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# Structure of Bis(triphenylphosphine)(*N*-ethoxycarbonyldithiocarbimato)palladium(II), Formed by the Reaction of Excess Ethoxycarbonyl Isothiocyanate with Palladium(0) in the Presence of Triphenylphosphine

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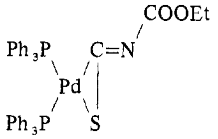
When a large excess of EtOCONCS is added to Pd(0) complexes in the presence of $PPh_3$ (Et = $C_2H_5$, Ph = $C_6H_5$), a compound of composition $Pd(S_2CNCOOEt)(PPh_3)_2$ is isolated. On the basis of an x-ray diffraction study the compound is shown to be bis(triphenylphosphine)(*N*-ethoxycarbonyldithiocarbimato)palladium(II). The compound crystallizes in space group $C_i^1$-$P\bar{1}$ of the triclinic system with two molecules in a unit cell of dimensions $a = 13.371$ (2) Å, $b = 13.741$ (3) Å, $c = 10.995$ (2) Å, $\alpha = 93.85$ (1)°, $\beta = 113.74$ (1)°, $\gamma = 95.30$ (1)°, and $V = 1829$ Å$^3$. The structure has been solved by the heavy-atom method and refined by full-matrix least-squares techniques to a final value of the conventional $R$ index on $F_o$ of 0.042 based on 5794 unique reflections having $F_o^2 \geq 3\sigma(F_o^2)$ collected by counter methods. The Pd atom is coordinated to two P atoms from the $PPh_3$ groups and to two S atoms of the $S_2C{=}NCOOEt$ dithiocarbimato ligand in approximately a square-planar fashion. The Pd–P distances are 2.306 (1) and 2.333 (1) Å, and the Pd–S distances are 2.316 (1) and 2.343 (1) Å. The S–Pd–S angle is 75.03 (4)°, while the P–Pd–P angle is 98.89 (4)°. All five atoms in the inner coordination sphere are within 0.1 Å of the best least-squares plane defined by these atoms. The S–C bond lengths are 1.742 (4) and 1.754 (4) Å and the C–N bond length is 1.282 (5) Å. The comparable parameters within the inner coordination sphere agree very well with those found in the bis(*N*-cyanodithiocarbimato)nickelate(II) anion. In addition, these parameters differ but little from those of typical dithiocarbamate complexes.

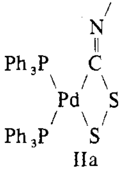
## Introduction

Our recent studies of the reactions of isocyanates[2] and isothiocyanates[3,4] with Rh(I) and Pd(0) complexes have revealed a varied and rich chemistry. That this chemistry can also be surprisingly complex is illustrated by the reactions of EtOCONCS[5] with Pd(0) in the presence of phosphines. When EtOCONCS is added in small excess to $Pd_2(dba)_3 \cdot CHCl_3$[5,6] and $PPh_3$ in benzene, a complex of composition $Pd(SCNCOOEt)(PPh_3)_2$ (I) is obtained in 80% yield. The complex is somewhat unstable in solution because of its tendency to lose the isothiocyanate ligand, but it is stable in the solid state; mp 108–112 °C dec; IR (KBr) $\nu(C{=}O)$ 1700 and $\nu(C{=}N)$ 1625 cm$^{-1}$. The structure of the complex is probably

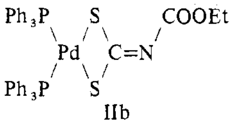


I

However, when the reaction is carried out with a (5–6)-fold excess of EtOCONCS, a complex of composition $Pd(S_2CNCOOEt)(PPh_3)_2$ (II) is obtained in 78% yield. This complex is very stable both in solution and in the solid state; mp 200–202 °C dec; IR (KBr) $\nu(C{=}O)$ 1706 and $\nu(C{=}N)$ 1537 cm$^{-1}$. The NMR spectra of these two complexes show only minor differences. On the basis of these spectroscopic results reasonable formulations for II are



IIa



IIb

The results of an x-ray diffraction study of compound II are presented here which indicate that it is correctly formulated as shown in IIb, a dithiocarbimato complex of Pd(II).

## Experimental Section

**Preparation of $Pd(S_2CNCOOEt)(PPh_3)_2$.** $PPh_3$ (400 mg, 1.53 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (200 mg, 0.193 mmol), and benzene (20 ml) were stirred under Ar at room temperature for 1.5 h. EtOCONCS (353 mg, 2.69 mmol) was slowly added to the resultant orange homogeneous solution. The color of the solution turned yellow. The solution was stirred for 2 h at room temperature. Solvent was removed under reduced pressure to give a reddish brown oil, to which ether (20 ml) was added. Pale yellow, crude product was isolated in 78% yield (283 mg) and was recrystallized from a mixed solvent of dichloromethane and ether to obtain yellow prisms: mp 200–202 °C dec; IR (KBr) 1706 ($\nu(C{=}O)$) and 1537 ($\nu(C{=}N)$) cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 1.18 (t, 3 H, $CH_3$), 4.08 (q, 2 H, $CH_2$) with $J = 7.0$ Hz, and 7.24 (m, 30 H, aromatic). Anal. Calcd for $C_{40}H_{35}NO_2P_2PdS_2$: C, 60.49; H, 4.44; N, 1.76; P, 8.07. Found: C, 60.41; H, 4.42; N, 1.98; P, 8.01.

