References and Notes

(1) J. Boersma and J. G. Noltes, Organozinc Coordination Chemistry, International Lead Zinc Research Organization, Inc., New York, N.Y., 1968.
(2) J. G. Noltes and J. Boersma, *J. Organomet. Chem.*, **7**, P6 (1967).
(3) E. R. Noller, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 184.
(4) J. G. Noltes and J. Boersma, *J. Organomet. Chem.*, **16**, 345 (1969).
(5) "CAD4-Users Manual", Enraf-Nonius, Delft, 1972.
(6) A. J. M. Duisenberg, Collected Abstracts of the First European Enraf-Nonius CAD4-Users Meeting, Paris, June 1974.
(7) The function minimized was $\sum(w(|F_o| - |F_c|))^2$. The refinement was on F. The unweighted and weighted residuals are defined as follows: $R_F = (\sum|F_o| - |F_c|)/(\sum|F_o|)$ and $R_{wF} = [(\sum w(|F_o| - |F_c|)^2)/(\sum w|F_o|^2)]^{1/2}$.
(8) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.
(9) H. M. Rietveld, Fysica Memo 153, RCN Petten, The Netherlands, 1966.
(10) D. J. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(11) R. F. Stewart, E. R. Davidson, and W. J. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(12) C. K. Johnson, "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(13) J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, "X-RAY SYSTEM", Technical Report TR-192, The Computer Science Center, University of Maryland, College Park, Md., 1972.
(14) The standard deviation in the mean value $\bar{X}$ was calculated with $\sigma(\bar{X}) = [\sum(X_i - \bar{X})^2/(n(n-1))]^{1/2}$.
(15) J. Boersma, A. L. Spek, and J. G. Noltes, *J. Organomet. Chem.*, **81**, 7 (1974).
(16) A. L. Spek, *Cryst. Struct. Commun.*, **3**, 535 (1973).
(17) C. J. Brown and D. E. C. Corbridge, *Acta Crystallogr.*, **7**, 711 (1954).
(18) P. Ganis, G. Avitabile, S. Migdal, and M. Goodman, *J. Am. Chem. Soc.*, **93**, 3328 (1971).
(19) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 281.
(20) J. M. O. Gorman, W. Shand, and V. Schomaker, *J. Am. Chem. Soc.*, **72**, 4222 (1950).
(21) J. Boersma, F. Verbeek, and J. G. Noltes, *J. Organomet. Chem.*, **33**, C53 (1971).
(22) K. Mollema, J. Boersma, and G. J. M. van der Kerk, to be submitted for publication.
(23) B. H. Bracher and R. W. H. Small, *Acta Crystallogr.*, **23**, 410 (1967).
(24) G. E. Coates and D. Ridley, *J. Chem. Soc. A*, 1064 (1966).

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Sulfur Chelates. 32.[1,2] Studies of the Solid-State Molecular Structure and Solution Structures and Dynamics of Bis(phosphine) Adducts of Platinum(II) 1,1-Dithiolates. Molecular Structures of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$, $Pt(S_2CO)(PPh_3)_2$, and $Pt(S_2CO)(diphos)\cdot{}^1/_4CHCl_3$

IVAN J. B. LIN, H. W. CHEN, and JOHN P. FACKLER, JR.*

Received June 29, 1977

NMR spectra are used to compare the solution structure of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ with its solid-state structure. The low-temperature solution structure is different from the structure of the crystalline solid, which is *trans*-PtS_2P_2 in its coordination about the metal. The low-temperature solution structure is that of the cation $[PtS_2CN(i\text{-}Bu)_2(PMe_2Ph)_2]^+$ with a free dithiolate anion. The structure of $Pt(S_2CO)(Ph_3P)_2$ and the diphos analogue show a *cis*-PtS_2P_2 coordination as indicated in spectral studies. They are formed by reacting the platinum(II) xanthate with the phosphine. Phosphine exchange and dithiolate exchange both occur in solutions containing $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$. The dithiolate ligand exchange is solvent dependent. Bimolecular phosphine exchange occurs with a larger rate constant than bimolecular dithiolate exchange and both of these processes appear faster than the bimolecular displacement of phosphine from $[Pt(S_2CNR_2)(PR_3)_2]^+$ by the dithiolate ligand.

Introduction

Our continued interest in the reactions[3,4] of phosphine bases with planar d^8 complexes has led us to reexamine[5] the behavior of bis(1,1-dithiolato)palladium(II) and -platinum(II) complexes in the presence of excess phosphine, using advanced NMR capabilities and single-crystal x-ray crystallography.

Various products are obtained when the ratio of phosphine to bis(1,1-dithiolato)M, M = Ni^{II}, Pd^{II}, or Pt^{II}, exceeds 2:1, depending upon the nature of the dithiolate ligand. Reacting the xanthate and dithiophosphate complexes with excess tertiary phosphine[5] gives the novel complexes $M(PR_3)_2(S_2CO)$ (M = Pd, Pt; R = alkyl or aryl) and $Pd(PR_3)_2[S_2P(O)OEt]$, respectively.

Stephenson and co-workers[10] have suggested a very reasonable mechanism for this reaction (1) involving the formation

$$M(S_2COR)_2 + 2L \rightleftharpoons L_2M(S_2COR)^+ + ROCS_2^-$$
$$ROCS_2^- + L_2M(S_2COR)^+ \rightarrow ROCS_2R + L_2MS_2CO \qquad (1)$$
$$M = Pd^{II}, Pt^{II}; L = \text{phosphine}$$

of an ionized dithiolate ligand.

Dithiocarbamate and dithiophosphinate complexes give bis(phosphine) adducts of stoichiometry $Pt(S_2CNR_2)_2(PR_3)_2$[10] and $M(S_2PR_2)_2(PR_3)_2$[7-9,11,12] (M = Pd, Pt; R = alkyl or aryl). Conductivity measurements and NMR studies[9,11,12] suggest that the bis(phosphine) adducts of bis(dithiophosphinato)-palladium(II) and -platinum(II) are ionic. The preliminary report of x-ray structural data of $[Pd(S_2PPh_2)(PEt_3)_2](S_2PPh_2)$ provided by Beevers and Fraser as cited by Alison et al.[9] indicated a structure with four-coordinate palladium in a cis ionic PdS_2P_2 configuration.

A subsequent paper by Alison et al.[10] has proposed that bis(phosphine) adducts of bis(dithiocarbamato)platinum(II) are also ionic compounds of type $[M(PR_3)_2Y]^+Y^-$ [Y being S_2PPh_2, S_2PMe_2, S_2CNR_2; M = Pd, Pt; PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3; R = Me, Ph, Et, *i*-Bu (Me = methyl, Et = ethyl, *i*-Bu = isobutyl, Ph = phenyl)]. The ionic formulation is suggested by the presence of IR spectral bands corresponding to those found in $NaS_2CNR_2\cdot3H_2O$ and by the ready synthesis of $[Pt(S_2CNR_2)(PR_3)_2]BPh_4$.

Our studies have shown that the solid-state structures of the dithiocarbamatoplatinum(II) complexes, $Pt(S_2CNR_2)_2(PR_3)_2$, are not cis ionic.[10a] IR studies, colors, and a single-crystal x-ray structure of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ (I) verify this conclusion. Thus a difference exists between the solid-state structures of the bis(phosphine) adducts of the dithiophosphinates and the dithiocarbamates.[10a]

Alison and Stephenson[10] reported the ^1H NMR studies of the bis(phosphine) adducts $Pt(S_2CNR_2)_2(PMePh_2)_2$ (R = methyl, ethyl). They found an equilibrium between the mono(phosphine) adduct and bis(phosphine) adduct with the equilibrium lying well to the right of eq 2. They report that

$$Pt(S_2CNR_2)(PR_3)_2^+ + S_2CNR_2^- \rightleftarrows Pt(S_2CNR_2)_2(PR_3) + PR_3 \quad (2)$$

the chemical shift of the N–CH_2 quartet (δ 3.74) in Pt-$[S_2CN(Et)_2]_2(PMePh_2)_2$ is identical with that for Pt-$[S_2CN(Et)_2]_2(PMePh_2)$ at room temperature. Another quartet of low intensity centered at δ 3.91 is attributed to the ionic complex. The methylphosphine resonance appears as a broad singlet at δ 1.84, indicative of rapid exchange between free and bound phosphine.

Since phosphine exchange in (2) which is rapid on the NMR time scale might be expected to cause an averaging of the N–CH_2 quartets on the ligands, we have pursued NMR studies using ^{31}P and ^{13}C as well as ^1H. These results are reported here.

