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# THE STRUCTURE OF $[(PPh_3)PdFe(SC_5H_4)_2] \cdot 0.5C_6H_5CH_3$: AN UNUSUAL HETEROBINUCLEAR COMPLEX CONTAINING A WEAK Fe → Pd DATIVE BOND

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## Summary

The structure of $[(PPh_3)PdFe(SC_5H_4)_2] \cdot 0.5C_6H_5CH_3$ has been determined by X-ray crystallography. This compound crystallizes in the monoclinic space group $C2/c$ with $a$ 39.258(5), $b$ 10.548(2), $c$ 13.612(4) Å, $\beta$ 101.69(2)°, $V$ 5519.7 Å$^3$ and $Z = 8$. On the basis of 3255 unique observations the structure has refined to $R = 0.040$ and $R_w = 0.046$. The complex is an unusual heterobinuclear Fe–Pd species in which the two metals are held together by the bridging cyclopentadienethiolato groups and what appears to be a dative Fe → Pd bond (2.878(1) Å).

## Introduction

There is considerable current interest in the chemistry of binuclear, mixed-metal complexes [1–4]. Not only should such species be capable of generating unique chemistry by virtue of the adjacent metals [5], but the different reactivities of the inequivalent metal centers should allow further modifications to the chemistry. For the adjacent metals to interact in a cooperative manner with substrate molecules it is imperative that they remain in close proximity during the reaction, and to ensure this, a variety of bridging groups has been utilized which hold the metals together and prevent fragmentation of the complexes [1,3,6–11].

An unusual heterobinuclear complex, in which the metals are bridged by two cyclopentadienethiolato groups, was prepared by Seyferth and coworkers [12] according to eq. 1. Although the expected product was the bisphosphine complex **1**, elemental analyses, NMR and mass spectral data suggested that the actual product was the monophosphine complex **2**. Such a species would have a 14 electron Pd center unless Fe → Pd dative bonding were invoked, and the lack of reactivity of **2** with $PPh_3$, CO and NO supported the dative-bonded formulation [12]. Owing to the

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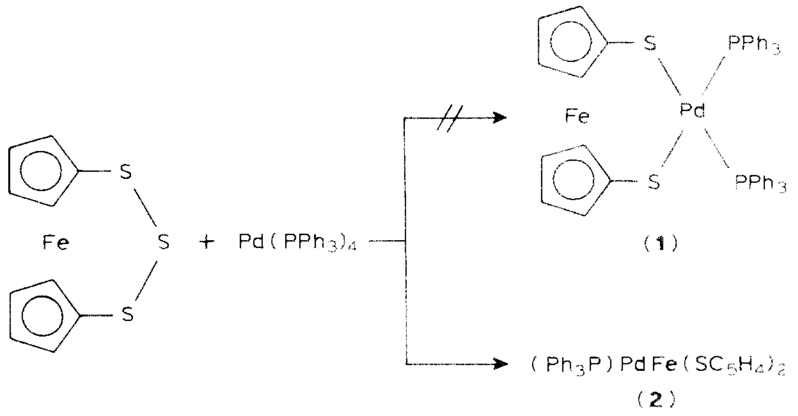


(1)

current interest in metal–metal dative bonds [13–17] and to the relative paucity of such species, the X-ray structure determination of **2** was undertaken in an attempt to confirm the nature of the bonding. This study, which has been briefly communicated [12], is reported herein.

## Experimental

### *X-Ray data collection*

Red-brown, plate-like crystals of $[(PPh_3)PdFe(SC_5H_4)_2]\cdot 0.5C_6H_5CH_3$, obtained by slow recrystallization from a cooled solution of the product in a $CH_2Cl_2$/toluene/hexanes mixture, were kindly supplied by Professor Seyferth and coworkers at M.I.T. A suitable crystal was mounted in a random orientation on a glass fiber. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 23 reflections, in the range $13.0° \leq 2\theta \leq 29.0°$, which were accurately centered on an Enraf–Nonius CAD4 diffractometer using Mo-$K_\alpha$ radiation. The $2/m$ diffraction symmetry and the systematic absences ($hkl$: $h+k$ odd; $h0l$: $l$ odd) are consistent with the space groups $Cc$ and $C2/c$. The centrosymmetric space group was chosen and later verified as the more probable one based on the successful refinement of the structure with acceptable thermal and positional parameters, reasonable agreement indices and by the location of all hydrogen atoms except those on the toluene methyl group.

Intensity data were collected with the CAD4 diffractometer in the bisecting mode by employing the $\omega$–$2\theta$ scan technique up to $2\theta = 52.0°$ with graphite-monochromated Mo-$K_\alpha$ radiation. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure time to assess possible crystal decomposition or movement. No significant variation in these standards was noted so no correction was applied to the data. A total of 5713 unique reflections was measured and processed in the usual way using a value of 0.04 for $p$ [18]; of these, 3255 were considered to be observed and were used in all subsequent calculations. Absorption corrections were applied to the data by using Gaussian integration [19]. See Table 1 for pertinent crystal data and the details of intensity collection.