This complex was also prepared from the reaction of $Pd(SCNCOOEt)(PPh_3)_2$ (50.6 mg, 0.066 mmol) with EtOCONCS (83.6 mg, 0.638 mmol) by stirring the mixture 3 h at room temperature. The resultant yellow powder (31.2 mg) yielded the same IR and NMR data as above.

**Preparation of $Pd(SCNCOOEt)(PPh_3)_2$.** $PPh_3$ (800 mg, 3.05 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (400 mg, 0.386 mmol) were stirred in benzene (20 ml) under Ar at room temperature. EtOCONCS (163 mg, 1.24 mmol) was added to the orange homogeneous solution. The reaction mixture immediately turned yellow. It was stirred for 2 h at room temperature. Evaporation of the benzene followed by the addition of ether (20 ml) caused the precipitation of pale yellow crystals in 80% yield. The complex is not stable in solution. Therefore, recrystallization was achieved from methylene chloride which contained a few drops of EtOCONCS and ether mixed solvent; mp 108–112 °C dec; IR (KBr) $\nu(C{=}O)$ 1700 and $\nu(C{=}N)$ 1625 cm$^{-1}$; NMR ($CDCl_3$) $\tau$ 2.8 (30 H, aromatic), 6.07 (q, 2 H, $CH_2O$), and 8.87 (t, 3 H, $CH_3$). Anal. Calcd for $C_{40}H_{35}NO_2SP_2Pd$: C, 63.04; H, 4.63; N, 1.84. Found: C, 62.98; H, 4.67; N, 1.83.

**Collection of X-Ray Intensity Data.** Preliminary Weissenberg and precession photographs failed to reveal any symmetry other than the expected center of inversion and the crystal was assigned to the triclinic system. General procedures for the determination of unit cell parameters and for the collection of intensity data have been given previously.[7,8] The compound $Pd(S_2CNCOOC_2H_5)(PPh_3)_2$, $C_{40}H_{35}NO_2P_2PdS_2$, has mol wt 794.21 and crystallizes in a Delaunay reduced cell of dimensions $a = 13.371$ (2) Å, $b = 13.741$ (3) Å, $c = 10.995$ (2) Å, $\alpha = 93.85$ (1)°, $\beta = 113.74$ (1)°, $\gamma = 95.30$ (1)°, and $V = 1829$ Å$^3$; $\rho_c = 1.442$ g/cm$^3$ and $\rho_o$ (by flotation in $ZnCl_2$ solution) = 1.45 (2) g/cm$^3$. The crystal selected for data collection had approximate dimensions 0.28 × 0.48 × 0.51 mm, calculated volume 0.0237 mm$^3$. Trial transmission factors ranged from 0.841 to 0.867, based on a linear absorption coefficient for Mo K$\alpha$ radiation of 7.30 cm$^{-1}$; accordingly no absorption correction was deemed necessary. Data were collected on a Picker FACS-I diffractometer using Mo K$\alpha$ radiation monochromatized from a mosaic graphite crystal. Details of data collection include the following: aperture 2.3 mm wide × 5.0 mm high, 34 cm from crystal; takeoff angle 2.5°;

**Table I.** Positional and Thermal Parameters for Nongroup Atoms of $Pd(S_2CNCOOEt)(PPh_3)_2$

| ATOM | X[A] | Y | Z | B11[B] | B22 | B33 | B12 | B13 | B23 |
|---|---|---|---|---|---|---|---|---|---|
| PD | -0.052699(21) | 0.227301(20) | -0.222022(26) | 3.95(2) | 3.71(2) | 5.87(4) | 0.51(1) | 2.18(2) | 0.56(2) |
| S(1) | 0.127282(82) | 0.208439(84) | -0.08593(11) | 4.45(7) | 6.08(7) | 8.49(11) | 1.19(6) | 2.16(7) | 1.06(7) |
| S(2) | 0.038961(94) | 0.225657(91) | -0.36416(11) | 6.65(9) | 6.96(8) | 8.92(12) | 1.58(6) | 4.82(9) | 1.40(8) |
| P(1) | -0.114196(79) | 0.214225(70) | -0.054916(95) | 4.53(7) | 3.53(5) | 6.54(10) | 0.56(5) | 2.60(7) | 0.59(6) |
| P(2) | -0.215957(80) | 0.257150(72) | -0.393540(95) | 4.51(7) | 3.76(6) | 6.27(10) | 0.56(5) | 1.93(7) | 0.65(6) |
| O(1) | 0.40607(37) | 0.18693(34) | -0.06257(50) | 12.96(42) | 8.70(33) | 21.16(73) | 5.37(31) | 5.83(45) | 2.76(39) |
| O(2) | 0.37334(43) | 0.33657(39) | -0.04594(81) | 11.92(50) | 8.48(37) | 57.2(18) | 4.38(34) | -13.18(78) | -8.91(65) |
| N | 0.25661(33) | 0.24076(30) | -0.22287(46) | 5.93(31) | 6.08(25) | 16.68(61) | 1.06(22) | 6.31(38) | 0.54(31) |
| C(1) | 0.16074(34) | 0.22672(29) | -0.22217(45) | 6.15(30) | 3.77(23) | 11.48(52) | 1.01(21) | 4.87(33) | 0.18(27) |
| C(2) | 0.34883(41) | 0.24819(39) | -0.10429(69) | 5.96(37) | 5.79(32) | 23.4(10) | 1.38(28) | 6.61(52) | 0.85(45) |
| C(3) | 0.4754(12) | 0.3692(15) | 0.0810(23) | 16.1(14) | 16.6(16) | 84.0(62) | 2.7(12) | -14.7(21) | 7.0(25) |
| C(4) | 0.4146(14) | 0.3539(19) | 0.1856(23) | 21.5(22) | 35.3(25) | 78.6(56) | -10.8(21) | -34.0(28) | 18.4(33) |