In addition, we report the detailed x-ray crystallographic study of dithiocarbonatobis(triphenylphosphine)platinum(II), the metal-containing product of reaction 1, as well as its bis(diphenylphosphine)ethylene, diphos, derivative.

Experimental Section

Physical Measurements. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were determined using a Laboratory Devices Mel-Temp melting point block and are reported uncorrected. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer, using KBr pellets. ^1H NMR spectra were recorded on Varian XL-100, Varian HA-100, and Varian A-60A spectrometers. Fourier-mode ^{31}P and ^{13}C NMR spectra were recorded on the Varian XL-100 operated at 40.5 and 25.16 MHz, respectively, with broad band proton decoupling unless otherwise specified. Deuterium solvents were used as internal ^2H locks.

Preparation of Materials. $PMePh_2$ and PMe_2Ph were purchased from Research Organic/Inorganic Chemical Co.; 90% ^{13}C-enriched carbon disulfide was purchased from Merck & Co., Inc. The complexes $Pt(S_2CNMe_2)_2(PMePh_2)_2$, $Pt(S_2CNMe_2)(PMePH_2)_2PF_6$, and $Pt(S_2CNMe_2)(PMe_2Ph)_2BPh_4$ were prepared as reported.[10] $NaS_2CN(i\text{-}Bu)_2{\cdot}3H_2O$, which has 30% carbon-13 enriched on the S_2CN carbon, was prepared by reacting 2.05 g of diisobutylamine with 0.85 g of sodium hydroxide and 1.5 g of 30% carbon-13 enriched carbon disulfide (by mixing 0.5 g of 90% enriched CS_2 with 1.0 g of reagent grade CS_2) as reported.[13,14] The carbon-13 enriched platinum complex was prepared by reacting K_2PtCl_4 with slightly more than two molar ratios of the carbon-13 enriched $NaS_2CN(i\text{-}Bu)_2{\cdot}3H_2O$ according to a literature[14] method. Preparations involving PMe_2Ph and $PMePh_2$ were carried out under nitrogen.

$Pt(S_2CNMe_2)_2(PMe_2Ph)_2$. In 20 mL of benzene solution, 0.22 g (0.5 mmol) of $Pt(S_2CNMe_2)_2$ was treated with 0.25 g (2.0 mmol) of PMe_2Ph. The solution was stirred and heated (70–80 °C) for 4 h. The hot solution was filtered to remove some unreacted Pt-$(S_2CNMe_2)_2$. Yellow hexagonal crystals were precipitated by slowly evaporating the filtrate. These were filtered off and dried under vacuum for more than 24 h; mp 139–141 °C. Anal. Calcd for $Pt(S_2CNMe_2)_2(PMe_2Ph)_2$: C, 37.12; H, 4.82; P, 8.70. Found: C, 38.09; H, 4.89; P, 8.57.

$Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$. In a solution of 30 mL of acetone/anhydrous ether (1:1 by volume), 0.3 g (0.5 mmol) of Pt-$[S_2CN(i\text{-}Bu)_2]_2$ was treated with 0.2 g (1.4 mmol) of PMe_2Ph. The solution was stirred for 10 min, and *n*-heptane was added until the solution became cloudy. Large yellow needle crystals formed. These were filtered off and dried under vacuum for more than 24 h; mp 115–118 °C. Anal. Calcd for $Pt[S_2CN(C_4H_9)_2]_2[PCH_3(C_6H_5)_2]_2$: C, 46.39; H, 6.66; N, 3.18. Found: C, 46.20; H, 6.73; N, 3.04.

$Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)$ (II). This compound, as used for NMR studies, was prepared by addition of a 1:1 molar ratio of PMe_2Ph to $Pt[S_2CN(i\text{-}Bu)_2]_2$ or a 1:1 molar ratio of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ to $Pt[S_2CN(i\text{-}Bu)_2]_2$. The compound was characterized in $CDCl_3$ solution by its NMR spectrum but was not isolated. ^{31}P NMR spectrum (−14 °C) 17.1 ppm (upfield relative to 85% H_3PO_4, t, J_{Pt-P} = 89.2); ^{13}C NMR spectrum (0 °C) δ 206.3 (t, J_{Pt-C} = 2.5, S_2CN), ~130 (complex, P–C_6H_5), 59.6 (s, N–CH_2), 26.8 (s, N–CH), 20.2 (s, N–CH_3), ~14 (complex, P–CH_3) (t = triplet, s = singlet).

$[Pt(S_2CN(i\text{-}Bu)_2)(PMe_2Ph)_2]BPh_4$ (III). To 0.5 g of Pt-$(PMe_2Ph)_2Cl_2$ in 10 mL of 95% alcohol, 0.25 g of $NaS_2CN(i\text{-}Bu)_2$ in 30 mL of 95% alcohol was added slowly with stirring. After the addition, the solution was filtered and 0.34 g of $NaBPh_4$ was added to the filtrate with stirring. A white precipitate was isolated. This was washed with 5 mL of 95% alcohol; mp 150–153 °C. Anal. Calcd for $C_{59}H_{64}NBP_2S_2Pt$: C, 59.14; H, 6.09. Found: C, 59.05; H, 5.96.

Attempted Preparation of $Pd(S_2CNEt_2)_2(PMe_2Ph)_2$. Neat PMe_2Ph was added to solid $Pd(S_2CNEt_2)_2$. Orange-red crystals were obtained which decomposed in both solution and solid state, presumably because of facile ligand dissociation.

$Pt(S_2CO)(PPh_3)_2$. This slightly yellow complex was obtained[5] by adding excess Ph_3P to a $CHCl_3$ solution of $Pt(S_2COC_2H_5)_2$, after storing several days at ~0 °C.

$Pt(S_2CO)(diphos){\cdot}{}^1/_4CHCl_3$. To a solution of 0.5 g of $Pt(S_2COEt)_2$ in $CHCl_3$, 0.5 g of bis(diphenylphosphine)ethylene (diphos) was added. After 30 min of stirring, the white precipitate which formed was filtered and vacuum dried. The crude product was recrystallized from $CHCl_3$. The melting point is 302 °C. $PtS_2CO(PPh_3)_2{\cdot}{}^1/_4CHCl_3$ was prepared by the same method. Its melting point is 274–276 °C.

X-Ray Structural Studies. Bis(diisobutyldithiocarbamato)bis-(triphenylphosphine)platinum(II). Single crystals of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ (I) suitable for x-ray study, were grown in an acetone–ether mixture by slow evaporation under nitrogen. An air-stable yellow crystal was mounted on a glass fiber in an arbitrary orientation. A clear acrylic plastic spray was used to coat the crystal. It was mounted on a Syntex $P2_1$ automatic four-circle diffractometer. The standard Syntex programs for crystal centering and indexing were used with Mo K$\bar{\alpha}$ (λ 0.71069 Å) radiation. A triclinic cell was selected and a least-squares orientation matrix was produced for data collection (Table I).

Table I. Crystal Data for $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ and $Pt(S_2CO)(Ph_3P)_2$

Compound	$Pt[S_2CN(i\text{-}Bu)_2]_2$-$(PMe_2Ph)_2$	$Pt(S_2CO)(Ph_3P)_2$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	6.632 (2)	11.161 (5)
b, Å	10.360 (4)	15.751 (6)
c, Å	15.896 (9)	10.331 (2)
α, deg	90.42 (4)	95.92 (3)
β, deg	102.72 (4)	74.85 (3)
γ, deg	108.29 (3)	108.87 (3)
Volume, Å^3	1008.04 (88)	1655 (1)
Formula wt, g/mol	880.21	811.80
Z	1	2
ρ(calcd), g/cm^3	1.45	1.63
ρ(measd), g/cm^3	1.42	1.63
Crystal size, mm^3	0.27 × 0.19 × 0.15	0.30 × 0.25 × 0.18
μ, cm^{-1}	39.65	28.89
2θ range, deg	0–50	0–45
No. of unique reflections	3351 with $I/\sigma(I) \geq 3$	3700 with $I/\sigma(I) \geq 3$

The intensity data were collected using a θ–2θ scan technique at variable scan rate from 2.0 to 29.3°/min. The background was measured for a time equal to half of the total scan time at a point 1° to each side of the Kα_1 and Kα_2 peaks, and the scan count was corrected for background. Three standard reflections, (003), (030), and (300), were measured after every 100 reflections and were used to correct the intensities with time.[15] Only small random fluctuations of these standard reflections were observed during the course of data collection.