TABLE 1

SUMMARY OF CRYSTAL DATA AND INTENSITY COLLECTION DETAILS

| | |
|---|---|
| Compound | $(PPh_3)PdFe(SC_5H_4)_2 \cdot 0.5C_6H_5CH_3$ |
| Formula weight | 662.9 |
| Formula | $PdFeS_2PC_{31.5}H_{27}$ |
| Space group | $C_{2h}^6-C2/c$ |
| Cell parameters | |
| $a$ (Å) | 39.258(5) |
| $b$ (Å) | 10.548(2) |
| $c$ (Å) | 13.612(4) |
| $\beta$ (°) | 101.69(2) |
| $V$ (Å$^3$) | 5519.7 |
| $Z$ | 8 |
| Density (g cm$^{-3}$) | 1.595 (calc), 1.59 (obs) |
| Crystal dimension (mm) | 0.052 × 0.293 × 0.262 |
| Crystal shape | monoclinic plate with short distance along $a^\star$ and faces of the forms {100}, {101}, {011}, {111} |
| Crystal volume (mm$^3$) | 0.0475 |
| Temperature (°C) | 23 |
| Radiation | Mo-$K_\alpha$ ($\lambda$ 0.71069 Å) graphite-monochromated |
| $\mu$ (cm$^{-1}$) | 13.905 |
| Range in absorption correction factors | 0.646–0.924 |
| Receiving aperture | $2.00 + 0.5\tan\theta$ mm wide by 4.0 mm high, 173 mm from crystal |
| Scan speed (° min$^{-1}$) | 10.058 to 0.891 |
| Scan width (°) | $0.50 + 0.350 \tan\theta$, in omega |
| $2\theta$ limits (°) | 1.0–52.0 |
| Unique data measured | 5713 |
| Unique data used ($F_0^2 \geqslant 3\sigma(F_0^2)$) | 3255 |
| Final number of parameters varied | 205 |
| Error in observation of unit weight ($GOF$) | 1.136 |
| $R$ [a] | 0.040 |
| $R_w$ | 0.046 |

[a] $R = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$, $R_w = [\Sigma w(| F_0 | - | F_c |)^2 / \Sigma w F_0^2]^{1/2}$.

### *Structure solution and refinement*

The structure was solved in space group $C2/c$ using standard Patterson, Fourier and least-squares techniques. All atoms, excluding the toluene methyl hydrogens, were ultimately located. Atomic scattering factors for non-hydrogen atoms [20] and hydrogen [21] were taken from the usual sources. Anomalous dispersion terms [22] for Pd, Fe, S and P were included in $F_c$. The carbon atoms of the $PPh_3$ phenyl groups were refined as rigid groups having idealized $D_{6h}$ symmetry, C–C distances of 1.392 Å and independent isotropic thermal parameters. All hydrogen atoms except the toluene methyl hydrogens, which were found to be disordered (vide infra), were input as fixed contributions. Their idealized positions were calculated after each cycle of refinement from the geometries of their attached carbon atom using a C–H distance of 0.95 Å. These hydrogen atoms were assigned isotropic

TABLE 2

ATOMIC POSITIONAL PARAMETERS ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR THE NON-GROUP ATOMS OF $[(PPh_3)PdFe(SC_5H_4)_2]\cdot 0.5CH_3C_6H_5$ [a]

| Atom | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| Pd | 3488.5(1) | 4329.8(5) | 2064.5(3) | 2.47 |
| Fe | 3028.2(2) | 6310.9(9) | 2447.5(6) | 2.55 |
| S(1) | 3229.6(5) | 3164(2) | 3148(1) | 3.51 |
| S(2) | 3709.9(4) | 5830(2) | 1146(1) | 3.67 |
| P | 3788.2(4) | 2661(2) | 1673(1) | 2.61 |
| C(1) | 2986(1) | 4542(6) | 3152(4) | 2.68 |
| C(2) | 2677(1) | 4864(7) | 2460(4) | 3.07 |
| C(3) | 2547(2) | 6009(7) | 2765(5) | 4.03 |
| C(4) | 2783(2) | 6434(7) | 3630(5) | 3.70 |
| C(5) | 3056(2) | 5546(6) | 3870(4) | 3.02 |
| C(6) | 3394(2) | 6741(6) | 1510(5) | 3.13 |
| C(7) | 3039(2) | 6868(7) | 999(4) | 3.47 |
| C(8) | 2874(2) | 7783(7) | 1490(6) | 4.47 |
| C(9) | 3117(2) | 8220(6) | 2332(6) | 4.27 |
| C(10) | 3431(2) | 7565(7) | 2376(5) | 4.10 |
| C(40) [b] | 5000 | 9632(15) | 2500 | 9.24 |
| C(41) | 5000 | 8232(14) | 2500 | 5.94 |
| C(42) | 4699(2) | 7509(11) | 2169(6) | 5.49 |
| C(43) | 4702(2) | 6225(12) | 2155(6) | 6.33 |
| C(44) | 5000 | 5564(14) | 2500 | 7.79 |

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. [b] Atoms C(40) is the toluene methyl group. C(41) to C(44) are the crystallographically independent toluene ring atoms.

thermal parameters of 1 Å$^2$ greater than the *B* (or equivalent isotropic *B*) of their attached carbon atom. All other non-group atoms were refined anisotropically.

The toluene molecules were found to occupy the 4(*e*) crystallographic diad axes and as a result the methyl hydrogens had to be at least two-fold disordered. In fact, the expected six half-weighted hydrogens were not unambiguously located suggesting further rotational disorder about the $C_{Me}$–$C_{Ph}$ bond.

On the final difference Fourier map the highest 20 peaks (1.60–0.58 e Å$^{-3}$) were in the vicinities of the rigid phenyl groups, the disordered methyl hydrogens and the heavier atoms (Pd, Fe, S and P). A typical carbon atom on earlier syntheses had a peak intensity of about 8.7 e Å$^{-3}$.

The final positional and thermal parameters of the individual non-hydrogen atoms appear in Table 2, the parameters for the carbon atoms of the rigid phenyl groups are given in Table 3. Anisotropic thermal parameters, hydrogen parameters, least-squares planes, and structure amplitudes are available from M.C. on request (Tables 6, 7, 8, and 9, respectively).

