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Polynuclear CS_2 Palladium Derivatives

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Compounds of empirical formula $MLCS_2$ (L = tertiary phosphine) have been known ever since the synthesis of the first carbon disulphide–transition metal complexes [1]. So far, such compounds have been reported for M = Ni [1–4] and M = Pt [5]. Herein we describe the preparation of the first palladium complexes of this stoichiometry, obtained by phosphine abstraction from $PdL_2(\eta^2\text{-}CS_2)$ precursors.

Addition of an equivalent amount of $[Pd(OCMe_2)bipy(C_6F_5)]ClO_4$ to a solution of $PdL_2(\eta^2\text{-}CS_2)$ in Me_2CO/CS_2 results in the precipitation (eqn. 1) of yellow solids of the general formula '$PdLCS_2$', ($L = PPh_3$, I, 66%; $L = P(p\text{-Tol})_3$, II, 24%).

$$PdL_2(\eta^2\text{-}CS_2) + [Pd(OCMe_2)bipy(C_6F_5)]ClO_4 \xrightarrow{Me_2CO/CS_2} \text{'}PdLCS_2\text{'} + [PdLbipy(C_6F_5)]ClO_4 \qquad (1)$$

When $L = PCy_3$, the tendency to form the betaine $Cy_3P^+CS_2^-$ offers an alternative route, since reaction (eqn. 2) of the $\eta^2\text{-}CS_2$ complex with an excess of carbon disulphide yields '$Pd(PCy_3)CS_2$' as a yellow powder (III, 90%).

$$Pd(PCy_3)_2(\eta^2\text{-}CS_2) + CS_2 \xrightarrow{Me_2CO} \text{'}Pd(PCy_3)CS_2\text{'} + Cy_3PCS_2 \qquad (2)$$

Although the three complexes precipitate as acetone solvates, this solvent can be removed by gently heating (50°, 24 hr) and their elemental analyses (Table I) are then in good agreement with the expected ones. These compounds are sparingly soluble in carbon disulphide; insoluble in ethanol, ether, acetone; and decompose in benzene, chloroform, dichloromethane giving a black deposit of metallic palladium. These solubility properties preclude molecular weight determinations and growth of crystals suitable for a structural study by X-ray diffraction. Therefore, besides the analytical data, only spectroscopic (i.r. and ^{31}P n.m.r.) information is available.

^{31}P n.m.r. spectra of I and III show a single peak, which requires all phosphines to be equivalent. Some more information can be obtained from the i.r. spectra, which show several bands due to the phosphine ligand (I: 1435vs, 1095vs, 1025m, 995m, 750sh s, 745vs, 705s, 690vs, 520vs, 500vs; II: 1715m, 1600m, 1515vs, 1510sh s, 1495vs, 1390m, 1305m, 1220m, 1185m, 1100vs, 1020m, 805vs, 710s, 705sh s, 645s, 640sh s, 630s, 615s, 515vs, 505vs; III: 1300m, 1265m, 1175s, 1100vs, 1000s, 915m, 895m, 880m, 850s, 845s, 740s, 705vs, 530m, 515s, 490m), being remarkable that complex I presents only two bands in the 500–550 cm^{-1} region, which excludes the possibility of two triphenylphosphine molecules being co-ordinated to any single palladium atom [6].

Compounds I–III also show several absorptions in the 1100–1200 cm^{-1} region, characteristic of $\nu(C{=}S)$ stretching (see Table I).

The known propensity of palladium(II) to be four-coordinate suggests our compounds to be polynuclear species with CS_2 groups bridging metallic centres. A number of structures have been proposed for a CS_2 bridge, only a few of which have been ascertained by means of diffraction techniques.

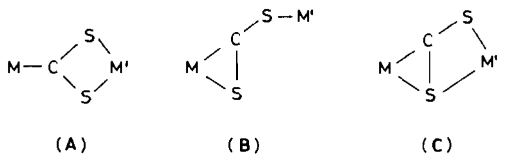

TABLE I. Analytical and Spectroscopic Data.