A total of 4243 reflections (including standard reflections and Friedel pairs of 00*l*, 00$\bar{l}$, and 0*kl*, 0$\bar{k}\bar{l}$) were collected, of which 3351 independent reflections had $I \geq 3\sigma(I)$, where the observed intensity *I* and standard deviation, $\sigma(I)$, are defined by the following expressions:

$$I = \left[\text{total scan count} - \frac{\text{sum of BG}}{\text{BG to scan ratio}}\right] \times \text{scan rate}$$

$$\sigma(I) = \left[\text{total scan count} + \frac{\text{sum of BG}}{\text{BG to scan ratio}}\right]^{1/2} \times \text{scan rate}$$

BG = background count

The data were corrected for Lorentz and polarization effects.[15] No absorption correction was made.

Determination of the Structure. Examination of a three-dimensional Patterson synthesis suggested that the platinum atom was located at (0, 0, 0). An initial structure factor calculation using the coordinates of the metal atom based on 1093 reflections with $I/\sigma(I) \geq 30$ yielded

Table II. Positional Parameters for $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$

Atom	x	y	z
Pt	0	0	0
S1	−0.0752 (3)	−0.0102 (2)	0.1370 (1)
S3	0.4134 (3)	0.1015 (2)	0.1801 (1)
P1	−0.0694 (3)	0.2047 (2)	−0.0067 (1)
C(N)	0.1737 (11)	0.0589 (6)	0.2108 (4)
N	0.1668 (9)	0.0777 (6)	0.2941 (3)
C1	0.3710 (12)	0.1423 (7)	0.3616 (4)
C2	0.4508 (15)	0.2999 (8)	0.3646 (5)
C3	0.6725 (17)	0.3515 (11)	0.4311 (7)
C4	0.2822 (20)	0.3602 (10)	0.3871 (8)
C5	−0.0419 (12)	0.0329 (7)	0.3222 (4)
C6	−0.1187 (14)	−0.1213 (8)	0.3345 (5)
C7	−0.3417 (16)	−0.1534 (11)	0.3586 (7)
C8	0.0445 (17)	−0.1614 (9)	0.4043 (6)
C9	0.0044 (13)	0.3071 (7)	−0.0948 (5)
C10	0.2219 (16)	0.3814 (11)	−0.0893 (7)
C11	0.2813 (21)	0.4605 (13)	−0.1571 (10)
C12	0.1201 (25)	0.4651 (11)	−0.2282 (8)
C13	−0.0940 (21)	0.3894 (10)	−0.2351 (6)
C14	−0.1527 (16)	0.3092 (8)	−0.1683 (5)
C15	−0.3554 (15)	0.1871 (9)	−0.0155 (6)
C16	0.0757 (20)	0.3245 (8)	0.0895 (6)

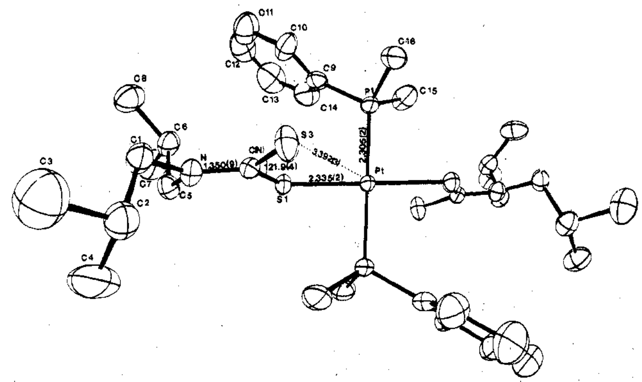


Figure 1. An ORTEP drawing of the complex $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$ showing the labeling scheme and selected bond distances and angles.

0.444 and 0.498 for $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \sum w(|F_o| - |F_c|)^2/\sum wF_o$, respectively. The scale factor and isotropic thermal parameter of platinum atom refined with two cycles of least squares using unit weight gave $R_1 = 0.21$ and $R_w = 0.27$. All nonhydrogen atoms were located from the Fourier map at this stage. After two cycles of isotropic refinement using 2434 reflections ($I/\sigma(I) \geq 10$) and unit weights for the scale factor, positional parameters and individual isotropic thermal parameters converged to values of 0.065 and 0.076 for R_1 and R_w, respectively.

Refinement was continued using 3351 reflections ($I/\sigma(I) \geq 3$) with scale factor, positional parameters, and individual anisotropic thermal parameters (except for platinum atom) at unit weight. Two cycles gave $R_1 = 0.063$ and $R_w = 0.071$. Successive anisotropic least-squares refinement cycles including all nonhydrogen atoms and anomalous dispersion corrections for the platinum scattering factor yielded $R_1 = 0.036$ and $R_w = 0.045$. The position shifts of the 22 refined atoms were less than 0.02 of their standard deviations in the last cycle. No effects caused by secondary extinction were observed in the final structure factors. The position and thermal parameters are listed in Table II and Table III. An ORTEP drawing of the structure appears in Figure 1.

Dithiocarbonatobis(triphenylphosphine)platinum(II). A single crystal of the compound was mounted on a glass fiber with epoxy and placed on a Syntex $P2_1$ diffractometer. The triclinic crystal system and unit cell dimensions were determined using monochromatized Mo K$\bar{\alpha}$ radiation. The density was measured by flotation in a $CHBr_3$ and CCl_4 mixture. The crystal data are collected in Table I. Intensity data were collected as described above.

Determination of the Structure. A three-dimensional Patterson was computed, from which the position of the platinum atom was obtained. A structure factor calculation based on the coordinates of this atom was used to generate a three-dimensional Fourier map. The sulfur and phosphorus atoms were located immediately. The carbon and oxygen atoms were located by using the structure factor calculations and a difference Fourier map based on the known locations of Pt, S, and P. Several cycles of anisotropic refinement (the phenyl carbons were refned only isotropically) incorporated with anomalous dispersion corrections for Pt, S, and P gave a final $R_1 = 4.5\%$ and $R_2 = 5.7\%$. The positional and thermal parameters are presented in Tables IV and V.

An ORTEP drawing of the complex $Pt(S_2CO)(PPh_3)_2$ is given in Figure 2. Some important bond lengths and bond angles are listed in Table VI.

Crystallographic Data for $Pt(S_2CO)(diphos)\cdot{}^1/_4CHCl_3$. Several crystals were examined by oscillation, Weissenberg, and precession methods. The systematic absences are consistent with the space group $P2_12_12_1$ (orthorhombic). The unit cell constants are $a = 20.777$ (3) Å, $b = 14.017$ (2) Å, $c = 10.323$ (1) Å, $\alpha = 90.00$ (1)°, $\beta = 90.00$ (3)°, and $\gamma = 90.00$ (3)°. The data set was collected by a Syntex $P2_1$ diffractometer. The data collection and reduction were as described above.

The heavy-atom position was found by the Patterson technique. The calculated R for the Pt atom was 0.16 for 698 reflections. Fourier

Table III. Thermal Parameters[a] with Estimated Standard Deviations for $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.0216 (3)	0.0060 (3)	0.0019 (3)	0.0045 (3)	0.0014 (3)	0.0003 (3)
S1	0.0254 (5)	0.0091 (3)	0.0022 (3)	0.0050 (3)	0.0021 (3)	0.0003 (3)
S3	0.0254 (6)	0.0182 (3)	0.0034 (3)	0.0058 (4)	0.0040 (3)	0.0001 (3)
P1	0.0310 (6)	0.0069 (3)	0.0030 (3)	0.0076 (3)	0.0025 (3)	0.0006 (3)
C(N)	0.0302 (3)	0.0078 (7)	0.0028 (3)	0.0067 (10)	0.0036 (6)	0.0011 (3)
N	0.0280 (18)	0.0111 (7)	0.0026 (3)	0.0048 (9)	0.0020 (5)	0.0004 (3)
C1	0.0309 (24)	0.0097 (8)	0.0027 (3)	0.0041 (11)	0.0001 (7)	0.0001 (4)
C2	0.0400 (30)	0.0104 (9)	0.0038 (4)	0.0032 (13)	0.0015 (8)	0.0000 (4)
C3	0.0426 (36)	0.0164 (14)	0.0062 (5)	−0.0008 (18)	−0.0015 (11)	−0.0013 (7)
C4	0.0591 (46)	0.0122 (12)	0.0091 (7)	0.0117 (19)	0.0034 (14)	−0.0004 (7)
C5	0.0292 (24)	0.0102 (3)	0.0033 (3)	0.0044 (11)	0.0045 (7)	0.0003 (4)
C6	0.0351 (27)	0.0116 (9)	0.0034 (3)	0.0044 (13)	0.0032 (8)	0.0014 (4)
C7	0.0371 (34)	0.0192 (15)	0.0074 (6)	0.0014 (18)	0.0077 (11)	0.0029 (8)
C8	0.0485 (37)	0.0141 (12)	0.0051 (4)	0.0094 (17)	0.0030 (10)	0.0030 (6)
C9	0.0319 (25)	0.0070 (7)	0.0048 (4)	0.0069 (11)	0.0042 (8)	0.0010 (4)
C10	0.0338 (32)	0.0177 (14)	0.0087 (7)	0.0078 (17)	0.0074 (12)	0.0033 (8)
C11	0.0513 (48)	0.0193 (18)	0.0111 (9)	0.0023 (23)	0.0127 (18)	0.0033 (10)
C12	0.0756 (61)	0.0138 (13)	0.0078 (7)	0.0087 (23)	0.0129 (17)	0.0035 (7)
C13	0.0674 (50)	0.0132 (12)	0.0055 (5)	0.0084 (20)	0.0063 (13)	0.0031 (6)
C14	0.0495 (35)	0.0104 (9)	0.0036 (4)	0.0062 (14)	0.0017 (9)	0.0015 (5)
C15	0.0421 (33)	0.0148 (11)	0.0070 (5)	0.0159 (16)	0.0087 (11)	0.0042 (6)
C16	0.0799 (53)	0.0087 (9)	0.0047 (4)	0.0112 (18)	0.0015 (12)	−0.0014 (5)