## Description of structure and discussion

This structure determination of $[(C_5H_4S)_2FePd(PPh_3)]\cdot 0.5C_6H_5CH_3$ confirms the monophosphine formulation **2**, suggested by elemental analyses, the mass spectral and $^1$H NMR data [12]. The unit cell of this compound contains eight formula units with four toluene molecules of crystallization. There are no unusual

TABLE 3

PARAMETERS FOR THE RIGID-GROUP ATOMS OF [(PPh$_3$)PdFe(SC$_5$H$_4$)$_2$]·0.5CH$_3$C$_6$H$_5$

*Derived parameters*

| Atom | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| C(11) | 0.4009(1) | 0.1816(4) | 0.2796(3) | 3.0(1) |
| C(12) | 0.4054(1) | 0.0507(4) | 0.2839(3) | 4.3(2) |
| C(13) | 0.4252(1) | −0.0051(3) | 0.3693(4) | 5.7(2) |
| C(14) | 0.4406(1) | 0.0700(5) | 0.4504(3) | 5.5(2) |
| C(15) | 0.4360(1) | 0.2009(5) | 0.4460(3) | 5.3(2) |
| C(16) | 0.4162(1) | 0.2567(3) | 0.3606(4) | 4.3(2) |
| C(21) | 0.3519(1) | 0.1472(4) | 0.0886(3) | 2.9(1) |
| C(22) | 0.3160(1) | 0.1473(4) | 0.0811(3) | 3.2(1) |
| C(23) | 0.29554(7) | 0.0558(4) | 0.0233(3) | 3.7(1) |
| C(24) | 0.3110(1) | −0.0358(4) | −0.0269(3) | 3.9(1) |
| C(25) | 0.3469(1) | −0.0360(4) | −0.0193(3) | 4.8(2) |
| C(26) | 0.36731(8) | 0.0555(4) | 0.0385(3) | 4.1(1) |
| C(31) | 0.4134(1) | 0.2948(4) | 0.0969(3) | 2.9(1) |
| C(32) | 0.4479(1) | 0.2645(4) | 0.1364(3) | 4.0(1) |
| C(33) | 0.47330(8) | 0.2860(5) | 0.0803(3) | 5.3(2) |
| C(34) | 0.4641(1) | 0.3380(5) | −0.0154(3) | 4.8(2) |
| C(35) | 0.4296(1) | 0.3683(4) | −0.0550(3) | 4.6(2) |
| C(36) | 0.40420(9) | 0.3468(4) | 0.0012(3) | 3.8(1) |

*Rigid group parameters*

| | $X_c$ [a] | $Y_c$ | $Z_c$ | Delta [b] | Epsilon | Eta |
|---|---|---|---|---|---|---|
| Ring 1 | 0.42072(7) | 0.1258(3) | 0.3650(2) | −0.188(3) | −2.733(3) | 0.906(3) |
| Ring 2 | 0.33143(7) | 0.0557(3) | 0.0309(2) | −2.027(3) | 2.719(3) | −0.513(3) |
| Ring 3 | 0.43875(8) | 0.3164(3) | 0.0407(2) | 1.094(4) | 2.473(2) | −1.085(4) |

[a] $X_c$, $Y_c$ and $Z_c$ are the fractional coordinates of the centroid 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 (1965) 511.

intermolecular contacts involving either the complex or the solvent molecules. Apart from the methyl group disorder, the toluene molecule is well behaved and quite unexceptional. A perspective view of the complex, with some relevant bond lengths and angles, is shown in Fig. 1. More complete bond length and angle tabulations are given in Tables 4 and 5, respectively.

The complex molecule is a rather unusual heterobinuclear Fe–Pd complex in which the metal centers are held together by the cyclopentadienethiolato groups (SC$_5$H$_4$) and what appears to be a dative Fe → Pd bond (vide infra). The SC$_5$H$_4$ ligands are $\eta^5$-bound through the carbon atoms in a pseudo-*trans* configuration to iron (much as in ferrocene and its derivatives) and are $\sigma$-bound to Pd through the sulfur atoms.

The coordination about Pd is a slightly distorted square plane in which the sulfur atoms are mutually *trans*, as are the PPh$_3$ group and the Fe atom of the ferrocenyl moiety. The major distortion from square planar geometry results because Pd lies towards the PPh$_3$ group, away from Fe such that the S–Pd–Fe angles are acute (see Fig. 1). In addition, the PPh$_3$ group is bent away from S(2) towards S(1) in order to relieve the interactions between phenyl ring 3 and S(2), which are eclipsed (S(2)–Pd–P–C(31) torsion angle = 8.10°). The most significant such non-bonded

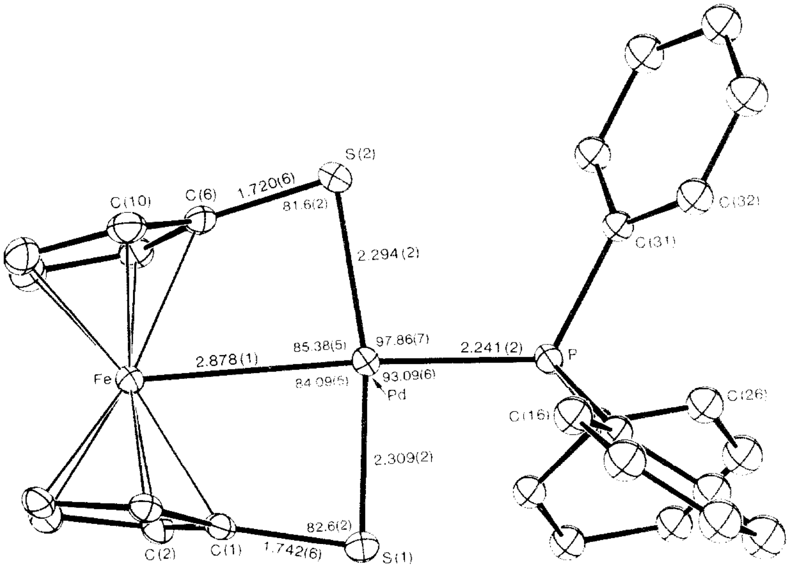


Fig. 1. A perspective view of [$(PPh_3)PdFe(SC_5H_4)_2$] showing the numbering scheme and some relevant parameters. Thermal ellipsoids are shown at the 20% level.

