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**Preliminary communication**

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# OXIDATIVE-ADDITION ACROSS A CARBON—SULFUR BOND: PLATINUM(0) COMPLEXES WITH ETHYLENE TRITHIOCARBONATE AND TRIMETHYLENE TRITHIOCARBONATE

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## Summary

Platinum(0) phosphine complexes $PtL_4$ (where L = $PPh_3$ or $PMePh_2$) undergo oxidative addition reactions with ethylene trithiocarbonate, $C_2H_4CS_3$, to give *cis*-$\overline{\mathrm{PtCS_2CH_2CH_2S}}(L)_2$ and with trimethylene trithiocarbonate, $(CH_2)_3CS_3$, to give *cis*-$\overline{\mathrm{PtCS_2CH_2CH_2CH_2S}}(PPh_3)_2$. These bidentate ligands are displaced by $CS_2$ giving the free trithiocarbonates and the known $CS_2$ complex $Pt(CS_2)(PPh_3)_2$. Dimethyl trithiocarbonate, $(CH_3S)_2CS$, does not undergo the same type of oxidative-addition reaction with $Pt(PPh_3)_4$, and ethylene carbonate shows no reactivity toward $Pt(PPh_3)_4$.

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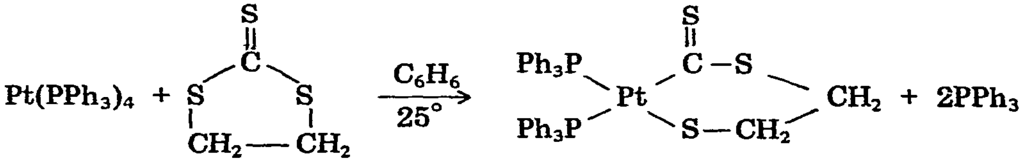
The complex $Pt(PPh_3)_4$ [1] undergoes a facile oxidative-addition reaction with $C_2H_4CS_3$ by cleavage of a carbon—sulfur bond to form a $Pt^{II}$ complex with a cyclic structure.

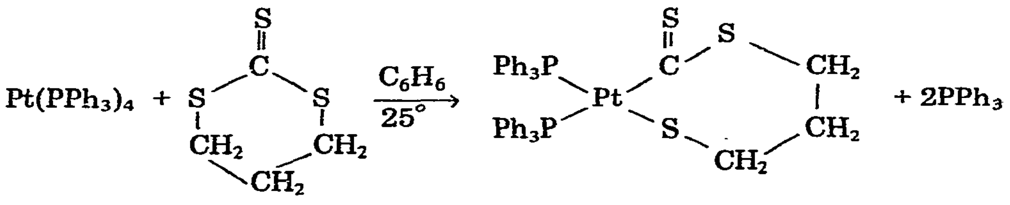


Reaction occurs instantly at room temperature upon adding a benzene solution of $C_2H_4CS_3$ to a stoichiometric amount of $Pt(PPh_3)_4$ in benzene under an inert atmosphere. Removal of solvent under vacuum and trituration of the residue with $Et_2O$ gave a white solid which was recrystallized from chloroform—hexane to give the product in nearly quantitative yield. The complex *cis*-$PtCS_2CH_2CH_2S(PPh_3)_2$ is an air-stable, white crystalline solid, m.p. 182° (dec.). (Anal. Found: C, 54.9; H, 4.1; S, 11.3. $C_{39}H_{34}P_2PtS_3$ calcd.: C, 54.7; H, 4.0; S, 11.3%.Mol. wt. osmometrically in benzene, Found: 860; calcd.: 856.)

The NMR spectrum of *cis*-$\overline{\mathrm{PtCS_2CH_2CH_2S}}(PPh_3)_2$ (in $CDCl_3$) shows complex multiplets at $\tau$7.5 and 6.9 (relative to TMS as internal standard) indicating non-equivalence of the ethylene protons in the bound ligand. The shielding effect of the $PPh_3$ ligands is shown by the relatively high field position of these multiplets compared to the singlet observed for free $C_2H_4CS_3$ at $\tau$6.02. The analogous methyldiphenylphosphine complex *cis*-$\overline{PtCS_2CH_2CH_2S}(PMePh_2)_2$ was prepared similarly from $Pt(PMePh_2)_4$. The NMR spectrum of this complex shows two separate resonances of equal intensity for the phosphine-methyl groups at $\tau$8.43 and 7.89 indicating the presence of two non-equivalent phosphine ligands. Each resonance occurs as a doublet due to coupling of the methyl protons with $^{31}P$ of the phosphine with $J(^{31}P{-}^{1}H)$ values of 8 and 10 Hz, respectively. Each of these doublets has satellite doublets due to splitting by $^{195}Pt$ with $J(^{195}Pt{-}^{1}H)$ values of 26 and 37Hz, respectively. The doublet resonance for each methyl is in agreement with a *cis* configuration for the phosphines [2]. The solid state (Nujol mull) IR spectrum of *cis*-$\overline{PtCS_2CH_2CH_2S}$-$(PPh_3)_2$ shows sharp bands at 1089 and 1100 cm$^{-1}$, one of which is probably due to $\nu(C{=}S)$. The IR spectrum of the complex in $CHCl_3$ shows only a single, strong absorption at 1095 cm$^{-1}$. However, a strong band at this position is commonly observed in $Pt^{II}$ complexes with $PPh_3$ ligands (e.g., *cis*-$PtCl_2(PPh_3)_2$ ) due to the in-plane C—H bending mode of the phenyl groups, and we believe that the $\nu(C{=}S)$ mode is not resolved from this band in the solution spectrum. The free ligand, $C_2H_4CS_3$, shows a strong $\nu(C{=}S)$ band at 1076 cm$^{-1}$.

