Thiocarbonyl Complexes of Iron:[1] Formation of Dinuclear Compounds by the Phosphine-Induced CO-CS Coupling in the Reaction of $Fe(CO)_4CS$ with $P(NMe_2)_3$. Molecular Structure of $Fe_2(CO)_6S_2COCP(NMe_2)_3$[†]

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Slow addition of $Fe(CO)_4CS$ to an excess of $P(NMe_2)_3$ affords the dinuclear complexes $Fe_2(CO)_6S_2COCP(NMe_2)_3$ (1) and $Fe_2(CO)_5(P(NMe_2)_3)S_2COCP(NMe_2)_3$ (2), the mononuclear complex $(Fe(CO)_2(P(NMe_2)_3)S_2COCP(NMe_2)_3$ (3), and the sulfur transfer product $S{=}P(NMe_2)_3$ (4). The iron compounds contain a new betaine-like ligand which is composed of $P(NMe_2)_3$, CS, CO, and an additional S atom and bonded to the iron atoms via the sulfur atoms: C-C bond formation between the CS group and one CO ligand has occurred. Complex 1 crystallizes in the space group *Pbca* with cell parameters $a = 1513.3(3)$ pm, $b = 1324.3(1)$ pm, $c = 2278.4(2)$ pm, and $Z = 8$. The dinuclear compounds 1 and 2 have a butterfly structure, and the ligand acts as a six-electron donor. ^{31}P, ^{13}C, and ^{1}H NMR and IR spectra are in accord with the structures.

Introduction

In the course of our studies concerning the chemical properties of $Fe(CO)_4CS$, we have recently shown that one or two CO groups can be replaced by classical tertiary phosphines to give $(CO)_3(CS)FePR_3$ and $(CO)_2(CS)Fe(PR_3)_2$ compounds in moderate yields. However, CO activation by amine oxides was necessary, although the presence of the strongly electron-withdrawing CS ligand should exert a labilizing effect on CO and should facilitate the introduction of more basic ligands. The procedure applied kept the more strongly bonded CS ligand unconverted. In the absence of the amine oxides only tarry materials were obtained.[2] Preferred replacement of CO instead of CS was also theoretically predicted to occur in transition-metal thiocarbonyl complexes.[3]

Attempts to introduce more basic donors such as phosphites or $P(NMe_2)_3$ in a similar manner have failed. In all cases we observed a desulfurization of the terminal CS group of $Fe(CO)_4CS$ and no product from a simple CO or CS replacement could be isolated. In contrast, $Fe(CO)_5$ usually produces mono- and disubstituted derivatives with nearly all phosphorus donors under thermal or photochemical conditions.[4] Desulfurization of a CS group terminally bonded to a transition metal has not yet been reported. Other desulfurization reactions in the coordination sphere of a metal are well-known, and phosphine-induced removal of the bridging sulfur atom from an η^2-CS_2 complex is the most common procedure for the preparation of transition-metal thiocarbonyl compounds, mainly of the heavier group 8 and 9 elements.[5]

In the present paper we describe the reaction of $Fe(CO)_4CS$ with $P(NMe_2)_3$ under modified conditions leading to the isolation of compounds with an unusual chelating ligand; preliminary results have been published recently.[6]

Results

Synthesis. Whereas phosphites reacted very slowly with $(CO)_4FeCS$ and the formation of the corresponding $S{=}P(OR)_3$ compounds could be monitored by ^{31}P NMR spectroscopy,[7] $P(NMe_2)_3$ immediately produced $S{=}P(NMe_2)_3$ (4) nearly quantitatively in an exothermic reaction when added to a solution of $Fe(CO)_4CS$ in pentane. However, the latter reaction is very complex and the results strongly depend on the reaction conditions. Thus, if a large excess of the aminophosphine is present during the reaction, a different pathway is achieved.

The dropwise addition of $Fe(CO)_4CS$ to an approximately 4-5-fold excess of $P(NMe_2)_3$ in pentane over 1 h produced a deep violet-brown solution along with a brown oily material. When the mixture stood for several days, violet crystals of 3 separated. Chromatography of the pentane solution on silanolized silica gel gave small amounts of the known complexes $(CO)_4FeP(NMe_2)_3$ (5) and $(CO)_3Fe(P(NMe_2)_3)_2$ (6), which have been identified by ^{31}P NMR, IR, and mass spectroscopy. Further elution with toluene produced a deep red oil, from which 1 crystallized after some weeks. The remaining oil has not

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[†] Dedicated to Professor H. Nöth on the occasion of his 65th birthday.