TABLE 4

SELECTED INTERATOMIC DISTANCES (Å) IN [$(PPh_3)PdFe(SC_5H_4)_2$]·$0.5CH_3C_6H_5$

| | | | |
|---|---|---|---|
| *Bonding distances* | | | |
| Pd–Fe | 2.878(1) | P–C(21) | 1.829(4) |
| Pd–P | 2.241(2) | P–C(31) | 1.837(5) |
| Pd–S(1) | 2.309(2) | C(1)–C(2) | 1.419(8) |
| Pd–S(2) | 2.294(2) | C(2)–C(3) | 1.406(9) |
| Fe–C(1) | 2.119(6) | C(3)–C(4) | 1.417(9) |
| Fe–C(2) | 2.060(6) | C(4)–C(5) | 1.410(9) |
| Fe–C(3) | 2.048(7) | C(1)–C(5) | 1.430(8) |
| Fe–C(4) | 2.041(6) | C(6)–C(7) | 1.432(9) |
| Fe–C(5) | 2.080(6) | C(7)–C(8) | 1.403(9) |
| Fe–C(6) | 2.154(6) | C(8)–C(9) | 1.411(10) |
| Fe–C(7) | 2.067(6) | C(9)–C(10) | 1.405(10) |
| Fe–C(8) | 2.039(7) | C(6)–C(10) | 1.448(8) |
| Fe–C(9) | 2.056(7) | C(40)–C(41) | 1.48(2) |
| Fe–C(10) | 2.080(7) | C(41)–C(42) | 1.40(1) |
| S(1)–C(1) | 1.742(6) | C(42)–C(43) | 1.35(1) |
| S(2)–C(6) | 1.720(6) | C(43)–C(44) | 1.36(1) |
| P–C(11) | 1.829(4) | | |
| *Non-bonding distances* | | | |
| Fe–Cp(1) [a] | 1.683 | S(1)–H(3) [c] | 2.88 |
| Fe–Cp(2) | 1.693 | S(1)–H(22) | 2.89 |
| H(5)–H(36) [b] | 2.27 | S(2)–H(43) | 3.04 |
| S(1)–C(11) | 3.494(5) | S(2)–H(36) | 3.04 |
| S(2)–C(36) | 3.332(5) | | |

[a] Cp(1) and Cp(2) are the centroids of cyclopentadienyl groups 1 and 2, respectively. [b] H(36) of the molecule at $x$, $1-y$, $1/2+z$. [c] H(3) of the molecule at $1/2-x$, $y-1/2$, $1/2-z$.

TABLE 5

SELECTED ANGLES (°) IN $[(PPh_3)PdFe(SC_5H_4)_2]\cdot 0.5CH_3C_6H_5$

| | | | |
|---|---|---|---|
| *Bond angles* | | | |
| Fe-Pd-S(1) | 84.09(5) | C(6)-C(7)-C(8) | 109.2(6) |
| Fe-Pd-S(2) | 85.38(5) | C(7)-C(8)-C(9) | 108.2(6) |
| Fe-Pd-P | 172.97(5) | C(8)-C(9)-C(10) | 108.4(6) |
| S(1)-Pd-S(2) | 168.60(7) | C(9)-C(10)-C(6) | 108.5(6) |
| S(1)-Pd-P | 93.09(6) | Pd-P-C(11) | 111.5(1) |
| S(2)-Pd-P | 97.86(7) | Pd-P-C(21) | 114.0(1) |
| Cp(1)-Fe-Cp(2) [a] | 165.20 | Pd-P-C(31) | 118.2(1) |
| Pd-Fe-Cp(1) | 98.20 | C(11)-P-C(21) | 105.9(2) |
| Pd-Fe-Cp(2) | 96.51 | C(11)-P-C(31) | 104.0(2) |
| Pd-S(1)-C(1) | 82.6(2) | C(21)-P-C(31) | 102.0(2) |
| Pd-S(2)-C(6) | 81.6(2) | P-C(11)-C(12) | 123.6(2) |
| S(1)-C(1)-C(2) | 126.5(5) | P-C(11)-C(16) | 116.2(2) |
| S(1)-C(1)-C(5) | 126.3(5) | P-C(21)-C(22) | 119.8(2) |
| S(2)-C(6)-C(7) | 126.8(5) | P-C(21)-C(26) | 120.2(1) |
| S(2)-C(6)-C(10) | 127.6(5) | P-C(3)-C(32) | 121.7(2) |
| C(5)-C(1)-C(2) | 107.3(5) | P-C(31)-C(36) | 118.4(2) |
| C(1)-C(2)-C(3) | 108.8(6) | C(40)-C(41)-C(42) | 122.9(7) |
| C(2)-C(3)-C(4) | 107.6(6) | C(42)-C(41)-C(42)′ [b] | 114.2(18) |
| C(3)-C(4)-C(5) | 108.7(6) | C(41)-C(42)-C(43) | 122.5(10) |
| C(4)-C(5)-C(1) | 107.6(5) | C(42)-C(43)-C(44) | 121.3(10) |
| C(10)-C(6)-C(7) | 105.5(6) | C(43)-C(44)-C(43) [b] | 118.3(25) |
| *Torsion angles* [c] | | | |
| C(1)-Cp(1)-Cp(2)-C(6) | 1.18 | S(1)-Pd-Fe-Cp(2) | 177.76 |
| C(2)-Cp(1)-Cp(2)-C(7) | 1.24 | S(1)-Pd-Fe-C(6) | 176.56 |
| C(3)-Cp(1)-Cp(2)-C(8) | 1.19 | S(2)-Pd-Fe-Cp(1) | -179.50 |
| C(4)-Cp(1)-Cp(2)-C(9) | 0.88 | S(2)-Pd-Fe-C(1) | -177.56 |
| C(5)-Cp(1)-Cp(2)-C(10) | 0.67 | S(1)-Pd-P-C(11) | -48.31 |
| S(1)-Cp(1)-Cp(2)-S(2) | 1.37 | S(1)-Pd-P-C(21) | 71.50 |
| S(1)-C(1)-C(6)-S(2) | 1.33 | S(1)-Pd-P-C(31) | -168.71 |
| S(1)-Pd-Fe-Cp(1) | -3.88 | S(2)-Pd-P-C(11) | 128.50 |
| S(1)-Pd-Fe-C(1) | -1.94 | S(2)-Pd-P-C(21) | -111.69 |
| S(2)-Pd-Fe-Cp(2) | 2.14 | S(2)-Pd-P-C(31) | 8.10 |
| S(2)-Pd-Fe-C(6) | 0.94 | C(41)-C(42)-C(43)-C(44) | 2.47 |

