

Synthesis and Molecular Structure of $[\text{K}(\text{18-crown-6})][(\text{CO})_4\text{FePPh}_2\text{CS}_2]$

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$[\text{K}(\text{18-crown-6})][(\text{CO})_4\text{FePPh}_2]$ **1** reacts with CS_2 to produce the adduct $[\text{K}(\text{18-crown-6})][(\text{CO})_4\text{FePPh}_2\text{CS}_2]$ **2** in high yield; an X-ray diffraction analysis confirms the phosphorus coordination of the $\text{PPh}_2\text{CS}_2^-$ ligand in **2** and shows weak contacts between the sulfur atoms and the potassium ion of the crown ether.

The ability of CS_2 to act as a donor to electron-deficient transition metal fragments and to accept electrons from nucleophilic species makes this molecule a versatile ligand in organometallic chemistry. Occupied π orbitals and vacant π^* orbitals generate exclusively $\eta^2\text{-C,S}$ -bonded transition metal compounds; an alternative end-on coordination mode has not been found.¹ $\eta^1\text{-C}$ -Bonded complexes are less familiar and have been obtained with several anionic transition metals.² Main group compounds containing a coordinatively active pair of electrons produce a variety of zwitterionic species with η^1 -coordination *via* the carbon atom.^{3–5} The addition compounds from both coordination modes have in many cases developed a rich coordination chemistry and numerous compounds with interesting new structural features have been prepared.¹ In particular, the zwitterionic phosphine adducts $\text{R}_3\text{P}^+\text{CS}_2^-$ have gained considerable attention because of the ability of these compounds to bind to metals in an η^1 , η^2 or η^3 manner.³ CS_2 is also capable of insertion reactions into various main group or transition metal M-X bonds and, depending on the nature of X, coordinated dithioesters, dithiocarbamates or similar types of compounds have been obtained.⁶

We now report the results of the reaction of $[\text{K}(\text{18-crown-6})][(\text{CO})_4\text{FePPh}_2]$ **1** with CS_2 . Similar to phosphines, the anion is equipped with a lone pair of electrons at the P atom and should act as a nucleophile. The diphenylphosphido complex **1** formed as one product upon treatment of $\text{Fe}(\text{CO})_5$ with KPPH_2 in THF in the presence of the crown ether.⁷ This work is part of our studies concerning the reactivity of $\text{Fe}(\text{CO})_5$ and $(\text{CO})_4\text{-FeCS}$ towards various nucleophiles.[†] The anion of **1** has been known for a long time, but there have been few reports about the chemistry of this compound.⁸

The reaction of **1** with excess CS_2 in THF under ambient conditions affords a red solution from which dark red crystals of $[\text{K}(\text{18-crown-6})][(\text{CO})_4\text{FePPh}_2\text{CS}_2]$ **2** could be isolated in 90% yield. Spectroscopic data indicate that the CS_2 molecule has added to the anion without bond breaking. The expected insertion into the Fe-P bond to give **3** has not occurred (Scheme 1). However, it is known from similar zirconium phosphido compounds that CS_2 inserts into the Zr-P bond to produce a phosphino dithioformato ligand, the phosphorus analogue of the dithiocarbamate, to act as a chelating ligand.⁹ The unusual coordination mode in **2** was confirmed by an X-ray analysis which shows that the anion $[(\text{CO})_4\text{FePPh}_2]^-$ coordinates at the carbon atom of the CS_2 molecule *via* the P atom. To our knowledge, this is the first case in which a transition metal

phosphido complex behaves like a phosphine towards CS_2 and does not insert the CS_2 molecule.

The IR spectrum of **2** is closely related to that of **1** but exhibits an additional strong band at 1030 cm^{-1} which can be assigned to the $\nu_{\text{as}}(\text{CS})$ vibration.[§] Two IR active $\nu(\text{CS})$ vibrations are expected,¹⁰ but the lower $\nu_{\text{s}}(\text{CS})$ band is probably hidden by strong bands of the crown ether. In the $\nu(\text{CO})$ region the spectrum shows three stretching frequencies of terminal CO groups at $2040(\text{s})$, $1950(\text{sh})$ and $1922(\text{vs})\text{ cm}^{-1}$ in the typical pattern of a $(\text{CO})_4\text{FeL}$ unit with the ligand L in an axial position. The ^{31}P NMR spectrum of **2** exhibits a resonance signal at δ 91.50. The coordination of **1** (δ $^{31}\text{P} = -2.38$) to the CS_2 molecule causes a downfield shift of more than 90 ppm. A similar shift is observed in going from three-coordinated PR_3 compounds to four-coordinated PR_3 adducts in which the free pair of electrons is involved in bonding to various electrophilic centres.¹¹ The same trend is observed going from KS_2CPPH_2 (δ 41.51¹²) to the $\text{Fe}(\text{CO})_4$ complex **2**.

