Preliminary communication

THE PREPARATION, STRUCTURE AND REACTIVITY OF A BRIDGING CARBON DISULPHIDE COMPLEX OF PLATINUM, $Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-}dppm)_2$

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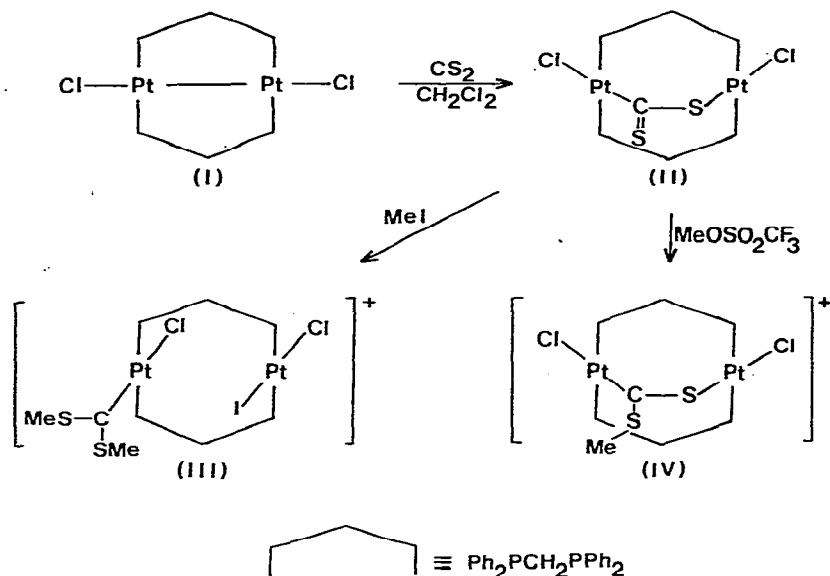
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Summary

$Pt_2Cl_2(\mu\text{-}dppm)_2$, (dppm = $Ph_2PCH_2PPh_2$) reacts with carbon disulphide to give $Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-}dppm)_2$, the structure of which has been determined and shown to contain CS_2 in an unusual C,S bridging mode. Despite coordination in this fashion, the chemistry of $Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-}dppm)_2$ parallels that of a typical $\pi\text{-}CS_2$ complex; thus with methyl iodide and methyltriflate the respective complexes $[Pt_2Cl_2I(C[SMe]_2)(\mu\text{-}dppm)_2]^+$ and $[Pt_2Cl_2(\mu\text{-}CS_2Me)(\mu\text{-}dppm)_2]^+$ result.

Carbon disulphide exhibits an interesting and varied chemistry with low-valent transition metal complexes [1]. To date, however, little effort has been directed toward investigating the reactivity of CS_2 and other heteroalkenes with transition metal cluster complexes. This research was undertaken to determine if CS_2 could be activated by a simple cluster complex and, if so, what patterns of reactivity would be exhibited by the ligated carbon disulphide.

$Pt_2Cl_2(\mu\text{-}dppm)_2$ [2] (I; Scheme 1) reacts with excess CS_2 in refluxing dichloromethane to yield golden-yellow, $Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-}dppm)_2$ (II). On refluxing in methyl iodide for a short time, II reacts to give the orange dithiocarbene complex, $[Pt_2Cl_2I(C[SMe]_2)(\mu\text{-}dppm)_2]I$ (III). Carbene formation can be prevented by the reaction of II with methyltriflate to give the yellow dithiomethyl ester cation, $[Pt_2Cl_2(\mu\text{-}CS_2Me)(\mu\text{-}dppm)_2]^+$ (IV). The structures assigned to III and IV are tentative only and are based upon the known structure of II (vide infra), and by analogy with the chemistry of complexes such as $Pt(\pi\text{-}CS_2)(PPh_3)_2$ [3] and $Os(\pi\text{-}CS_2)(CO)_2(PPh_3)_2$ [4].

The IR and ^1H NMR data for the complexes prepared are collected in Table 1. All complexes exhibit medium intensity IR bands in the 900—1000 cm^{-1} range, which can be attributed to either $\nu(C{=}S)$ or $\nu(C{-}S)$. The value of 985 cm^{-1} observed for $Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-}dppm)_2$ is perhaps the

Cl——Pt———Pt——Cl $\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{CS}_2}$

(I)

(II)

Mel

$\text{MeOSO}_2\text{CF}_3$

(III)

(IV)

$\equiv \text{Ph}_2\text{PCH}_2\text{PPh}_2$

SCHEME 1

TABLE 1

IR [a] and ^{1}H NMR DATA FOR NEW COMPLEXES

Compound [b]	$\nu(C{=}S)$ or $\nu(C{-}S)$ (cm^{-1})	δ(SMe)
Pt$_2$Cl$_2$(μ-CS$_2$)(μ-dppm)$_2$ (II)	985m	—
[Pt$_2$Cl$_2$I(C[SMe]$_2$)(μ-dppm)$_2$]$^+$(III)	995m, 955m, 840w	2.11 [c]
[Pt$_2$Cl$_2$(μ-CS$_2$Me)(μ-dppm)$_2$]$^+$ (IV)	985m, 965w, 945w	2.02 [d]
[Pt$_2$I$_3$(C[SMe]$_2$)(μ-dppm)$_2$]$^+$ (V)	990m, 955m	2.11 [c]

[a] Nujol mulls. [b] All complexes reported have satisfactory elemental analyses. Yields are all in the range 75—90%. [c] DMSO-d_6. [d] CD$_2$Cl$_2$.

most significant in that it is somewhat lower than the value generally observed in η^2-CS$_2$ complexes ($\sim$ 1150 cm^{-1}) and more in keeping with the ν_{max}(C=S) value of 1010 cm^{-1} observed for Fp—C(S)S—Fp (Fp = (η^5-C$_5$H$_5$)-Fe(CO)$_2$) [5].