[a] The form of the thermal epllisoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Positional Parameters for $Pt(S_2CO)(PPh_3)_2$

Atom	*x*	*y*	*z*
Pt	0.27057 (4)	0.24303 (4)	0.49114 (4)
S1	0.3649 (3)	0.2869 (2)	0.2683 (3)
S2	0.4387 (3)	0.1797 (2)	0.4163 (3)
P1	0.2104 (3)	0.1933 (2)	0.7057 (3)
P2	0.1238 (3)	0.3197 (2)	0.5108 (3)
C	0.4762 (12)	0.2302 (9)	0.2556 (13)
O	0.5614 (10)	0.2229 (8)	0.1613 (10)
C11	0.3128 (12)	0.1355 (8)	0.7474 (12)
C12	0.3781 (13)	0.1647 (9)	0.8505 (12)
C13	0.4549 (16)	0.1165 (11)	0.8783 (16)
C14	0.4670 (17)	0.0403 (12)	0.7996 (17)
C15	0.4015 (15)	0.0094 (11)	0.6982 (16)
C16	0.3236 (13)	0.0571 (9)	0.6720 (13)
C21	0.0483 (11)	0.1102 (7)	0.7515 (11)
C22	−0.0069 (12)	0.0796 (8)	0.8834 (12)
C23	−0.1310 (13)	0.0172 (9)	0.9149 (13)
C24	−0.1968 (13)	−0.0183 (9)	0.8139 (14)
C25	−0.1406 (13)	0.0091 (9)	0.6831 (14)
C26	−0.0170 (12)	0.0734 (8)	0.6500 (12)
C31	0.2218 (11)	0.2870 (7)	0.8268 (11)
C32	0.1265 (12)	0.2920 (8)	0.9417 (12)
C33	0.1517 (14)	0.3669 (10)	0.0304 (15)
C34	0.2709 (15)	0.4350 (10)	0.0012 (15)
C35	0.3642 (14)	0.4308 (10)	0.8850 (15)
C36	0.3394 (13)	0.3561 (9)	0.7960 (13)
C41	0.0068 (11)	0.3286 (8)	0.6697 (11)
C42	−0.1038 (13)	0.2548 (9)	0.7106 (13)
C43	−0.1918 (15)	0.2576 (11)	0.8361 (13)
C44	−0.1710 (17)	0.3347 (12)	0.9165 (18)
C45	−0.0654 (16)	0.4090 (11)	0.8745 (16)
C46	0.0265 (13)	0.4076 (9)	0.7523 (13)
C51	0.0142 (11)	0.2748 (8)	0.3983 (11)
C52	−0.0810 (12)	0.3126 (9)	0.3954 (13)
C53	−0.1675 (14)	0.2756 (10)	0.3117 (14)
C54	−0.1589 (14)	0.1987 (10)	0.2352 (14)
C55	−0.0676 (13)	0.1588 (9)	0.2420 (13)
C56	0.0229 (12)	0.1967 (8)	0.3209 (12)
C61	0.2136 (11)	0.4368 (8)	0.4637 (11)
C62	0.1890 (12)	0.4814 (8)	0.3707 (12)
C63	0.2613 (13)	0.5734 (9)	0.3462 (14)
C64	0.3525 (13)	0.6177 (9)	0.4197 (13)
C65	0.3786 (15)	0.5737 (10)	0.5138 (15)
C66	0.3090 (13)	0.4816 (10)	0.5399 (14)

syntheses led to the locations of all 32 nonhydrogen atoms. However, after several cycles of full-matrix isotropic refinement, the *R* factor remained at 0.10 for the full data (2203 reflections). The solvent molecules were located by difference Fourier and Fourier syntheses. Refinement was discontinued at $R = 0.086$. The occupancy factor for the solvent was found to be 0.25. The bond distances and angles in the Pt complex are not seriously affected by the solvent molecule. The structure is substantially the same as found[16] for $Pt(S_2CO)(PPh_3)_2$.

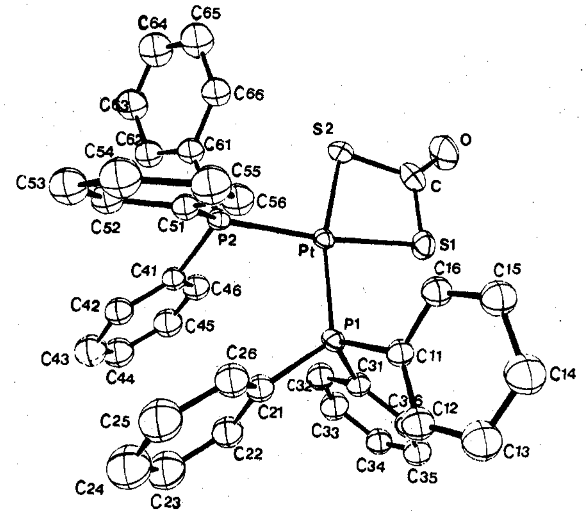


Figure 2. An ORTEP drawing of $Pt(S_2CO)(PPh_3)_2$.

Structural Results

The structures of $Pt(S_2CO)(PPh_3)_2$ and $Pt(S_2CO)$(diphos) establish the formation of sulfur-bonded dithiocarbonates from the reaction of xanthates with phosphines.[5,17] The short C=O distance (1.195 Å) is consistent with the spectroscopic studies reported earlier.[17] This distance is somewhat shorter than ketonic[20] C=O bonds and about 6 pm shorter than the C=O distances reported recently[18] for the rhodium(III) complex, $K[Rh(S_2CO)_2(PMe_2Ph)_2]$, where the phosphines are trans. The short C=O distance in the platinum(II) species presumably reflects the π electron withdrawing effects of the phosphine ligands, each trans to sulfur atoms in the dithiolate ligand.

Stephenson and co-workers[6] recently described the structure of $(AsPh_4)Pt(S_2COC_2H_5)_3$. Like the bis(phosphine) adduct of $Pt[S_2CN(i\text{-}Bu)_2]_2$ reported here, the xanthate anion also contains two dangling dithiolate ligands. However, in the bis(phosphine) complex the unidentate dithiolate ligands are trans. This result was anticipated from spectroscopic studies which suggested that an ionic formulation was incorrect in the solid state.

