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Syntheses and Structure of Bis(pentamethylcyclopentadienyl)-dithiophosphinato Complexes

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ABSTRACT

*Bis(pentamethylcyclopentadienyl)phosphane Cp^*_2PH reacts with sulfur under basic conditions to give the corresponding dithiophosphinate salts M^+ $CP^*_2PS_2^-$ (***5*** *$M^+ = HNEt_3^+$,* ***6*** *$M^+ = Li^+$), which are formed via the intermediate $CP^*_2P(S)H$ (***4****). Both salts on treatment with cobalt(II) chloride give rise to the transition metal dithiophosphinate* **7**. *The structures of this new type of diorganodithiophosphinate complexes in the solid state have been investigated.* © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8**: 521–525, 1997

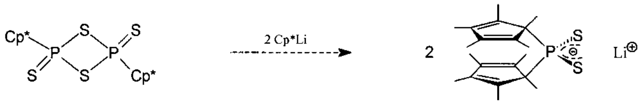
INTRODUCTION

Transition metal complexes containing organodithiophosphinate ligands have found use in a variety of technical [1,2] and clinical applications [3]. The bidentate nature of the organodithiophosphinate anions exhibits an interesting complexation behavior, in which the anion may act as a chelating or bridging ligand [4]. The latter binding mode is favored in coordination polymers [5]. In this article, we report syntheses, reactivity, and crystal structures of pentamethylcyclopentadienyl dithiophosphinates. The extraordinary electronic and steric properties of the pentamethylcyclopentadienyl substituent [6] cause unusual geometric features in such complexes.

RESULTS AND DISCUSSION

Organodithiophosphinates can be generated from the corresponding organodithiophosphinic acids. These are readily available starting either from suitable phosphanes or phosphoranes [7,8]. However, the latter route is unsuitable for the case of pentamethylcyclopentadienyl dithiophosphinates, since the corresponding dithioxophosphorane (**1**) in its monomeric or dimeric form is currently unknown (Scheme 1).

The conversion of the readily available bis(pentamethylcyclopentadienyl)thiophosphinic acid chloride **2** (Scheme 2) [9] via nucleophilic displacement



SCHEME 1

Dedicated to Prof. William Edwin McEwen on the occasion of his seventy-fifth birthday.

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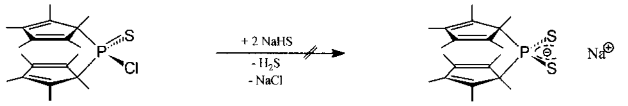


SCHEME 2

also fails, due to the steric congestion of the pentamethylcyclopentadienyl substituent.

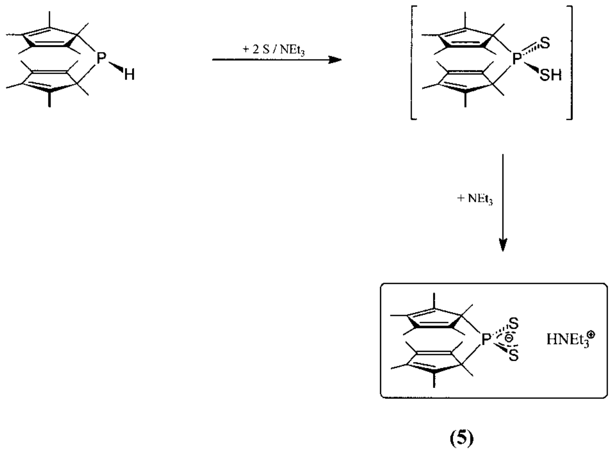
In contrast, the sulfuration of bis(pentamethylcyclopentadienyl)phosphane **3** [10] yields the desired pentamethylcyclopentadienyldithiophosphinate anion. However, the classical sulfuration procedure at high temperature is unsuitable in our case, since the dithiophosphinic acid that is formed decomposes under these conditions. Therefore, a modified procedure at low temperature has been used, in which the sulfur is activated by a base such as triethylamine. Thus, the reaction under basic conditions furnishes directly the ammonium salt **5** of the dithiphosphinic acid. The use of organolithium compounds leads to the corresponding lithium salt **6** of this acid. The reaction proceeds via the intermediate formation of pentamethylcyclopentadienylphosphanesulfide **4.** The latter can be isolated as the main product, if only one equivalent of sulfur is used under the same conditions (Schemes 3 and 4).