[a] Cp(1) and Cp(2) are the centroids of cyclopentadienyl groups 1 and 2, respectively. [b] Atoms C(42)′ and C(43)′ are related to C(42) and C(43), respectively, by the symmetry operation $1-x$, $y$, $1/2-z$. [c] Torsion angles are the conformation angles about the central bond shown.

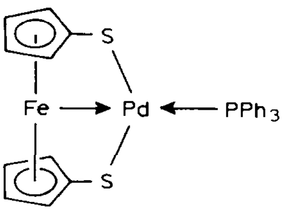
contact (3.332(5) Å), between S(2) and C(36), is much smaller than the Van der Waals distance of ca. 3.70 Å and in the absence of the observed distortion would be even less favorable. Atom S(1), on the other hand, is staggered with regard to the other phenyl groups (Table 5) resulting in less severe interactions involving these groups; the shortest S(1)-phenyl carbon contact (S(1)-C(11) 3.494(5) Å) is significantly longer than that observed for S(2). The Pd-S distances (av. 2.302 Å) appear normal although they are at the short end of the range observed (2.288(3)-2.431(3) Å) in a variety of mono- and dithiolato $Pd^{II}$ complexes [23-27]. Similarly the Pd-P distance (2.241(2) Å) is one of the shortest observed in typical Pd-$PPh_3$ complexes (2.230(4)-2.344(2) Å) [25,28-33] and is also shorter than such distances obtained in several compounds in which the phosphine ligand is coordinated *trans* to another metal (2.271–2.296 Å) [34–36]. These short Pd–S and Pd–P distances may be a consequence of the coordinative unsaturation at Pd which would result in these electron donating ligands being tightly bound to the electron deficient metal center.

The geometry about Fe is surprisingly close to that of ferrocene even though Pd seems to be coordinated to the iron center: the two eclipsed $SC_5H_4$ groups are only 19.6° from parallel. This small tilt of the $SC_5H_4$ groups away from the Pd atom results in a rather large Cp(1)–Fe–Cp(2) [37] angle of 165.2°. By comparison, in other bis(cyclopentadienyl) metal complexes, $Cp_2ML_n$, in which one or more groups, $L_n$, are bound to the metal, the Cp–M–Cp angles are within the range 126–143° [38–44]. The relatively small tilt of the $SC_5H_4$ groups in the present species may suggest that the Fe–Pd interaction is weak. It is also possible that this small tilt represents a compromise between the electronic requirements of the Fe, Pd and S atoms. A significantly greater tilt of the $SC_5H_4$ groups would result in longer (and presumably less favorable) Pd–S contacts, and C–S–Pd angles which are even more acute than those presently observed.

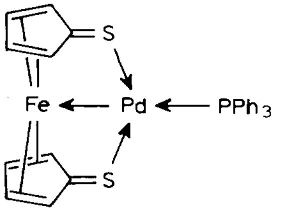
The parameters within the cyclopentadienethiolato groups are essentially as expected; for example, the average C–C distance of 1.42 Å compares well with the predicted value of 1.43 Å [45] and the C–C–C angles (av. 108.0°) are quite typical. Both S–C distances (1.742(6) and 1.720(6) Å) appear normal [23–27] but show some shortening suggesting a slight degree of multiple bond character. A normal S–C single bond involving an $sp^2$ carbon might be expected at about 1.77 Å [46]. In both $SC_5H_4$ ligands the rings are tilted such that the carbons bound to sulfur are furthest from Fe whereas those at the opposite side of the Cp rings (C(3), C(4), C(8) and C(9)) are closest to Fe. Nevertheless, the range in Fe–C distances (2.154(6)–2.039(7) Å) again appears to be normal. Although the Cp rings are close to being planar (see supplementary Table 8), calculations excluding the carbon atoms bound to S indicate that these carbon atoms are outwardly displaced from the planes of the other Cp carbon atoms by 0.037(6) Å for Cp ring 1 and 0.059(6) Å for Cp ring 2. Similarly S(1) and S(2) are displaced 0.148(2) and 0.212(2) Å from these same planes. The greater distortion of Cp ring 2 is probably due to its steric interactions with phenyl ring 3 (vide supra).

