

REACTIONS OF CARBON DISULPHIDE WITH PALLADIUM(0) COMPLEXES

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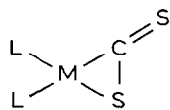
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Summary

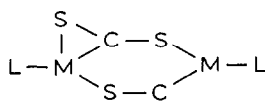
The reaction of PdL_n ($n = 3$, $\text{L} = \text{P}^t\text{BuPh}_2$; $n = 2$, $\text{L} = \text{P}^t\text{Bu}_2\text{Ph}$, P^tBu_3 , PCy_3) with CS_2 in hexanes results in precipitation of either $\text{Pd}(\eta^2\text{-CS}_2)\text{L}_2$ ($\text{L} = \text{P}^t\text{BuPh}_2$, PCy_3) or $\text{Pd}_2(\mu\text{-CS}_2)_2\text{L}_2$ ($\text{L} = \text{P}^t\text{Bu}_2\text{Ph}$, P^tBu_3). The monomeric complexes $\text{Pd}(\text{CS}_2)\text{L}_2$ are unstable in a CS_2 solution and convert to the corresponding doubly CS_2 -bridged dimeric complexes $\text{Pd}_2(\text{CS}_2)_2\text{L}_2$. It is the steric bulk of the phosphine ligands that appears to control which type of product initially precipitates. Reaction of the trinuclear clusters $\text{Pd}_3(\text{CO})_3\text{L}_3$ with CS_2 gives the dimeric complexes $\text{Pd}_2(\text{CS}_2)_2\text{L}_2$. The molecular structure of $\text{Pd}_2(\text{CS}_2)_2(\text{P}^t\text{Bu}_2\text{Ph})_2$ has been determined by a single crystal X-ray analysis. Crystals of the complex are monoclinic, space group $P2_1/c$ (a 10.373(2) b 13.684(1), c 12.173(2) Å, β 94.04(7)°) with two centrosymmetrically related dimers per unit cell. The final agreement indices (172 variables, 2071 reflections) are $R = 0.032$ and $R_w = 0.038$. The $\text{PPd}(\text{CS}_2)_2\text{PdP}$ core is essentially planar with each CS_2 ligand π -bonded through the $\text{C}=\text{S}$ linkage to one metal atom and σ -bonded to the other through the second S atom.

Introduction

There is an extensive coordination chemistry of carbon disulphide with the CS_2 ligand exhibiting a variety of bonding modes [1]. Interest in the area has been stimulated by the versatility of this ligand and the belief that it may serve as a model for the activation of CO_2 . Initial research by Baird and Wilkinson [2], and Mason and Rae [3] revealed that the Pd and Pt complexes $\text{M}(\text{CS}_2)(\text{PPh}_3)_2$ contained $\eta^2\text{-CS}_2$



(a)



(b)

Where M is a Ni subgroup metal and L is a phosphine ligand

ligands (type **a**), and reported [2] the empirical formula of a Ni complex to be $\text{Ni}(\text{CS}_2)(\text{PPh}_3)$. The Ni complex was subsequently shown by X-ray crystallography [4] to be $\text{Ni}_2(\text{CS}_2)_2(\text{PPh}_3)_2$ with $\mu\text{-CS}_2$ ligands (type **b**).

There have been no examples of type **a** Ni complexes reported although attempts have been made to prepare them [1]. We have recently described [5] the preparation of Pd and Pt doubly CS_2 -bridged dimeric complexes, type **b**, by the reaction of the trinuclear complexes $\text{M}_3(\text{CO})_3\text{L}_3$ and CS_2 . Complexes of Pd and Pt with type **b** stoichiometry have also been isolated from the reaction of metal-phosphine monomeric compounds and CS_2 [6,7,8]. We now report our results on the factors that determine which type of CS_2 complex forms for Pd.