REACTIVITY

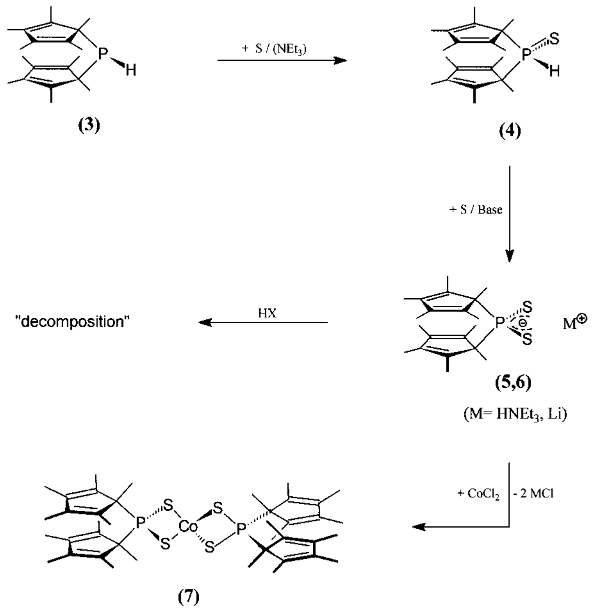
The dithiophosphinates normally can be converted easily into the corresponding acids by protonation using strong acids. However, in the case of **5** and **6,** the reaction with dilute acids, such as HCl or HBF_4 in ether and *p*-toluenesulfonic acid in toluene at low temperature (−80°C), fails. Several other products were formed instead, which were not characterized. This decomposition may be explained by condensation reactions involving elimination of H_2S and Cp*H.

The reactions of cobalt(II) chloride with the dithiophosphinate salts **5** and **6** in THF solution afford cleanly the desired transition metal dithiophosphinates, which are soluble in organic solvents and can be separated from the LiCl formed.

The cobalt(II) dithiophosphinate salts exhibit a very intensive and characteristic green color in solution, as well as in the solid state. However, the characterization of these salts by standard NMR spectroscopy is not successful, due to the paramagnetic nature of such complexes. Therefore, the identity of the cobalt(II) dithiophosphinate **7** was established by an X-ray diffraction study.



SCHEME 3



SCHEME 4

CRYSTAL STRUCTURES

The dithiophosphinates **5** and **6** differ in the coordination behavior of the cations (Figures 1 and 2). While in the ammonium salt **5** there is only a weak and anisobidentate interaction between the ammonium proton and the sulfur atoms [H(1)–S(1): 233(3) pm; H(1)–S(2): 307(6) pm], in the corresponding lithium salt the cation is bonded in a slightly distorted isobidentate manner [Li(1)–S(1): 249.6(6) pm; Li(1)–S(2): 248.2(5) pm]. Moreover, the formula unit in **5** occurs isolated in the solid state, while in compound **6,** two units are bridged by two DME molecules (see Tables 1 and 2).

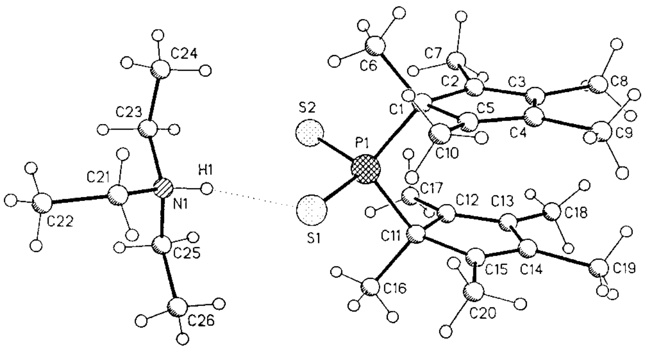


FIGURE 1 Molecular structure of **5** in the solid state.