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X $10^3$.

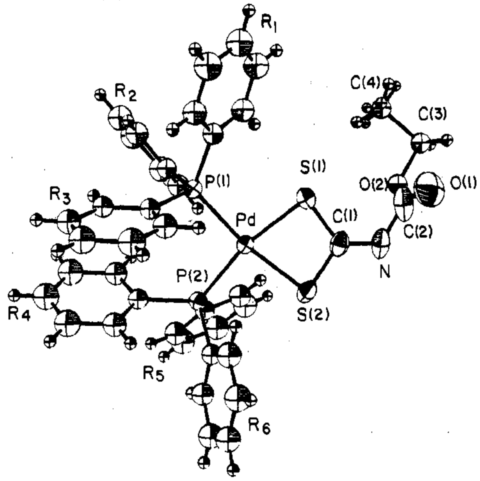


**Figure 1.** Perspective view of the $Pd(S_2CNCOOEt)(PPh_3)_2$ molecule showing the numbering scheme. The vibrational ellipsoids are drawn at the 50% probability level except for atoms O(2), C(3), and C(4), which are drawn with $B = 3.0$ Å$^2$, and for the H atoms.

scan speed 2.0°/min; scan range from 0.7° below the $K\alpha_1$ peak to 0.8° above the $K\alpha_2$ peak; background counts for 10 s at each end of the scan range; 6471 unique data collected out to 50° in $2\theta$, past which point few intensities were above background; six standard reflections collected every 100 reflections showing variations within counting statistics.

**Solution and Refinement of the Structure.** By using a value for $p$ of 0.04[7] the data were processed to yield 5794 unique reflections having $F_o^2 > 3\sigma(F_o^2)$. Only these reflections were used in subsequent calculations.

Computer programs, sources of scattering factors and anomalous terms, and calculational procedures have been noted previously.[9] The positions of the Pd and the four atoms immediately surrounding it were determined from a sharpened, origin-removed Patterson function. The usual procedure of full-matrix least-squares refinements interspersed with difference Fourier syntheses revealed the positions of all of the remaining nonhydrogen atoms. Space group $C_i^1$-$P\bar{1}$ was assumed. After initial anisotropic refinement of all nonhydrogen nongroup atoms a difference Fourier synthesis revealed the positions of all of the hydrogen atoms of the phenyl groups and the hydrogen atoms of the methine carbon atom, as well as the positions of a set of six half hydrogen atoms on the methyl group. The location of these hydrogen atoms justifies the assumption of the centrosymmetric space group. The final refinement model of 181 variables included fixed contributions for the H atoms (C–H = 0.95 Å, $B(\mathrm{H}) = B_{\mathrm{iso}}(\mathrm{C}) + 1$ Å$^2$) and anisotropic parameters for all nonhydrogen atoms except for the carbon atoms of the six phenyl rings which were refined isotropically, each phenyl ring being refined as a rigid group. This refinement converged to values of $R$ and $R_w$ of 0.042 and 0.064, respectively, and to an error in an observation of unit weight of 2.36 e.

The largest peak on the final difference Fourier map is 0.9 e/Å$^3$, about 25% the height of a typical C atom. All major peaks on this map were associated with the C atoms of the phenyl groups, a normal observation after rigid-body refinement. Although the thermal parameters of portions of the ethoxy moiety are high enough to suggest some disorder, the final difference Fourier map showed no significant features in that area. Examination of $\sum w(|F_o| - |F_o|)^2$, the function minimized in the refinements, as a function of $|F_o|$, setting angles, and Miller indices revealed no unusual trends. Of the 677 reflections having $F_o^2 < 3\sigma(F_o^2)$ and omitted from the calculations, ten have $Q > 4\sigma(F_o^2)$ and five have $Q > 5\sigma(F_o^2)$, where $Q = |F_o^2 - F_c^2|$.