Experimental

All reactions were performed under an N_2 atmosphere. Solvents were dried and distilled under N_2 prior to use. P^iBuPh_2 was purchased from Strem Chemicals Inc, while $\text{P}^i\text{Bu}_2\text{Ph}$ and P^iBu_3 were synthesised by literature methods [9–11] as were PdL_2 [12] (where $\text{L} = \text{P}^i\text{Bu}_3$, P^iBuPh_2 and PCy_3), $\text{Pd}_3(\text{CO})_3\text{L}_3$ [12] (where $\text{L} = \text{P}^i\text{Bu}_3$, PCy_3 and $\text{P}^i\text{Bu}_2\text{Ph}$) and $\text{Pd}(\text{CS}_2)(\text{PPh}_3)_2$ [2]. The IR spectra, as Nujol mulls, were recorded on a Pye Unicam SP102S spectrometer. The ^{31}P NMR were recorded on a Bruker WP80 at 32.8 MHz, with chemical shifts measured, relative to external $\text{P}(\text{OMe})_3$ in $\text{CO}(\text{CD}_3)_2$.

Preparation of $\text{Pd}(\text{CS}_2)(\text{PCy}_3)_2$ (1a)

1.00 g of $\text{Pd}(\text{PCy}_3)_2$ was dissolved in 75 ml of hexanes and 5 ml of CS_2 added. Immediately a yellow-orange precipitate formed. The mixture was stirred for 15 min filtered and the product washed with hexanes (yield 0.79 g, 70%).

Preparation of $\text{Pd}(\text{CS}_2)(\text{P}^i\text{BuPh}_2)_2$ (2a)

1.50 g of $\text{Pd}(\text{C}_5\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)$ [13] was dissolved in toluene and to it three equivalents of P^iBuPh_2 (5.13 g) was added. The mixture was heated at 70°C for 1 h. The solvents were removed under vacuum, 125 ml of hexanes was added and the solution was filtered off. To this solution 10 ml of CS_2 was added; immediately a yellow precipitate formed. The solution was stirred for 30 min, and the product isolated by filtration and washed with hexanes (yield 2.73 g, 58%).

Preparation of $\text{Pd}_2(\text{CS}_2)_2(\text{P}^i\text{BuPh}_2)_2$ (2b)

As above for **2a** except instead of adding CS_2 the hexane solution was exposed to an atmosphere of CO for 20 min. A red-violet coloured precipitate $\text{Pd}_3(\text{CO})_3\text{-(P}^i\text{BuPh}_2)_3$ formed, which was filtered and washed with hexane. This was added to 20 ml of hexanes and 3 ml of CS_2 . Immediately a yellow-orange precipitate formed, which filtered and recrystallised from CS_2 , CH_2Cl_2 and hexane (yield 2.39 g, 90%).

Preparation of $\text{Pd}_2(\text{CS}_2)_2\text{L}_2$ ($\text{L} = \text{P}^i\text{Bu}_2\text{Ph}$ (3a); P^iBu_3 (4b))

1.50 g of PdL_2 was dissolved in 75 ml of hexanes and to it 5 ml of CS_2 was added. Immediately a yellow precipitate formed. This was filtered and recrystallised from CS_2 , CH_2Cl_2 and hexanes (yield 0.77 g, 70%).

Reactions of $Pd_3(CO)_3L_3$ with CS_2 ($L = PCy_3$, P^iBu_2Ph and P^iBu_3)

0.20 g of $Pd_3(CO)_3L_3$ was added to 15 ml of hexanes and 2 ml of CS_2 . Immediately a yellow-orange precipitate formed. This was stirred for 30 min and the products (**1b**, **3b** or **4b**) were isolated by filtration (yield 90%).

The analytical data for compounds **1–4** are given in Table 1.

X-Ray study of $Pd_2(\mu-CS_2)_2(P^iBu_2Ph)_2$

Brownish-yellow crystals of $Pd_2(CS_2)_2(P^iBu_2Ph)_2$ were obtained by recrystallization from CS_2 /hexane mixtures. A photographic examination showed the crystals belonged to the monoclinic space group $P2_1/c$, C_{2h}^5 , No. 14 [14]. Crystal data are presented in Table 2.

A crystal of equant habit was chosen for data collection and mounted on an Enraf–Nonius CAD4F diffractometer. Three standard reflections, monitored every 3.8 h during data collection, showed no decomposition had occurred. Details of the experimental conditions are summarized in Table 2. Eight crystal faces were identified as the forms {100}, {010} and {001}.

A total of 3218 reflections was measured. The recorded intensities were corrected for Lorentz and polarization effects and a standard deviation $\sigma(I)$ was assigned to each intensity (I), using the data reduction program of the SPD package [15]. The data were not corrected for absorption. Of the data collected 2071 unique reflections with $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

The positional coordinates for the Pd atom were readily obtained from a three-dimensional Patterson synthesis. A series of difference Fourier syntheses and least-squares refinements revealed the positions of the remaining 18 non-hydrogen atoms.

