

Reactivity of $[Fe_2(CO)_6(\mu-S_2)]$ toward a Base-Containing Diphosphine $(Ph_2PCH_2)_2NCH_3$: Formation of Diiron Carbonyl Compounds Having Polydentate Heterofunctionalized Phosphine $(PNS = Ph_2PCH_2N(CH_3)CH_2S)$ and Bidentate Thiophosphinito $(Ph_2PS = PS)$ Bridges

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Reaction of the base-containing diphosphine $(Ph_2PCH_2)_2NCH_3$ with $[Fe_2(CO)_6(\mu-S_2)]$ (1) yielded at room temperature the novel compound $[Fe_2(CO)_4(\mu-\kappa^1:\kappa^1-SPPh_2)\{\mu-\kappa^2:\kappa^2-SCH_2N(Me)CH_2-PPh_2\}]$ (2) resulting from S–S and P–C bond cleavage concomitant with P–S and C–S bond formation. Experiments at low temperature allowed the isolation of an intermediate species, $[Fe_2(CO)_5-(\mu-\kappa^1:\kappa^1-SPPh_2)\{\mu-\kappa^2:\kappa^1-SCH_2N(Me)CH_2PPh_2\}]$ (3), differing from 2 by the coordination mode of the PNS ligand and the presence of one additional carbonyl group. When the reaction was performed in the presence of an excess of *t*BuNC, an analogous compound of 3 was obtained. The X-ray analysis of this species, 4, revealed that an isocyanide replaced a carbonyl ligand in the axial position at one iron center.

Introduction

In quest for [2Fe2S] or [2Fe3S] electrocatalyst species, bioinspired by the active site of [FeFe]-hydrogenases, for the reduction of protons to dihydrogen, the chemistry of organometallic carbonyl diiron molecules with a sulfur environment has been widely investigated during the past decade.¹ The recent and fast advances in the understanding of the functioning of the active site of [FeFe]-hydrogenases have been possible because of the numerous and systematic studies concerning bis-thiolate hexacarbonyl diiron chemistry that have been performed during the last forty years.² In this context, the μ -dithio-bis(tricarbonyl iron) complex $[Fe_2(CO)_6(\mu-S_2)]$ (1)³ is one of the major precursors of bioinspired models of the H-cluster because it allows obtaining easily functionalized dithiolate (aza- and oxa-dithiolate) diiron molecules.⁴

It is well known that the chemical activity of **1** is mainly centered on the dithio bridge. In the presence of reducing reagents, such as LiBHEt₃, the single S-S bond is broken, giving a bridging disulfido species that could be protonated at the sulfur atoms to afford a dihydrosulfido compound (Scheme 1).⁵

In the continuity of our work concerning the use of bidentate ligands, such as diphosphine, phenanthroline, and N-heterocyclic carbene, in diiron molecules having a propane- or aza-dithiolate bridge,⁶ we have explored the reactivity of the dithio precursor **1** toward diphosphine in view to synthesize novel dissymmetrically substituted diiron systems containing a simple dithio functionality as a bridge.

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50°C, 4h

We report here the reaction of the complex $[Fe_2(CO)_6-(\mu-S_2)]$ (1) with the base-containing diphosphine $(Ph_2PCH_2)_2-NCH_3$ that leads to the formation of novel compounds featuring a bridging polydentate heterofunctionalized phosphine (PNS = $Ph_2PCH_2N(CH_3)CH_2S$) and a bidentate thiophosphinito μ -Ph_2PS group.