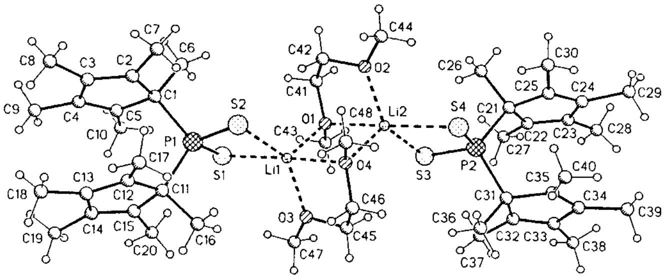


FIGURE 2 Molecular structure of **6** in the solid state.

TABLE 1 Geometric Parameters of **5**

Bond Lengths (pm)		*Bond Angles (°)*	
P1–C1	190.3 (7)	C1–P1–C11	110.7 (3)
P1–C11	190.4 (8)	C1–P1–S1	108.1 (2)
P1–S1	200.1 (2)	C1–P1–S2	109.2 (2)
P1–S2	198.5 (2)	C11–P1–S1	109.0 (2)
N1–H1	91 (3)	C11–P1–S2	108.5 (2)
S1–H1	233 (3)	S1–P1–S2	111.4 (1)
S2–H1	307 (6)	N1–H1–S1	167 (6)
N1–S1	323.0 (6)	N1–H1–S2	118 (5)
N1–S2	359. (6)		

TABLE 2 Geometric Parameters of **6**

Bond Lengths (pm)		*Bond Angles (°)*	
P1–C1	189.5 (3)	C1–P1–C11	111.6 (1)
P1–C11	190.1 (3)	C1–P1–S1	108.3 (1)
P2–C21	189.4 (3)	C1–P1–S2	110.0 (1)
P2–C31	190.5 (3)	C11–P1–S1	109.4 (1)
P1–S1	200.3 (1)	C11–P1–S2	108.0 (1)
P1–S2	201.0 (1)	S1–P1–Li1	55.9 (1)
P2–S3	201.0 (1)	S2–P1–Li1	55.5 (1)
P2–S4	200.5 (1)	C21–P2–C31	111.1 (1)
S1–Li1	249.6 (6)	C21–P2–S3	108.4 (1)
S2–Li1	248.2 (5)	C21–P2–S4	110.0 (1)
S3–Li2	244.2 (6)	C31–P2–S3	109.5 (1)
S4–Li2	254.5 (6)	C31–P2–S4	108.6 (1)
Li1–Li2	324.7 (8)	S3–P2–Li2	53.4 (1)
		S4–P2–Li2	56.3 (1)

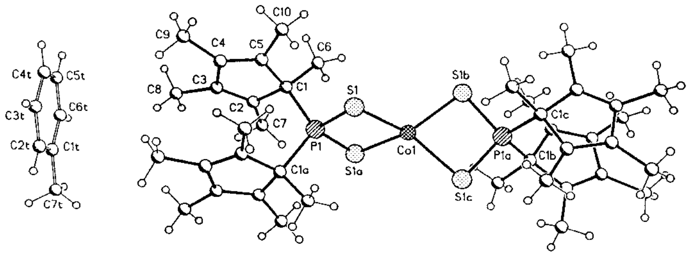


FIGURE 3 Molecular structure of **7** in the solid state.

TABLE 3 Geometric Parameters of **7**

P1–C1	188.5 (4)	C1–P1–C1a	113.9 (2)
P1–S1	203.1 (1)	C1–P1–S1	109.6 (1)
S1–Co1	232.5 (1)	C1–P1–S1a	109.7 (1)
		S1–P1–S1a	103.9 (1)
		S1–Co1–S1a	86.9 (1)
		Si–Co1–S1b/c	121.8 (1)
		P1–S1–Co1	84.6 (1)

The dithiophosphinate anion shows in both salts an almost parallel arrangement of the pentamethylcyclopentadienyl rings and almost ideal tetrahedral geometry at the phosphorus center. The P–S bond lengths are influenced only marginally by the nature of the cation. The slightly widened P–C bond lengths (190 pm), however, seem to be a general feature in Cp* compounds.