The Fe–Pd distance (2.878(1) Å) is rather long for a single bond but corresponds, we suggest, to a weak dative Fe → Pd bond. This bond is necessary to give Pd a favorable 16e configuration; without it a very unsaturated and reactive 14e configuration would result. Although the Fe–Pd distance is long (it is significantly greater than those observed in clusters containing Fe–Pd single bonds (2.599(1)–2.698(1) Å) [47]), it is not unreasonably long for such a bond; Pd–Pd bonding distances up to 2.790(2) Å [48] and Fe–Fe bonding distances up to 2.890(6) Å [49] have been reported. Somewhat similar weak iron–metal interactions have also been noted in silver and copper dimethylaminomethylferrocene complexes [50,51], (3.091(3) and 2.945(5) Å, respectively) and in $[(C_5H_5)Fe(C_5H_4Au_2(PPh_3)_2)]^+$ (2.818(9) Å [52]). It is also significant that rather small tilts of the Cp rings (6.5 to 16°) were again observed in these latter compounds and that the largest tilt, in the gold complex, seems to correspond to the strongest metal–iron interaction and corresponds closely to the value which we observe in the Fe–Pd complex.

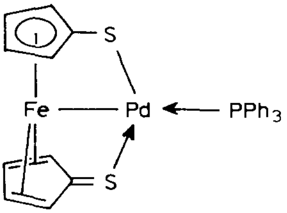
Although we have suggested that the bonding in the present complex involves a dative Fe → Pd bond, this is based only on the consideration of the $Fe(C_5H_4S)_2$ moiety as a ferrocene-like system with an 18-electron iron. Other canonical forms



( I )



(II)



(III)

which should be considered are shown in structures II and III. Structure I is the electronic form we have considered in our previous discussions; however, structure II may also be a significant contributor to the actual electronic structure, having an electron-deficient 16-electron iron, until the 2-electron donor bond from the 16-electron palladium is considered. Such a structure would certainly explain the somewhat shortened C–S bonds (vide supra), which suggest some multiple-bond character, and also the tilting of the Cp–S planes, which suggests a weaker bonding of the sulfur-bound carbons to the iron. The C–C bond lengths within the Cp rings also show tendencies consistent with this canonical structure, but not at a statistically significant level; such small differences could well be masked by thermal vibration of the ring atoms. Structure II is therefore a plausible alternative. Structure III and its obvious "twin" (with the localized double bonds on the other ring) show a more conventional metal–metal bond, with one electron contributed from each metal, and would be consistent with the same bonding distance trends as structure II. The actual structure may in fact have significant contributions from all three resonance forms.

The crystal structures of several [1]-, [2]- and [3]-ferrocenophanes provide useful comparisons with the parameters of the present compound. Of these, the [3]-ferrocenophanes generally display significantly smaller tilts of the Cp rings from the parallel configuration (8.8–12.5° for $C_3$ bridges [53–57], 2.4–6.2° for bridges involving large heteroatoms) [11,58–63] than those for [2]-ferrocenophanes (about 23°) [64–67] or [1]-ferrocenophanes (16.6–27.1°; heteroatom bridges only) [68,69]. The tilts for the [1]- and [2]-ferrocenophanes clearly result from the short bridge lengths, which pinch the cyclopentadienyl groups together at the bridge location. For the carbon-bridged [3]-ferrocenophanes, the smaller tilts are due to the increased bridge length and flexibility, whereas for the heteroatom-bridged [3]-ferrocenophanes, the rings are actually forced apart very slightly at the bridges, but the angles remain small due to the flexibility of the bridges. In the present compound the bridge is also three atoms in length, but has a rigid structure by virtue of the pseudo-*trans* alignment of the thiolate sulfurs about Pd, and the Pd–Fe bond. This rigidity forces the Cp groups apart, causing them to tilt significantly away from the bridge. The ferrocenophane structures which probably offer the best comparisons with the present compound are [Fe($C_5H_4S$)$_2$S] [58] and [Fe($C_5H_4S$)$_2$Se] [59], in which the Pd($PPh_3$) unit of the present molecule is replaced by S and Se, respectively, [Fe($C_5H_4AsMe_2$)$_2$Ni$I_2$(CO)] [60] and a series of closely related complexes by Cullen and coworkers [11,62,63], containing cyclopentadienephosphine bridging groups. The major difference between all of these compounds and [($C_5H_4S$)$_2$FePd-($PPh_3$)] is the angle at the central bridging atom (S, Se, Ni, Mo, Rh, or Pd), which ranges from about 93 to 104° in the above species. In all cases involving metals at the bridgehead position the substituted cyclopentadienyl groups are bound *cis* to the bridging metal, whereas in the present compound the arrangement is almost *trans* (S(1)–Pd–S(2) 168.60(7)°). The strain induced by this pseudo-*trans* arrangement causes the large tilt (19.6°) of the Cp rings, compared to smaller tilt angles of between 2 and 6.2° for the above ferrocenophanes.