Table V. Thermal Parameters[a] for $Pt(S_2CO)(Ph_3P)_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.0057 (5)	0.0019 (5)	0.0053 (5)	0.0007 (5)	−0.0012 (5)	−0.0004 (5)
S1	0.0091 (5)	0.0052 (5)	0.0068 (5)	0.0020 (5)	−0.0004 (5)	0.0013 (5)
S2	0.0071 (5)	0.0035 (5)	0.0084 (5)	0.0020 (5)	−0.0012 (5)	−0.0007 (5)
P1	0.0063 (5)	0.0020 (5)	0.0058 (5)	0.0008 (5)	−0.0014 (5)	−0.0003 (5)
P2	0.0058 (5)	0.0021 (5)	0.0058 (5)	0.0010 (5)	−0.0014 (5)	−0.0005 (5)
C	0.0082 (14)	0.0044 (7)	0.0082 (15)	0.0012 (8)	−0.0009 (12)	−0.0016 (8)
O	0.0114 (12)	0.0105 (8)	0.0106 (12)	0.0056 (8)	0.0017 (10)	−0.0004 (8)

Atom	*B*, Å^2	Atom	*B*, Å^2	Atom	*B*, Å^2
C11	3.21 (23)	C31	2.75 (21)	C51	2.83 (21)
C12	4.03 (26)	C32	3.52 (24)	C52	3.64 (24)
C13	5.53 (34)	C33	4.90 (30)	C53	4.53 (28)
C14	6.04 (36)	C34	5.13 (31)	C54	4.54 (29)
C15	5.33 (32)	C35	4.90 (30)	C55	3.85 (25)
C16	3.90 (26)	C36	4.00 (26)	C56	3.32 (23)
C21	2.63 (20)	C41	3.17 (22)	C61	2.96 (22)
C22	3.24 (23)	C42	3.89 (25)	C62	3.52 (24)
C23	3.92 (26)	C43	5.51 (33)	C63	4.36 (28)
C24	4.12 (26)	C44	6.19 (37)	C64	4.12 (27)
C25	4.16 (27)	C45	5.52 (34)	C65	5.13 (32)
C26	3.47 (24)	C46	4.00 (26)	C66	4.31 (27)

[a] Thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table VI. Some Bond Lengths and Angles in $Pt(S_2CO)(Ph_3P)_2$

	Lengths, Å		
Pt-S1	2.347 (3)	S2-C	1.803 (14)
Pt-S2	2.326 (4)	C-O	1.195 (16)
Pt-P1	2.280 (3)	P1-C11	1.825 (16)
Pt-P2	2.288 (4)	C11-C12	1.401 (20)
S1-C	1.755 (16)		
	Angles, Deg		
S1-Pt-S2	75.2 (2)	S1-C-S2	106.6 (7)
S1-Pt-P1	170.6 (2)	S2-C-O	124.8 (9)
P1-Pt-P2	98.7 (2)	Pt-P1-C11	115.9 (5)
P2-Pt-S2	165.4 (2)	Pt-P1-C21	114.9 (5)
S1-C-O	128.6 (9)	C11-P1-C31	102.7 (6)

Table VII. C⩦N Stretching Frequencies[a] in cm^{-1} of Some Phosphine Adducts of Platinum(II) Dithiocarbamates

Compd	ν(C⩦N)
$Pt(S_2CNMe_2)_2(PMePh_2)_2$	1482
$Pt(S_2CNMe_2)(PMePh_2)_2PF_6$	1562
$Pt(S_2CNMe_2)_2(PMe_2Ph)_2$	1478
$Pt(S_2CNMe_2)(PMe_2Ph)_2BPh_4$	1572
$(S_2CNMe_2)_2$	1495[b]
$Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$	1465
$Pt(S_2CN(i\text{-}Bu)_2)(PMe_2Ph)_2BPh_4$	1520

[a] Recorded using KBr pellets. [b] N. K. Wilson, *J. Phys. Chem.*, 75, 1067 (1971).

Table VIII. Bond Lengths (Å) and Bond Angles (deg) in $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$

	Bond Lengths		
Pt-S1	2.335 (2)	P1-C16	1.838 (8)
Pt-P1	2.305 (2)	C(N)-N	1.349 (9)
S1-C(N)	1.734 (6)	N-C1	1.488 (8)
S3-C(N)	1.692 (8)	N-C5	1.485 (10)
P1-C9	1.823 (8)	C1-C2	1.547 (11)
P1-C15	1.821 (11)		
	Some Nonbonded Distances		
Pt-S3	3.392 (3)	S1-S3	2.994 (3)
	Bond Angles about Metal Atom		
S1-Pt-P1	87.2 (1)	Pt-P1-C15	113.6 (4)
Pt-S1-C(N)	106.5 (3)	Pt-P1-C16	113.9 (4)
Pt-P1-C9	116.8 (3)		
	Monodentate Ligand		
S1-C(N)-S3	121.9 (4)	N-C(N)-S3	121.6 (5)
S1-C(N)-N	116.6 (5)		
	Phosphine		
C9-P1-C15	104.6 (4)	C16-P1-C9	102.6 (4)
C9-C14-C13	120.5 (7)	C16-P1-C15	103.8 (5)

The infrared spectra of the cis bis(phosphine) ionic compounds, $Pt(S_2CNR_2)(PR_3)_2^+X^-$ ($X^- = PF_6^-$ and BPh_4^-), have characteristically high C⩦N stretching frequencies which are not found in $Pt(S_2CNR_2)_2(PR_3)_2$ (Table VII). Furthermore, cis phosphine ionic compounds, $Pt(S_2CNR_2)(PR_3)_2^+X^-$, are colorless, as are most other cis phosphineplatinum(II) complexes.[19] (The Pt(II) anion of ethyl xanthate is yellow, although it contains two cis dangling dithiolate ligands.)

While the coordinated Pt–P and Pt–S distances reported in these complexes are normal,[21–24] with trans Pt–P bonds 1–2 pm shorter than cis Pt–P bonds, the nonbonded Pt–S3 distance (Table VIII) in $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ is unusually short (3.392 Å). It is shorter than the dangling Pt···S distance found in $Pt(S_2CC_6H_4C_3H_7)_2(PMePh_2)$,[25] $Pd(S_2PPh_2)_2(PPh_3)$,[9] and $Ru(S_2CNMe_2)_3(NO)$[26] (Table IX). This distance is less than the sum of van der Waals radii of sulfur[27] and platinum[28] atoms (3.92 Å), suggesting a weak interaction (see Figure 3). The perpendicular distance of S3 from the Pt–P1–S1 plane is 2.903 Å. The distance from Pt to the projection point of the dangling sulfur atom onto the plane is 1.751 Å. S3 does not lie directly above the platinum. The dangling Pt–S3 axis makes an angle of ~45° with a line perpendicular to the equatorial plane at the platinum position. The dihedral angle between the S1–C(N)–S3 plane and the Pt–P1–S1 plane is 83.9°.

Table IX. Nonbonded Metal–Dangling Sulfur Distances

Compd	Distance, Å
$Pt(S_2CC_6H_4C_3H_7)_2PMePh_2$	3.580[a]
$Pd(S_2PPh_2)_2PPh_3$	>3.5[b]
$Ru(S_2CNMe_2)_3NO$	3.633[c]
$Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$	3.392 (3)
$Pt(S_2CNEt_2)_2PPh_3$	3.457 (5)[d]
$Pt(S_2P(OEt)_2)_2PPh_3$	3.955 (9)[d]
$Pt(S_2COEt)_2PPh_3$	>4.5[d]
$[AsPh_4]Pt(S_2COC_2H_5)_3$	4.85, 4.97[e]

[a] D. R. Swift, Ph.D. Thesis, Case Western Reserve University, 1970. [b] Reference 7. [c] A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966). [d] To be submitted for publication from our laboratories. [e] Reference 6.

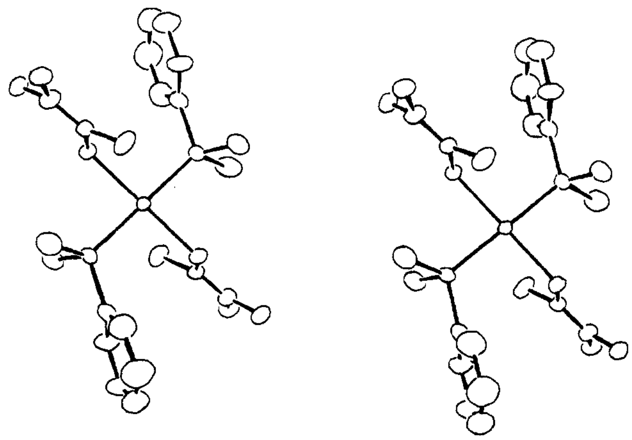
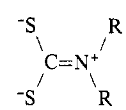


Figure 3. A stereopair representation of $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$. Only the α carbons of the isobutyl groups are represented.

The sulfur–sulfur "bite" distance of 2.994 Å and the S1–C(N)–S3 angle of 121.9° are comparable with those found in $NaS_2CNEt_2{\cdot}3H_2O$[29] and tetramethylthiuram disulfide.[30,31] These values, however, are larger than those found for bidentate ligands in $M(S_2CNR_2)_2$.[32,33] The S1–C(N) and S3–C(N) distances of the monodentate ligand are 1.734 and 1.691 Å, respectively. These sulfur–carbon bonds exhibit some double bond character, being longer than a C=S double bond (1.558 Å) and shorter than the C—S single bond (1.81 Å).

