A General Synthetic Route for Platinum Cluster Compounds containing Carbonyl and Tertiary Phosphine Ligands and a Study of their Reactions with Unsaturated Inorganic Molecules

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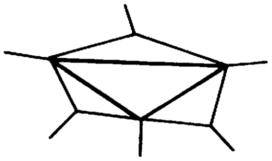
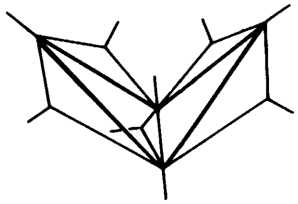
The reduction of *cis*-[$PtCl_2(CO)(PR_3)$] (R = a variety of alkyl or aryl groups) by zinc dust or sodium tetrahydroborate under a carbon monoxide atmosphere is an efficient high-yield method for the formation of tri-, tetra-, and penta-nuclear clusters, which is superior in yield, convenience, and generality to other methods. The nuclearity of the cluster formed appears to be the result of a subtle interplay between the steric and electronic properties of the phosphine and, in the case of triphenylphosphine at least, is altered by the presence of free ligand. Reactions of some of the above clusters with the unsaturated inorganic molecules SO_2, CS_2, and COS are reported. In some reactions the initial cluster framework is retained with concomitant complete or partial substitution of the bridging carbonyl ligands but in other cases either cluster aggregation or degradation is observed.

The cluster chemistry of low-valent platinum has been a topic of considerable recent structural,[1,2] spectroscopic,[3,4] and theoretical[5,6] interest. The majority of reported clusters contain both carbonyl and tertiary phosphine ligands and a number of 42- and 44-electron trinuclear,[7–9] 58-electron tetranuclear,[7,10–12] and 70-electron pentanuclear[13,14] clusters have been structurally characterised. Some representative examples are illustrated in (**1**)—(**3**). The common structural feature in these clusters is the Pt_3 triangular unit since the structures of the larger clusters may be derived by the fusion of these triangles.[15] Other platinum clusters containing only carbonyl ligands[16,17] or isocyanide ligands[18,19] have also been structurally characterised as have a number of platinum phosphine hydride clusters.[20,21] A considerable number of mixed-metal clusters containing platinum have also been synthesised.[1,2]



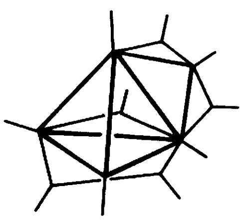
(1)

[$Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3$]



(2)

[$Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4$]



(3)

[$Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4$]

The chemical properties of these clusters have not been widely reported, although Bender and Braunstein[22] have investigated their interconversion on chromatographic columns. To some extent the study of these cluster compounds has been hampered by the lack of a convenient high-yield general synthetic route. The reported syntheses generally start with mononuclear platinum compounds which have two co-ordinated phosphines per platinum. Some representative examples are shown in equations (1)—(3).

$$3[PtH_2(PR_3)_2] \xrightarrow[C_6H_6]{CO} [Pt_3(\mu\text{-}CO)_3(PR_3)_3] + 3H_2 + 3PR_3 \quad (1)$$

$$5[Pt(CO)_2(PR_3)_2] \xrightarrow[EtOH]{heat} [Pt_3(\mu\text{-}CO)_3(PR_3)_4] + 2[Pt(PR_3)_3] + 7CO \quad (2)$$

$$[PtCl_2(PR_3)_2] + 2Na[Mn(CO)_5] \longrightarrow [Pt_5(CO)(\mu\text{-}CO)_5(PR_3)_4] + [Mn_2(CO)_{10-x}(PR_3)_x] \quad (x = 0\text{—}2) \quad (3)$$

All of these routes have certain disadvantages. Reactions of type (1)[23] are restricted to complexes of bulky phosphines, which are also good σ donors (*e.g.* R = C_6H_{11} or Bu^t), for which the dihydride complex is known. In addition, the reaction is accompanied by the formation of mononuclear side products, which are difficult to separate from the cluster.[24] Reactions of the type (2)[7] employ platinum itself as a phosphine scavenger, leading to low yields of the cluster which must be separated from the mononuclear by-product. Reactions of the type (3)[13,14] utilise air-sensitive and expensive carbonyl anions as both reducing agents and phosphine scavengers and again the platinum clusters must be separated from the phosphine-substituted metal carbonyls by chromatography which can cause cluster interconversion.[22]

In this paper we report the development of high-yield syntheses of platinum carbonyl phosphine cluster compounds, starting from mononuclear precursors with only a single phosphine which effectively eliminates the problems referred to above.

Results and Discussion

The Platinum(II) *Precursor*.—The mononuclear precursor selected was of the type *cis*-[$PtCl_2(CO)(PR_3)$]. These

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Table 1. Coupling constants (Hz) for some *triangulo*-triplatinum clusters

Cluster	$^1J(^{195}Pt-^{31}P)$	$^2J(^{195}Pt-^{31}P)$	$^3J(^{31}P-^{31}P)$
$[Pt_3(\mu-CO)_3(PBu^n_3)_3]$[a]	4 425	444	60
$[Pt_3(\mu-CO)_3\{P(CH_2CH_2CN)_3\}_3]$[a]	4 489	466	61
$[Pt_3(\mu-CO)_3\{P(C_6H_{11})_3\}_3]$[b]	4 412	430	58
$[Pt_3(\mu-CO)_3(PPr^i_3)_3]$[b]	4 422	430	56

[a] This work. [b] Ref. 3.

compounds may be readily synthesised in a number of ways, *e.g.* equations (4)—(6) (cod = cyclo-octa-1,5-diene). In our experience reaction (4) was found to be the most convenient and effective route.