Other angles and distances in the present compound indicate that it has other associated steric strains. The C–S–Pd angles in this Pd complex are very acute, averaging 82.1°, while the comparable angles average 102.8 and 102.3° for the S and Se species, and around 120° for all metal-bridged species. The severe strain indicated in the present compound strongly supports the existence of Fe–Pd bonding in this complex. Furthermore, the sulfur atoms in the present compound are displaced 0.15 and 0.21 Å out of the Cp ring planes, away from the iron, while the sulfur atoms are coplanar with the Cp rings in the S-bridged species and only 0.04 Å out of the plane with the Se-bridged species. In the nickel arsine complex the arsenic atoms are only 0.00 and 0.06 Å out-of-plane towards the iron. In ferrocenylphosphine complexes of Cullen, a large variation in the positions of the phosphorus atoms relative to the Cp planes was observed [11,62,63]; these deviations from planarity seem to be due to the bulk of the phosphine substituents. Clearly in the present compound such arguments cannot be used, since there are no substituents other than the Cp ring on sulfur and the complex is rather free of severe steric interactions other than those noted, which are brought about the Fe → Pd interaction. A similar direction and magnitude of displacement was also observed in Sn[($SeC_5H_4$)$_2$Fe]$_2$ [61], in which the selenium atoms are displaced outward from the Cp planes by 0.25 Å; this displacement was attributed to the large sizes of the Sn and Se atoms, which also prevented the ferrocene moieties from pivoting to relieve the strain. In the present Pd complex, the outward displacement of the S atoms from their Cp planes indicates that the palladium atom does not restrict the Cp–Fe–Cp angle from bending more; on the contrary, it seems that more bending would relieve the outward strain at C(1) and C(6). Since steric reasons cannot account for the angle at iron, some more subtle electronic influences must favour a more nearly linear Cp–Fe–Cp angle. The observed geometry strongly supports the existence of an Fe–Pd bond, since without it the Pd atom could adopt a trigonal arrangement in which the strain at the sulfur atoms would be relieved. Such a mode is certainly plausible, as illustrated by the arsine and phosphine complexes [11,60,62,63] in which angles at the bridgehead metals, approximating 90°, were observed. In view of this, it is rather surprising that one more triphenylphosphine ligand was not retained, to give an unremarkable *cis*-(bisphosphine bisthiolato) complex. In either this geometry or the trigonal geometry previously mentioned, the palladium atom could pucker away from the $FeS_2$ plane, affording further relief of steric strain. In addition, it seems that in a *cis* geometry the strain could be further relieved by twisting of the Cp rings to give a staggered arrangement as in several of the ferrocenylphosphine species. As noted earlier the Cp rings in the present compound are almost exactly eclipsed.

In conclusion, it seems clear that the structural and chemical [12] evidence suggests some form of Fe–Pd bonding. Of the three bonding formulations noted (I–III), we favour formulation I, containing an Fe → Pd dative bond.

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## References

1 D.A. Roberts and G.L. Geoffroy in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, Vol. 6, (1982) pp. 763–877 and references therein.
2 C.P. Casey and R.M. Bullock, Organometallics, 3 (1984) 1100.
3 W.C. Mercer, R.R. Whittle, E.W. Burkhardt and G.L. Geoffroy, Organometallics, 4 (1985) 68.
4 C.P. Casey and R.M. Bullock, J. Mol. Catal., 14 (1982) 283.
5 E.L. Muetterties, T.N. Rodin, E. Band, C. Brucker and W.R. Pretzer, Chem. Rev., 79 (1979) 91.
6 R. Choukroun and D. Gervais, J. Organomet. Chem., 266 (1984) C37.
7 A.T. Hutton, P.G. Pringle and B.L. Shaw, Organometallics, 2 (1983) 1889.
8 B. Delavaux, B. Chaudret, F. Dahan and R. Poilblanc, Organometallics, 4 (1985) 935.
9 R.G. Ball, F. Edelmann, G.-Y. Kiel, J. Takats and R. Drews, Organometallics, 5 (1986) 829.
10 C.P. Casey, R.M. Bullock, W.C. Fultz and A.L. Rheingold, Organometallics, 1 (1982) 1591.
11 I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig and J. Trotter, Organometallics, 4 (1985) 972.
12 D. Seyferth, B.W. Hames, T.G. Rucker, M. Cowie and R.S. Dickson, Organometallics, 2 (1983) 472.
13 F.W.B. Einstein, R.K. Pomeroy, P. Rushman and A.C. Willis, Organometallics, 4 (1985) 250.
14 F.W.B. Einstein, T. Jones, R.K. Pomeroy and P.J. Rushman, J. Am. Chem. Soc., 106 (1984) 2707.
15 F.W.B. Einstein, R.K. Pomeroy, P. Rushman and A.C. Willis, J. Chem. Soc., Chem. Commun., (1983) 854.
16 H.B. Chin, M.B. Smith, R.D. Wilson and R. Bau, J. Am. Chem. Soc., 96 (1974) 5285.
17 L.W. Arndt, M.Y. Darensbourg, T. Delord and B.T. Bancroft, J. Am. Chem. Soc., 108 (1986) 2617.
18 R.J. Doedens and J.A. Ibers, Inorg. Chem., 6 (1967) 204.
19 In addition to local programs and modifications, a package of programs from the University of British Columbia was used, including: FASTFO, a modified version of FORDAP, the Fourier summation program by A. Zalkin; BUCILS, a structure factor and least-squares refinement program descended from ORFLS; BICABS, an absorption correction program which uses the Coppens–Leiserowitz–Rabinovitch logic for Gaussian integration; ORTEP, the plotting program by C.K. Johnson; ORFFE, the program for calculating bond lengths, angles and associated standard deviations by W. Busing and H.A. Levy.
20 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, 1974; Vol. IV, Table 2.2A.
21 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
22 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
23 P.M. Bailey, S.H. Taylor and P.M. Maitlis, J. Am. Chem. Soc., 100 (1978) 4711.
24 O. Piovesana, L, Sestili, C. Bellitto, A. Flamini, M. Tomassini, P.F. Zanazzi and A.R. Zanzari, J. Am. Chem. Soc., 99 (1977) 5190.

25 J. Ahmed, K. Itoh, I. Matsuda, F. Ueda, Y. Ishii and J.A. Ibers, Inorg. Chem., 16 (1977) 620.

26 H.W. Chen and J.P. Fackler, Inorg. Chem., 17 (1978) 12.

27 D.M. Roundhill, S.G.N. Roundhill, W.B. Beaulieu and U. Bagchi, Inorg. Chem., 19 (1980) 3365.

28 Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Jap., 52 (1979) 737.