The substantial difference in C—S bond distances and the longer C⩦N bond distance found in the monodentate dithiocarbamate ligand suggest that the symmetrical thioureide resonance form IV contributes less in the monodentate dtc



IV

ligands than in the bidentate ligands.

NMR Results

^{13}C NMR Studies of $Pt(S_2CNR_2)_2(PMe_2Ph)_2$. Two ^{13}C NMR spectra of 30% carbon-13 enriched $Pt[S_2CN(i\text{-}Bu)_2]_2$ in $CDCl_3$ at 32 °C are shown in Figure 4. The assignment is straightforward. The signals at 20.1, 26.9, and 56.4 ppm are for the γ, β, and α carbons of the isobutyl groups. The 1:4:1 triplet at 213.0 ppm is assignable to the C⩦N carbon, coupled to ^{195}Pt ($I = {}^1/_2$, natural abundance = 33%). These

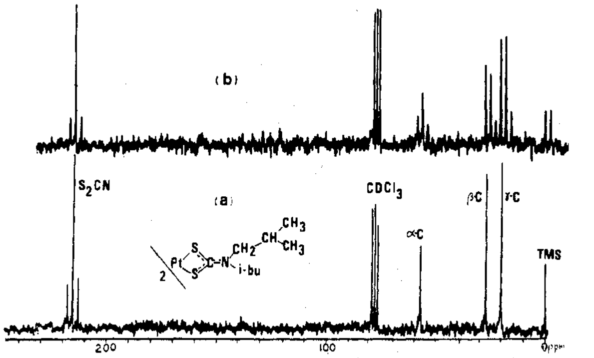


Figure 4. ^{13}C NMR spectra of $Pt(S_2CN(i\text{-}Bu)_2)_2$ with 30% carbon-13 enriched at the S_2CN carbon at 32 °C in $CDCl_3$: (a) with broad band proton decoupled, (b) without proton decoupled.

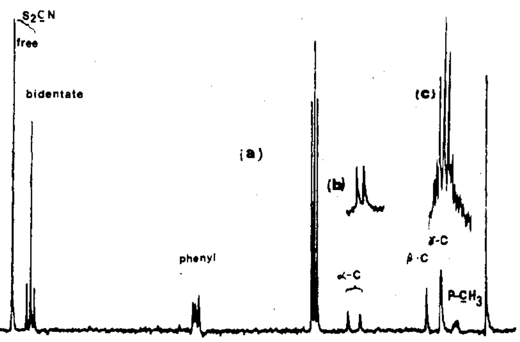


Figure 5. (a) ^{13}C NMR spectrum of $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$ in $CDCl_3$ at −58 °C. (b) Phosphine region, less than 1:1 molar ratio of PMe_2Ph was added to the sample in (a). (c) P–CH_3 carbon resonance of $[PtS_2CN(i\text{-}Bu)_2(PMe_2Ph)_2]BPh_4$ at 32 °C.

assignments are supported by spectrum (b) recorded without proton decoupling. Thus the γ carbons become a 1:4:4:1 quartet, the β carbons become a 1:1 doublet, the α carbons become a 1:2:1 triplet, and the C⋯N carbon resonance remains a 1:4:1 triplet.

Upon dissolving 0.2 g of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ (I) in 3.5 mL of $CDCl_3$, the ^{13}C NMR spectrum at −58 °C shows two different types of C⋯N carbon resonances with relative intensity of 1:1, a singlet at 213.0 ppm, and a 1:4:1 triplet at 204.8 ppm. There are two different α and γ carbon resonances at 62.1, 56.6 and 20.5, 19.9 ppm with 1:1 intensity, respectively, an unresolved signal at δ 26.5 for the β carbon resonance, and an approximate five-line pattern at δ 14.0 for the P–CH_3 carbons (Figure 5a). When the temperature is raised to −37 °C the C⋯N carbon resonances broaden. At 4°, they merge to a singlet at 209.7 ppm, a small signal arises at 206.4 ppm (Figure 6a–d), and the P–CH_3 carbon resonance becomes a 1:1 doublet. The two types of isobutyl carbon resonances also collapse to an equivalent set from −58 to +4 °C. The low intensity of this region, however, is not as informative as the C⋯N carbon. Upon addition of ~0.03 g of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)$ (II) to the above solution at 4 °C, a sharp 1:4:1 triplet arises at δ 206.4 (spectrum e). If a drop (less than 1:1 molar ratio) of PMe_2Ph is added to I in $CDCl_3$, the ^{13}C NMR spectrum at −58 °C shows that the isobutyl carbon resonances are not affected, whereas the P–CH_3 resonance becomes a sharp doublet at δ 14.1 (Figure 5b). For comparison, the P–CH_3 carbon resonance of $[Pt(S_2CN(i\text{-}Bu)_2)(PMe_2Ph)_2]BPh_4$ (III) is also shown in Figure 5c.

^{31}P NMR Studies of $Pt(S_2CNR_2)_2(PMe_2Ph)_2$ (R = Isobutyl). The proton noise decoupled ^{31}P NMR spectrum in $CDCl_3$ (~0.065 M) at −60 °C shows a sharp 1:4:1 triplet at 18.3 ppm (Figure 7a–c with Pt satellites omitted) upfield relative to 85% H_3PO_4. This is assignable to the coordinated phosphines which are coupled to the ^{195}Pt. The chemical shift

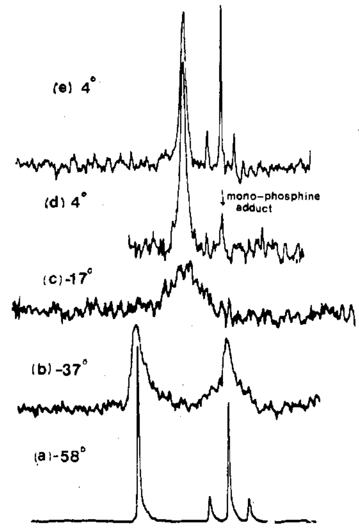


Figure 6. Variable-temperature ^{13}C NMR spectra (a–d) of $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$ at the S_2CN carbon. (e) Small amount of $Pt(S_2CN(i\text{-}Bu)_2)_2PMe_2Ph$ was added.

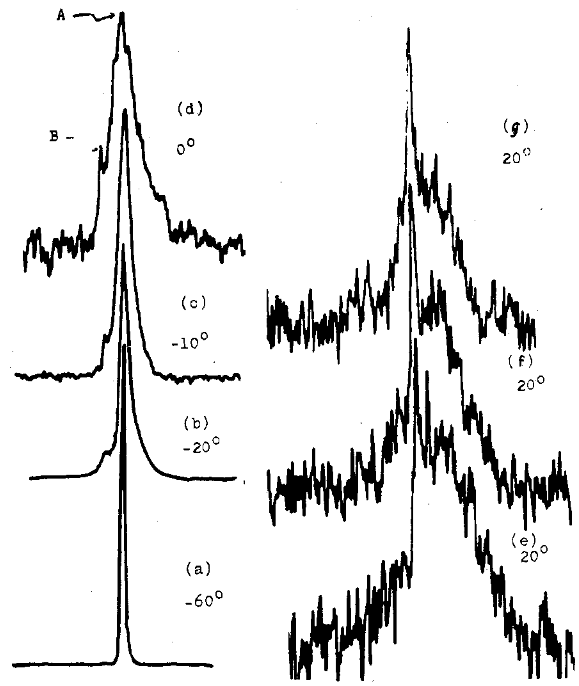


Figure 7. Variable-temperature ^{31}P NMR spectra of $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$ in $CDCl_3$ (a–e) (The satellites due to the ^{195}Pt are omitted. A, the resonance assigned to the cis ionic form. B, the additional peak arises above −20 °C.), (f) a small amount of $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)$ was added, and (g) 1 mL of toluene was added to sample f.

and coupling constant of resonance A are comparable to that found in III.

When the temperature is increased, resonance A begins to broaden (Figure 7). At −20 °C, there is a small sharp peak (resonance B) in addition to the broadening of resonance A. At 20 °C, resonance B broadens slightly, increasing in intensity, while resonance A further broadens, decreasing in intensity. Addition of ~0.02 g of II to this solution increases the intensity of resonance B (spectrum 7f). Addition of ~1 mL of toluene to the above solution further increases the intensity of resonance B accompanied by slight broadening of both resonances A and B (Figure 7g).