$$[Pt(cod)Cl_2] + CO + PR_3 \xrightarrow[(ii)\,Et_2O]{(i)\,CHCl_3} [PtCl_2(CO)(PR_3)] \qquad \text{(4)[25]}$$

$$K[PtCl_3(C_2H_4)] + CO + PR_3 \xrightarrow{Me_2CO,\ C_6H_6} [PtCl_2(CO)(PR_3)] \qquad \text{(5)[26]}$$

$$[Pt_2Cl_4(PR_3)_2] + CO \xrightarrow{C_6H_6} [PtCl_2(CO)(PR_3)] \qquad \text{(6)[27]}$$

The known compounds *cis*-$[PtCl_2(CO)(PR_3)]$, where PR_3 = PPh_3, PMe_2Ph, PBu^n_3, or $P(C_6H_{11})_3$, were prepared in this manner and identified on the basis of analytical, i.r., and melting point data[26,27] (see Experimental section). In addition the compound *cis*-$[PtCl_2(CO)\{P(CH_2CH_2CN)_3\}]$, which does not appear to have been previously reported, was synthesised and characterised by analytical and i.r. data.

The Reducing Agent.—We have shown that the compounds *cis*-$[PtCl_2(CO)(PR_3)]$ are reduced under mild conditions [1 atm (101 325 Pa) of carbon monoxide] to give cluster compounds in good yields (60—80%). A variety of reducing agents were examined. The best results were obtained with either zinc dust [with tetrahydrofuran (thf) or acetone as solvent] or sodium tetrahydroborate (with methanol as solvent). Both of these reducing agents have previously proved to be effective in the synthesis of mononuclear platinum(0) compounds when the phosphine is present in excess as shown in equations (7)[28] and (8).[29]

$$[PtCl_2(PR_3)_2] \xrightarrow[thf]{CO,\ Zn} [Pt(CO)_2(PR_3)_2] \qquad (7)$$

$$[PtCl_2(PR_3)_2] + 2PR_3 \xrightarrow[EtOH]{NaBH_4} [Pt(PR_3)_4] \qquad (8)$$

The BH_3·thf complex also proved to be a satisfactory reducing agent for cluster formation, but sodium amalgam was too powerful and brought about reduction to the metal. Having established general synthetic routes for preparing platinum phosphine cluster compounds, the following paragraphs describe some specific syntheses.

$[Pt_3(\mu-CO)_3(PBu^n_3)_3]$. When a suspension of *cis*-$[PtCl_2(CO)(PBu^n_3)]$ in methanol was saturated with CO and $NaBH_4$ added, a deep red solution was immediately obtained from which a red crystalline solid was isolated. This was shown to be the *triangulo*-triplatinum cluster $[Pt_3(\mu-CO)_3(PBu^n_3)_3]$ (yield 64%) on the basis of analytical and i.r. evidence and in particular by measurement of its characteristic[3,30] $^{31}P-\{^1H\}$ n.m.r. spectrum. The coupling constants obtained are given in Table 1, together with those of some related clusters whose n.m.r. spectra have been described in the literature.[3]

$[Pt_3(\mu-CO)_3\{P(CH_2CH_2CN)_3\}_3]$. A solution of *cis*-$[PtCl_2(CO)\{P(CH_2CH_2CN)_3\}]$ in acetone was stirred overnight with zinc dust under CO to give a red solution from which an orange-red solid was isolated. The analytical and i.r. data were consistent with the formulation $[Pt_3(\mu-CO)_3\{P(CH_2CH_2CN)_3\}_3]$ (yield 73%) and this was confirmed by the $^{31}P-\{^1H\}$ n.m.r. spectrum. The relevant coupling constants are given in Table 1.

$[Pt_3(\mu-CO)_3\{P(C_6H_{11})_3\}_3]$. This compound was prepared from $[PtCl_2(CO)\{P(C_6H_{11})_3\}]$ by both methods given above. The reaction using $NaBH_4$ proceeded as for $[PtCl_2(CO)(PBu^n_3)]$ except that the product was insoluble in methanol and had to be extracted into benzene. The reduction using zinc dust proceeded as for $[PtCl_2(CO)\{P(CH_2CH_2CN)_3\}]$, but was much slower, requiring 4 d for completion at ambient temperature. In both cases the yield was at least 60% and the i.r., analytical, and $^{31}P-\{^1H\}$ n.m.r. properties of the product agree with those published.[3,23]

$[Pt_4(\mu-CO)_5(PMe_2Ph)_4]$. When a suspension of *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ in methanol was saturated with CO and treated with $NaBH_4$ a deep red solution was immediately obtained from which a red crystalline solid was isolated. The i.r. spectrum of this solid matched that of an authentic[7] sample of $[Pt_4(\mu-CO)_5(PMe_2Ph)_4]$ (**2**) and the analytical data were also consistent with this formulation as was the $^{31}P-\{^1H\}$ n.m.r. spectrum which has recently been reported by Pregosin and coworkers.[12] The yield was 80%.

$[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$. When a solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ in thf was saturated with CO and stirred for 6 h with zinc dust a deep red solution was obtained from which a reddish brown crystalline solid was isolated. This was identified as $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$ (**3**) on the basis of analytical data and its very characteristic[14] i.r. spectrum. The yield was 76%.

$[Pt_3(\mu-CO)_3(PPh_3)_4]$. When *cis*-$[PtCl_2(CO)(PPh_3)]$ in thf solution was reduced with zinc dust under CO in the presence of a one-third mol equivalent of free PPh_3 the red-brown trinuclear cluster $[Pt_3(\mu-CO)_3(PPh_3)_4]$ was isolated in 80% yield rather than $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$. The trinuclear cluster was characterised on the basis of i.r.[7] and analytical data.