Results and Discussion

The reaction of $[Fe_2(CO)_6(\mu-S_2)]$ (1) with 1 equiv of (Ph₂PCH₂)₂NCH₃ was performed in CH₂Cl₂ at 20 °C. IR and ${}^{31}P{}^{1}H$ NMR monitoring revealed that 1 is readily transformed within 1 h. The ³¹P{¹H} NMR spectrum of the solution indicates a mixture of three compounds (2, 3, and 3'), each of them characterized by a doublet of doublets with coupling constants lower than 8 Hz (Figure 1). A prolonged ³¹P{¹H} NMR monitoring for several hours showed the gradual disappearance of signals of 3 and 3' over time. After 36 h, only the phosphorus signals of 2 were detected. The synthesis of 2 can also be carried out by heating the reaction mixture in toluene at 50 °C for 4 h. After crystallization in CH₂Cl₂-hexane, 2 was obtained pure as an orange powder with moderate yields (60%). The IR spectrum of 2 in CH₂Cl₂ displays four strong bands at 1991, 1952, 1926, and 1897 cm⁻¹ in the ν (CO) region. ¹H NMR shows the signals of phenyl and methyl groups at the expected chemical shifts with a ratio of 20:3. Each proton of the methylene groups of the diphosphine (Ph₂PCH₂)₂NCH₃ appears as a multiplet between 5 and 2 ppm. The ${}^{31}P{}^{1}H$ NMR indicates that the two phosphorus atoms are inequivalent and the coupling constant $J_{\rm PP}$ of 7.3 Hz does not accord with that of a typical chelated diphosphine at one iron center.6a

These spectroscopic data are compatible with the results of a single-crystal X-ray diffraction study of **2**. Single crystals of **2** were obtained at -20 °C from a dichloromethane-hexane (1:1) solution. Their X-ray analysis reveals that the S–S bond in **1** and one P–C bond in the diphosphine have been cleaved with concomitant formation of P–S and S–C bonds, giving the two bridging Ph₂PS (PS) and Ph₂PCH₂N-(CH₃)CH₂S (PNS) ligands (Figure 2). Relatively facile P–C cleavage at diiron centers has been previously reported.⁷ **2** is isostructural with rare complexes having a butterfly $\{Fe_2(\mu - \mu)\}$ SR) $(\mu - \mu - \kappa^1 : \kappa^1 - SPPh_2)$ core with triangular Fe₂P and tetragonal Fe₂P₂ wings, recently reported by Song et al and which are obtained through the reaction of the S-centered anion $[Fe_2(CO)_6(\mu-SR)(\mu-S)]^-$ with Ph₂PCl.⁸ The geometry around each iron atom could be described as a distorted trigonal bipyramid supplemented by a Fe-Fe single bond (2.6315(7) Å), two carbonyl groups, and a bridging sulfur atom of the PNS group lying in the equatorial plane. The major structural features of 2 are the bridging bidentate thiophosphinito Ph₂PS group and the new polydentate heterofunctionalized phosphine Ph₂PCH₂N(CH₃)CH₂S ligand, which are coordinated to the diiron site in a μ - κ^{1} : κ^{1} and μ - κ^{2} : κ^{2} fashion, respectively. The six-membered heterometallacycle {FePCNCS} adopts a chair conformation that is constrained due to the coordination of the nitrogen atom to the second iron center.

In order to identify the kinetic products of the reaction, 3 and 3', the reaction between 1 and 1 equiv of $(Ph_2PCH_2)_2$ -NCH₃ was realized in CH₂Cl₂ at low temperature (-45 °C). After 15 min of stirring, the red solution was evaporated, giving a red powder. ${}^{31}P{}^{1}H$ NMR of a CDCl₃ solution of this powder indicates only the presence of the two expected species 3 and 3', with a ratio of 80:20. The ¹H NMR spectrum of this mixture in CDCl₃ indicates that each of these species is characterized by a set of signals similar to that observed for 2, which can be assigned to C₆H₅, CH₂, and CH₃ groups with the expected ratio 20H/4×1H/3H, suggesting that the structures of these three compounds are very close. The cooling at -20 °C of a solution of 3-3' in dichloromethane-hexane (1:1) afforded single crystals that were analyzed by X-ray diffraction and assigned arbitrarily to 3. The analysis revealed that the main difference between the structures of 2 and 3 is the coordination of the PNS ligand that is now bound to the diiron site through the bridging sulfur atom and the PPh₂ group in a μ - κ^2 : κ^1 fashion (Figure 3).