Compound		Found (calc.)		$\delta(^{31}P)$	i.r. (1100–1200 cm^{-1} region)
		%C	%H		
I	$[Pd(PPh_3)CS_2]_x$	51.12 (51.30)	3.54 (3.40)	24.1	1115br vs, 1135br vs, 1155s
II	$[PdP(p\text{-Tol})_3CS_2]_x$	53.66 (54.27)	4.34 (4.35)	–	1115vs, 1130vs, 1155s
III	$[Pd(PCy_3)CS_2]_x$	48.88 (49.29)	7.37 (7.18)	37.3	1120vs, 1140vs, 1150br s

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Coordination as a metallodithiocarboxylato(S,S)-metal [7] (A) has been found [8–10] to exhibit two characteristic absorptions in the 920–940 and 870–880 cm^{-1} regions, assignable respectively to the symmetric or assymmetric stretching modes of the CS_2 moiety.

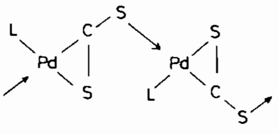
Coordination of the exocyclic sulphur atom of a η^2-CS_2 complex to a second metal centre leads [11–13] to dinuclear complexes (B) which show a single absorption in the 1100–1200 cm^{-1} region, at a frequency close to that found in the mononuclear starting material.

Another coordination mode (C) has been found [12–14] for $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)]^{2+}$, which does not show 'i.r. bands attributable to C=S stretching modes'.

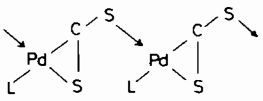
Only recently [4], the structure of $[Ni(PPh_3)CS_2]_2$ has been elucidated, in which two nickel atoms are bridged through the *exo* sulphur atom of two η^2-CS_2 ligands (and not through the *endo* sulphur atoms as had been proposed earlier).

Though the i.r. absorptions due to triphenylphosphine in I and $[Ni(PPh_3)CS_2]_2$ coincide, both spectra differ very much in the 1100–1200 cm^{-1} region since the latter only presents one band at 1125 cm^{-1} (s).

Therefore, our compounds must have a different structure, and we think them to be polymer species of type (E) or (F).



(E)



(F)

We think it noteworthy that compounds of this type '$PdLCS_2$' could only be isolated for L = PPh_3, $P(p\text{-}Tol)_3$, PCy_3, and not for other tertiary phosphines (PEt_3, PBu_3, $PEtPh_2$, $P(p\text{-}C_6H_4OMe)_3$, $P(p\text{-}C_6H_4Cl)_3$), in agreement with the results found for nickel [3].

Besides, compounds I and III react with stoichiometric amounts of the respective phosphines regenerating the η^2-CS_2 starting complex, (as identified by their i.r. spectra), whereas III does not react with either PPh_3 or PCy_3.

References

1 M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 865 (1967).

2 E. Uhlig and W. Poppitz, *Z. Chem., 19,* 191 (1979).

3 M. G. Mason, P. N. Swepston and J. A. Ibers, *Inorg. Chem., 22,* 411 (1983).

4 C. Bianchini, C. A. Ghilardi, A. Meli, S. Midollini and A. Orlandini, *Chem. Commun.,* 753 (1983).

5 D. H. Farrar, R. Taylor and A. Walker, *Inorg. Chim. Acta, 64,* L195 (1982).

6 S. H. Mastin, *Inorg. Chem., 13,* 1003 (1974).

7 J. M. Lisy, E. D. Dobrzynski, R. J. Angelici and J. Clardy, *J. Am. Chem. Soc., 97,* 656 (1975).

8 W. P. Fehlhammer and H. Stolzenberg, *Inorg. Chim. Acta, 44,* L151 (1980).

9 W. P. Fehlhammer, A. Mayr and H. Stolzenberg, *Ang. Chem. Int. Ed. Eng., 18,* 626 (1976).

10 H. Stolzenberg, W. P. Fehlhammer and P. Dixneuf, *J. Organomet. Chem., 246,* 105 (1983).

11 T. G. Southern, U. Oehmichen, J. Y. LeMarouille, H. LeBozec, D. Grandjean and P. Dixneuf, *Inorg. Chem., 19,* 2976 (1980).

12 C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, *Inorg. Chem., 19,* 2968 (1980).

13 J. Amaudrut, J. Sala-Pala, J. E. Guerchais, R. Mercier and J. Douglade, *J. Organomet. Chem., 235,* 301 (1982).

14 C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, *Ang. Chem. Int. Ed. Eng., 18,* 673 (1979).