Factors affecting Cluster Nuclearity.—The results described above have demonstrated that the nuclearity of the cluster obtained by the reduction of *cis*-$[PtCl_2(CO)(PR_3)]$ is sensitive to the steric and/or electronic requirements of the tertiary phosphine. The other synthetic routes to platinum clusters have also resulted in clusters of differing nuclearity depending on the phosphine used.[7—10,13,14]

Consider first the case of the trinuclear $[Pt_3(\mu-CO)_3(PR_3)_3]$ clusters. Previously it has been suggested[23,30] that such clusters are stable only with phosphines which have a large cone angle[31,32] such as $P(C_6H_{11})_3$ (170°) or PBu^t_3 (182°). This work indicates, however, that this is primarily a reflection of the mode of synthesis employed since the dihydride precursors involved [reaction (1)] are available only for such bulky phosphines as discussed above. Thus both PBu^n_3 and $P(CH_2CH_2CN)_3$, which have relatively small cone angles (132° in each case[31]), have been shown to form stable clusters of the type $[Pt_3(\mu-CO)_3(PR_3)_3]$. It is not clear exactly what favours the formation of such clusters since although $P(C_6H_{11})_3$, PBu^t_3, and PBu^n_3 are strong σ-donor and poor π-acceptor ligands, $P(CH_2CH_2CN)_3$ is anomalous in this respect in that it has an extremely low basicity arising from the electron-withdrawing character of the cyano-groups.[33]

Use of phosphines such as PPh_3 and PMe_2Ph with intermediate cone angles and electronic parameters destabilises clusters of the type $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$. Traces of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ have been identified[34] as a minor product of the reaction of $[Pt(C_2H_4)_2(PPh_3)]$ with $[Rh(\eta\text{-}C_5Me_5)(CO)_2]$ and the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum at room temperature was indicative of rapid phosphine exchange. This phenomenon is not observed for other examples of $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ reported above and elsewhere[3,30] but is consistent with the fact that the stable trinuclear cluster compounds formed with these two phosphines are $[Pt_3(\mu\text{-}CO)_3(PR_3)_4]$.[7]

In the absence of an excess of ligand, these phosphines appear to favour the formation of $[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$ and $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$ respectively, an observation common to this and other[7,12–14] synthetic methods.

Having developed general synthetic routes to these platinum carbonyl clusters we now go on to describe some of their reactions with small inorganic molecules.

Reactions of Platinum Clusters with Unsaturated Inorganic Molecules.—The known platinum cluster compounds owe their stability to a suitable combination of π-acceptor ligands, and clusters with various phosphines, isocyanides, CO, and SO_2 in terminal and/or bridging modes of bonding have been isolated. In their pioneering work on the synthesis of carbonyl phosphine clusters, Chatt and Chini[7] observed that some of the clusters reacted further with free phosphine and CO. Examples are shown in reactions (9) ($L = PEt_3$, $PMePh_2$, or PPh_3) and (10).

$$[Pt_3(\mu\text{-}CO)_3L_4] + 5L \longrightarrow 3[Pt(CO)L_3] \quad (9)$$

$$2[Pt_3(\mu\text{-}CO)_3(PPh_3)_4] + 3CO \longrightarrow [Pt_4(\mu\text{-}CO)_5(PPh_3)_4] + 2[Pt(PPh_3)_2(CO)_2] \quad (10)$$

It was apparent from these and other similar observations that some unsaturated inorganic molecules can promote interconversion of platinum clusters which may or may not require fragmentation of the cluster. Therefore it was of interest to investigate a number of reactions with such molecules to determine some of the factors which influence the stability of platinum clusters towards fragmentation.

Farrar and co-workers[35] have investigated the exchange of phosphine ligands in the compounds $[Pt_3(\mu\text{-}CO)_3L_3]$ where L is a bulky phosphine such as $P(C_6H_{11})_3$, PPr^i_3, or PBu^t_3. They found that the phosphines L readily and quickly exchange with a less bulky phosphine L′ and, depending on how much of the free phosphine L′ is used, various amounts of mixed-phosphine triangles are formed. These observations apply to very bulky phosphines. The Pt_3 cluster compounds were all stable to fragmentation in the presence of a large excess of free phosphine and no mononuclear compounds were detected, in contrast to the results of Chatt and Chini[7] with the smaller phosphine PPh_3.

Secondly, we[36] have found that $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ reacts readily with 2,6-xylyl isocyanide ($CNC_6H_3Me_2$-2,6) to give either $[Pt_3(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)_3(CNC_6H_3Me_22,6)_2\{P(C_6H_{11})_3\}]$ or $[Pt_3(\mu\text{-}CO)(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)_2(CNC_6H_3Me_2\text{-}2,6)\{P(C_6H_{11})_3\}_2]$ depending on the isocyanide to cluster ratio employed in the reaction.

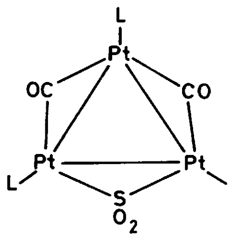
Finally, we have described elsewhere[37] some reactions of carbonyl phosphine cluster compounds with SO_2. This reaction is used as a facile synthetic route to SO_2 cluster compounds of platinum and involves the apparently simple replacement of carbonyl ligands by SO_2. In all the syntheses reported so far, no intermediate or alternative products have been detected and there is no evidence to suggest that the Pt_3 triangle is broken at all in the reaction. This is true not only for the simple Pt_3 triangles, but also for the few known examples in higher clusters. In fact, in reaction (11) of SO_2 with $[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$ the precise substitution of only the three least hindered carbonyl ligands with no change in the Pt_5 framework is evidence against a fragmentation mechanism. In the case of the trinuclear cluster $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$, replacement of CO by SO_2 was accompanied by loss of one terminal phosphine ligand to give $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$.

$$[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4] \xrightarrow[\text{PhMe, 60 °C}]{SO_2} [Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(PPh_3)_4] \quad (11)$$

It is thought that, as bridging ligands, CO and SO_2 have quite similar electronic properties; SO_2 is the better σ donor but CO is the better π acceptor.[38] Therefore it is logical to see whether the conversion of CO-bridged Pt_3 triangular clusters into their SO_2-bridged equivalents could be reversed by treating the SO_2 clusters with CO gas. We[37] have carried out the reaction of $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ with CO. This is a peculiar example since the carbonyl precursor $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ contains four phosphine ligands and, therefore, cannot be regenerated by this method. One possible product, $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$, has been shown to be electron deficient and not easily isolated.[34] The product actually obtained in good yield (80% based on Pt) from this reaction was the pentanuclear cluster $[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$, which is the same as that usually synthesised in the presence of limited amounts of triphenylphosphine as reported earlier in this paper. Such a conversion of a Pt_3 cluster to a Pt_5 cluster necessarily involves fragmentation of the Pt_3 triangle. In this case the cause is the relatively low basicity of the triphenylphosphine.