The structure refinement [15], by full-matrix least-squares techniques on F , proceeded smoothly. Hydrogen atoms were included in the final cycles but not refined. Idealized positional coordinates for the H atoms were computed by assuming either sp^2 or sp^3 staggered geometries and C–H bond distances of 0.95 and 1.0 Å respectively. The refinement converged at $R_1 = \Sigma||F_0| - F_c||/\Sigma|F_0| = 0.0323$ and $R_2 = (\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2)^{1/2} = 0.0385$ (2071 unique data and 172 variables).

TABLE 1
ANALYTICAL DATA FOR COMPOUNDS 1–4

Compound	Formula	Analysis (Found (calcd.)(%))	
		C	H
1a	$C_{37}H_{66}P_2S_2Pd$	57.2 (59.79)	8.9 (8.96)
2a	$C_{33}H_{38}P_2S_2Pd$	58.3 (59.46)	5.5 (5.70)
1b	$C_{38}H_{66}P_2S_4Pd_2$	48.8 (49.28)	7.2 (7.20)
2b	$C_{34}H_{38}P_2S_4Pd_2$	50.3 (48.11)	4.8 (4.48)
3b	$C_{30}H_{46}P_2S_4Pd_2$	44.2 (44.50)	5.6 (5.74)
4b	$C_{26}H_{54}P_2S_4Pd_2$	40.4 (40.56)	7.1 (7.09)

TABLE 2

CRYSTAL DATA AND EXPERIMENTAL CONDITIONS ASSOCIATED WITH DATA COLLECTION

Molecular formula	$C_{15}H_{23}PS_2Pd$ $F_w = 404.85$
System	Monoclinic
Space group	$P2_1/c$
Cell constants	a 10.373(2) Å b 13.684(1) Å c 12.173(2) Å β 94.04(7)°
Cell volume	1723.6 Å ³
Density (calculated)	1.56 g cm ⁻³
Z	4
$\mu(Mo-K_{\alpha})$	13.7 cm ⁻¹
Radiation	Mo- K_{α} , graphite monochromatized
Wavelength (Å)	0.71073
Temperature (°C)	23
Approximate crystal dimensions (cm)	0.021 × 0.017 × 0.009
Number and 2θ range of centered reflections	21, 20 < 2θ < 30°
Data collected	hkl and $h\bar{k}l$, for $0 < 2\theta < 50^\circ$
Scan mode	$\theta:2\theta$
Scan width (deg.)	0.80
Maximum scan time (sec.)	75
Prescan rate (deg. min ⁻¹)	11
Acceptance ratio $\sigma(I)/I$	0.04

TABLE 3

ATOMIC POSITIONAL AND THERMAL PARAMETERS (Estimated standard deviations are given in parentheses, and correspond to the least significant digit(s). Positional parameters are given as fractional coordinates. $B(\text{\AA}^2) = (\frac{4}{3}) \times [a^2 B_{1,1} + b^2 B_{2,2} + c^2 B_{3,3} + ab(\cos \gamma) B_{1,2} + ac(\cos \beta) B_{1,3} + bc(\cos \alpha) B_{2,3}]$

Atom	x	y	z	$B(\text{\AA}^2)$
Pd	0.08358(3)	0.00724(3)	0.34695(3)	2.135(6)
S(1)	-0.1090(1)	-0.0313(1)	0.2486(1)	3.45(3)
S(2)	0.1905(1)	0.0417(1)	0.5157(1)	2.97(3)
P	0.2515(1)	0.01872(9)	0.22072(9)	2.19(2)
C(1)	-0.0948(5)	-0.0238(3)	0.3836(4)	2.44(9)
C(11)	0.2312(5)	-0.0872(3)	0.1287(4)	2.6(1)
C(12)	0.1777(5)	-0.1708(4)	0.1719(4)	3.3(1)
C(13)	0.1647(6)	-0.2553(4)	0.1085(5)	4.1(1)
C(14)	0.2026(7)	-0.2567(4)	0.0044(5)	4.8(1)
C(15)	0.2529(6)	-0.1751(5)	-0.0403(5)	4.6(1)
C(16)	0.2689(5)	-0.0908(4)	0.0223(4)	3.4(1)
C(21)	0.4258(5)	0.0065(4)	0.2741(4)	3.8(1)
C(22)	0.4306(5)	-0.0825(5)	0.3517(5)	4.3(1)
C(23)	0.4690(6)	0.0961(5)	0.3399(5)	5.3(2)
C(24)	0.5179(5)	-0.0135(5)	0.1849(5)	5.1(2)
C(31)	0.2239(6)	0.1328(4)	0.1356(4)	3.3(1)
C(32)	0.3323(6)	0.1673(4)	0.0661(5)	4.7(1)
C(33)	0.1022(6)	0.1185(5)	0.0610(5)	4.8(1)
C(34)	0.1975(8)	0.2149(4)	0.2171(6)	6.0(2)