The final positional and thermal parameters for the nongroup atoms are given in Table I. Table II contains information on the atoms of the rigid groups. Table III presents data on the idealized hydrogen atoms. Root-mean-square amplitudes of vibration are presented in Table IV.[10] The values of $10|F_o|$ and $10|F_c|$ (in electrons) are given in Table V.[10]

## Discussion

The structure determined in this study is shown in perspective view in Figure 1 together with the labeling scheme. The molecular structure corresponds to IIb; the compound is bis(triphenylphosphine)(*N*-ethoxycarbonyldithiocarbimato)palladium(II). Figure 2 shows a stereoview of the two well-separated molecules in the unit cell. Figure 3 presents a projection of the molecule, together with some important bond distances and angles. A more complete listing of distances and angles may be found in Table VI. As judged by the agreement among the six P–ring C distances, the standard deviations, as estimated from the inverse matrix, are reasonable. However, owing to high thermal motion of the atoms of the ethoxy group, bond distances and angles in this portion

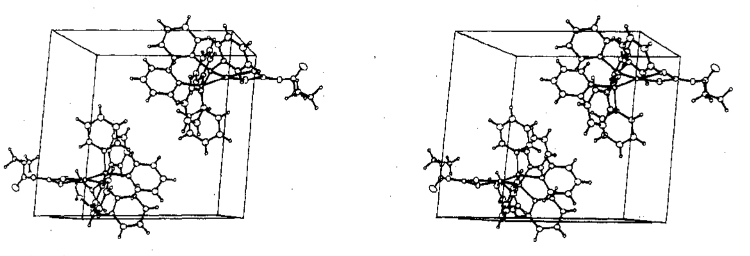


**Figure 2.** Stereoview of a unit cell of $Pd(S_2CNCOOEt)(PPh_3)_2$. The $x$ axis goes from left to right, the $y$ axis goes into the paper, and the $z$ axis goes from bottom to top. The vibrational ellipsoids are drawn at the 20% probability level except for O(2), C(3), and C(4) (3.0 Å$^2$) and the H atoms (1.0 Å$^2$).

**Table II.** Derived Parameters for the Rigid-Group Atoms and Rigid-Group Parameters of $Pd(S_2CNCOOEt)(PPh_3)_2$

| ATOM | X | Y | Z | B,A$^2$ | ATOM | X | Y | Z | B,A$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| R1C1 | -0.01865(20) | 0.17781(19) | 0.10333(21) | 2.96(7) | R4C1 | -0.35080(18) | 0.24187(20) | -0.38400(28) | 2.98(7) |
| R1C2 | 0.07804(22) | 0.24133(17) | 0.17571(27) | 3.80(8) | R4C2 | -0.37627(21) | 0.31481(17) | -0.31116(28) | 3.84(8) |
| R1C3 | 0.14871(20) | 0.22297(21) | 0.30282(27) | 4.50(9) | R4C3 | -0.47849(24) | 0.30543(21) | -0.30465(32) | 4.84(10) |
| R1C4 | 0.12268(23) | 0.14108(23) | 0.35753(22) | 4.84(10) | R4C4 | -0.55526(19) | 0.22312(24) | -0.37097(35) | 5.07(11) |
| R1C5 | 0.02598(25) | 0.07756(19) | 0.28515(28) | 4.94(10) | R4C5 | -0.52979(21) | 0.15019(19) | -0.44380(31) | 4.87(10) |
| R1C6 | -0.04468(20) | 0.09593(18) | 0.15804(27) | 3.74(8) | R4C6 | -0.42756(23) | 0.15956(18) | -0.45031(28) | 3.93(8) |
| R2C1 | -0.14668(23) | 0.32730(16) | 0.00885(26) | 2.92(7) | R5C1 | -0.20759(22) | 0.38357(16) | -0.43722(29) | 3.16(7) |
| R2C2 | -0.13383(25) | 0.41502(20) | -0.04273(25) | 3.79(8) | R5C2 | -0.30253(18) | 0.42132(21) | -0.51702(31) | 4.25(9) |
| R2C3 | -0.15304(28) | 0.50215(16) | 0.01139(31) | 4.90(10) | R5C3 | -0.29476(21) | 0.51427(22) | -0.55816(31) | 5.14(10) |
| R2C4 | -0.18509(29) | 0.50156(17) | 0.11710(32) | 5.03(10) | R5C4 | -0.19205(27) | 0.56947(18) | -0.51949(34) | 5.04(11) |
| R2C5 | -0.19794(27) | 0.41383(21) | 0.16868(26) | 4.63(10) | R5C5 | -0.09710(20) | 0.53173(21) | -0.43969(34) | 5.04(10) |
| R2C6 | -0.17873(25) | 0.32670(17) | 0.11456(27) | 3.83(8) | R5C6 | -0.10487(18) | 0.43878(21) | -0.39855(29) | 4.03(8) |
| R3C1 | -0.23279(17) | 0.12021(16) | -0.11017(27) | 2.80(7) | R6C1 | -0.24336(23) | 0.17622(18) | -0.54569(21) | 2.95(7) |
| R3C2 | -0.33211(20) | 0.13466(15) | -0.10328(27) | 2.94(7) | R6C2 | -0.30473(24) | 0.20257(16) | -0.67192(26) | 3.69(8) |
| R3C3 | -0.41726(17) | 0.05702(19) | -0.14311(30) | 3.75(8) | R6C3 | -0.33024(24) | 0.13673(21) | -0.78530(20) | 4.30(9) |
| R3C4 | -0.40309(20) | -0.03508(16) | -0.18983(31) | 4.43(9) | R6C4 | -0.29437(26) | 0.04455(19) | -0.77243(23) | 4.34(9) |
| R3C5 | -0.30377(24) | -0.04953(15) | -0.19671(31) | 4.70(10) | R6C5 | -0.23299(26) | 0.01819(16) | -0.64619(29) | 4.80(10) |
| R3C6 | -0.21862(18) | 0.02812(19) | -0.15688(30) | 3.81(8) | R6C6 | -0.20749(24) | 0.08403(20) | -0.53282(22) | 4.17(9) |