It was shown above that $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ can be synthesised from $[PtCl_2(CO)(PPh_3)]$ if an extra one-third mol of phosphine per mol of platinum is added. Therefore, it was decided to repeat the reaction of $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ in benzene solution with CO in the presence of an additional one-third mol equivalent of PPh_3. In this case there was a rapid colour change from dark to pale orange and an orange microcrystalline solid was isolated. This was shown to be the mixed SO_2/CO triangular cluster $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PPh_3)_3]$ on the basis of analytical, i.r., and most conclusively $^{31}P\text{-}\{^1H\}$ n.m.r. data. The n.m.r. spectrum of this cluster was very similar to that of the $P(C_6H_{11})_3$ analogue discussed in more detail below and reproduced in Figure 1. No product was observed which contained the extra phosphine. Nor was there any suggestion of either a pentanuclear cluster or a binuclear complex. It seems, therefore, that the presence of the free phosphine in this reaction may suppress total fragmentation of the Pt_3 triangle.

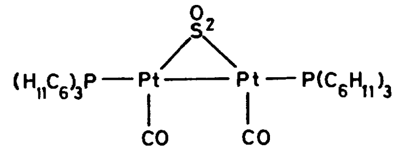
In order to make a better judgement in the interconversion of CO and SO_2 cluster compounds, the reaction of $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]$ with CO was investigated. The bulky and relatively basic phosphine $P(C_6H_{11})_3$ favours the isolation of the 42-electron carbonyl cluster $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ from our general synthetic route above. Carbon monoxide gas was bubbled through a benzene solution of $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]$ at room temperature for 2 min only. There was an immediate colour change from orange to yellow. A yellow crystalline solid was isolated, the i.r. spectrum of which contained bands due to bridging CO as well as SO_2 ligands. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this product clearly showed it to be the trinuclear cluster $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)\{P(C_6H_{11})_3\}_3]$, **(4)**.



(4)

The n.m.r. parameters of this cluster are given in Table 2. The observed and calculated $^{31}P-\{^1H\}$ n.m.r. spectra are given in Figure 1.

In an attempt to replace the third SO_2 ligand with CO the reaction was repeated over prolonged periods of time at 60 °C. In addition to the spectrum of $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)\{P(C_6H_{11})_3\}_3]$ identical to that obtained previously an additional set of lines was obtained in the $^{31}P-\{^1H\}$ n.m.r. spectrum of the resulting yellow solid, indicating the product to be a mixture of the trinuclear cluster and a second compound. This latter species contains only two symmetrically arranged platinum phosphine units and the magnitudes of the coupling constants indicate that it is based on an approximately linear P–Pt–Pt–P moiety. This compound was not isolated but, in view of the spectroscopic evidence, the most probable structure is that shown in (5). The $^{31}P-\{^1H\}$ n.m.r. data are given in Table 3 and the spectrum is illustrated in Figure 2.



(5)

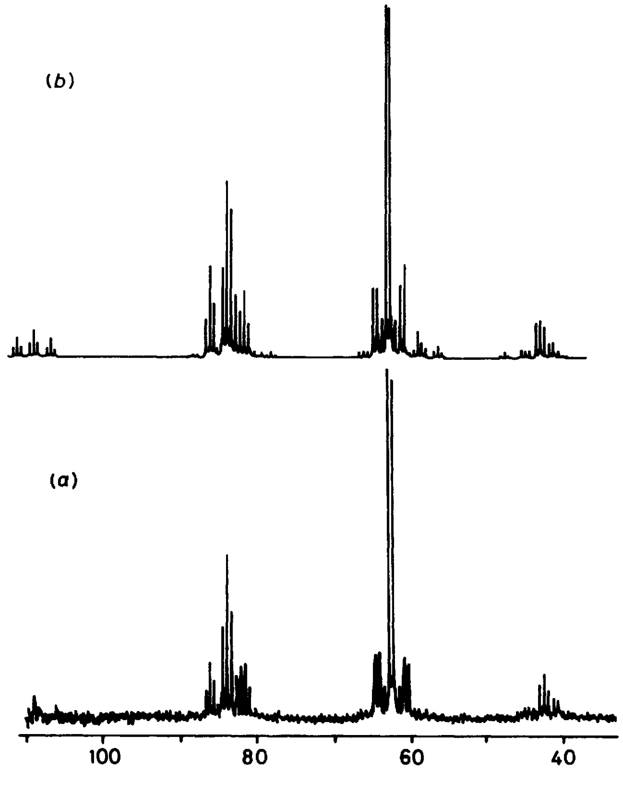
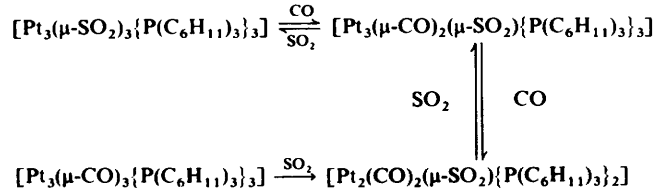