The ^{31}P NMR spectrum of ~0.019 M I in acetone-d_6 at −70 °C also shows a slightly broadened 1:4:1 triplet at 19.0 ppm. On heating, this resonance broadens and collapses. The

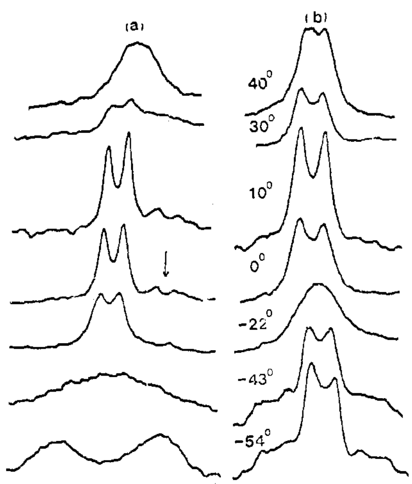


Figure 8. Variable-temperature ^1H NMR spectra of $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$ in $CDCl_3$ (100 MHz): (a) $N-CH_2$ region, (b) $P-CH_3$ region. The mark ↓ indicates the presence of $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)$.

broadening at a given temperature is greater in acetone than in $CDCl_3$.

^1H NMR Studies of *trans*-$Pt(S_2CNR_2)_2(PMe_2Ph)_2$. Results of ^1H NMR studies of the bis(phosphine) compounds in $CDCl_3$ are also very interesting. When R = isobutyl ($\sim 10^{-2}$ M), at −54 °C, there are two broad signals (δ 3.97, 3.58 ppm) at the $N-CH_2$ proton region, an approximate triplet of doublets (δ 1.72) at the $P-CH_3$ proton region, and a broad signal for the methine (δ 2.36) and the methyl (δ 0.95) protons. When the temperature is increased to −22 °C, the two broad $N-CH_2$ signals collapse to a broad doublet, and the $P-CH_3$ protons give a broad signal. At 0 °C the $N-CH_2$ doublet sharpens, accompanied by the appearance of another doublet while the $P-CH_3$ resonance sharpens to a doublet. On further heating (48 °C), the $N-CH_2$ protons collapse to a broad peak again, and the $P-CH_3$ protons also broaden. The variable-temperature ^1H NMR spectra are shown in Figure 8.

The ^1H NMR spectrum of I in toluene-d_8 ($\sim 10^{-2}$ M) is qualitatively similar to the spectrum in $CDCl_3$, although a lower temperature is required to obtain a limiting spectrum. A spectrum at −90 °C is comparable with the spectrum in $CDCl_3$ at −54 °C. At probe temperature the $N-CH_2$ and $(N)CH_3$ protons are sharp, with broadening occurring above 35 °C. The $P-CH_3$ probe temperature signal compares with the signal in $CDCl_3$ at ~0 °C.

The ^1H NMR spectrum of III ($\sim 10^{-2}$ M) in $CDCl_3$ shows a sharp doublet for the $N-CH_2$ protons (δ 3.54), a multiplet for the CH protons (δ 2.27), a sharp doublet for the $(N)CH_3$ protons (δ 0.97), a deceptive triplet (1:4:1) of doublets (1:1) (δ 1.34) for the $P-CH_3$ protons, and a complex resonance at δ 7.2 ppm for the phenyl protons. Upon addition of more than one molar ratio of $NaS_2CN(i\text{-}Bu)_2 \cdot 3H_2O$ to the above solution at ~32° C. additional peaks arise. These are attributed to the sodium salt, and no appreciable line shape change is observed for the resonances assigned to III. However, in acetone-d_6, upon addition of a saturated solution of the sodium salt, only one set of sharp isobutyl resonances is observed, and the $P-CH_3$ proton resonance becomes a doublet with $^2J_{P-H} \simeq$ 11 Hz.

Discussion of the NMR Spectra

The low-temperature ^{13}C NMR spectrum of I shows two different types of dithiocarbamate ligand resonances having equal intensities. In the S_2CN carbon region an upfield triplet, assigned to a coordinated dithiocarbamate, has $^2J_{C-Pt} = 89$ Hz; a downfield singlet is assigned to the ionic ligand. From the ^{13}C spectra of $Pd(PR_3)_2X_2$ complexes, Nelson et al.[34,35] show that the phosphine methyl resonances for nonexchanging cis isomers may appear as a quintet, a triplet, a doublet of doublets, or a doublet. For platinum complexes, the $P-CH_3$ carbon spectra are complicated by the coupling with ^{195}Pt. In the case of a cis phosphineplatinum complex III, an approximate five-line pattern is observed (Figure 5b). This is similar to the low-temperature spectrum of I. Thus the $P-CH_3$ carbon signal of I is consistent with a cis phosphine configuration. *The conclusion is that I has an ionic formulation at low temperature in solution, a result which is solvent dependent.*

Upon heating the solution of I above −58 °C (in $CDCl_3$), the ^{13}C signals of the S_2CN carbon in the coordinated and uncoordinated ligands coalesce, indicating exchange. The small peak that arises at 4 °C in the S_2CN carbon region is assigned to the mono(phosphine) adduct II. This is supported by spectrum e in Figure 6, which shows that addition of the mono(phosphine) adduct increases the intensity of the small peak. The close similarity of the chemical shift and coupling constant with II further confirms this conclusion. From Figure 6e it can be seen that although the free and coordinated dtc ligand exchange is fast on the NMR time scale, the resonance of II remains sharp. The exchange of the free and bidentate dtc ligands (from −58 to +4 °C) does not directly involve II. Thus reaction 2 which forms II is not kinetically important from −58 to +4 °C.

The NMR data suggest that a dithiolate exchange reaction (3) dominates the kinetics from −50 to 0 °C. An intermediate

$$Pt(S_2CN^*R_2)(PR_3)_2^+ + S_2CNR_2^- \rightleftharpoons Pt(S_2CNR_2)(PR_3)_2^+ + S_2CN^*R_2^- \quad (3)$$

such as represented by the solid-state structure of I or its cis analogue (which could not be detected in this work) could account for the magnetic equivalence observed.

The ^{13}C NMR spectrum of I at −58 °C, in which the $P-CH_3$ spectrum shows a five-line pattern, changes to a sharp doublet in the presence of a small amount of added phosphine. The S_2CN carbon resonance (chemical shift or ^{2}Pt–C coupling) does not change. Thus bimolecular phosphine exchange occurs with the cation of I, which is the cation of III, without the concomitant loss of the dithiolate ligand, eq 4. This is

$$Pt(S_2CNR_2)(P^*R_3)_2^+ + PR_3 \rightleftharpoons Pt(S_2CNR_2)(PR_3)(P^*R_3) + P^*R_3 \quad (4)$$

consistent with the bidentate nature of the dithiolate coordination. The ^{31}P NMR spectrum also supports the conclusion[36] that the bimolecular rate constant for phosphine exchange with the cation of I is larger than the rate constant for dithiolate exchange. The addition of $NaS_2CN(i\text{-}Bu)_2 \cdot 3H_2O$ to III in acetone-d_6 produces conditions which demonstrate that (3) can occur.

The ^1H and ^{31}P data also support the conclusions reached from the ^{13}C studies. They are as follows. (a) *The dominant low-temperature form of I in solution is the ionic species, the cation of III.* No evidence for appreciable amounts of either the cis or trans neutral species is obtained, even though the trans species crystallizes from the solution. (b) *The dithiolate exchange reaction occurs more rapidly in acetone-d_6 or toluene than in $CDCl_3$.* (c) *The phosphine exchange with I appears more favorable kinetically than the dithiolate exchange.* (d) *The bimolecular processes implied by eq 3 and 4 both appear faster than eq 2.*[37]

In particular, since eq 2 and 3 involve the same reactants, the relative importance of rupturing the Pt–S and Pt–P bonds needs to be considered. As expected from trans effects originating from the π-accepting ability of the phosphine, the Pt–S bond ruptures with a lower activation energy than the Pt–P bond. Since eq 2 and 4 have the same leaving group, the slower rate of eq 2 further suggests that the nucleophilic reactivity of phosphine toward Pt(II) is greater than that of the dithiocarbamate anion.[38]

Acknowledgment. Support for this work was received from the National Institutes of Health, GM 19050-06, and the Sohio Foundation for the NMR studies, and the National Science Foundation, CHE 76-18709, and the General Electric Foundation for the crystallographic investigations. J.P.F. also thanks the John S. Guggenheim Foundation for a Fellowship and the University of Cambridge through Professor Jack Lewis for an opportunity to write up these studies.