TABLE 4
SUMMARY OF ^{31}P NMR AND IR SPECTROSCOPIC DATA

Complex	$\delta(^{31}\text{P})^a$	$^2J(\text{P-Pd-P})$ (Hz)	(CS_2) (cm^{-1})
1a ^b	41.04, 25.99	14.65	1173, 1161, 620
2a ^b	41.68, 55.08	20.14	1170, 1150, 620
1b ^c	36.84		1140, 1120, 1100
2b ^c	44.43		1170, 1150, 1125, 715
3b ^c	64.51		1150, 1135, 1110, 710
4b ^c	81.21		1175, 1150, 1125

^a Chemical shifts are in ppm downfield from H_3PO_4 . ^b ^{31}P NMR spectra were recorded in CS_2 solution at -60°C . ^c ^{31}P NMR spectra were recorded in $\text{CH}_2\text{Cl}_2/\text{CS}_2$ solution at 22°C .

In the final cycle no shift exceeded 0.01 of its standard deviation. The error in an observation of unit weight is 1.09 electrons. A statistical analysis of R_2 over various ranges of $|F_0|$, $\lambda^{-1} \sin\theta$ and reflection parities showed no abnormal trends. A total difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance. Final positional and B thermal parameters for the non-H atoms are given in Table 3.

Supplementary material available. A weighted least-squares plane of the $\text{PPd}(\text{CS}_2)_2\text{PdP}$ core, hydrogen atom parameters, anisotropic thermal parameters and structure amplitudes as $10|F_0|$ vs. $10|F_c|$ have been deposited *.

Results

Preparation of the CS_2 complexes

$\text{Pd}(\text{PPh}_3)_4$ is known to react with CS_2 in refluxing diethyl ether to give the $\eta^2\text{-CS}_2$, monomeric complex $\text{Pd}(\text{CS}_2)(\text{PPh}_3)_2$ [2] (type a). We have found that $\text{Pd}(\text{PCy}_3)_2$ and $\text{Pd}(\text{P}^t\text{BuPh}_2)_n$ [16] also react with CS_2 , in hexanes at 23°C , to precipitate the analogous compounds $\text{Pd}(\text{CS}_2)_2\text{L}_2$ ($\text{L} = \text{PCy}_3$, **1a**; P^tBuPh_2 , **2a**). Complexes **1a** and **2a**, unlike $\text{Pd}(\text{CS}_2)(\text{PPh}_3)_2$, react further when dissolved in CS_2 eliminating a phosphine ligand and forming the doubly- CS_2 bridged, dimeric species $\text{Pd}_2(\text{CS}_2)_2\text{L}_2$ ($\text{L} = \text{PCy}_3$, **1b**; P^tBuPh_2 , **2b**). The $\eta^2\text{-CS}_2$ monomeric complexes were not observed in the reaction of PdL_2 ($\text{L} = \text{P}^t\text{Bu}_2\text{Ph}$; P^tBu_3) with CS_2 in hexane but rather the dimeric complexes $\text{Pd}_2(\text{CS}_2)_2\text{L}_2$ ($\text{L} = \text{P}^t\text{Bu}_2\text{Ph}$, **3b**; P^tBu_3 , **4b**) formed immediately. Reaction of the trinuclear clusters $\text{Pd}_3(\text{CO})_3\text{L}_3$ ($\text{L} = \text{PCy}_3$, P^tBuPh_2 , $\text{P}^t\text{Bu}_2\text{Ph}$, P^tBu_3) with CS_2 , in hexanes, results in immediate formation of the $\mu\text{-CS}_2$ dimers $\text{Pd}_2(\text{CS}_2)_2\text{L}_2$ (**1b**, **2b**, **3b**, **4b**, respectively).