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Figure 1. ${}^{31}P{}^{1}H$ NMR spectrum (in CDCl₃) of a mixture of 2, 3, and 3' (\triangle and *) arising from the reaction of [Fe₂(CO)₆(μ -S₂)] (1) with 1 equiv of (Ph₂PCH₂)₂NCH₃ in CH₂Cl₂ at 20 °C.



Figure 2. View of the molecule of $[Fe_2(CO)_4{\{\mu-\kappa^1:\kappa^1-SPPh_2\}}](\mu-\kappa^2:\kappa^2-SCH_2N(Me)CH_2PPh_2]]$ (**2**·2CH₂Cl₂) showing 50% probability ellipsoids. CH₂Cl₂ molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1–Fe2, 2.6315(7); Fe1–S1, 2.2697(9); Fe2–S1, 2.2633(10); Fe1–S2, 2.3541(10); Fe2–P2, 2.2035(10); Fe1–P1, 2.1738(10); P2–S2, 2.0393(12); Fe2–N1, 2.093(3); C51–S1, 1.827(4); Fe2–S1–Fe1, 70.97(3); P2–S2–Fe1, 88.46(4); S2–P2–Fe2, 104.58(5).

It has to be pointed out that the PPh_2 group of the PNS ligand lies in the equatorial plane instead of the axial position. An additionnal carbonyl ligand completes the coordination sphere of the iron atom at which the amine

functionality is not coordinated (Figure 3), and the metallacycle adopts the favored chair conformation with the methyl group in equatorial position. This structure suggests that the transformation of 3 into 2 consists in the replacement of one carbonyl group by the amine functionality of the PNS group (Scheme 3). We tentatively assign 3' to an isomer that may differ by the coordination of the PPh₂ group in an axial position as depicted in Scheme 3. According to our experimental results, it was not possible to specify whether 3 or 3' is the major or the minor product of this mixture. The ${}^{31}P{}^{1}H{}$ NMR spectrum of a sample, in $CDCl_3$, of 3-3' stored as a powder at -20 °C during one month indicates the presence of 2 in the mixture. This reveals that even in these conditions of storage the decarbonylation process occurs. Such a transformation of 3-3' into 2 was confirmed on stirring a dichloromethane solution of a mixture of 3-3' for a few hours at room temperature, as shown in Scheme 3.

The reaction of 1 with $(Ph_2PCH_2)_2NCH_3$ in CH_2Cl_2 at room temperature was also performed in the presence of tBuNC in the hope of isolating stable analogues of 3-3', by replacing a carbonyl group by the more electron-donating isocyanide ligand. Such substitutions were previously involved when phosphine ligands react with $[Fe_2(CO)_6(\mu X_2$] (X = S, Se) complexes to lead to mono- and disubstituted derivatives [Fe₂(CO)_{6-x} $L_x(\mu$ -X₂)] (x = 1, 2).⁹ A mixture of 2, 3-3', and new compounds 4-4' was obtained according to NMR analysis. The ${}^{31}P{}^{1}H$ NMR spectrum of a solution of this mixture in CDCl₃ displays two novel sets of two apparent singlets (at 85.5 and 50.0 ppm for the major product and 79.4 and 54.7 ppm for the minor one, with a ratio of 60:40), which were assigned to compounds 4 and 4'. ¹H NMR data of these species could not be assigned with a sufficient accuracy to report them. It was not possible to separate satisfactorily all products by chromatography on silica gel. The cooling at -30 °C of the reaction solution in dichloromethane after addition of hexane afforded single