Registry No. I, 64900-48-7; II, 64872-66-8; III, 64872-68-0; $Pt(S_2CNMe_2)_2(PMe_2Ph)_2$, 64872-69-1; $Pt(S_2CO)(PPh_3)_2$, 25787-94-4; $Pt(S_2CO)(diphos)\cdot{}^1/_4CHCl_3$, 64872-70-4; $Pt(S_2CNMe_2)_2(PMePh_2)_2$, 64872-71-5; $[Pt(S_2CNMe_2)(PMePh_2)_2]PF_6$, 64872-72-6; $[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$, 40587-91-5; $Pt(S_2CNMe_2)_2$, 40545-11-7; $Pt[S_2CN(i\text{-}Bu)_2]_2$, 64872-73-7; $Pt(PMe_2Ph)_2Cl_2$, 30759-88-7; $Pt(S_2COEt)_2$, 19965-15-2; ^{13}C, 14762-74-4.

Supplementary Material Available: Positional and thermal parameters of $PtS_2CO(diphos)\cdot{}^1/_4CHCl_3$, Table A-1; significant bond lengths and angles for $PtS_2CO(diphos)\cdot{}^1/_4CHCl_3$, Table A-2; and structure factor tables for all three compounds, Tables A-3–A-5 (84 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Abstracted from the thesis of I. J. B. Lin submitted in partial fulfillment of the requirements for the Ph.D. degree at Case Western Reserve University, Oct 1975.
(2) Part 31: H. W. Chen, J. P. Fackler, Jr., D. P. Schussler, and L. D. Thompson, *J. Am. Chem. Soc.*, in press.
(3) J. P. Fackler, Jr., I. J. B. Lin, and J. Andrews, *Inorg. Chem.*, **16**, 450 (1977).
(4) Selenium NMR studies of diselenocarbamates of Pt(II) and Pd(II) with added phosphines are producing results which qualitatively are similar to the results reported in this paper. W.-H. Pan and J. P. Fackler, Jr., to be submitted for publication.
(5) J. P. Fackler, Jr., and W. C. Seidel, *Inorg. Chem.*, **8**, 1631 (1969).
(6) M. C. Cornock, R. O. Gould, C. L. Jones, J. D. Owen, D. F. Steele, and T. A. Stephenson, *J. Chem. Soc.*, 496 (1977).
(7) T. A. Stephenson and B. D. Faithful, *J. Chem. Soc. A*, 1504 (1970).
(8) J. M. C. Alison and T. A. Stephenson, *Chem. Commun.*, 1092 (1970).
(9) J. M. C. Alison, T. A. Stephenson, and R. O. Gould, *J. Chem. Soc., A*, 3690 (1971).
(10) (a) J. M. C. Alison and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 254 (1973). (b) With very bulky phosphines, ionic PtS_2P_2 species appear to be formed in the solid state with the dithiocarbamates (T. A. Stephenson and co-workers). Steric factors presumably are important in helping to determine the solid state and solution structures whenever bulky ligands are involved.
(11) D. F. Steele and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 2124 (1973).
(12) F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **9**, 629 (1970).
(13) R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, **11**, 2435 (1972).
(14) D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 233 (1970).
(15) A complete list of the various crystallographic programs used can be found in H. W. Chen and J. P. Fackler, Jr., *Inorg. Chem.*, in press. The possibility that a trans isomer crystal was selected from a cis–trans mixture was considered. Microscopic examination of a large sample of crystals showed that >99% of them were of the same yellow color and crystal shape. Several crystals grown from different sample preparations gave identical cell dimensions.
(16) See H. W. Chen, Ph.D. Thesis, Case Western Reserve University, 1977.
(17) J. M. Burke and J. P. Fackler, Jr., *Inorg. Chem.*, **11**, 2744 (1972); J. M. Burke, Ph.D. Thesis, Case Western Reserve University, 1972.
(18) R. O. Gould, A. M. Gunn, Van der Hauk, and E. M. Thijs, *J. Chem. Soc., Dalton Trans.*, 1713 (1976).
(19) G. Booth, *Adv. Inorg. Chem. Radiochem.*, **6**, 1 (1964).
(20) O. Kennard and D. G. Watson, Ed., "Molecular Structures and Dimensions", International Union of Crystallography, Vol. 1, N. V. A. Oosthoek's Uitgevers Mij, Utrecht, 1972.
(21) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).
(22) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.
(23) M. Bair, G. Hartwell, Jr., R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Commun.*, 92 (1967).
(24) A. Z. Amannov, G. A. Kukina, and M. A. Poria-Koshits, *J. Struct. Chem. (Eng. Transl.)*, **8**, 149 (1967).
(25) D. R. Swift, Ph.D. Thesis, Case Western Reserve University, 1970.
(26) A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966).
(27) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1968, pp 421–425.
(28) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 791 (1962).
(29) M. Colapietro, A. Momenicano, and A. Vaciago, *Chem. Commun.*, 572 (1968).
(30) I. L. Karle, J. A. Estlin, and K. Britts, *Acta Crystallogr.*, **22**, 273 (1967).
(31) H. C. Brinkhoff and A. M. Grotens, *Recl. Trav. Chim. Pays-Bas*, **111**, 252 (1971).
(32) (a) B. B. Owen, R. C. Miller, C. E. Milner, and H. L. Cogan, *J. Phys. Chem.*, **65**, 2065 (1961); (b) M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 619 (1965).
(33) (a) G. Peyronel and A. Pignedoli, *Acta Crystallogr.*, **23**, 398 (1967); (b) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970).
(34) D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Nucl. Chem. Lett.*, **10**, 727 (1974), and references contained therein.
(35) A. W. Verstuyft, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, **14**, 1495 (1975).
(36) The ^{31}P resonance shows an exchange of the cation of I, without involving II. The resonance of II remains sharp while that of I becomes broadened.
(37) The line broadening of the dithiocarbamate resonance according to eq 3 is given by $\tau_{CF}^{-1} = k_3[S_2CNR_2]$. For eq 4, the $\tau_{CF}^{-1} = k_4[PR_3]$. The ^{13}C spectrum of I at −58 °C in the presence of less than a molar equivalent of added phosphine shows fast phosphine exchange and slow dithiocarbamate exchange. With $k_4[PR_3] > k_3[S_2CNR_2]$ and $[PR_3] < [S_2CNR_2]$, $k_4 > k_3$.
(38) Conductivity measurements in dichloromethane and nitromethane show that the complexes $Pt(S_2PPh_2)_2(PR_3)_2$ are 1:1 electrolytes. The mull and solution IR spectra are identical, suggesting that the same species is retained in solution. On removal of solvent, the bis(phosphine) adduct is recovered. At −20 °C the ^{31}P NMR spectrum of $Pt(S_2PMe_2)_2(PPh_3)_2$ in a $CDCl_3$ solution consists of a triplet (1:4:1) of triplets (1:2:1) at −93.36 ppm, A, a singlet at −34.32 ppm, B, and a triplet (1:4:1) of doublets (1:1) at −17.05 ppm, C. The relative intensity of A, B, and C is 1:1:2. The spectrum is consistent with an ionic formulation. The triplet of triplets in region A is assignable to the coordinated dithiophosphinate ligand in which the phosphorus signal is coupled to ^{195}Pt, giving a resultant 1:4:1 triplet. This triplet is further split by the two phosphine phosphorus atoms. The singlet in region B is assignable to the free dithiophosphinate ligand. The triplet of doublets in region C is assignable to the two cis phosphines. When the temperature is increased to 3 °C, the signals in region A and region B broaden and in region C are a sharp 1:4:1 triplet. At 43 °C the signals in regions A and B further broaden and the triplet in region C remains sharp. At this stage additional peaks arise which are attributed to decomposition. At 63 °C, signals of the coordinated and free dithiophosphinate ligands merge to a broad peak at ca. −65 ppm. These results suggest a rapid exchange of coordinated ligand with free ligand: $Pt(S_2PMe_2)(PPh_3)_2]^+ + S_2PMe_2{}^{*-} \rightleftharpoons [Pt(S_2PMe_2{}^*)(PPh_3)_2]^+ + S_2PMe_2^-$. This exchange is faster than the phosphine dissociation process: $[Pt(S_2PMe_2)(PPh_3)_2]^+ + S_2PMe_2^- \rightleftharpoons [Pt(S_2PMe_2)_2(PPh_2)] + PPh_3$.