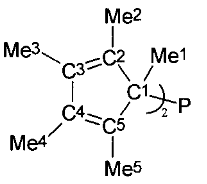
In the transition metal complex **7**, two dithiophosphinate ligands are coordinated to one metal center in an orthogonal arrangement (Figure 3). They are both bound in a perfectly isobidentate manner [S(1/1a/1b/1c)–Co: 232.5(1) pm], which has not been observed for cobalt(II) so far (Table 3). In contrast to the salts **5** and **6**, there is a considerable distortion from the tetrahedral geometry at the phosphorus and the cobalt centers, probably as a consequence of the strong metal–sulfur interaction. Thus, the S–P–S bond angle is reduced to 103.9(1)°, and the corresponding P–S bond lengths are widened slightly by 3 pm compared to **5** and **6.** The angle S–Co–S, in which both sulfur atoms belong to the same dithiophosphinate ligand, shows a value of only 87°, while the corresponding angle in which the sulfur atoms belong to different anions is widened to 122°.

This distortion from the tetrahedral geometry presumably results from the large steric congestion of the anionic ligands and should therefore be characteristic for dimeric structures of bis(pentamethylcyclopentadienyl)-substituted dithiophosphinates.

EXPERIMENTAL

All manipulations were carried out with exclusion of air and moisture in an inert gas atmosphere (argon). Solvents were dried using standard procedures.

NMR: Bruker AMX 300; ^{31}P: 121.5 MHz, external standard 85% H_3PO_4; ^{1}H: 333.1 MHz, external standard TMS; ^{13}C: 75.5 MHz, external standard TMS; ^{7}Li: 115.9, external standard 1.5 M LiBr; positive sign denotes shifts to lower frequencies; −MS: Kratos Instruments Concept 1H, Kratos Instruments MS 50, VG Instruments VG 12-250 (EI, 70 eV). Melting points were determined in sealed glass capillaries and are uncorrected. The numbering of the hydrogen and carbon atoms within the Cp* rings is denoted as depicted below.



Bis(pentamethyl-2,4-cyclopentadien-1-yl)phosphanesulfide (4)

To a solution of 4.0 g (13 mmol) of phosphane **3** in 20 mL toluene was added 0.42 g (13 mmol) of sulfur and 1.8 mL of triethylamine. The mixture was stirred at room temperature for 2 hours, and the product was crystallized from the resulting solution at −30°C. Yield: 3.2 g (73%); mp: 121–123°C. $^{31}P\{^{1}H\}$ NMR (C_6D_6): $\delta = 36.2$ (s). ^{1}H NMR (C_6D_6): $\delta = 5.58$ (d, $^{1}J_{HP}$: 424.1 Hz, 1H, P*H*), 1.79 (s, 6H), 1.71 (s, 6H), 1.44 (s, 6H), 1.38 (s, 6H) (Me^{2-5}), 1.42 (d, $^{3}J_{HP}$: 22.4 Hz, 6H, Me^{1}).

^{13}C NMR (C_6D_6): $\delta = 138.3$ (d, J_{CP}: 7.1 Hz), 137.9 (d, J_{CP}: 4.7 Hz), 135.3 (s), 134.6 (s) (C^{2-5}), 61.5 (d, $^{1}J_{CP}$: 30.3 Hz, C^{1}), 19.7 (d, $^{2}J_{CP}$: 2.2 Hz, Me^{1}), 12.8 (s), 12.1 (s), 11.7 (s), 11.5 (s) (Me^{2-5}). MS (*m/z*) (%): 334 (3) [M^+], 301 (10) [$M^+ - S - H$], 166 (20) [$M^+ - S - Cp^*$], and other fragments.