29 Y. Zenitani, K. Inoue, Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Jap., 49 (1976) 1531.

30 Y. Zenitani, H. Tokunan, Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Jap., 51 (1978) 1730.

31 M. Horike, Y. Kai, N. Yasuoka and N. Kasai, J. Organomet. Chem., 72 (1974) 441

32 G. Del Piero and M. Cesari, Acta Crystallogr., Sect. B., B35 (1979) 2411.

33 K. Miki, Y. Kai, N. Yasuoka and N. Kasai, J. Organomet. Chem., 165 (1979) 79.

34 P.W. Jolly, C. Krüger, K.-P. Schick and G. Wilke, Z. Naturforsch. B, 35 (1980) 926.

35 Y. Kobayashi, Y. Iitaka and H. Yamazaki, Acta Crystallogr. Sect. B., B28 (1972) 899.

36 A. Ducruix, H. Felkin, C. Pascard and G.K. Turner, J. Chem. Soc., Chem. Commun., (1975) 615.

37 Cp(1) and Cp(2) refer to the centroids of the cyclopentadiene groups.

38 M. Cowie and M.D. Gauthier, Inorg. Chem., 19 (1980) 3142.

39 T. Jones, A.J.L. Hanlan, F.W.B. Einstein and D. Sutton, J. Chem. Soc., Chem. Commun., (1980) 1078.

40 A.J. Schultz, K.L. Stearley, J.M. Williams, R. Mink and G.D. Stucky, Inorg. Chem., 16 (1977) 3303.

41 N.I. Kirillova, A.I. Gusev and Yu.T. Struchkov, Zh. Strukt. Khimii, 13 (1972) 473.

42 F. van Bolhuis, E.J.M. de Boer and J.H. Teuben, J. Organomet. Chem., 170 (1979) 299.

43 K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton and G.V. Rees, Acta Crystallogr., Sect. B., B30 (1974) 2290 and references therein.

44 K. Prout, S.R. Critchley and G.V. Rees, Acta Crystallogr., Sect. B., B30 (1974) 2305.

45 G. Fachinetti, C. Floriani, F. Marchetti and M. Mellini, J. Chem. Soc., Dalton Trans., (1978) 1398.

46 A typical S–$CH_3$ single bond is given as 1.81 Å in International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, 1974; Vol. III, Table 4.2.6. The difference in covalent radii between *sp*$^2$ and *sp*$^3$ carbon is 0.04 Å.

47 G. Longoni, M. Manassero and M. Sansoni, J. Am. Chem. Soc., 102 (1980) 3242.

48 R.G. Holloway, B.R. Penfold, R. Colton and M.J. McCormick, J. Chem. Soc., Chem. Commun., (1976) 485.

49 F.W.B. Einstein and J. Trotter, J. Chem. Soc. (A), (1967) 824.

50 A.N. Nesmeyanov, N.N. Sedova, Yu.T. Struchkov, V.G. Andrianov, E.N. Stakheeva and V.A. Sazonova, J. Organomet. Chem., 153 (1978) 115.

51 A.N. Nesmeyanov, Yu.T. Struchkov, N.N. Sedova, V.G. Andrianov, Yu.V. Volgin and V.A. Sazonova, J. Organomet. Chem., 137 (1977) 217.

52 V.G. Andrianov, Yu.T. Struchkov and E.R. Rossinskaya, Zh. Strukt. Khim., 15 (1974) 74.

53 N.D. Jones, R.E. Marsh and J.H. Richards, Acta Crystallogr., 19 (1965) 330.

54 C. Lecomte, Y. Dusasoy, J. Protas, C. Moise and J. Tirouflet, Acta Crystallogr., Sect. B, B29 (1973) 488.

55 P. Batail, D. Grandjean, D. Astruc and R. Dabard, J. Organomet. Chem., 102 (1975) 79.

56 G. Lecomte, Y. Dusasoy, J. Protas and C. Moise, Acta Crystallogr., Sect. B, B29 (1973) 1127.

57 L.D. Spaulding, M. Hillman and G.J.B. Williams, J. Organomet. Chem., 155 (1978) 109.

58 B.R. Davis and I. Bernal, J. Cryst. Mol. Struct., 2 (1972) 107.

59 A.G. Osborne, R.E. Hollands, J.A.K. Howard and R.F. Bryan, J. Organomet. Chem. 205 (1981) 395.

60 C.G. Pierpont and R. Eisenberg, Inorg. Chem., 11 (1972) 828.

61 A.G. Osborne, R.E. Hollands, R.F. Bryan and S. Lockhart, J. Organomet. Chem., 226 (1982) 129.

62 W.R. Cullen, T.-J. Kim, F.W.B. Einstein and T. Jones, Organometallics, 2 (1983) 714.

63 W.R. Cullen, T.-J. Kim, F.W.B. Einstein and T. Jones, Organometallics, 4 (1985) 346.

64 K. Yasufuku, K. Aoki and H. Yamazaki, Inorg. Chem., 16 (1977) 624.

65 R.A. Abramovitch, J.L. Atwood, M.L. Good and B.A. Lampert, Inorg. Chem., 14 (1974) 3085.

66 M.B. Laing, and K.N. Trueblood, Acta Cryst., 19 (1965) 373.

67 M.R. Churchill and K.G. Lin, Inorg. Chem., 12 (1973) 2274.

68 H. Stoeckli-Evans, A.G. Osborne and R.H. Whiteley, J. Organomet. Chem., 194 (1980) 91.

69 I.R. Butler, W.R. Cullen, F.W.B. Einstein, S.J. Rettig and A.J. Willis, Organometallics, 2 (1983) 128.