Inorganica Chimica Acta, 44 (1980) L151–L152
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

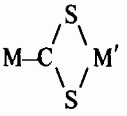
Isocyanide- and Heteroallene-bridged Metal Complexes. III. Reactions of $Pd(\eta^2\text{-}CS_2)(PPh_3)_2$ with Metal Compounds. 'Coordination Isomerism' in Metallodithiocarboxylato Metal Complexes

WOLF PETER FEHLHAMMER und HERIBERT STOLZENBERG

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-8520 Erlangen, F.R.G.

Received October 12, 1979

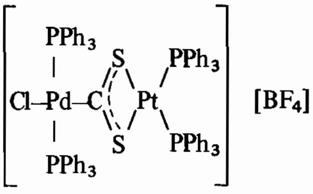
Recently, we reported on the systematic formation of metallodithiocarboxylato metal complexes by reaction of the metal–CS_2 species $[Fe(\eta\text{-}C_5H_5)(CO)_2CS_2]^-$ and $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ with higher valent metal compounds. It has been shown that the particular CS_2-bridging mode



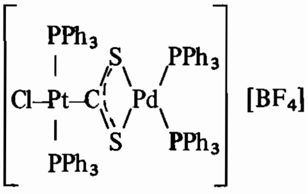
which combines the elements of both a dithiocarbene metal and a metal S,S'-dithiolate, may serve as a rather general building unit for a variety of stable di- and trinuclear metal complexes [1].

We have now extended our investigations to include Wilkinson's palladium complex $Pd(\eta^2\text{-}CS_2)(PPh_3)_2$, (I) [2], of which no chemistry has been described so far. Oxidative addition of iodine occurs with loss of CS_2 to give $PdI_2(PPh_3)_2$; similarly, $PdCl_2(PPh_3)_2$ is produced by the reaction of I with $HgCl_2$. On the other hand, if I is reacted with the chlorine bridged complex $[PdCl(PPh_3)_2]_2[BF_4]_2$ in a 2:1 molar ratio, CS_2 is incorporated in the reaction product $[(Ph_3P)_2ClPd(CS_2)Pd(PPh_3)_2][BF_4]$, which is the palladium analog of Angelici's platinum compound [3].

The dinuclear heterometallic product II of the reaction with the corresponding platinum complex $[PtCl(PPh_3)_2]_2[BF_4]_2$ turns out to be an isomer of III, which has been synthesized earlier from $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ and $[PdCl(PPh_3)_2]_2[BF_4]_2$ (2:1) [1].



(II)



(III)

The two complexes, having merely their palladium and platinum coordination sites interchanged, represent a rare example of 'coordination isomerism', more frequently encountered in salt-like compounds with both complex cations and anions. Hence, II and III are very similar, though definitely not identical (see Tables I and II).

As expected, III containing a Pt–C bond is slightly more stable than II with the carbene moiety coordinated to palladium. A striking decrease in thermal stability, however, parallels the stepwise replacement in the CS_2-bridged complexes of platinum by palladium, as reflected by a total ~100 °C drop in the decomposition points (Table I).

A characteristic two band pattern is found in the IR-spectra of the complexes $[(Ph_3P)_2ClM(CS_2)M'(PPh_3)_2][BF_4]$ (M,M' = Pd, Pt), which we assign to the antisymmetric (930 ± 10 cm^{-1}) and symmetric (875 ± 5 cm^{-1}) CS_2-stretching vibrations (Table I). Further significant FIR* as well as Raman** data comprise the $\nu(M\text{–}C)$ (435–465 m, cm^{-1}), $\nu_{as,s}(MS_2)$ (320–325 sst, 300–315 m–st, cm^{-1}), and $\nu(M\text{–}Cl)$ (~290 m–st, cm^{-1}) vibrations.

The ^{31}P nmr spectra are given in Table II. The number and relative intensities of the signals in combination with the appearance of ^{195}Pt satellites allow the unequivocal assignment of chemical shifts and couping constants to each of the four different types of phosphane ligands (Table II). The observed $^1J(Pt\text{–}P)$ values are consistent with the accepted rule $J_{cis} > J_{trans}$ [4]. Furthermore, these data prove the *trans*-configuration at the carbene carrying metal and the equivalence of the *cis*-triphenylphosphane ligands on the chelated metal, which in turn provides

---

*Polyethylene discs, Polytec FIR 30.

**Polycrystalline, Cary Model 82.

TABLE I. Characteristic IR Data (KBr, cm^{-1}) of $[(Ph_3P)_2ClM(CS_2)M'(PPh_3)_2][BF_4]$.