X-Ray quality crystals of **2** have been obtained by layering a THF solution of the salt with pentane.[¶] The molecular structure of the compound is shown in Fig. 1. The structure of the anion confirms the exclusive bonding of the phosphorus atom to the iron without an $\text{Fe}\cdots\text{S}$ interaction. Two nearly equal $\text{K}\cdots\text{S}$ contacts of 341.6(2) and 338.6(2) pm are responsible for the potassium atom being extruded by 67.9 pm out of the best plane of the O atoms of the crown ether ligand. These contacts are probably the reason why a CS_2 insertion into the Fe-P bond and a Fe-S coordination or the formation of a chelating ligand with CO substitution did not occur. The P-CS_2 bond is only 5 pm longer than the bond of the P atom to the phenyl carbon atoms

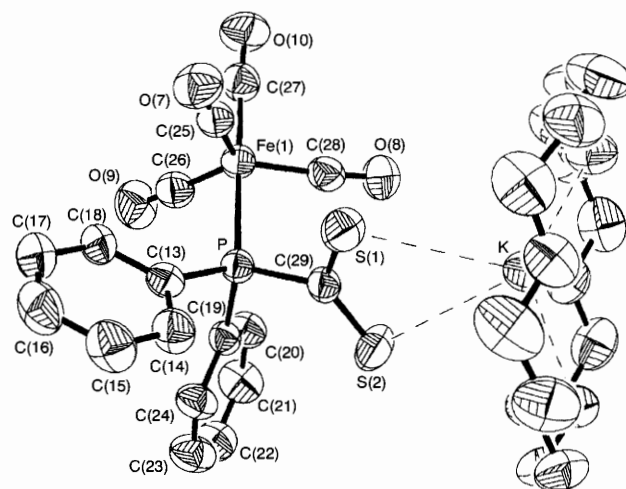
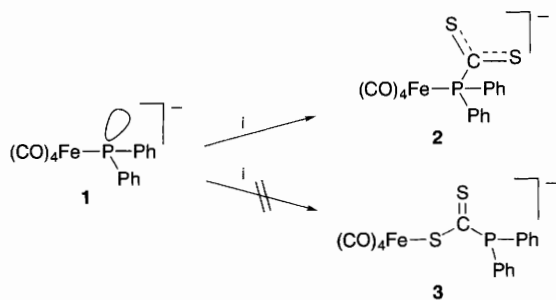


Fig. 1 ORTEP drawing of the molecular structure of $[\text{K}(\text{18-crown-6})][(\text{CO})_4\text{FePPh}_2\text{CS}_2]$ **2**, with 50% thermal ellipsoids. Relevant distances (pm) and angles ($^\circ$) are: Fe-P 225.9(1), $\text{C}(29)\text{-P}$ 186.6(4), $\text{C}(29)\text{-S}(1)$ 167.3(4), $\text{C}(29)\text{-S}(2)$ 165.5(4), $\text{Fe-C}(27)$ 177.2(5), $\text{Fe-C}(25)$ 178.0(4), $\text{Fe-C}(26)$ 177.2(5), $\text{Fe-C}(28)$ 178.8(5), $\text{K}\cdots\text{S}(1)$ 338.6(2), $\text{K}\cdots\text{S}(2)$ 341.6(2); $\text{Fe-P-C}(29)$ 112.0(1), $\text{P-Fe-C}(25)$ 88.5(1), $\text{P-Fe-C}(26)$ 91.0(2), $\text{P-Fe-C}(28)$ 89.3(1), $\text{P-Fe-C}(27)$ 177.7(1), $\text{S}(1)\text{-C}(29)\text{-S}(2)$ 127.9(3), $\text{S}(2)\text{-C}(29)\text{-P}$ 117.5(2), $\text{S}(1)\text{-C}(29)\text{-P}$ 114.5, $\text{C}(13)\text{-P-C}(19)$ 102.5(1), $\text{C}(25)\text{-Fe-C}(28)$ 118.2(2), $\text{C}(25)\text{-Fe-C}(26)$ 120.8(2), $\text{C}(26)\text{-Fe-C}(28)$ 118.2(2).



Scheme 1 Reagents and conditions: i, CS_2 in THF, 25 $^\circ\text{C}$, 1 h

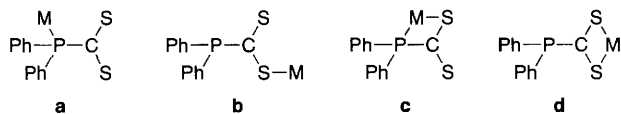


Fig. 2 Possible coordination modes a–d of the chelating ligand $[\text{Ph}_2\text{PCS}]^-$ towards one metal atom (M = electron deficient transition metal fragment)

and corresponds to a normal single bond. The C–S bond lengths are only slightly different, and are nearly identical with the C–S distances in $[\text{NEt}_4][(\text{CO})_5\text{WPPh}_2\text{CS}_2]$, in which no further contact of atoms to the S atoms have been found.¹³ The PCS_2 unit is planar, the sum of bond angles at the carbon atom is 359.9° indicating sp^2 hybridization. The geometry is closely related to that of the adduct Et_3PCS_2 .¹⁴ The CS_2 plane forms a dihedral angle of 66.5° with the Fe–P–C plane.