RIGID GROUP PARAMETERS

| GROUP | $X_C$[A] | $Y_C$ | $Z_C$ | DELTA[B] | EPSILON | ETA |
|---|---|---|---|---|---|---|
| RING 1 | 0.05201(16) | 0.15945(14) | 0.23043(19) | -0.6822(18) | 2.9417(17) | 0.8305(19) |
| RING 2 | -0.16589(16) | 0.41443(14) | 0.06297(19) | -0.4040(32) | 2.1835(16) | 2.0800(32) |
| RING 3 | -0.31794(15) | 0.04257(13) | -0.15000(17) | 0.7217(16) | -2.6157(18) | -3.1662(19) |
| RING 4 | -0.45303(16) | 0.23250(15) | -0.37748(19) | -0.3065(19) | -2.5985(18) | 2.5830(22) |
| RING 5 | -0.19982(17) | 0.47652(15) | -0.47836(20) | 1.5326(16) | 3.0516(20) | -0.3642(20) |
| RING 6 | -0.26886(15) | 0.11038(14) | -0.65906(19) | 0.5673(20) | 2.7168(16) | -2.0855(20) |

[A] $X_C$, $Y_C$, AND $Z_C$ ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

**Table III.** Idealized Positional Coordinates for Hydrogen Atoms

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| | | | Phenyl Groups | | | | |
| $HR_1C_2$ | 0.096 | 0.297 | 0.139 | $HR_4C_2$ | −0.324 | 0.371 | −0.266 |
| $HR_1C_3$ | 0.215 | 0.266 | 0.353 | $HR_4C_3$ | −0.496 | 0.356 | −0.255 |
| $HR_1C_4$ | 0.171 | 0.129 | 0.445 | $HR_4C_4$ | −0.625 | 0.217 | −0.366 |
| $HR_1C_5$ | 0.009 | 0.022 | 0.323 | $HR_4C_5$ | −0.582 | 0.094 | −0.488 |
| $HR_1C_6$ | −0.110 | 0.053 | 0.109 | $HR_4C_6$ | −0.410 | 0.109 | −0.499 |
| $HR_2C_2$ | −0.113 | 0.415 | −0.116 | $HR_5C_2$ | −0.373 | 0.384 | −0.544 |
| $HR_2C_3$ | −0.146 | 0.562 | −0.025 | $HR_5C_3$ | −0.360 | 0.540 | −0.613 |
| $HR_2C_4$ | −0.199 | 0.561 | 0.154 | $HR_5C_4$ | −0.187 | 0.634 | −0.548 |
| $HR_2C_5$ | −0.220 | 0.414 | 0.241 | $HR_5C_5$ | −0.027 | 0.570 | −0.413 |
| $HR_2C_6$ | −0.187 | 0.267 | 0.150 | $HR_5C_6$ | −0.040 | 0.414 | −0.344 |
| $HR_3C_2$ | −0.342 | 0.198 | −0.071 | $HR_6C_2$ | −0.330 | 0.265 | −0.681 |
| $HR_3C_3$ | −0.485 | 0.067 | −0.138 | $HR_6C_3$ | −0.372 | 0.155 | −0.872 |
| $HR_3C_4$ | −0.461 | −0.088 | −0.216 | $HR_6C_4$ | −0.312 | −0.000 | −0.850 |
| $HR_3C_5$ | −0.294 | −0.112 | −0.228 | $HR_6C_5$ | −0.208 | −0.045 | −0.638 |
| $HR_3C_6$ | −0.151 | 0.018 | −0.162 | $HR_6C_6$ | −0.165 | 0.066 | −0.447 |
| | | | Ethyl Group | | | | |
| $H_1C(3)$ | 0.510 | 0.428 | 0.077 | $H_2C(3)$ | 0.527 | 0.317 | 0.086 |
| $H_1C(4)$ | 0.466 | 0.395 | 0.265 | $H_1'C(4)$ | 0.469 | 0.339 | 0.264 |
| $H_2C(4)$ | 0.350 | 0.384 | 0.147 | $H_2'C(4)$ | 0.354 | 0.311 | 0.146 |
| $H_3C(4)$ | 0.405 | 0.291 | 0.196 | $H_3'C(4)$ | 0.398 | 0.421 | 0.198 |

of the molecule are not representative.

