Carbon Subsulphide Complexes of the Platinum Metals

By A. P. GINSBERG* and W. E. SILVERTHORN

(*Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey* 07974)

Summary Carbon subsulphide undergoes oxidative addition with *trans*-$IrCl(CO)(RPh_2P)_2$ (R = Ph,Et), $[Ir(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]Cl$, and $Pt(Ph_3P)_{3\text{ or }4}$.

CARBON SUBSULPHIDE, the linear molecule S:C:C:C:S, has been known since 1893,[1] but its chemistry has been very little studied. We report on the reaction of carbon subsulphide with co-ordinatively unsaturated, low-valent platinum-metal complexes.

Some of the new compounds are listed in the Table. Satisfactory microanalyses (C, H, S, and P) have been obtained for all compounds listed. In preparing these compounds, all solvents were degassed, and manipulations were carried out under a nitrogen or argon atmosphere. The reactions are:

$$\textit{trans}\text{-}IrCl(CO)(Ph_3P)_2 + C_3S_2 \xrightarrow[\text{Benzene}]{5^\circ} \quad \text{(I)}$$

$$\textit{trans}\text{-}IrCl(CO)(EtPh_2P)_2 + 3C_3S_2 \xrightarrow[\text{Benzene}]{25^\circ} \quad \text{(II)}$$

$$[\mathrm{Ir(Ph_2PCH_2\cdot CH_2\cdot PPh_2)_2]Cl},x\mathrm{H_2O} + \mathrm{C_3S_2} \xrightarrow[\mathrm{CH_2Cl_2}]{-10^\circ} \mathrm{(III)}$$

$$[\mathrm{Ir(Ph_2PCH_2\cdot CH_2\cdot PPh_2)_2]Cl},x\mathrm{H_2O} + 2\mathrm{C_3S_2} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{reflux}} \mathrm{(IV)}$$

$$\mathrm{Pt(Ph_3P)_{3\ or\ 4}} + \mathrm{C_3S_2} \xrightarrow[\mathrm{Et_2O}]{-15^\circ} \mathrm{(V)}$$

$$\mathrm{(V)} + \mathrm{C_3S_2} \xrightarrow[\mathrm{CHCl_3}]{\text{reflux}} \mathrm{(VI)}$$

In the i.r. spectrum of free (liquid) C_3S_2, a very strong band at 2065 cm.$^{-1}$ has been assigned as $\nu(C{=}C)$ (ν_4,Σ_u^+) and a strong band at 1019 cm.$^{-1}$ as $\nu(C{=}S)$ (ν_3,Σ_u^+).[2] The compounds with one mole of C_3S_2 per metal atom, (I), (III), and (V), all have a very strong i.r. absorption at 1980—1995 cm.$^{-1}$. We assign this as $\nu(C{=}C)$ of the bound C_3S_2. The occurrence of this band at nearly the same frequency in (I), (III), and (V) suggests that the bonding of C_3S_2 is similar in these three compounds. Evidence that the C_3S_2 molecule retains its identity in the complexes with one mole of C_3S_2, is provided by the observation that the i.r. spectrum of a bromoform solution of (III) has strong $\nu(C{=}C)$ bands due to both free and bound C_3S_2; a chloroform solution of (III) has only a very weak absorption attributable to free C_3S_2, but a strong one due to bound C_3S_2 at the same frequency as in the solid state.

Carbon sulphide complexes with iridium and platinum

	Formula	Colour	Selected i.r. data (KBr discs)
(I)	$IrCl(CO)(Ph_3P)_2(C_3S_2)$[a]	light brown	2030s,[f] 1985vs,[g] 1960sh,[g] 855m,[h] 665sh[h]
(II)	$[IrCl(CO)(EtPh_2P)_2(C_3S_2)_3]_n$[b]	purple	2030s,[i] ~1450s, 1280m, 1255m
(III)	$[Ir(Ph_2PCH_2\cdot CH_2\cdot PPh_2)_2(C_3S_2)]Cl,3H_2O$[c]	yellow	1980vs,[g] 840m,[h] 635sh[h]
(IV)	$\{[Ir(Ph_2PCH_2\cdot CH_2\cdot PPh_2)_2(C_3S_2)_2]Cl\}_n$[d]	purple	~1425s, 1275m, 1250sh
(V)	$Pt(Ph_3P)_2(C_3S_2)$[a]	red-brown	1995vs,[g] 935wm,[h] 775m,[h] 370w[f]
(VI)	$[Pt(Ph_3P)_2(C_3S_2)_2,CHCl_3]_n$[e]	purple	~1400s, ~1280

[a] Too unstable for molecular weight measurements.