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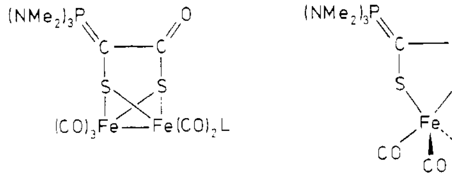
Chart I



1: L = CO

2: L = $P(NMe_2)_3$

3

yet been crystallized but was identified as the dinuclear compound **2** from the spectroscopic data (Chart I).

The chromatographic workup procedure finally gave a deep violet band of additional **3**; however, it decomposed on the column. Further extraction of the oily residue with various solvents did not produce any other defined compound. No complex with a CS ligand could be detected.

The compounds **1**–**3** contain a new chelating ligand which is composed of an unconverted $P(NMe_2)_3$ unit, CO, CS, and an additional S atom and is bonded to the metal atoms via the two sulfur atoms.

Spectroscopic Studies. The complexity of the reaction becomes apparent by monitoring the pentane solution of the initial reaction mixture by ^{31}P NMR spectroscopy. About 15 signals of different intensities indicate that many phosphorus-containing compounds have formed. However, most of them have not yet been identified; an intense signal at 82.5 ppm was indicative of **4**.

The ^{31}P NMR spectrum **1** shows a singlet at 54.85 ppm. The shift is consistent with the phosphine ligand being bonded to a carbon atom as in $[CH_3P(NMe_2)_3]^+$ (60.0 ppm) or in the ylide $CH_2{=}P(NMe_2)_3$ (70.8 ppm). **2** exhibits a closely related signal at 55.83 ppm and an additional signal at 159.61 ppm that indicates the presence of a second aminophosphine bonded to the iron atom as in **5** (157.1 ppm)[8] or **6** (172.9 ppm).[9] A similar pair of signals was recorded for the mononuclear compound **3** at 54.56 and 167.53 ppm.

The ^{13}C NMR spectrum of **1** exhibits a doublet for the methyl protons of the ylidic-bonded $P(NMe_2)_3$ group. One single peak in the CO region for the two equivalent $Fe(CO)_3$ units (not ^{13}C enriched) indicates fluxional behavior of the three chemically different CO groups. The spectrum of **2** shows two *N*-methyl doublets and three signals in the carbonyl region, of which two are doublets according to couplings to the P atom. The singlet shows the $Fe(CO)_3$ group to be fluxional, and the doublets are consistent with the loss of fluxionality at the side of the molecule bearing the phosphine ligand.[10] Relative to **1**, the CO resonances of **2** are shifted downfield, as a consequence of the substitution of a π-accepting CO group for the mainly σ-donating $P(NMe_2)_3$. The signals for the ylidic carbon atom and that for the ring C=O group of **1**–**3** could not be located.

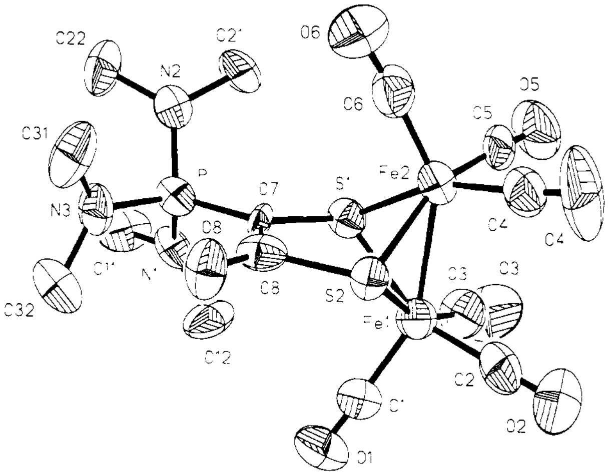


Figure 1. Perspective drawing of the molecular structure of $Fe_2(CO)_6S_2COCP(NMe_2)_3$ (**1**) (XP,[11] 50% thermal ellipsoids), showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

The ^1H NMR spectra of **1**–**3** are consistent with the structures proposed and show two types of NMe_2 protons for **2** and **3** but one doublet for **1**.

