Mn(CO)_3(Ph_2PH)X]$ is a known process [10]. The components were separated by TLC. $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}H)]$ (trace) and *fac*-$[Mn(CO)_3(Ph_2PH)_2Cl]$ were isolated. The IR ν(CO) spectrum of the latter was in agreement with literature data [10].

(iii) A 2:1 reaction mixture of $[Mn(CO)_5Cl]$ and Ph_2PSiMe_3 in THF was monitored by IR spectroscopy over a 48 h period. After 75 min, ν(CO) bands due to $[Mn(CO)_5Cl]$, $[Mn(CO)_4(Ph_2PSiMe_3)Cl]$ (**IVa**) and $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (**Va**) were observed. The bands due to the first two components slowly disappeared over the 48 h period. The solvent was removed to yield compound **Va**, which was recrystallized from toluene, as an orange solid.

(f) [Mn(CO)$_5$Br] + Ph$_2$PSiMe$_3$ in Hexane

The ligand Ph_2PSiMe_3 was injected through a rubber septum into a refluxing solution of $[Mn(CO)_5Br]$ in hexane (1:1 reacting ratio). An immediate evolution of gas bubbles occurred. The IR spectrum showed mainly unreacted $[Mn(CO)_5Br]$ and some $[Mn(CO)_4(Ph_2PH)Br]$. Further heating for 30 min produced $[Mn(CO)_4(Ph_2PSiMe_3)Br]$ (**IVb**), and a trace of $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**Vb**). The mixture was hydrolyzed and its ^{31}P NMR spectrum taken, showing the presence of $[Mn(CO)_4(Ph_2PH)Br]$ and a trace of **Vb** as the only phosphorus-containing compounds.

(g) [Mn(CO)$_5$Br] + Ph$_2$PSiMe$_3$ in DME

The silylphosphine (2.43 mmol) was added to a warm solution of $[Mn(CO)_5Br]$, (3.36 mmol) in DME (60 cm^3), to give an orange solution. After 10 min, the solution was red. It was cooled and methanol was added to hydrolyze the silylphosphine. The solvent was removed under vacuum, giving an orange residue which was separated by column chromatography (eluant, 1:1 toluene/cyclohexane) into orange $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**Vb**) (0.2 mmol), $[Mn(CO)_4(Ph_2PH)Br]$ (1.26 mmol) and a minor amount of yellow $[Mn(CO)_3(Ph_2PH)_2Br]$.

(h) Reaction of $[Mn(CO)_4(Ph_2PSiMe_3)Br]$ (IVb) with $[Mn(CO)_5Cl]$

Compound **IVb** was prepared *in situ* in THF, using a 1:1 molar ratio of Ph_2PSiMe_3 and $[Mn(CO)_5Br]$. A ^{31}P NMR spectrum of the solution showed the presence of **IVb**, $[Mn(CO)_3(Ph_2PH)_2Br]$ and excess Ph_2PSiMe_3. The solution was transferred under N_2 to a flask containing $[Mn(CO)_5Cl]$ in THF. IR spectroscopy showed the formation of $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**Vb**), over a period of two days. This product was separated by TLC and characterized by IR, ^{31}P NMR and mass spectroscopy. Yield, 15%, based on $[Mn(CO)_5Br]$ taken.

(i) Reaction of $[Mn(CO)_4(Ph_2PSiMe_3)I]$ (IVc) with $[Mn(CO)_5Cl]$

A toluene solution of $[Mn(CO)_5I]$ (0.34 mmol) was allowed to react with Ph_2PSiMe_3 (1:1 molar ratio) for 1.5 h, forming $[Mn(CO)_4(Ph_2PSiMe_3)I]$ (**IVc**) in solution. $[Mn(CO)_5Cl]$ (0.26 mmol) was added, the solution was allowed to stand for 3 h at ambient temperatures, then heated to 80 °C for 10 min to complete the reaction. The solvent was removed under vacuum and the residue was taken up in CH_2Cl_2 (0.5 cm^3) and separated by TLC (eluant 1:1, petrol/chloroform) into $[Mn_2(CO)_{10}]$ (trace), $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}I)]$ (0.09 mmol), $[Mn(CO)_5Cl]$ (trace) and $[Mn(CO)_4(Ph_2PH)I]$ (0.06 mmol). A small amount of CH_2Cl_2-insoluble material was found to be $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$.