M	M'	F. °C (dec.)	ν_{as}, ν_s (CS_2)	$\Delta\nu$	I_{as}/I_s
Pt	Pt	254–257	939 m–s, 874 m	65	1 : 0.6
Pt	Pd	208–213	932 m–s, 872 m	60	1 : 0.6
Pd	Pt	191–196	923 m, 879 m	44	1 : 0.9
Pt	Pd	158–163	920 m, 879 m	41	1 : 1.0

TABLE II. ^{31}P Nmr Data of $[(Ph_3P)_2ClM(CS_2)M'(PPh_3)_2][BF_4]$ (CD_2Cl_2, 85% H_3PO_4 ext.).

M	M'	'*trans*-MP_2'		'*cis*-$M'P_2$'		I_1/I_2
		δ_1 [ppm]	$^1J(Pt–P)$ [Hz]	δ_2 [ppm]	$^1J(Pt–P)$ [Hz]	
Pt	Pt	−20.0	2900	−16.1	3060	1 : 1
Pt	Pd	−18.5	2950	−30.3	–	1 : 1
Pd	Pt	−24.3	–	−15.6	3090	1 : 1
Pd	Pd	−20.8	–	−30.5	–	1 : 1

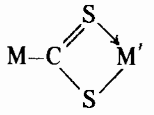
T

TABLE III. Characteristic IR Data (KBr, cm^{-1}) of $(Ph_3P)_2M(SCS)M'(CO)_5$, (IV)

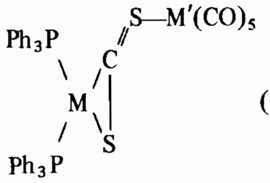
M	M'	F. °C (dec.)	$\nu(CO)[A_1][B_1][E][A_1']$	$\nu(C{=}S)^a$	$\nu(C–S)^a$
Pt	Cr	145–152	2055 s, 1978 m, 1920 vs, 1888 vs	1137 m	674 w
Pt	W	172–176	2060 s, 1974 m, 1917 vs, 1878 vs	1134 m	668 sh
Pd	Cr	108–113	2057 s, 1980 m, 1926 vs, 1890 vs	1175 m	
Pd	W	113–116	2060 s, 1975 m, 1918 vs, 1881 vs	1171 m	658 w

[a] $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$: 1142 vs, 652 m; $Pd(\eta^2\text{-}CS_2)(PPh_3)_2$: 1177 vs, 636 m, cm^{-1}.

evidence for the equivalent nature of the two S atoms of the bidentate ligand, thus precluding any asymmetric formulation such as



Addition of $M'(CO)_5thf$(M' = Cr, W) to I affords the dark orange complexes IVa which, in contrast to the corresponding yellow platinum compounds IVb [1], are very labile in solution. The IR spectra (Table III) support theproposed structure of an intact



(IVa, M = Pd, IVb, M = Pt)

$M(\eta^2\text{-}CS_2)(PPh_3)_2$ molecule acting as a monodentate S-donor ligand through the 'exo-sulfur atom'. The same kind of CS_2-bridging has meanwhile been ascertained by X-ray structure analyses of $[(Triphos)Co(SCS)Cr(CO)_5]$ [5] and $(R_3P)_2(CO)_2Fe(SCS)Mn(CO)_2Cp$ [6].

Experimental

General procedure for $[(Ph_3P)_2ClM(CS_2)M'(PPh_3)_2][BF_4]\cdot(CH_3)_2CO$

Under an atmosphere of dry nitrogen CH_2Cl_2 solutions of 2 mmol $M(\eta^2\text{-}CS_2)(PPh_3)_2$ and 1 mmol $[M'Cl(PPh_3)_2]_2[BF_4]_2$ [7] are mixed and stirred for about 1 hr. The reaction mixture is then filtered through cellulose and evaporated to dryness. The residue is recrystallized twice from acetone/petrol ether to give yellow air-stable needles (70–90%) containing one molecule of acetone per formula.

Acknowledgements

We gratefully acknowledge support of our work by Prof. Dr. H. Behrens, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. M. Moll for recording the ^{31}P nmr spectra.

References

1 W. P. Fehlhammer, A. Mayr, and H. Stolzenberg, *Angew. Chem., 91,* 661 (1979).
2 M. C. Baird and G. Wilkinson, *J. Chem. Soc. A,* 865 (1967).
3 J. M. Lisy, E. D. Dobrzynski, R. J. Angelici, and J. Clardy, *J. Am. Chem. Soc., 97,* 656 (1975).
4 P. S. Pregosin and R. W. Kunz: '^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes', (NMR, Basic Principles and Progress, Vol. 16), Springer-Verlag, Berlin, 1979.
5 C. Bianchini, A. Meli, A. Orlandini, and L. Sacconi, *Inorg. Chim. Acta, 35,* L375 (1979).
6 P. Dixneuf, personal communication.
7 W. Beck and K. V. Werner, *Chem. Ber., 104,* 2901 (1971); C. Eaborn, N. Farrell, J. L. Murphy, and A. Pidcock, *J. Chem. Soc. Dalton Trans.,* 58 (1976).