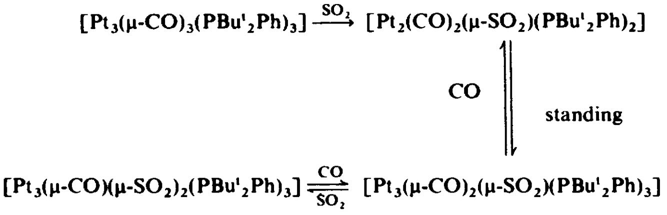
Figure 1. Observed (*a*) and calculated (*b*) $^{31}P-\{^1H\}$ n.m.r. spectra of $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)\{P(C_6H_{11})_3\}_3]$ (**4**)

Evidently, this attempt at recovering the carbonyl cluster from its SO_2 equivalent has not gone to completion. Both of the above reactions were reversed on treatment with SO_2, giving $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]$ as the only isolable product. These results suggest the series of reactions in Scheme 1. Recently Farrar and co-workers[35] have investigated the reaction of SO_2 with $[Pt_3(\mu\text{-}CO)_3(PBu^t_2Ph)_3]$, a carbonyl cluster with a particularly bulky phosphine which is also a good σ donor. They observed a similar sequence of reactions which are summarised in Scheme 2. The main difference between these two schemes is that with $P(C_6H_{11})_3$ the fully CO-substituted cluster could not be obtained whereas for PBu^t_2Ph the fully SO_2-substituted cluster was not obtained. Farrar was also able to observe both of the mixed triangular clusters $[Pt_3(\mu\text{-}CO)_x(\mu\text{-}SO_2)_{3-x}(PBu^t_2Ph)_3]$ (x = 1 or 2). It is probable that neither of the schemes gives all of the intermediate compounds and that each interconversion of triangular clusters occurs *via* a binuclear species.



$$\begin{tikzcd}
{[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]} \arrow[r, shift left, "CO"] & {[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)\{P(C_6H_{11})_3\}_3]} \arrow[l, shift left, "SO_2"] \arrow[d, shift left, "CO"] \\
{[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]} \arrow[r, "SO_2"] & {[Pt_2(CO)_2(\mu\text{-}SO_2)\{P(C_6H_{11})_3\}_2]} \arrow[u, shift left, "SO_2"]
\end{tikzcd}$$

Scheme 1.



$$\begin{tikzcd}
{[Pt_3(\mu\text{-}CO)_3(PBu^t_2Ph)_3]} \arrow[r, "SO_2"] & {[Pt_2(CO)_2(\mu\text{-}SO_2)(PBu^t_2Ph)_2]} \arrow[d, shift left, "standing"] \\
{[Pt_3(\mu\text{-}CO)(\mu\text{-}SO_2)_2(PBu^t_2Ph)_3]} \arrow[r, shift left, "CO"] & {[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PBu^t_2Ph)_3]} \arrow[l, shift left, "SO_2"] \arrow[u, shift left, "CO"]
\end{tikzcd}$$

Scheme 2.

Interconversion of the various observed complexes involving fragmentation and aggregation reactions is easily achieved with modest changes in conditions because the CO and SO_2 ligands react at similar rates and give products of comparable stabilities. The influence of the phosphine appears to be such that the

Table 2. $^{31}P-\{^1H\}$ N.m.r. data for $[Pt_3(\mu-CO)_2(\mu-SO_2)\{P(C_6H_{11})_3\}_3]$, (4)

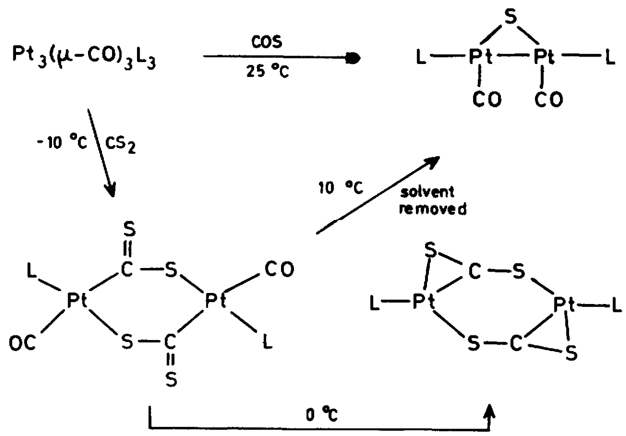
$\delta(^{31}P^1)$/p.p.m.	82.2	$^2J(Pt^2P^1)$/Hz	449
$\delta(^{31}P^{2,2'})$/p.p.m.	61.9	$^2J(Pt^2P^{2'})$/Hz	301
$^1J(Pt^1P^1)$/Hz	5 134	$^3J(P^1P^2)$/Hz	51
$^1J(Pt^2P^2)$/Hz	4 055	$^3J(P^2P^{2'})$/Hz	62
$^2J(Pt^1P^2)$/Hz	372		

Table 3. $^{31}P-\{^1H\}$ N.m.r. data for $[Pt_2(CO)_2(\mu-SO_2)\{P(C_6H_{11})_3\}_2]$, (5), and $[Pt_2(\mu-S)(CO)_2(PPh_3)_2]$, (6)

	(5)	(6)
$\delta(^{31}P)$/p.p.m.	29.2	21.1
$^1J(PtP)$/Hz	3 854	3 161
$^2J(PtP)$/Hz	297	122
$^3J(PP)$/Hz	67	149

smaller, less basic phosphines allow fast and complete reaction with CO or SO_2 gas to give complete substitution, possibly without the need for fragmentation. The bulky phosphines, such as $P(C_6H_{11})_3$ and PBu^t_2Ph, which are also better σ donors, favour fragmentation of the Pt_3 triangle, giving both trinuclear and binuclear products but without easily reacting to completion. In particular, reactions of these compounds have revealed no mononuclear products. On the other hand, in the case of PPh_3, provided there is sufficient phosphine present, fragmentation of the triangle is not necessary but, in the presence of an excess of phosphine, degradation to mononuclear species is quite likely.