The Pd atom is four-coordinate, being bound in roughly a square-planar fashion to the P atoms of the $PPh_3$ groups and to the two S atoms of the dithiocarbimate ligand. Table VII lists some important least-squares planes and interplanar angles. Note that the $PdS_2P_2$ portion of the molecule is essentially planar (plane no. 3), exhibiting only a very small tetrahedral distortion. Distortion from square-planar coordination about Pd(II) occurs mainly as a result of the small S(1)–Pd–S(2) bite angle of 75.03 (4)°, with a corresponding P(1)–Pd–P(2) angle of 98.89 (4)°. The Pd–P distances of 2.306 (1) and 2.333 (1) Å appear to differ significantly from one another, as do the Pd–S distances of 2.316 (1) and 2.343 (1) Å. This may result from packing effects: the phenyl groups on atom P(2) are tilted more toward the P(2) and S(2) atoms than are those attached to atom P(1) toward the P(1) and S(1) atoms. In any event, the Pd–P distances are typical of those found in a variety of Pd complexes.[11-19] Moreover, the Pd–S distances are close to those found in $Pd(CS_2)(PPh_3)_2$[20] (2.305 (11) Å), in $Pd_2(S_2CSCMe_3)_2(SCMe_3)_2$ (2.313 (3) and 2.330 (3) Å), a dimer,[21] and in the trimers[21,22] $Pd(S_2CPh)_2$ (2.320 (3)–2.343 (3) Å) and $Pd_3(S_2CSEt)_3(SEt)_3$ (2.331 (4)–2.349 (5) Å).

As predicted from an infrared spectral study of *N*-cyanodithiocarbimates[23] and as found in the $Ni(S_2CNCN)_2^{2-}$ anion[24] the metal–$S_2C$ ring system in the present complex is essentially planar (plane no. 2, Table VII). A comparison of the inner portion of the metal–dithiocarbimate system here with that found in the $Ni(S_2CNCN)_2^{2-}$ anion[24] shows reasonable agreement (S–C = 1.754 (4) and 1.742 (4) vs. 1.69 (2) and 1.75 (3) Å; C=N = 1.282 (5) vs. 1.29 (3) Å; S–C–N = 128.2 (4) and 123.3 (4) vs. 132 (2) and 120 (2)°). As noted

**Table VI.** Selected Bond Distances (Å) and Angles (deg) in $Pd(S_2CNCOOEt)(PPh_3)_2$

| | | | |
|---|---|---|---|
| | Distances | | |
| Pd-S(1) | 2.316 (1) | Pd-S(2) | 2.343 (1) |
| Pd-P(1) | 2.306 (1) | Pd-P(2) | 2.333 (1) |
| S(1)-C(1) | 1.754 (4) | S(2)-C(1) | 1.742 (4) |
| P(1)-$R_1C_1$ | 1.832 (2) | P(2)-$R_4C_1$ | 1.842 (3) |
| P(1)-$R_2C_1$ | 1.822 (3) | P(2)-$R_5C_1$ | 1.839 (3) |
| P(1)-$R_3C_1$ | 1.815 (2) | P(2)-$R_6C_1$ | 1.831 (3) |
| O(1)-C(2) | 1.180 (6) | C(3)-C(4) | 1.668 (31) |
| O(2)-C(2) | 1.283 (7) | O(2)-C(3) | 1.510 (18) |
| N-C(1) | 1.282 (5) | N-C(2) | 1.377 (7) |
| S(1)· · ·S(2) | 2.837 (2) | | |
| | Angles | | |
| S(1)-Pd-S(2) | 75.03 (4) | P(1)-Pd-P(2) | 98.89 (4) |
| S(1)-Pd-P(1) | 94.27 (4) | S(2)-Pd-P(2) | 92.00 (4) |
| P(1)-Pd-S(2) | 168.66 (4) | S(1)-Pd-P(2) | 166.56 (5) |
| Pd-S(1)-C(1) | 87.96 (14) | Pd-S(2)-C(1) | 87.41 (14) |
| Pd-P(1)-$R_1C_1$ | 117.2 (1) | Pd-P(2)-$R_4C_1$ | 123.5 (1) |
| Pd-P(1)-$R_2C_1$ | 116.1 (1) | Pd-P(2)-$R_5C_1$ | 112.13 (8) |
| Pd-P(1)-$R_3C_1$ | 109.8 (1) | Pd-P(2)-$R_6C_1$ | 109.77 (10) |
| $R_1C_1$-P(1)-$R_2C_1$ | 99.1 (1) | $R_4C_1$-P(2)-$R_5C_1$ | 101.9 (1) |
| $R_1C_1$-P(1)-$R_3C_1$ | 104.0 (1) | $R_4C_1$-P(2)-$R_6C_1$ | 101.8 (1) |
| $R_2C_1$-P(1)-$R_3C_1$ | 109.5 (1) | $R_5C_1$-P(2)-$R_6C_1$ | 106.1 (1) |
| S(1)-C(1)-S(2) | 108.5 (2) | C(2)-O(2)-C(3) | 122.8 (9) |
| C(1)-N-C(2) | 119.6 (5) | N-C(2)-O(1) | 127.4 (6) |
| N-C(1)-S(1) | 128.2 (4) | N-C(1)-S(2) | 123.3 (4) |
| C(4)-C(3)-O(2) | 96.2 (1.2) | O(1)-C(2)-O(2) | 121.8 (6) |
| O(2)-C(2)-N | 110.6 (5) | | |
| | Torsion Angles | | |
| C(1)-S(1)-Pd-S(2) | 6.8 (1) | S(1)-Pd-S(2)-C(1) | -6.9 (1) |
| Pd-S(2)-C(1)-S(1) | 9.3 (2) | S(2)-C(1)-S(1)-Pd | -9.4 (2) |