The IR spectrum of **1** shows five strong absorptions in the region of terminal CO groups; two bands of equal intensities are recorded for the two CO groups of **3**. For **1**–**3** strong bands in the ketone region can be attributed to the $\nu(C{=}O)$ vibration of the ring CO group at 1644 (**1**), 1610 (**2**), and 1525 cm^{-1} (**3**). The shift to lower frequencies by more than 100 cm^{-1} in **3** is surprising and corresponds approximately to the shift on going from an ester to an amide CO vibration. This means that electron delocalization has increased in **3**, leading to a more polar character of the CO bond.

Molecular Structure of 1. A single-crystal X-ray crystallographic analysis of **1** has been performed to confirm its molecular structure. The molecular structure of **3** with the same ligand has been published in a previous paper.[6] Crystals of **1** were obtained from slow evaporation of a toluene solution. Figure 1 shows a perspective view of the molecular structure; crystal data, selected bond angles and distances, and atomic parameters for **1** are presented in Tables I–III, respectively.

The $Fe_2(CO)_6$ moiety in **1** is bridged by the new betaine ligand $S{=}C(O^-)C({=}S)P^+(NMe_2)_3$, and coordination to the metal atoms occurs via the sulfur atoms. The Fe_2S_2 core of the molecule has a butterfly arrangement, and the two Fe_2S planes form a dihedral angle of 79.88°. The atoms S(1), S(2), C(7), C(8), O(8), and P are essentially in one plane; the deviations of the atoms from the best S_2C_2 plane are collected in Table IV. The deviations of the iron atoms from the best plane of the ligand are 126(1) and −124(1) pm, respectively. The two Fe_2S planes are perpendicular to the ligand plane.

The nonbonding S···S separation of 287.7 pm is comparable to that in other compounds in which a bridge of two atoms connects the sulfur atoms and is longer than in similar compounds with a single atom bridge. However, in **3**, where the S atoms coordinate at one Fe atom, the nonbonding separation has increased to 302 pm.

Distances and angles within the ligands of **3** and **1** are very similar, and a comparison of the important parameters

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Table I. Crystallographic Data for 1

compd	$Fe_2(CO)_6(\mu\text{-}S_2COCP(NMe_2)_3)$
formula	$C_{16}H_{36}FeN_6P_2S_2$
space group	*Pbca*, orthorhombic
Z	8
cell params	
a, pm	1513.1(3)
b, pm	1324.3(1)
c, pm	2278.4(2)
V, pm^3	4567 × 10^6
d_{calcd}, g/cm^3	1.59
temp, °C	20
radiation	Cu Kα, graphite monochromated
diffractometer	CAD4
no. of rflns for the determination of cell params	24
scan range, deg; scan method	$2 < \theta < 65$; ω scan
no. of indep rflns	3733
no. of obsd rflns	1483 ($F_o > 4\sigma(F_o)$)
cor	Lorentz and polarizn factor, numeric abs cor for μ = 78.7 cm^{-1} [11]
structure determination	direct methods[10]
refinement	H atoms of the CH_3 groups calcd as rigid groups with different fixed isotropic temp factors for each methyl group (C–H = 96 pm, H–C–H = 109.5°)
programs	SHELXTL,[1] PLATON[12–14]
atomic factors	
R,[a] %	6.2
R_w,[b] %	4.1
wR,[c] %	3.5

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w^{1/2}||F_o| - |F_c||)/(\sum w^{1/2}|F_o|)$; $w = 1/\sigma^2(F)$. [c] $wR = [(\sum w(|F_o| - |F_c|)^2/(\sum wF_o^2)]^{1/2}$.

is shown in Table V. The change from being a chelating donor to one metal to acting as a donor to two metals is accompanied by an increase of nearly all bond distances with the exception of the C—C bond, which slightly shortens from 143 pm in **3** to 137 pm in **1**, suggesting a slightly increasing double-bond character.