The products have been characterized by IR and ^{31}P NMR spectroscopy, elemental analysis and in the case of **3b** X-ray crystallography. The instability of **1a** and **2a** in solution made it difficult to obtain analytically pure samples. Spectroscopic data are presented in Table 4.

* See NAPS document no. 04235 for 26 pages of supplementary material. Order from NAPS % Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only \$9.55 for photocopies or \$4.00 for microfiche. Outside the U.S. and Canada add postage of \$4.50 for the first 20 pages, and \$1.00 for each page thereafter. \$1.50 for microfiche postage.

The complexes exhibit strong infrared absorptions in the regions of 620 to 720 cm^{-1} and 1100 and 1175 cm^{-1} which are typical of both $\eta^2\text{-CS}_2$ complexes [2,17] and $\mu\text{-CS}_2$ complexes [4,5]. Previous researchers have assigned these regions to the M-C-S ring and *exo*-(C=S) vibrations respectively [17]. As a general observation complexation of the *exo*-S atom in monomeric $\eta^2\text{-CS}_2$ compounds is reflected in a slight lowering of the *exo*-(C=S) frequency and a raising of the frequency assigned to the in-ring vibration.

The observation of an AX ^{31}P NMR spectrum for type **a** complexes and a single ^{31}P resonance in type **b** is consistent with the assigned structures.

Reaction of $\text{Pd}(\text{CS}_2)_2\text{L}_2$ with CS_2

The complexes **1a** and **2a** were each dissolved in $\text{CH}_2\text{Cl}_2/\text{CS}_2$ at -60°C and their ^{31}P NMR spectra were monitored at 10°C interval (every 15 min) as the solutions were warmed to room temperature. Both complexes gave an AX spectrum, with narrow line widths, at -53°C .

The ^{31}P NMR spectrum of **2a** had reached coalescences at -5°C and then sharpened with increasing temperature giving a one line, fast exchange, spectrum at 10°C . Resonances associated with **2b** and free P^tBuPh_2 first began to appear at -43°C . The reaction to produce **2b** proceeded with increasing temperature and was complete after 30 min at 23°C . There were no observable intermediates.

At -43°C a broadened AX spectrum was recorded for **1a** indicating the onset of a slow exchange process. However unlike **2a**, coalescence was not observed for **1a**. The broadened spectrum collapsed into the base line at -23°C . Resonances assigned to **1b** and $\text{PCy}_3 \cdot \text{CS}_2$ appeared at -13°C and continued to grow in with increasing time and temperature.

*Description of the structure of **3b***

Differences in the number and intensity of the 1100 to 1175 cm^{-1} IR active CS_2 vibrations between the Pd and Pt [5,8] type **b** complexes led us to confirm the structure of the Pd dimeric complexes by a single crystal X-ray analysis of **3b**. The crystal structure consists of discrete dimeric molecules for the closest intermolecular distance is 2.28 Å between C(1) and H(13)(C(13)) in the equivalent position (x , $1/2 - y$, z). A perspective view of the molecule together with the atom numbering scheme is given in Fig. 1. Selected intramolecular dimensions are present in Table 5.

The complex **3b** possesses a crystallographically imposed centre of inversion. The two centrosymmetrically related $\text{Pd}(\text{P}^t\text{Bu}_2\text{Ph})$ fragments are held together by two doubly bridging CS_2 moieties. Each CS_2 group is π -bonded through a C=S linkage to one metal atom and σ -bonded to the other through the *exo*-S atom resulting in a six-membered ring. A weighted least-squares plane calculation reveals the planarity of the $\text{PPd}(\text{CS}_2)_2\text{PdP}$ core (largest deviation 0.107(1) Å).

The angles subtended at the Pd atom are consistent with a highly distorted square-planar coordination geometry. The Pd-P distance, 2.408(1) Å, is longer than the value of 2.349(2) Å found for the Pt analogue. This and other dimensions associated with the phosphine ligand are normal [5,18,19].