Complex **2** contains the little studied diarylphosphinodithioformate anion $[\text{Ph}_2\text{PCS}_2]^-$ as a ligand. In principle, three coordinatively active pairs of electrons are available allowing the coordination modes a–d in Fig. 2 to one transition metal with $[\text{Ph}_2\text{PCS}_2]^-$ acting as a two or four electron donor. As yet, only examples for structures **b**, **c**, and **d** have been found. A dialkylarsinodithioformate tungsten complex in which the ligand is bonded in the coordination mode **c** has also been described.¹⁵ An additional M–C interaction as found in complexes with the $\text{S}_2\text{C–PCy}_3$ ligand would also be possible. The related dithiocarbamate ligands only form complexes according to **b** and **d** because the lone pair of electrons of the amino group is coordinatively inactive but is involved in π bonding to the carbon atom.

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Footnotes

† The similar reaction with $(\text{CO})_4\text{FeCS}$ afforded only a dark brown material, from which no defined product could be separated.

‡ The only known compound with a similarly bonded Ph_2PCS_2 ligand is the complex $[\text{NEt}_4][\text{W}(\text{CO})_5\text{PPh}_2\text{CS}_2]$ but which has been obtained via the reaction of $(\text{CO})_5\text{WPPh}_2\text{H}$ with BuLi in the presence of CS_2 .¹³

§ Selected data for **2**: IR (nujol)/ cm^{-1} $\nu(\text{CO})$: 2040s, 1950sh, 1922vs; $\nu(\text{CS})$: 1030s. ^{31}P NMR (THF): δ 91.50. Satisfactory C, H elemental analysis obtained.

¶ Crystal data for **2**. $\text{C}_{29}\text{H}_{34}\text{FeKO}_{10}\text{PS}_2$, triclinic, space group $P\bar{1}$, $a = 1271.5(1)$, $b = 1348.6(1)$, $c = 1367.2(1)$ pm, $\alpha = 87.89(1)$, $\beta = 62.31(1)$, $\gamma = 73.54(1)^\circ$. $V = 1978.4 \text{ \AA}^3$, $Z = 2$, $D_c = 1.351 \text{ g cm}^{-3}$, $\mu = 6.8 \text{ cm}^{-1}$ (Mo-K α), 4710 observed reflections, $\theta_{\text{max}} = 26.32$. The structure was solved using direct methods, a series of successive difference Fourier maps and least-square refinements which ended in $R1 = 0.0417$ and $wR2 = 0.1198$ (SHELXL-93).¹⁶ Around the symmetry centres $1/2$, $1/2$, $1/2$ and $0,0,0$ the crystal contains strongly disordered solvent molecules (THF). The corresponding electron density maxima, which could not be assigned to single molecules, have been refined as carbon atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- C. Bianchini, C. Mealli, A. Meli and M. Sabat, *Stereochemistry of Organometallic and Inorganic Compounds*, ed. I. Bernal, Elsevier, Oxford, Amsterdam, New York, Tokyo, 1986, vol. 1, p. 146.
- J. E. Ellis, R. W. Fennel and E. A. Flom, *Inorg. Chem.*, 1976, **15**, 2031.
- D. Miguel, V. Riera, J. A. Miguel, M. Gomez and X. Solans, *Organometallics*, 1991, **10**, 1683.
- M. L. Ziegler, H. Weber, B. Nuber, and O. Serhadle, *Z. Naturforsch., Teil B*, 1987, **42**, 1411.
- N. Kuhn, H. Bohnen and G. Henkel, *Z. Naturforsch., B Chem. Sci.*, 1994, **49**, 1473.
- I. S. Butler and A. F. Fenster, *J. Organomet. Chem.*, 1974, **66**, 161.
- W. Petz and F. Weller, manuscript in preparation.
- Gmelin, *Handbuch der Anorganischen Chemie, Fe Organische Verbindungen B2*, 1978, 52.
- E. Hey, M. F. Lappert, J. L. Atwood and S. G. Bott, *J. Chem. Soc., Chem. Commun.*, 1987, 421.
- K. Dehnicke, U. Müller and J. Weidlein, *Schwingungsspektroskopie*, Georg Thieme Verlag, Stuttgart, New York, 1982.
- H. Inoue, T. Nakagome, T. Kuroiwa, T. Shirai and E. Fluck, *Z. Naturforsch., B Chem. Sci.*, 1987, **42**, 573.
- E. M. Vaquez-Lopez, A. Sanchez, J. S. Casas and J. Sordo, *J. Organomet. Chem.*, 1992, **438**, 29.
- K.-H. Yih, Y.-C. Lin, M. C. Cheng, and Y. Wang, *J. Chem. Soc., Chem. Commun.*, 1993, 1380.
- T. N. Margulis and D. H. Templeton, *J. Chem. Phys.*, 1962, **36**, 2311.
- M. Luksza, S. Himmel and W. Malisch, *Angew. Chem.*, 1983, **95**, 418.
- G. M. Sheldrick, SHELXL-93, Program for crystal structure analysis, University of Göttingen, 1993.