The ligand common to **3** and **1** exhibits remarkable differences in the orientation of the amino groups in the solid state. Whereas in **1** one nitrogen (N(3)) is in a position cis to the carbonyl oxygen atom, an approximate trans position is found in **3**. In Table IV the deviations of atoms from the best planes formed by the C_2S_2 unit are compared. It shows that in **1** planarity is achieved for seven atoms with deviations below 10 pm. In **3** the phosphorus atom P(1) and the trans nitrogen of the C-bonded $P(NMe_2)_3$ group are turned out of the plane to the same side by 20 and 64 pm, respectively. This deviation from ligand planarity in the solid state is probably caused by packing effects, due to the less symmetric $Fe(CO)_2P(NMe_2)_3$ metal fragment in **3** with respect to the symmetric $Fe_2(CO)_6$ fragment in **1**.

Whereas **1** has a noncrystallographic plane of symmetry, the ligand arrangement in **3** in the solid state is trigonal bipyramidal with one CO group in the axial position and the other one in the equatorial position, thus producing no symmetry plane. This leads to chirality at iron in **3**, and according to the centrosymmetric space group $P2_1/n$, the four molecules in the unit cell consist of two pairs of racemates.

Discussion

The Ligand. The new unusual ligand in **1**–**3** can be considered as a betaine which is formally the result of an adduct of the unknown ylide S=C=P(NMe$_2$)$_3$ at COS.

Table II. Selected Distances and Angles in $Fe_2(CO)_6S_2COCP(NMe_2)_3$ (1)

	Distances (pm)		
Fe(1)–Fe(2)	249.9(3)	C(7)–C(8)	137(2)
Fe(1)–S(1)	224.7(3)	C(8)–O(8)	124.6(14)
Fe(1)–S(2)	226.4(4)	C(7)–P	174.5(10)
Fe(2)–S(1)	225.0(4)	P–N(1)	165.8(10)
Fe(2)–S(2)	225.6(3)	P–N(2)	165.6(10)
Fe(1)–C(1)	176.2(14)	P–N(3)	164.2(9)
Fe(1)–C(2)	182(2)	C(1)–O(1)	113(2)
Fe(1)–C(3)	179.2(12)	C(2)–O(2)	114(2)
Fe(2)–C(4)	183(2)	C(3)–O(3)	113.2(14)
Fe(2)–C(5)	183.1(11)	C(4)–O(4)	111(2)
Fe(2)–C(6)	176.6(14)	C(5)–O(5)	112.1(14)
S(1)–C(7)	178.0(9)	C(6)–O(6)	116(2)
S(2)–C(8)	188.1(12)		
	Angles (deg)		
Fe(2)–Fe(1)–S(1)	56.3(1)	N(1)–P–N(2)	110.3(5)
Fe(2)–Fe(1)–S(2)	56.28(9)	N(1)–P–N(3)	109.3(5)
Fe(1)–Fe(2)–S(2)	56.6(1)	N(2)–P–N(3)	103.8(5)
Fe(1)–Fe(2)–S(1)	56.2(1)	S(1)–Fe(1)–C(1)	105.6(5)
S(1)–Fe(2)–S(2)	79.4(1)	S(1)–Fe(1)–C(2)	153.9(5)
S(1)–Fe(1)–S(2)	79.3(1)	S(1)–Fe(1)–C(3)	89.6(5)
Fe(1)–S(1)–Fe(2)	67.5(1)	S(2)–Fe(1)–C(1)	102.0(4)
Fe(1)–S(2)–Fe(2)	67.1(1)	S(2)–Fe(1)–C(2)	89.3(5)
Fe(2)–Fe(1)–C(1)	151.8(4)	S(2)–Fe(1)–C(3)	159.1(4)
Fe(2)–Fe(1)–C(2)	97.9(5)	S(1)–Fe(2)–C(4)	159.2(4)
Fe(2)–Fe(1)–C(3)	102.8(4)	S(1)–Fe(2)–C(5)	92.7(4)
Fe(1)–Fe(2)–C(4)	103.0(5)	S(1)–Fe(2)–C(6)	99.1(5)
Fe(1)–Fe(2)–C(5)	100.7(4)	S(2)–Fe(2)–C(4)	88.0(4)
Fe(1)–Fe(2)–C(6)	147.3(5)	S(2)–Fe(2)–C(5)	156.6(4)
Fe(2)–S(1)–C(7)	102.5(4)	S(2)–Fe(2)–C(6)	101.4(5)
Fe(1)–S(1)–C(7)	105.2(3)	C(1)–Fe(1)–C(2)	99.7(7)
Fe(2)–S(2)–C(8)	102.1(4)	C(1)–Fe(1)–C(3)	98.0(6)
Fe(1)–S(2)–C(8)	102.0(4)	C(2)–Fe(1)–C(3)	93.4(6)
S(1)–C(7)–C(8)	116.1(8)	C(4)–Fe(2)–C(5)	92.5(6)
S(2)–C(8)–O(8)	114.7(8)	C(4)–Fe(2)–C(6)	99.6(7)
O(8)–C(8)–C(7)	133(1)	C(5)–Fe(2)–C(6)	101.6(6)
S(1)–C(7)–P	120.8(6)	Fe(1)–C(1)–O(1)	178(1)
P–C(7)–C(8)	122.7(8)	Fe(1)–C(2)–O(2)	178(1)
S(2)–C(8)–C(7)	112.3(8)	Fe(1)–C(3)–O(3)	178(1)
N(1)–P–C(7)	108.1(6)	Fe(2)–C(4)–O(4)	176(1)
N(2)–P–C(7)	112.7(5)	Fe(2)–C(5)–O(5)	177(1)
N(3)–P–C(7)	112.7(5)	Fe(2)–C(6)–O(6)	176(1)