Characterization of Manganese Complexes

$[Mn(CO)_4(Ph_2PSiMe_3)Cl]$, **IVa**, δ ^{31}P in THF, −13.8, Δ (δ ^{31}P) = −42 ppm. $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$, **Va**, $\nu(CO)$ in cyclohexane, 2097 w, 2078 m, 2021 vs, 2008 s, 1956 s; δ ^{31}P in $CDCl_3$, 1.6. The mass spectrum showed the parent ion at m/e = 524/526, together with fragments corresponding to the sequential loss of eight CO groups and the μ-Ph_2P group. $[Mn(CO)_4(Ph_2PSiMe_3)Br]$, **IVb**, δ ^{31}P in THF, −14.3, Δ (δ ^{31}P) = −41.6 ppm. $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)$, **Vb**, $\nu(CO)$ in cyclohexane, 2095 w, 2075 m, 2018 vs, 2006 s, 1959 s; δ ^{31}P in $CDCl_3$, −10.8. The mass spectrum showed the parent ion doublet at m/e = 598, 600, corresponding to the presence of $^{79,81}Br$ isotopes, and the stepwise loss of eight CO groups and the μ-PPh_2 group. $[Mn(CO)_4(Ph_2PSiMe_3)I]$, **IVc**, δ ^{31}P in THF, −14.3, Δ (δ ^{31}P) = −41.6 ppm. $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}I)]$, **Vc**, $\nu(CO)$ in cyclohexane, 2089 w, 2069 m, 2014 vs, 2002 s, 1962 s; δ ^{31}P in $CDCl_3$, −28.2. $[Mn(CO)_4(Ph_2PH)X]$, δ ^{31}P data, X = Cl, 34.5 ppm, $J(PH)$ = 367 Hz, Δ (δ ^{31}P) = −74.4 ppm; X = Br, δ ^{31}P, 33.5, $J(PH)$ = 364 Hz, Δ (δ ^{31}P) = −73.4 ppm; X = I, δ ^{31}P, 34.2, $J(PH)$ = 373 Hz, Δ (δ ^{31}P) = −74.1 ppm; $\nu(CO)$, X = Br, 2091 m, 2026 s, 2015 s, 1959 m. $[Mn_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}H)]$, $\nu(CO)$ in hexane, 2093 m, 2063 m, 2010 vs, 1999 m, 1965 s; δ ^{31}P in $CDCl_3$, +156 ppm. *fac*-$[Mn(CO)_3(Ph_2PH)_2X]$; X = Cl, $\nu(CO)$ in $CHCl_3$, 2035 s, 1970 m, 1914 m; δ ^{31}P (in $CDCl_3$), 42.2, $J(PH)$ = 318 Hz, Δ (δ ^{31}P) = −82.1 ppm; X = Br, $\nu(CO)$, 2036 s, 1972 m, 1915 m; δ ^{31}P, 49.0, Δ (δ ^{31}P) = −88.9 ppm; X = I, $\nu(CO)$, 2030 s, 2010 m, 1910 m. $[MnRe(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$ (**III**). $\nu(CO)$ in cyclohexane, 2105 w, 2082 m, 2076 w, 2019 vs, 2005 m, 1955 m; δ ^{31}P in $CDCl_3$, −57.8; the mass spectrum showed species corresponding to the loss of Cl and eight consecutive CO groups, as well as fragments attributed to the formation and breakdown of the recombination species $[M_2(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Br)]$.

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