In addition to their observations on the reactions of $[Pt_3(\mu-CO)_3(PBu^t_2Ph)_3]$ with SO_2, Farrar and co-workers[35] have reported that the same carbonyl cluster reacts readily with CS_2 and COS to give complexes of lower nuclearity. Their findings are summarised in Scheme 3.



Scheme 3. L = PBu^t_2Ph

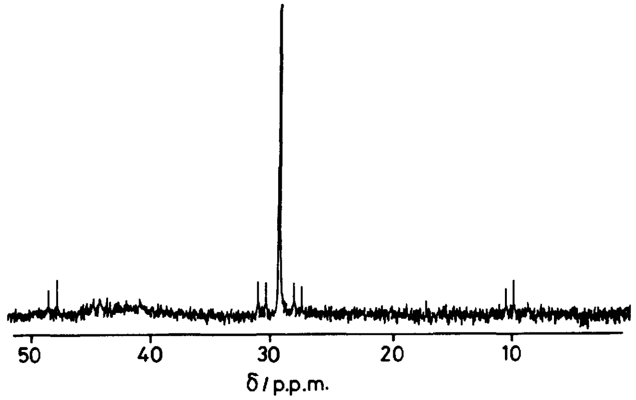


Figure 2. $^{31}P-\{^1H\}$ N.m.r. spectrum of $[Pt_2(CO)_2(\mu-SO_2)\{P(C_6H_{11})_3\}_2]$, (5)

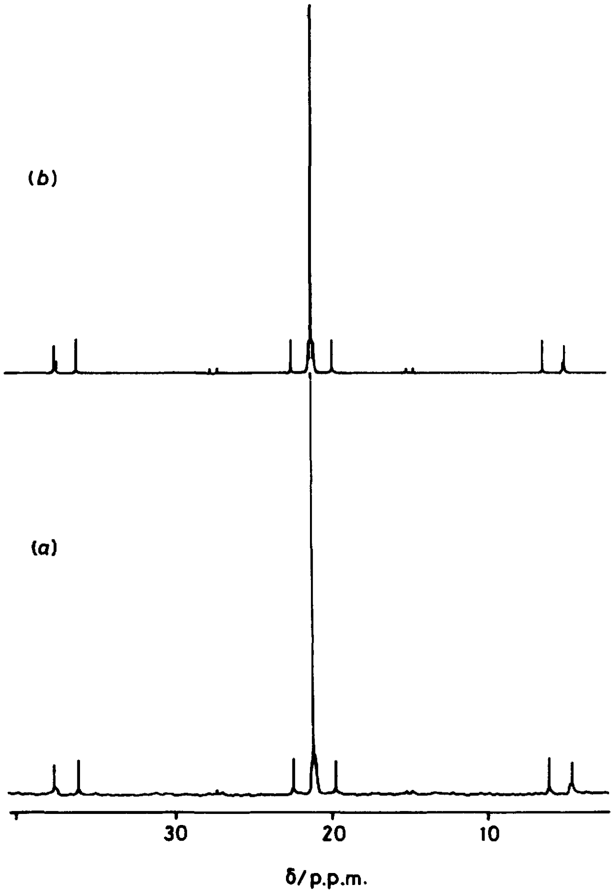
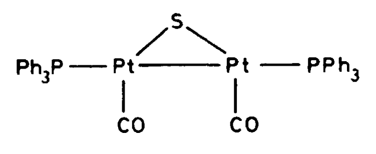


Figure 3. Observed (*a*) and calculated (*b*) $^{31}P-\{^1H\}$ n.m.r. spectra of $[Pt_2(\mu-S)(CO)_2(PPh_3)_2]$, (6)

It was of interest therefore to investigate the reactions of $[Pt_3(\mu-CO)_3(PPh_3)_4]$ with CS_2 and COS. The reaction with CS_2 proceeded rapidly even at −10 °C. The only cluster compound isolated was the now familiar pentanuclear cluster $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$, identified on the basis of its characteristic i.r. spectrum. It would appear that CS_2 merely acts as a phosphine abstractor and that PPh_3, unlike PBu^t_2Ph, does not have sufficient σ-donor ability and/or steric bulk to stabilise a platinum CS_2 complex. In the reaction with COS however, exactly analogous results were obtained with the PBu^t_2Ph and PPh_3 clusters and the binuclear complex $[Pt_2(\mu-S)(CO)_2(PPh_3)_2]$, (6), was isolated in good yield (84%) after 24 h at room temperature. The product was identified on the basis of i.r. and $^{31}P-\{^1H\}$ n.m.r. spectroscopic evidence. The n.m.r.



(6)

data are given in Table 3 and the observed and calculated spectra in Figure 3. The form of the ^{31}P-{^{1}H} n.m.r. spectrum is similar to that of $[Pt_2(CO)_2(\mu\text{-}SO_2)\{P(C_6H_{11})_3\}_2]$ (**5**), shown in Figure 2, but the coupling constants show some variation (Table 3). These may reflect differences in the electronic nature of the μ-S and $\mu\text{-}SO_2$ bridging ligands or varying deviations from linearity in the P–Pt–Pt–P units in the two complexes.

It is clear therefore that the platinum phosphine carbonyl clusters show a wide diversity in their reactions with small unsaturated inorganic molecules.

Experimental

All reactions were carried out in Schlenk tubes under an atmosphere of nitrogen unless otherwise stated. All solvents were degassed before use and all chemicals were used as supplied. Methanol used for $NaBH_4$ reductions was pre-dried over $Mg(OMe)_2$. Microanalyses were performed in these laboratories. Infrared spectra were recorded on a Pye Unicam SP2000 or a Perkin-Elmer 1710 FT-IR spectrometer as Nujol mulls between KBr discs and calibrated using polystyrene film. ^{31}P-{^{1}H} N.m.r. spectra were recorded on a Bruker WH90 or JEOL FX90Q spectrometer operating at 36.43 MHz or a Bruker AM250 spectrometer operating at 101.26 MHz. Trimethyl phosphate was used as an external reference with chemical shifts taken as positive to high frequency of the reference.