Betaine-like species have earlier been postulated to be intermediates in the Wittig reaction,[15] but they have not been identified. In the dinuclear compounds **1** and **2** this betaine acts as a six-electron donor to two metal atoms, whereas in the mononuclear species **3** only the donation of four electrons is necessary to one metal center. This behavior is a common feature for all ligands of the general type E=C(R)-C(R)=E (E = O, S, NR, PR). Coordination to a mononuclear center can be described with different oxidation states, M^n or M^{n+2} (Scheme I), of the central metal atom. Touchard and Dixneuf described a similar pair of compounds, in which a bidentate tetrathiooxalato ligand (R = SMe, E = S, and M = $Fe(CO)_2P(C_6H_5)_3$) is involved. It was obtained by the dimerization of a η^2-S=CSMe radical complex formed from a one-electron-reduction process.[16]

1 and **2** belong to the large family of the well-known "butterfly" derivatives $Fe_2(CO)_6(\mu\text{-}S\text{-}A\text{-}S)$. The sulfur atoms in these kinds of compounds can be bridged by various groups A, consisting of C_1, C_2, C_n, B_1, B_2 fragments, of transition metals with further ligands or even of a single bond, as in the neutral compound $Fe_2(CO)_6S_2$.[17] In the

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Table III. Atomic Parameters for $Fe_2(CO)_6S_2COCP(NMe_2)_3$ (1)

atom	*x*	*y*	*z*	U_{eq}/U_{iso}, Å^2
Fe(1)	0.6443(1)	0.3202(2)	0.07590(7)	0.0572(8)
Fe(2)	0.5465(1)	0.1722(2)	0.05568(7)	0.0531(7)
S(1)	0.4960(2)	0.3263(3)	0.0803(1)	0.049(1)
S(2)	0.6169(2)	0.1962(2)	0.1418(1)	0.045(1)
P	0.3816(2)	0.3773(3)	0.1873(1)	0.048(1)
O(1)	0.7030(7)	0.4830(8)	0.1510(4)	0.099(5)
O(2)	0.8158(6)	0.2247(9)	0.0467(5)	0.125(6)
O(3)	0.6417(7)	0.4323(8)	−0.0346(3)	0.124(5)
O(4)	0.6695(7)	0.0053(9)	0.0309(5)	0.140(7)
O(5)	0.5113(6)	0.2046(8)	−0.0703(3)	0.101(5)
O(6)	0.3934(7)	0.0560(8)	0.0954(4)	0.113(6)
O(8)	0.5321(5)	0.2332(6)	0.2416(3)	0.065(4)
N(1)	0.3962(8)	0.4992(7)	0.1739(4)	0.057(5)
N(2)	0.2843(6)	0.3398(7)	0.1622(4)	0.050(4)
N(3)	0.3741(7)	0.3595(8)	0.2585(4)	0.061(4)
C(1)	0.6818(9)	0.419(1)	0.1213(5)	0.074(7)
C(2)	0.749(1)	0.260(1)	0.0588(5)	0.079(7)
C(3)	0.6411(9)	0.389(1)	0.0081(5)	0.077(6)
C(4)	0.625(1)	0.071(1)	0.0401(6)	0.075(7)
C(5)	0.5226(8)	0.192(1)	−0.0223(5)	0.065(6)
C(6)	0.4545(9)	0.099(1)	0.0780(6)	0.070(7)
C(7)	0.4696(6)	0.3113(8)	0.1559(4)	0.032(4)
C(8)	0.5277(8)	0.2544(9)	0.1884(5)	0.052(5)
C(11)	0.3246(9)	0.572(1)	0.1844(6)	0.088(7)
C(12)	0.485(1)	0.547(1)	0.1638(7)	0.089(7)
C(21)	0.2735(8)	0.318(1)	0.0997(4)	0.089(6)
C(22)	0.1984(8)	0.359(1)	0.1930(5)	0.080(7)
C(31)	0.3449(8)	0.261(1)	0.2819(5)	0.089(7)
C(32)	0.4266(9)	0.419(1)	0.3007(5)	0.094(7)