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Figure 3. View of the molecule of $[Fe_2(CO)_5(\mu - \kappa^1 : \kappa^1 - SPPh_2) \{\mu - \kappa^2 : \kappa^1 - SCH_2N(Me)CH_2PPh_2\}]$ (**3**·CH₂Cl₂) showing 50% probability ellipsoids. CH₂Cl₂ is omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1-Fe2, 2.6569(6); Fe1-S1, 2.2349(9); Fe2-S1, 2.2629(9); Fe1-S2, 2.3640(9); Fe2-P2, 2.2644(9); Fe1-P1, 2.2074(9); P2-S2, 2.0368(11); C51-S1, 1.828(3); Fe2-S1-Fe1, 72.41(3); P2-S2-Fe1, 88.62(4); S2-P2-Fe2, 106.06(4).



crystals of **4**. The X-ray analysis revealed that **4** has a structure similar to that of **3** with a six-membered metallacycle {FePCNCS} in a chair conformation, which is coordinated to the diiron core in a μ - κ^2 : κ^1 fashion through sulfur and phosphorus atoms. The *t*BuNC ligand replaces a carbonyl group in an axial position at one iron atom (Figure 4).

The IR spectrum of a solution of these single crystals in dichloromethane displays a ν (CN) band at 2147 cm⁻¹ and three strong ν (CO) bands at 1990, 1952, and 1916 cm⁻¹. No replacement of one carbonyl group with an isocyanide in 1 or 2 was observed in the same experimental conditions. This suggests that 3 and 3' are the precursors of the isocyanide compounds 4 and 4', as summarized in Scheme 4. As we did for 3 and 3', we propose that 4 and 4' are two isomers differing by the equatorial or axial position of the PPh₂ group of the metallacycle as depicted in Scheme 4, but their difference could also be related to equatorial or axial coordination of the *t*BuNC ligand.

It has to be pointed out that single crystals of a side product were obtained in some crystallization attempts. Their X-ray analysis revealed that the diphosphine disulfide molecule, $\{Ph_2P(S)CH_2\}_2NMe$ (5) (see Figure 5 in Supporting Information), is formed in some experiments. The formation of 5 is not uncommon, but to the best of our knowledge its structure has never been reported. **5** could be obtained by sulfurization of the diphosphine due to either partial decomposition of **1** or the presence of sulfur-containing impurities in the reactional mixture. NMR data of **5** in CDCl₃ were similar to those of a sample obtained by straigthforward reaction of the diphosphine with sulfur. The signal of the two equivalent phosphorus atoms is observed as a singlet at 35.6 ppm in the ³¹P{¹H} NMR spectrum (CDCl₃). A ¹H NMR recording shows typical signals of C₆H₅, CH₂, and CH₃ groups (see experimental data).

Conclusion

Novel diiron complexes with polydentate heterofunctionalized (PNS) phosphine and bidentate thiophosphinito ligands have been obtained from the reaction of $[Fe_2(CO)_6-(\mu-S_2)]$ (1) with the base-containing diphosphine (Ph₂-PCH₂)₂NCH₃. Unfortunately, their unstability in acidic media and reducing conditions limits their use as electrocatalysts for the reduction of protons. Use of robust chelating ligands with a lower affinity toward sulfur such as 1,10phenanthroline and other cyclic base-containing diphosphines is now under investigation.



Figure 4. View of the molecule of $[Fe_2(CO)_4(tBuNC)(\mu-\kappa^2:\kappa^1-SPPh_2)\{\mu-\kappa^2:\kappa^1-SCH_2N(Me)CH_2PPh_2\}]$ (4·C₆H₁₄) showing 50% probability ellipsoids. Hexane is omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1–Fe2, 2.6350(10); Fe1–S1, 2.2501(14); Fe2–S1, 2.2583(14); Fe1–S2, 2.3534(14); Fe2–P2, 2.2384(14); Fe1–P1, 2.2067(15); P2–S2, 2.0449(17); C51–S1, 1.824(5); Fe2–C65, 1.886(6); C65–N60, 1.139(6); Fe2–S1–Fe1, 71.53(4); P2–S2–Fe1, 88.98(6); S2–P2–Fe2, 105.78(7).