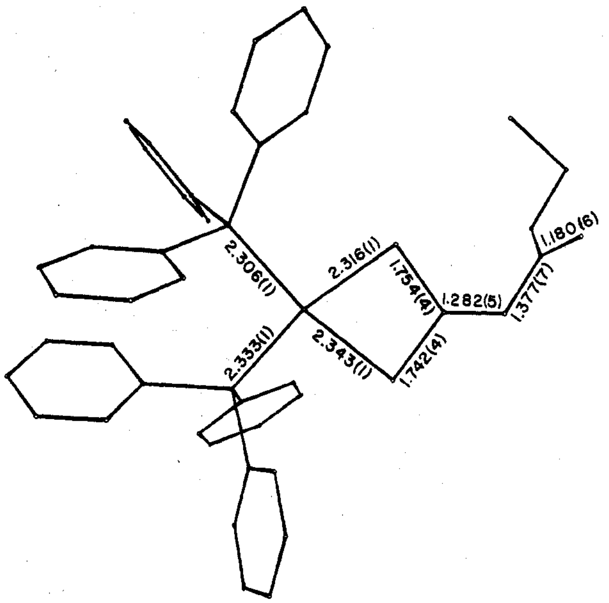
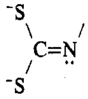
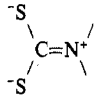


**Figure 3.** A molecule of $Pd(S_2CNCOOEt)(PPh_3)_2$ with selected bond distances and angles. H atoms are omitted for clarity.

by Cotton and Harris[24] there are no significant differences between any of the corresponding distances or angles in the central $Ni(S_2CN)_2$ portions of their $Ni(S_2CNCN)_2^{2-}$ dithiocarbimate anion and an *N,N*-diethyldithiocarbamate complex of Ni, $Ni(S_2CNEt_2)_2$.[25] These results, together with the actual distances and angles involved, suggested to them that the best hybrid descriptions of the dithiocarbimate (III) and dithiocarbamate (IV) ligands in that instance were



III



IV

There appear to be no palladium–dithiocarbamate structures with which to compare the present structure. But our results

**Table VII.** Weighted Least-Squares Planes

Deviations from Planes,[a] Å

| | Plane | | | | | |
|---|---|---|---|---|---|---|
| Atom | 1 | 2 | 3 | 4 | 5 | 6 |
| Pd | 0.392 | 0.0006 (3) | 0.0004 (3) | 0.0023 (3) | 0 (0) | 0 (0) |
| S(1) | 0.000 (1) | −0.011 (1) | 0.076 (1) | −0.042 (1) | −0.110 | 0 (0) |
| S(2) | 0.000 (1) | −0.013 (1) | −0.094 (1) | −0.053 (1) | 0.129 | 0 (0) |
| P(1) | 0.57 | −0.14 | −0.042 (1) | −0.10 | 0 (0) | −0.15 |
| P(2) | 0.85 | 0.15 | 0.045 (1) | 0.18 | 0 (0) | 0.15 |
| O(1) | −0.77 | −0.03 | 0.08 | −0.13 | −0.13 | 0.01 |
| N | 0.004 (4) | 0.47 | 0.47 | 0.384 (4) | −0.47 | 0.49 |
| C(1) | −0.008 (4) | 0.190 (4) | 0.19 | 0.134 (4) | −0.19 | 0.21 |

Equations of Planes[b]

| Plane | *A* | *B* | *C* | *D* |
|---|---|---|---|---|
| 1 | −1.838 | 13.468 | 1.417 | 2.451 |
| 2 | 0.925 | 13.293 | 0.537 | 2.853 |
| 3 | 0.947 | 13.105 | 1.123 | 2.679 |
| 4 | 0.655 | 13.327 | 0.655 | 2.847 |
| 5 | −0.945 | −13.016 | −1.366 | −2.606 |
| 6 | 1.014 | 13.280 | 0.500 | 2.854 |

Dihedral Angles, Deg

| Planes | Angle | Planes | Angle |
|---|---|---|---|
| 1-2 | 11.9 | 2-6 | 0.4 |
| 1-3 | 12.5 | 3-4 | 3.5 |
| 1-4 | 10.7 | 3-5 | 178.6 |
| 1-5 | 167.1 | 3-6 | 3.5 |
| 1-6 | 12.3 | 4-5 | 175.2 |
| 2-3 | 3.4 | 4-6 | 1.6 |
| 2-4 | 1.2 | 5-6 | 175.2 |
| 2-5 | 175.2 | | |

[a] If no standard deviation is given for the distance of an atom from the plane, the atom was not used to define the plane. [b] Plane equation: $Ax + By + Cz - D = 0$, where $x, y, z$ are in triclinic coordinates.

suggest that III is an adequate description for the present dithiocarbimate structure as well.