The Pd-C(1) distances, 1.980(5) Å, is equivalent to the value 1.970(6) Å found in the complex $\text{Pt}_2(\text{CS}_2)_2(\text{P}^t\text{Bu}_2\text{Ph})_2$ [5], however the Pd-S(1) bond length, 2.316(1) Å, is significantly shorter than the distance observed in the related Pt complex,

2.337(2) Å. The two Pd–S bond distances, 2.316(1) and 2.313(1) Å, are indistinguishable as are the two C–S bond lengths, 1.643(5) and 1.650(5) Å. All parameters associated with the CS₂ ligand are comparable to those found not only for the Pt analogue [5], but also for the Pd and Pt monomeric complexes (type a) [3,19]. Thus the σ -bonding of the *exo*-S atom and the geometric requirements of a six-membered ring have no drastic effect on the geometry of the CS₂ ligand.

Discussion

The reactions are summarized in Scheme 1, where $n = 2, 3$ or 4 depending on L. It is the steric bulk of the phosphine ligands which apparently controls the

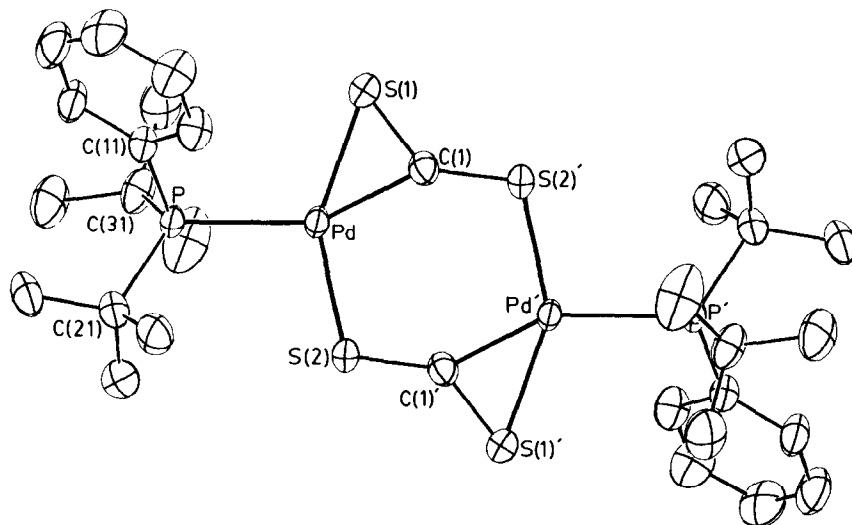
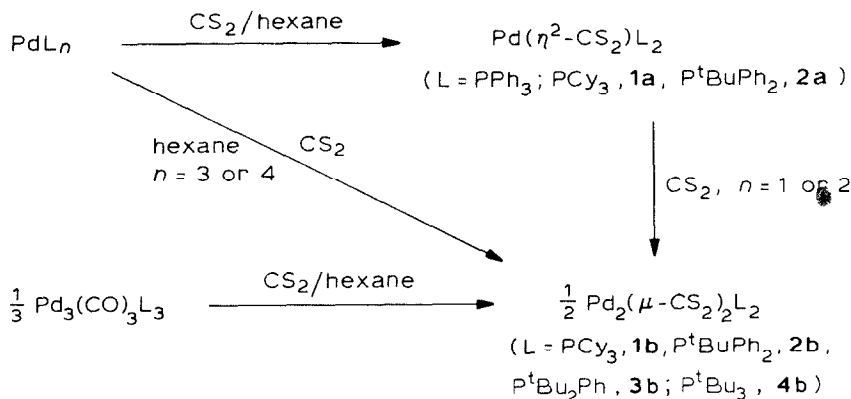


Fig. 1. An ORTEP drawing of Pd₂(CS₂)₂(P^{*t*}Bu₂Ph)₂ plotted as 50% probability thermal ellipsoids, with H-atoms omitted.

TABLE 5
SELECTED BOND DISTANCES (Å) AND ANGLES (deg.)