Table IV. Deviation of Atoms (in pm) from the Best Plane Formed by the Elements S(1), S(2), C(7), and C(8) of 1 and the Corresponding Atoms of 3

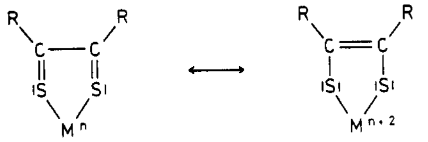
1		3[a]	
atom	dev	atom	dev
S(1)	1.4	S(1)	2.1
S(2)	−1.3	S(2)	−2.0
C(7)	−2.9	C(1)	−4.4
C(8)	2.8	C(2)	4.3
O(8)	8.4	O(1)	11.7
P	2.8	P(1)	−20.0
N(3)	9.4	N(11)	−64.0
		Fe	0.2

[a] The atoms of 3 are numbered as shown in ref 6.

Table V. Comparison of Corresponding Distances (Å) and Angles (deg) of the Ligand in 1 and 3

	1	3	*d*(1–3)
S(1)–C(7)	1.780(9)	1.750(7)	0.03
C(7)–C(8)	1.37(2)	1.43(1)	−0.06
C(8)–O(8)	1.24(1)	1.246(14)	0.006
C(7)–P	1.745(10)	1.727(7)	0.018
C(8)–S(2)	1.881(12)	1.778(8)	0.103
S(1)···S(2)	2.88	3.02	−0.14
S(1)–C(7)–P	120.8(6)	115.3(4)	5.5
C(7)–C(8)–S(2)	112.3(8)	115.5(6)	−3.2
S(1)–C(7)–C(8)	116.1(8)	117.8(5)	−1.7
P–C(7)–C(8)	122.7(8)	126.8(6)	−4.1
O(8)–C(8)–S(2)	114.7(8)	119.0(6)	−4.3
C(7)–C(8)–O(8)	133.0(10)	125.5(7)	7.5

Scheme I



case of 1 and 2, the bridging unit A is the unknown ylide-like compound $O{=}C{=}C{=}P(NMe_2)_3$ and 1 can formally be considered to be the result of a [2 + 2] cycloaddition of this species with $Fe_2(CO)_6S_2$. Structural parameters are known for similar compounds with the C_1 fragments CO,[18] CH_2,[19,20] $CHCH_2Ac$,[21] and C=;[22] the structures of compounds with C_2 fragments as bridging groups are known for A = CH_2CH_2[23] and PhC=CPh.[24] All parameters of 1 concerning the $Fe_2(CO)_6S_2$ core are in accordance with the parameters of the latter species, including nonbonded S···S interactions.

1 and 2 can also be viewed as derivatives of the class of β-keto ylides $O{=}C(R)C(R'){=}P(NMe_2)_3$, in which R and R′ are the units $Fe_2S_2(CO)_6$ and $Fe_2S_2(CO)_5P(NMe_2)_3$, respectively.

Mechanistic Considerations. The preferred formation of the chelating ligand of 1–3 from the starting materials cannot be understood, and the mechanism of formation is as yet unknown. Some suggestions, however, can be made if known reactions between carbonyls, CS_2, phosphines, and phosphine sulfides are taken into account.