Computer simulations of n.m.r. spectra were carried out using a program developed by Professor R. K. Harris, then of the University of East Anglia, and adapted for use on the Oxford University VAX system by Dr. A. E. Derome.

The following compounds were prepared by standard literature methods: $[Pt(cod)Cl_2]$,[39] $K[PtCl_3(C_2H_4)]$,[40] *cis*-$[PtCl_2(CO)(PPh_3)]$, *cis*-$[PtCl_2(CO)(PMe_2Ph)]$, *cis*-$[PtCl_2(CO)\{P(C_6H_{11})_3\}]$,[25] and *cis*-$[PtCl_2(CO)(PBu^n{}_3)]$.[26]

Syntheses.—*cis*-$[PtCl_2(CO)\{P(CH_2CH_2CN)_3\}]$. This compound was prepared by a modification of the published[25] synthesis of *cis*-$[PtCl_2(CO)(PR_3)]$. The complex $[Pt(cod)Cl_2]$ (0.32 g, 0.86 mmol) was dissolved in chloroform (40 cm^3) and CO was bubbled through this solution for 1 h to give a pinkish solution. A solution of $P(CH_2CH_2CN)_3$ (0.16 g, 0.83 mmol) in hot chloroform (30 cm^3) was added dropwise over 30 min with stirring. The yellow solid which precipitated was washed with fresh chloroform and then recrystallised from acetone–propan-2-ol. Yield: 0.34 g (81%), m.p. 202—203 °C (Found: C, 24.2; H, 2.7; N, 7.6. $C_{10}H_{12}Cl_2N_3OPPt$ requires C, 24.6; H, 2.5; N, 8.6%). I.r. spectrum: ν_{CN} 2 240m, ν_{CO} 2 100s cm^{-1}.

$[Pt_3(\mu\text{-}CO)_3(PBu^n{}_3)_3]$. A suspension of *cis*-$[PtCl_2(CO)(PBu^n{}_3)]$ (0.4 g, 0.81 mmol) in methanol (30 cm^3) was saturated with CO. A solution of $NaBH_4$ (0.16 g, 4.2 mmol) in methanol (20 cm^3), also saturated with CO, was added under CO, giving a deep red solution. The mixture was brought to boiling and filtered under CO. Reduction of the volume under vacuum, followed by standing at −40 °C, resulted in the precipitation of red microcrystals of $[Pt_3(\mu\text{-}CO)_3(PBu^n{}_3)_3]$. The solid was washed with water and a little cold methanol. Yield: 0.22 g (64%) (Found: C, 36.4; H, 6.6. $C_{39}H_{81}O_3P_3Pt_3$ requires C, 36.7; H, 6.4%). I.r. spectrum: ν_{CO} 1 800(sh) and 1 788vs cm^{-1}. ^{31}P-{^{1}H} N.m.r. in C_6H_6 solution: $\delta(^{31}P)$ 24.4 p.p.m.

$[Pt_3(\mu\text{-}CO)_3\{P(CH_2CH_2CN)_3\}_3]$. A solution of *cis*-$[PtCl_2(CO)\{P(CH_2CH_2CN)_3\}]$ (0.32 g, 0.66 mmol) in acetone (30 cm^3) was saturated with CO and zinc dust (0.21 g, 3.2 mmol) was then added. The solution was stirred under CO for 18 h during which time it became first green then red. The excess of zinc dust was then filtered off and the filtrate evaporated to dryness *in vacuo*. The resulting orange solid was washed well with dichloromethane and methanol and then dissolved in acetone. Addition of ethanol to this solution gave, on standing, red crystals of $[Pt_3(\mu\text{-}CO)_3\{P(CH_2CH_2CN)_3\}_3]$. Yield: 0.20 g (73%) (Found: C, 29.4; H, 2.9; N, 9.4. $C_{30}H_{36}N_9O_3P_3Pt_3$ requires C, 28.8; H, 2.9; N, 10.1%). I.r. spectrum: ν_{CO} 1 790br s cm^{-1}. ^{31}P-{^{1}H} N.m.r. in acetone solution: $\delta(^{31}P)$ 16.1 p.p.m.

$[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$. (*a*) *By zinc dust reduction*. A solution of *cis*-$[PtCl_2(CO)\{P(C_6H_{11})_3\}]$ (0.32 g, 0.56 mmol) in thf (30 cm^3) was saturated with CO and zinc dust (0.32 g, 4.9 mmol) was then added. The solution was stirred under CO for 4 d during which time it became first green then red. The excess of zinc dust was filtered off and the filtrate evaporated to dryness *in vacuo*. The resulting orange solid was extracted into benzene and filtered. Addition of ethanol to this solution gave, on standing, red crystals of $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$. Yield: 0.18 g (63%).

(*b*) *By* $NaBH_4$ *reduction*. A suspension of *cis*-$[PtCl_2(CO)\{P(C_6H_{11})_3\}]$ (0.32 g, 0.56 mmol) in methanol was saturated with CO. Sodium tetrahydroborate (0.15 g, 3.9 mmol) was added under CO to give a dark brown suspension. The mixture was brought to boiling and then filtered. The brown residue was extracted into benzene to give a red solution which was filtered. Addition of ethanol to this solution gave, on standing, red crystals of $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$. Yield: 0.17 g (60%) [Found: C, 47.9; H, 6.7 (solvated with benzene). $C_{63}H_{105}O_3P_3Pt_3$ requires C, 47.6; H, 6.6%]. I.r. spectrum: ν_{CO} 1 769s (lit.,[3] 1 770s cm^{-1}). ^{31}P-{^{1}H} N.m.r. in C_6H_6 solution: $\delta(^{31}P)$ 66.9 (lit.,[3] 69.8 p.p.m. from H_3PO_4).