Bond	Distance	Bond	Distance
Pd–P	2.408(1)	C(1)–S(1)	1.643(5)
Pd–C(1)	1.980(5)	C(1)–S(2)'	1.650(5)
Pd–S(1)	2.316(1)	P–C(11)	1.835(5)
Pd–S(2)	2.313(1)	P–C(21)	1.886(5)
		P–C(31)	1.884(5)

Atoms	Angle	Atoms	Angle
P–Pd–S(1)	108.74(4)	S(1)–C(1)–S(2)'	135.9(3)
P–Pd–C(1)	152.5(1)	Pd–P–C(11)	106.3(2)
P–Pd–S(2)	103.30(4)	Pd–P–C(21)	119.6(2)
C(1)–Pd–S(1)	44.1(1)	Pd–P–C(31)	108.4(2)
C(1)–Pd–S(2)	104.0(1)	C(11)–P–C(21)	101.9(2)
Pd–C(1)–S(2)'	145.1(3)	C(11)–P–C(31)	108.2(2)
C(1)'–S(2)–Pd	110.7(2)	C(21)–P–C(31)	111.6(3)



SCHEME 1

reaction. Monomeric $\text{Pd}(\eta^2\text{-CS}_2)\text{L}_2$ complexes are not observed for the larger phosphines, $\text{P}^t\text{Bu}_2\text{Ph}$ or P^tBu_3 . The type **a** complexes can be isolated for the smaller ligands, PPh_3 , PCy_3 or P^tBuPh_2 , however the latter two react quickly in $\text{CH}_2\text{Cl}_2/\text{CS}_2$ to give the dimeric compounds **1b** and **2b**. There is no correlation between basicity [20] and formation of **b**-type complexes. The fact that **1a** is observed while “**3a**” is not (even though PCy_3 and $\text{P}^t\text{Bu}_2\text{Ph}$ have the same cone angle [21]) we ascribe to the over-simplification in defining a phosphine ligand as a solid cone [21]. It has been shown that in trigonal planar complexes containing *cis*- PR_2Ph ligand, the phenyl groups adopt a ‘graphite-like’ interaction forcing the R-groups to point directly towards the third coordination site [22]. Thus for type **a** complexes $\text{P}^t\text{Bu}_2\text{Ph}$ would have a larger steric requirement than PCy_3 . Equilibrium constants for the dissociation of phosphine in PdL_n complexes also indicate that PCy_3 is a smaller ligand than $\text{P}^t\text{Bu}_2\text{Ph}$ [23].

The complex $\text{Pd}(\text{CS}_2)(\text{PPh}_3)_2$ is stable in solution although at temperatures higher than -60°C the P atom environments are exchanging in the ^{31}P NMR experiment [24]. By contrast **1a** and **2a** decompose in solution in the absence of CS_2 and convert to the complexes **1b** and **2b** when CS_2 is present. Variable temperature ^{31}P NMR of **1a** and **2a** in $\text{CH}_2\text{Cl}_2/\text{CS}_2$, shows that the first process to occur on warming of a solution is one in which the P nuclear environments are interchanged. In the case of **1a** the reaction to form the CS_2 dimer **1b** is complete before coalescence of the original **1a** resonances occurs. However a coalescence temperature of approximately -5°C was observed for **2a** as the reaction to produce **2b** occurs more slowly. The PCy_3 ligand is more basic and more sterically demanding than P^tBuPh_2 . These two factors apparently offset each other and it could be the formation of $\text{PCy}_3 \cdot \text{CS}_2$ which accelerates the conversion of **1a** to **1b**.

The process by which the P spins are interchanged may be associated with either fluxionality of the CS_2 ligand or exchange of the phosphine ligands. Free phosphine liberated during formation of the dimeric complexes may be involved in this process although $\text{Pd}(\text{CS}_2)(\text{PPh}_3)_2$ is also fluxional and does not spontaneously form a dimeric complex. There is evidence which suggests that the type **b** complex $\text{Pd}_2(\text{CS}_2)_2(\text{PPh}_3)_2$ does form in the presence of phosphine acceptors [8]. While the exchange process may be related to the basicity of the phosphine ligand, formation of type **b** complexes appears to be related to the steric bulk of the phosphine ligands.

The known Ni- and Pt-CS₂ chemistry is consistent with our conclusions on the factors affecting the Pd system. The comparatively short metal-phosphorus bonds for first row transition metal elements would accentuate the phosphine ligands steric requirements for Ni complexes and this results in only type **b** compounds forming [1,4]. The Pt-CS₂ chemistry exactly parallels the results found for Pd. Both **a** and **b** complexes have been prepared for PCy₃, while PPh₃ gives only a type **a** compound and P^tBu₃ a type **b** [5,6,7].

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