The mechanism of formation of the present complex, especially the abstraction of the "extra S atom" from the medium, remains unaccounted for. The compound can be formed by reaction of excess EtOCONCS with the initially formed Pd(SCNCOOEt)$(PPh_3)_2$. Whether the organic fragment, EtOOCNC, is trapped by $PPh_3$ is a possibility that is now under study.

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**Registry No.** $Pd(S_2CNCOOEt)(PPh_3)_2$, 61202-76-4; Pd-$(SCNCOOEt)(PPh_3)_2$, 61202-77-5; $Pd_2(dba)_3$, 52409-22-0.

**Supplementary Material Available:** Table IV, the root-mean-square amplitudes of vibration, and Table V, the structure amplitudes (41 pages). Ordering information is given on any current masthead page.

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# Crystal and Molecular Structure of 1,1′-(Tetraphenyl-*o*-phenylene)ferrocene

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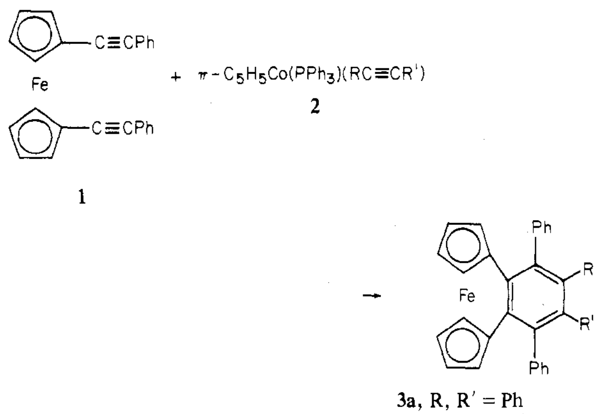
1,1′-(Tetraphenyl-*o*-phenylene)ferrocene, $C_{40}H_{28}Fe$, crystallizes in the monoclinic of space group $P2_{1/a}$, and four molecules in the unit cell with $a = 24.342$ (7), $b = 10.959$ (5), $c = 11.397$ (5) Å, and $\beta = 112.69$ (3)°. A single-crystal x-ray structural analysis has been completed. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located, the final discrepancy indices being $R_1 = 5.40$ % and $R_2 = 6.25$ % for 2939 independent reflections. The cyclopentadienyl rings in the ferrocene moiety are eclipsed and tilted by 23.7°.

## Introduction

Reaction of 1,1′-bis(phenylethynyl)ferrocene (**1**) with acetylene–cobalt complexes (**2**) yielded 1,1′-(*o*-phenylene)-ferrocene, (*o*-phenylene)-[2]ferrocenophane, derivatives (**3**).



1

2

3a, R, R′ = Ph
b, R = Ph; R′ = $CO_2CH_3$
c, R, R′ = $CO_2CH_3$

The structures **3** have been presented on the basis of their microanalyses and spectral properties.[1] In particular, the $^1H$ NMR spectra exhibited a set of $A_2B_2$ patterns associated with the ferrocenyl rings for **3a** and **3c** and two broad signals attributable to the overlap of two sets of $A_2B_2$ patterns for **3b**.

It has been known that the splitting of the $A_2B_2$ signals of the ferrocenyl protons[2] and the electronic spectra, especially the band corresponding to $\lambda_{max}$ 440 nm of $(C_5H_5)_2Fe$, correlate to ring-tilt distortion angle in [*m*]ferrocenophane.[3] Structural features of the ferrocene and benzene moiety of **3a**, a new [2]ferrocenophane with the shortest bridging group, e.g., two $sp^2$ carbons, are of great interest in connection with the large splitting ($\Delta\delta = 0.87$) of the $A_2B_2$ signals and $\lambda_{max}$ 466 nm ($\epsilon = 470$) of this compound. We now report the crystal structure of **3a**.

## Experimental Section

Recrystallization of air-stable **3a**, $C_{40}H_{28}Fe$, from hexane/methylene chloride gave well-formed columnar crystals suitable for x-ray studies. Precession and Weissenberg photography indicated that the crystals were monoclinic with the systematic absence of $h0l$, $h = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with space group $P2_{1/a}$. Cell constants of $a = 24.342$ (7) Å, $b = 10.959$ (5) Å, $c = 11.397$ (5) Å, and $\beta = 112.69$ (3)° were determined from high-order reflections on a Rigaku four-circle automated diffractometer. The unit cell volume is 2805.0 Å$^3$, yielding a calculated density of 1.337 g cm$^{-3}$ for $M = 564.5$ and $Z = 4$. [The experimental density is 1.38 (10) g cm$^{-3}$ by flotation