The reaction is probably initiated by a nucleophilic addition of the aminophosphine at the thiocarbonyl carbon atom in the first step to give an unstable adduct. A similar attack was also proposed in the reaction of $P(NMe_2)_3$ with CS_2, which ultimately leads to an insertion of CS_2 into all three PN bonds.[25] Some adduct material decomposes into 4, probably forming a highly reactive $(CO_4Fe{\equiv}C$ fragment. Replacement of one CO group by the sulfide 4 followed by an S-transfer from coordinated 4 to an adjacent CO group could lead to a further intermediate of the composition $(CO)_2Fe(\eta^2\text{-}S{=}C{=}P(NMe_2)_3)(\eta^2\text{-}S{=}C{=}O)P(NMe_2)_3$. A subsequent C—C coupling between the CS carbon atoms in the coordination sphere of the metal could generate 3. The dinuclear complex 1 may be formed upon action of a $Fe(CO)_4$ fragment on one of the intermediates. 2 is derived from 3 by insertion of the 14-electron fragment $Fe(CO)_3$ into one of the Fe—S bonds.

The transition metal carbonyl induced desulfurization of $S{=}PR_3$ compounds was observed earlier by the reaction of $S{=}P(C_6H_5)_3$ or $Se{=}P(C_6H_5)_3$ with $Fe(CO)_5$, producing both a mixture of $(CO)_4FeP(C_6H_5)_3$ and $(CO)_3Fe(P(C_6H_5)_3)_2$ and no species with a coordinated phosphine selenide or sulfide.[7]

Although some of the intermediates proposed have stable parallels in the literature, the mechanism remains speculative at the present time, because a reaction product containing the 20-electron fragment $(CO)_4Fe{\equiv}C$ which should be generated after splitting off 4 from the adduct could not be isolated. The isolobal relationship $S{=}C \leftarrow\!\!\!\!\circ\!\!\!\!\rightarrow (CO)_4Fe{\equiv}C$ accounts for a highly reactive species and is probably responsible for the tarry, CO-containing material, additionally isolated. An alternative pathway would be the transfer of the former CS carbon atom to phosphines with formation of the known bis-ylide $(NMe_2)_3P{=}C{=}P$-

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$(NMe_2)_3$, but a signal for this compound (27.72 ppm[26]) could not be detected. Another route to the butterfly unit via the reactive intermediate $S{=}Fe(CO)_4$ was pointed out recently by Ando et al.[27]

Probably as a result of the strong desulfurizing properties of $P(NMe_2)_3$, no complex with an intact CS ligand (terminal or bridging) has yet been isolated. Products which arise from splitting of a PN bond as occurs with CS_2 could also not be detected.

Experimental Section

General Data. The reactions were carried out under an atmosphere of dry nitrogen in dried and degassed solvents. Column chromatography was performed with a 200 × 20 mm column packed with silanolized silica gel (Merck). The IR spectra were run on a Perkin-Elmer 457 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 300 instrument. The electron injection (EI) mass spectrum was measured on a CH7 MAT instrument. Microanalyses were performed by the analytical service of the Fachbereich Chemie der Universität Marburg (Marburg, Germany). $Fe(CO)_4CS$ was prepared as described in the literature;[28] commercially available $P(NMe_2)_3$ (Merck) was used without further purification.

Reaction of $Fe(CO)_4CS$ with $P(NMe_2)_3$. To a solution of 2 mL of $P(NMe_2)_3$ in about 50 mL of pentane was added dropwise at 0 °C with vigorous stirring a solution of 410 mg (1.93 mmol) of freshly prepared $Fe(CO)_4CS$ in 20 mL of pentane over a period of 40–50 min. The resulting violet-brown solution was stirred for an additional 1 h and then allowed to stand for 4 days in the dark. Violet crystals of **3** separated along with a brown oily material. The crystals were separated by filtration. The solution was decanted from the brown oily material; removal of all volatile products from the violet solution left a violet oil, which was extracted with about 40 mL of pentane. The residue was identified as impure **3** and recrystallized from toluene/pentane at −20 °C. IR: $\nu(C{=}O)$ 1525 (m) cm^{-1}; terminal CO 1977 (s), 1920 (s) cm^{-1}. ^{31}P NMR (C_6D_6): 54.56 (PC), 167.53 (PFe) ppm. Anal. Calcd for $C_{16}H_{36}FeN_6P_2S_2$: C, 35.43; H, 6.69; N, 15.50. Found: C, 34.35; H, 6.43; N, 15.03.