However, apart from the rather diagnostic bands of the C(SMe)$_2$ ligand in III [3], the infrared frequencies quoted in Table 1 can only be considered of limited use in assigning structures to these complexes. This is especially so in the case of IV which also exhibits a maximum at 985 cm^{-1}. Monoalkylation of other CS$_2$ complexes has been observed to have varying effects on ν(C=S) [4]. Thus, methylation of Ru(η^2-CS$_2$)(CO)$_2$(PPh$_3$)$_2$ on the exocyclic S atom results in a drop in ν(C=S) of only 3 cm^{-1} whereas alkylation of Os(η^2-CS$_2$)-(CO)$_2$(PPh$_3$)$_2$ results in a drop of 45 cm^{-1}. The structure assigned to IV is therefore based upon that found for Ru(η^2-CS$_2$Me)(CO)$_2$(PPh$_3$)$_2$ [6].

In the ^{1}H NMR spectra, the methylene resonances of II—V were observed as broad, unresolved doublets between δ 3.5 and 5.0 ppm. The limited solubility of these complexes and the complexity of the expected ABMM$'$NN$'$XY pat-

tem made resolution of these multiplets beyond the means of our instrumentation. However, the fact that a broad doublet is observed for all complexes at least eliminates monomeric formulations. The methyl resonances observed for III, IV and V (vide infra) are quite typical for complexes of this type [4]. Evidence for the existence of *syn* and *anti* isomers of the $C(SMe)_2$ group in III and IV was not observed owing to interference from solvent absorption bands.

In view of the difficulties associated with unambiguously assigning structures based on IR and ^1H NMR data, an X-ray structural determination of II was initiated. Crystals of $Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-dppm})_2$ are monoclinic, a 13.87, b 14.66, c 26.28 Å, β 104.12°, $Z = 4$, space group $P2_1/c$. Intensity data were collected on a CAD-4 Diffractometer using monochromatic Mo-K_α radiation (λ = 0.70169 Å). A total of 4760 unique reflections were measured of which 967 having $I > 3\sigma(I)$ were used. The structure was solved by the direct method using the SHELX system [7] and the data were reduced by routine procedures [8]. The structure was refined by large block full matrix least squares techniques with anisotropic temperature factors assigned to the platinum atoms. Hydrogen atoms were not located. Final refinement converged at R = 0.058.

The inner coordination geometry of II is depicted in Fig. 1. The geometry around each platinum atom is essentially square planar and the Pt—Pt distance of 3.094 Å indicates the absence of a Pt—Pt bond. The geometry of the CS_2 moiety is similar to that observed in $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ [9], as are the Pt(1)C(1) and Pt(2)S(2) bond lengths. Unfortunately, little can be said about the internal dimensions of the CS_2 group since the large e.s.d.'s preclude any comparison of the C(1)S(1) and C(1)S(2) bond lengths.

Many thiocarbonyl complexes have been synthesized through modification of suitable compounds containing the $\eta^2\text{-}CS_2$ and $\eta^2\text{-}CS_2Me$ ligands [1]. It was anticipated that II and IV could be so modified. However, reaction of II

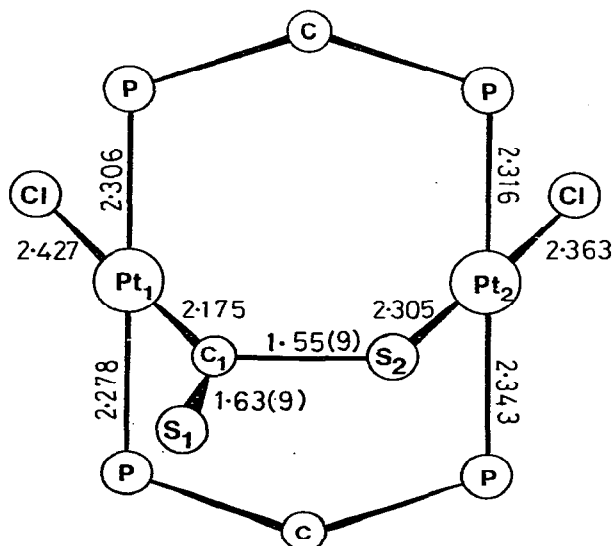Fig. 1. Inner coordination geometry of compound II.

with excess PPh_3 lead to loss of CS_2 and isolation of $[Pt_2(PPh_3)_2(\mu\text{-dppm})_2]^{2+}$ [10]. To date no isolable products have been obtained from the reaction of IV with either LiI, HCl or $NaBH_4$.

In view of the greater reactivity observed for $Pt_2I_2(\mu\text{-dppm})_2$ [2], it is perhaps surprising to note that this compound does not form a stable CS_2 adduct. That there is some interaction is evidenced by the fact that salts of the cation, $[Pt_2I_3(C[SMe]_2)(\mu\text{-dppm})_2]^+$ (V), can be isolated from the reaction of $Pt_2I_2(\mu\text{-dppm})_2$ with methyl iodide and CS_2. The instability of the CS_2 adduct of $Pt_2I_2(\mu\text{-dppm})_2$ is perhaps ascribable to greater steric interaction between the iodide ligands and the dppm phenyl groups on forming the pseudo-"A frame" structure, II.

Further work on this system and others involving the interaction of heterocumulenes with transition metal cluster complexes is in progress.

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