Triethylammonium Bis(pentamethyl-2,4-cyclopentadien-1-yl)dithiophosphinate (5)

3.5 g (12 mmol) of the phosphane **3** was dissolved in a mixture of 20 mL of toluene and 3.2 mL (25 mmol) of triethylamine. After the addition of 0.8 g (25 mmol) of sulfur at room temperature, the mixture was stirred for 1 hour and insoluble components were filtered off. The isolated crude product was washed with pentane and recrystallized from toluene.

Yield: 4.1 g (73%); mp: 284–287°C. $^{31}P\{^{1}H\}$ NMR (C_6D_6): $\delta = 85.2$ (s). ^{1}H NMR (C_6D_6): $\delta = 2.57$ (q, $^{3}J_{HH}$: 7.3 Hz, 6H, NCH_2CH_3), 2.01 (d, $^{3}J_{HP}$: 19.2 Hz, 6H, Me^{1}), 1.94 (s, 12H), 1.93 (s, 12H) (Me^{2-5}), 0.88 (t, $^{3}J_{HH}$: 7.3 Hz, 9H, NCH_2CH_3). ^{13}C NMR (C_6D_6): $\delta = 139.9$ (s), 136.0 (d, J_{CP}: 7.9 Hz) (C^{2-5}), 65.2 (d, $^{1}J_{CP}$: 34.7 Hz, C^{1}), 45.3 (s, NCH_2CH_3), 21.6 (d, $^{2}J_{CP}$: 0.8 Hz, Me^{1}), 14.4 (s), 12.1 (s)(Me^{2-5}), 8.8 (s, NCH_2CH_3).

Lithium-bis(pentamethyl-2,4-cyclopentadien-1-yl)dithiophosphinate (6)

0.5 g (16 mmol) of elemental sulfur was added to a solution of 2.4 g (8 mmol) of Cp^*_2PH in 15 mL ether, and the mixture was treated with 16 mmol of methyllithium (10.5 mL of a 1.6 M solution in ether) at −10°C (nascent methane gas!). The precipitated product was filtered off, washed with ether, and recrystallized from dimethoxyethane (DME). Yield: 5.0 g (81%); mp: 307–310°C. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta =$ 90.7 (s). ^{1}H NMR ($CDCl_3$): $\delta = 1.98$ (s, 12H), 1.65 (s, 12H) (Me^{2-5}), 1.37 (d, $^{3}J_{HP}$: 19.9 Hz, 6H, Me^{1}). ^{13}C NMR ($CDCl_3$): $\delta = 138.8$ (s), 136.5 (d, J_{CP}: 8.2 Hz) (C^{2-5}), 64.1 (d, $^{1}J_{CP}$: 32.5 Hz, C^{1}), 20.7 (s, Me^{1}), 13.6 (s), 11.9 (s) (Me^{2-5}). ^{7}Li NMR (DME): $\delta = -2.56$.

Bis[bis(pentamethyl-2,4-cyclopentadien-1-yl)dithiophosphinato] Cobalt (II) (7)

A mixture of 1.2 g (9 mmol) of $CoCl_2$ and 8.4 g (18 mmol) of salt **5** or 6.7 g (18 mmol) of salt **6** in 50 mL THF was stirred at room temperature for 2 hours. After filtration and evaporation of the solvent, the product was crystallized from toluene at −30°C to give **7** as green prisms. Yield: 4.1 g (58%); mp: 323–326°C.

X-ray Structure Determination of 5, 6, *and* 7

The structures were solved by direct methods. Nonhydrogen atoms were refined anisotropically. Details of data collection and refinement are given in Table 4. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopold-