$[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$. A suspension of *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ (0.79 g, 1.8 mmol) in methanol (60 cm^3) was saturated with CO. A solution of vacuum-dried $NaBH_4$ (0.7 g, 18 mmol) in methanol (40 cm^3), also saturated with CO, was added rapidly under CO giving a red solution and a brown precipitate. The mixture was stirred under CO for 30 min, then brought to boiling to give a red solution which was filtered, whilst hot, under CO. On cooling and standing, $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$ was deposited as red, needle-like crystals which were washed well with water, then a little methanol and dried *in vacuo*. Yield: 0.54 g (80%) (Found: C, 30.5; H, 3.0. $C_{37}H_{44}O_5P_4Pt_4$ requires C, 30.2; H, 3.0%). I.r. spectrum: ν_{CO} 1 800s and 1 775s (lit.,[7] 1 800s and 1 779s cm^{-1}).

$[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$. A solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ (0.20 g, 0.36 mmol) in thf (50 cm^3) was saturated with CO. An excess of zinc dust (0.47 g, 7.2 mmol) was added and the reaction mixture stirred under CO at room temperature for 6 h. The colour of the solution changed to green and finally deep red. The excess of zinc dust was filtered off and the solution was evaporated to dryness *in vacuo*. The residue was extracted with benzene (30 cm^3). Concentration of this solution followed by the addition of methanol gave $[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$ as reddish brown microcrystals. Yield: 0.12 g (76%) (Found: C, 42.1; H, 2.6. $C_{78}H_{60}O_6P_4Pt_5$ requires C, 42.7; H, 2.7%). I.r. spectrum: ν_{CO} 1 998vs, 1 895w, 1 860s, 1 812s, and 1 787vs (lit.,[13] 1 998vs, 1 899m, 1 858s, 1 812s, and 1 788vs cm^{-1}).

$[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$. To a stirred solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ (0.20 g, 0.36 mmol) in thf (50 cm^3), triphenylphosphine (0.03 g, 0.12 mmol) was added. The reaction mixture was saturated with CO and an excess of zinc dust (0.30 g, 4.6 mmol) was added. This mixture was stirred under an atmosphere of CO for 4 h during which the colour of the solution changed to pale green and finally to red. The excess of zinc dust was filtered off and the solvent removed *in vacuo*. The residue was extracted with acetone and concentration of this solution to low volume gave red crystals of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$. A second crop was obtained on addition of methanol to the filtered acetone solution. Yield: 0.17 g (80%) (Found: C, 51.6; H, 3.4. $C_{75}H_{60}O_3P_4Pt_3$ requires C, 52.4; H, 3.5%). I.r. spectrum: ν_{CO} 1 860mw, 1 800s, and 1 790s (lit.,[7] 1 854w, 1 803s, and 1 788s cm^{-1}).

Substitution by CO *of* SO_2 *in* $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$.—The compound $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]\cdot PhMe\cdot SO_2$ (0.23 g, 0.13 mmol) was dissolved in benzene (25 cm^3) to give an orange solution. On addition of PPh_3 (12 mg, 0.04 mmol) the colour darkened to red. Carbon monoxide was then bubbled through the solution which immediately became yellow and then orange again. The solvent was removed *in vacuo* and the solid recrystallised from diethyl ether–methanol to give $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PPh_3)_3]\cdot C_6H_6$ as orange microcrystals. Yield: 0.16 g (76%) (Found: C, 47.9; H, 3.5. $C_{62}H_{51}O_4P_3Pt_3S$ requires C, 47.4; H, 3.3%). I.r. spectrum: ν_{CO} 1 790vs and 1 850w; ν_{SO_2} 1 263m and 1 094s cm^{-1}.

Reaction of $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]$ *with* CO.—The compound $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]\cdot C_6H_6$ (0.12 g, 0.07 mmol) was dissolved in benzene (20 cm^3) and CO bubbled through the solution for 2 min during which time the solution changed from orange to yellow. The solvent was removed *in vacuo* and the solid recrystallised from diethyl ether–methanol to give $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)\{P(C_6H_{11})_3\}_3]\cdot C_6H_6$. Yield: 0.08 g (70%) (Found: C, 46.0; H, 6.5. $C_{62}H_{105}O_4P_3Pt_3S$ requires C, 45.8; H, 6.5%). I.r. spectrum: ν_{CO} 1 785vs and 1 842s; ν_{SO_2} 1 070s and 1 087w cm^{-1}. $^{31}P\text{-}\{^1H\}$ N.m.r. in CD_2Cl_2 solution: $\delta(^{31}P)$ 82.2 (1 P) and 61.9 (2 P) p.p.m.

Reactions of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$.—*With* CS_2. The compound $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ (0.10 g, 0.06 mmol) was dissolved in CH_2Cl_2 (15 cm^3) and cooled to −15 °C. Carbon disulphide (five drops) was added with stirring whereupon the solution darkened from orange to deep red. The solvent was removed *in vacuo* and the residue allowed to warm to room temperature. Recrystallisation from CH_2Cl_2–hexane gave $[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$ as a brown powder. Yield: 0.04 g (55% based on Pt).

With COS. The compound $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ (0.10 g, 0.06 mmol) was dissolved in CH_2Cl_2 and COS bubbled through the solution for 10 min. The solution was stirred under an atmosphere of COS for 24 h, concentrated to low volume under reduced pressure, and ethanol added to precipitate a yellow solid. The compound $[Pt_2(\mu\text{-}S)(CO)_2(PPh_3)_2]$ was obtained on recrystallisation from CH_2Cl_2–hexane. Yield: 0.06 g (72% based on Pt) (Found: C, 45.1; H, 3.1. $C_{38}H_{30}O_2P_2Pt_2S$ requires C, 45.5; H, 3.0%). I.r. spectrum: ν_{CO} 2 030s and 1 990s cm^{-1}. $^{31}P\text{-}\{^1H\}$ N.m.r. in CD_2Cl_2 solution: $\delta(^{31}P)$ 21.1 p.p.m.

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