The pentane solution was subjected to column chromatography (silanolized silica gel/pentane). Pentane eluted a yellow band which gave a mixture of small amounts of **5** and **6**.

Further elution with toluene yielded a red band, which gave a red oil after evaporation of the solvent. When this oil was allowed to stand for about 3 weeks under Ar, red crystals were obtained, which were identified as **1**. IR (Nujol): $\nu(C{=}O)$ 1644 (s) cm^{-1}; terminal CO 2073 (s), 2025 (s), 1996 (vs), 1985 (vs), 1972 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 2.07 (d, CH_3N, $J(P,H)$ = 9.67 Hz). ^{13}C NMR (C_6D_6): δ 36.80 (d, CH_3N, $J(P,C)$ = 4.53 Hz), 209.76 (s, CO). ^{31}P NMR (toluene-d_8): 54.58 ppm. Anal. Calcd for $C_{14}H_{18}Fe_2N_3O_7PS_2$: C, 30.73; H, 3.32; N, 7.68. Found: C, 30.93; H, 3.32; N, 7.98. The remaining red oil was identified as **2**. IR (Nujol): $\nu(C{=}O)$ 1610 cm^{-1}; terminal CO 2045 (s), 1968 (vs), 1955 (sh), 1932 (s) cm^{-1}. ^1H NMR (toluene-d_8): δ 2.20 (CH_3N, $J(P,H)$ = 9.64 Hz), 2.59 (CH_3N, $J(P,H)$ = 8.86 Hz). ^{13}C NMR: δ 37.03 (CH_3N, $J(P,C)$ = ca. 4 Hz), 38.97 (CH_3N, $J(P,C)$ = ca. 4 Hz), 212.37 (s, CO), 217.37 (d, CO, $J(P,C)$ = 25.14 Hz), 218.00 (d, CO, $J(P,C)$ = ca. 20 Hz). Mass spectrum: m/z 654 $[M - CO]^+$, 598 $[M - 3\ CO]^+$, 542 $[M - 5\ CO]^+$. The average yields from several runs were about 8% of **3** and about 15% of **1** and **2** with respect to $Fe(CO)_4CS$; **5** and **6** were only formed in trace amounts.

X-ray Data Collection. A red crystal (0.08 × 0.21 × 0.49 mm) was sealed in a glass capillary and mounted on a CAD4 diffractometer (Enraf-Nonius, Delft, The Netherlands) equipped with Cu Kα radiation. Least-squares refinement of the data of 24 reflections ($25° < \theta < 40°$) yielded accurate cell parameters. Intensity data collection was done using the ω-scan mode. Twenty-five percent of the peak width was measured on each side of the peak to get the background level. Every 2 h two standard reflections were scanned for intensity control. Orientation was checked every 250 reflections by scanning two selected reflections. As no significant variation was detected, it was not necessary to apply any correction. A total of 4177 reflections were scanned ($2° < \theta < 65°$: h, 0–13; k, 0–17; l, 0–26), including 384 systematically absent ones. Selection for σ ($F_o > 4\sigma_{F_o}$) left 1483 observed reflections, which were subjected to a numeric absorption correction.[11]

Structure Solution. Systematic absences indicated the orthorhombic space group *Pbca*, which was confirmed in the course of the calculation. Fe, S, and several light-atom positions were obtained by direct methods;[11] the rest of the light-atom positions resulted from subsequent least-squares and difference Fourier syntheses, whereas all hydrogen atoms were calculated as part of rigid groups with tetrahedral geometry (C–H = 96 pm, H–C–H = 109.5°) and with different fixed isotropic thermal parameters for each methyl group. The other atoms were refined anisotropically. Full-matrix refinement converged at $R = 6.2\%$ with $R_w = 4.1\%$ and $wR = 3.5\%$. The highest peak in the final difference Fourier map was 0.43 Å^3. The positional and equivalent thermal parameters are given in Table III. Table I contains a summary of X-ray experimental data; the complete anisotropic thermal parameters are available as supplementary material (see the paragraph at the end of the paper).

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Supplementary Material Available: Tables of atomic positions, equivalent isotropic thermal parameters, and anisotropic thermal displacement coefficients (2 pages). Ordering information is given on any current masthead page.

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