[b] Osmometric molecular weight measurements in chloroform (37°) give $n \approx 5{\cdot}3$.

[c] Conductivity measurements (0°), over the range 2—13 g./l. in acetonitrile, indicate that this compound is a 1 : 1 electrolyte and that the cation is monomeric.

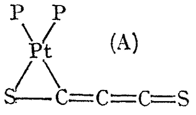
[d] Conductivity (25°) and osmometric (37°) measurements over the range 1·6—13 g./l. in acetonitrile solution indicate that this compound is a 1 : 1 electrolyte with $n = 1$. However, osmometer measurements over the same concentration range in chloroform solution give $n = 2{\cdot}6$.

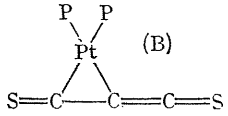
[e] Osmometer measurements in chloroform (37°) give n = 4—5, but appreciable decomposition took place.

[f] ν(CO); [g] $\nu(C = C)$; [h] ν(CS); [i] ν(MS), tentative assignment.

Compound (I) has a single ν(CO) frequency at 2030 cm.$^{-1}$ as compared to 1967 cm.$^{-1}$ for ν(CO) in $IrCl(CO)(Ph_3P)_2$. The shift of ν(CO) to higher frequency suggests that in (I), and also presumably in (III) and (V), the C_3S_2 has undergone oxidative addition to the metal.[3] Structures A and B, drawn for the Pt compound (V), show the two possible modes of oxidative addition.

Structure (A) is analogous to the known structure of $Pt(Ph_3P)_2CS_2$[4] and (B) is analogous to the recently suggested structure of $Pt(Ph_3P)_2(CH_2{:}C{:}CH_2)$.[5,6] Both (A) and (B) should give a $\nu(C{=}C)$ absorption in the region observed. The medium bands at 855, 840, and 935 cm.$^{-1}$ in, respectively,


(A)


(B)

(I), (III), and (V), are reasonably assigned as ν(CS) for the $C{=}C{=}S$ grouping in either (A) or (B) [*cf.*, $\nu(CS)$ = 859 cm.$^{-1}$ in $O{=}C{=}S$]. Compound (V) has a medium band at 775 cm.$^{-1}$ which could be due to the second ν(CS) frequency expected for both (A) and (B); a corresponding band has been found at 665 cm.$^{-1}$ for (I) and at 635 cm.$^{-1}$ for (III). A weak band at 370 cm.$^{-1}$ in the spectrum of (V) inclines us to favour structure (A), since it could then be assigned as ν(PtS) [*cf.*, the tentative assignment of ν(PtS) at 313 cm.$^{-1}$ in $Pt(Ph_3P)_2CS_2$ [7]].

The compounds with more than one mole of C_3S_2 per metal atom are characterized by a strong band in the 1400—1450 cm.$^{-1}$ region which is partially obscured by phosphine ligand absorptions. They also have two medium intensity bands in the 1250—1280 cm.$^{-1}$ region. Compound (II) has a ν(CO) band shifted 90 cm.$^{-1}$ to higher frequency compared to ν(CO) in $IrCl(CO)(EtPh_2P)_2$. As before, this suggests that oxidative addition to the metal has taken place in (II) and presumably also in (IV) and (VI). It seems unlikely that more than one C_3S_2 molecule reacts directly with each metal atom, and we assume that only one C_3S_2 adds to the metal and then additional carbon subsulphide interacts with the already bound molecule. The products appear to be oligomeric.

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