TABLE 4 Crystallographic Data

	5	***6**DME***	***7**Toluene***
Formula	$C_{26}H_{46}NPS_2$	$C_{28}H_{50}LiO_4PS_2$	$C_{47}H_{68}CoP_2S_4$
Formula weight	467.73	462.59	882.12
Habit	rod-shaped	prisms	prisms
Color	colorless	colorless	blue-green
Crystal size (mm)	$0.60 \times 0.40 \times 0.35$	$0.70 \times 0.50 \times 0.35$	$0.50 \times 0.40 \times 0.30$
Crystal system	orthorhombic	triclinic	tetragonal
Space group	$Pna2_1$ (No. 33)	P-1 (No. 2)	$I4_1/a$ (No. 88)
Unit cell **a** (Å)	13.346(3)	8.838(2) $\alpha = 65.76(2)°$	14.628(5)
b (Å)	14.822(3)	18.025(4) $\beta = 78.39(2)°$	14.628(5)
c (Å)	13.926(3)	18.651(4) $\gamma = 79.62(2)°$	22.663(6)
Volume ($Å^3$)	2754.7(10)	2638(1)	4849(3)
Z	4	4	4
Density (Mg/m^3)	1.128	1.165	1.208
Absorption coefficient (mm^{-1})	0.264	0.279	0.622
F(000)	1024	1000	1884
Diffractometer	Nicolet R3m	Nicolet R3m	Nicolet R3m
Wavelength	0.71073 Å (Mo $K\alpha$)	0.71073 Å (Mo $K\alpha$)	0.71073 Å (Mo $K\alpha$)
Temperature	293(2) K	293(2) K	293(2) K
$2\theta_{max}$	50°	50°	45°
Index ranges	$-2 < h < 15$ $-;17 < k < 2$ $-2 < l < 16$	$-10 < h < 10$ $-19 < k < 21$ $0 < l < 22$	$-13 < h < 15$ $-13 < k < 15$ $-16 < l < 24$
Reflections collected	4047	9661	6559
Independent reflections	2962 ($R_{int} = 0.034$)	9348 ($R_{int} = 0.064$)	1599 ($R_{int} = 0.055$)
Refinement on	F^2	F^2	F^2
Data/restraints/parameters	2962/2/287	9348/0/565	1599/13/128
Goodness-of-fit on F2	1.153	0.902	1.006
Final *R* indices [R_1 for $I > 2\sigma(I)$]	$R1 = 0.062$ $wR2 = 0.184$	$R1 = 0.054$ $wR2 = 0.148$	$R1 = 0.045$ $wR2 = 0.133$
Largest diff. peak and hole ($eÅ^{-3}$)	0.311 and −0.315	0.534 and −0.259	0.500 and −0.228

hafen (FRG) on quoting the depository numbers CSD-406888 (**5**), CSD-406886 (**6**), and CSD-406887 (**7**).

REFERENCES

[1] (a) W. Kuchen, J. Metten, DBP 1166191, Chemische Fabriken Kalk, 1964; (b) W. Kuchen, J. Metten, DBP 1137732, Chemische Fabriken Kalk, 1963.

[2] (a) J. P. Milionis, F. I. Arthen, DPB 1233134, American Cyanamid Co., 1967; (b) H. Jenkner, DBP 1242857, Chemische Fabriken Kalk, 1967.

[3] I. Haiduc, C. Silvestru, M. Gielen, *Bull. Soc. Chim. Belg., 92,* 1983, 187–189.

[4] I. Haiduc, *Rev. Inorg. Chem., 3,* 1981, 353–370.

[5] W. Kuchen, H. Hertel, *Angew. Chem., 81,* 1969, 127–135; *Angew. Chem. Int. Ed. Engl., 8,* 1969, 89–97.

[6] J. Ebels, Diploma Thesis, University of Bonn, 1993.

[7] K. Issleib, G. Döll, *Z. Anorg. Allg. Chem., 324,* 1963, 259–269.

[8] (a) K. Diemert, W. Kuchen, *Angew. Chem., 83,* 1971, 544; *Angew. Chem. Int. Ed. Engl., 10,* 1971, 508–509; (b) W. Kuchen, H. Keck, *Z. Naturforsch., 31b,* 1976, 437–441.

[9] (a) T. A. Mastryukova, A. E. Shipov, M. I. Kabachnik, *Zh. Obshch. Khim., 31,* 1961, 507–512; (b) L. Malatesta, *Gazz. Chim. Ital., 77,* 1947, 509–518.

[10] H. M. Schiffner, Ph.D. Thesis, University of Bonn, 1991.