Oxidative-addition reactions of $Pt^0$ with $ClCS_2Et$ [3], $ClCSNMe_2$ [4], and ClCSOMe [5] are known to give a metal-bonded thiocarbonyl function ($PtC\leqslant^{S}$) via cleavage of the carbon—chlorine bond, and this is typical of the reactivity of many halogen-containing organic compounds toward platinum group metal complexes in low oxidation states. In order to determine whether or not the cleavage of carbon—sulfur bonds in trithioesters, as occurs with $C_2H_4CS_3$, is typical of the reactivity of all trithioesters, we examined the reaction of $(CH_3S)_2CS$ [6] with $Pt(PPh_3)_4$, and found that cleavage of a carbon—sulfur bond by $Pt^0$ does not occur. The unstable orange colored solid isolated from this reaction was not fully characterized. However, when this reaction was followed by NMR, only a sharp singlet at $\tau$3.54 was observed to appear for the product. This clearly indicates that cleavage of a carbon—sulfur bond in $(CH_3S)_2CS$ to give $Pt(SCH_3)(CS_2CH_3)(PPh_3)_2$ does not occur. It therefore seems that the specific reactivity of $C_2H_4CS_3$ toward $Pt^0$ which we observe is not general for trithioesters.

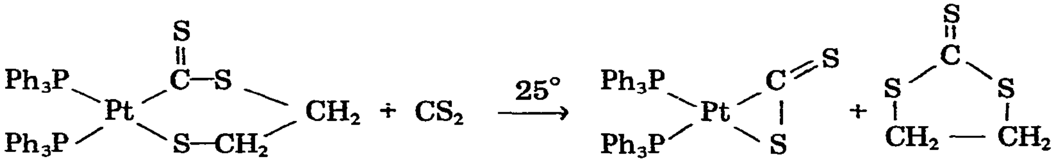
In order to determine if carbon—sulfur bond cleavage in $C_2H_4CS_3$ is a result of ring strain in the 5-membered ring structure, we examined the reactivity of the 6-membered ring compound, $(CH_2)_3CS_3$ [8]. It was found that reaction occurred readily with carbon—sulfur bond cleavage to give the analogous complex.



The product *cis*-$\overline{PtCS_2CH_2CH_2CH_2S}(PPh_3)_2$ is a stable, yellow crystalline solid, m.p. 200° (dec.). (Anal. Found: C, 54.3; H, 4.18; S, 10.1; Cl, 1.02. $C_{40}H_{36}P_2PtS_3 \cdot 0.1\ CHCl_3$ calcd.: C, 54.6; H, 4.13; S, 10.9; Cl, 1.20%.) The NMR spectrum (in $CDCl_3$) shows three complex multiplets for the methylene protons at $\tau$8.1, 7.4, and 6.7.

While it appears that the reactivity of $C_2H_4CS_3$ and $(CH_2)_3CS_3$ as contrasted with $(CH_3S)_2CS$ cannot be ascribed to ring strain, their tendency to oxidatively add to $Pt^0$ may be attributed to the formation of a stable chelate ring. Such a chelate ring could also be formed by the oxygen analog, ethylene carbonate, $C_2H_4CO_3$. It, however, does not react with $Pt(PPh_3)_4$ in $C_6H_6$ solution at 25°.

The complex *cis*-$\overline{PtCS_2CH_2CH_2S}(PPh_3)_2$ reacts with $CS_2$ to form the known adduct $Pt(CS_2)(PPh_3)_2$ [7] and free $C_2H_4CS_3$.



These products were easily identified in solution by the strong bands in the IR spectrum at 1157 and 1076 cm$^{-1}$ corresponding to $\nu$(C=S) of $Pt(CS_2)(PPh_3)_2$ and free $C_2H_4CS_3$, respectively, and by the singlet in the NMR spectrum at $\tau$6.02 for free $C_2H_4CS_3$. Complete ligand displacement occurs within 20 minutes at 25° when the complex is dissolved in $CS_2$, and over a period of about 10 h when $CS_2$ is added to a solution of the complex in either $C_6H_6$ or $CHCl_3$. The analogous *cis*-$\overline{PtCS_2CH_2CH_2CH_2S}(PPh_3)_2$ reacts similarly with $CS_2$ to give $Pt(CS_2)(PPh_3)_2$ and free $(CH_2)_3CS_3$.

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