Experimental Section

General Procedures. All the experiments were carried out under an inert atmosphere, using Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. $[Fe_2(CO)_6(\mu-S_2)]^3$ and $(Ph_2PCH_2)_2$ -NCH₃ (PNP)¹⁰ were prepared according to reported procedures. Other reagents were purchased from the usual commercial suppliers and used as received. The NMR spectra (${}^{1}H$, ${}^{31}P$) were recorded at room temperature in CDCl₃ solution with Bruker DRX 500, Bruker AMX 400, or AC300 spectrometers and were referenced to SiMe₄ (${}^{1}H$) and H₃PO₄ (${}^{31}P$). The infrared spectra were recorded on a Nicolet Nexus Fourier transform spectrometer. Chemical analyses were made by the Service de Microanalyses ICSN, Gif sur Yvette, France.

Crystal data (Table 1) for compounds **2**, **3**, **4**, and **5** were collected on a Oxford Diffraction X-Calibur-2 CCD diffractometer, equipped with a jet cooler device and graphite-monochromated Mo K α radiation ($\alpha = 0.71073$ Å). The structures were solved and refined by standard procedures.¹¹

Preparation of 2. In a 250 mL round-bottom flask, 250 mg $(0.73 \times 10^{-3} \text{ mol})$ of $[\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)]$ (1) was reacted with 1 equiv of PNP (320 mg) in toluene (50 mL) at 50 °C for 4 h. The solvent was then evaporated to dryness under vacuum, and the residue was solubilized in dichloromethane—hexane (1:1). After overnight crystallization at -20 °C, **2** was obtained as orange crystals (yield: 315 mg, 60%). Data for **2** are as follows. IR (CH₂Cl₂, cm⁻¹): ν (CO) 1991(s), 1952(vs), 1926(s), 1897(s). ¹H NMR (CDCl₃, 25 °C): δ 7.97–7.21 (m, 20H, C₆H₅), ({4.60 (m, 1H), 3.46 (m, 1H), 2.87 (m, 1H), 2.47 (m, 1H)}, PCH₂NCH₂S), 2.64 (s, 3H, NCH₃). ³¹P{¹H} NMR (CDCl₃, 25 °C): δ 82.0 (d, J = 7.3 Hz), 80.1 (d, J = 7.3 Hz). Anal. Calcd for C₃₁H₂₇Fe₂NO₄-P₂S₂·1.5CH₂Cl₂: C, 46.32; H, 3.58; N, 1.66. Found: C, 46.36; H, 3.81; N, 1.56.

Preparation of 3–3'. A 200 mg (0.58 10^{-3} mol) portion of **1** was reacted with 1 equiv of PNP (320 mg) in CH₂Cl₂ (5 mL) at -45 °C for 15 mn. The orange solution turned readily to red. The solvent was then evaporated to dryness under vacuum, and the residue was solubilized in dichloromethane–hexane (1:1). After overnight crystallization at -20 °C, **3–3'** were obtained as

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Table 1. Crystall	lographic Data fo	or Complexes 2,	3, 4, and 5
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	$2 \cdot 2 CH_2 Cl_2$	$3 \cdot CH_2Cl_2$	$4 \cdot C_6 H_{14}$	5
empirical formula	$C_{33}H_{31}Cl_4Fe_2NO_4P_2S_2$	$C_{33}H_{29}Cl_2Fe_2NO_5P_2S_2$	$C_{42}H_{50}Fe_2N_2O_4P_2S_2$	C ₂₇ H ₂₇ NP ₂ S ₂
fw	885.15	828.23	884.60	491.56
temperature/K	170(2)	170(2)	170(2)	170(2)
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	Pbca	$P2_1/n$	$P2_{1}/c$
a(A)	16.5283(8)	15.9177(4)	19.1289(10)	15.3111(8)
b(A)	14.1976(5)	17.2413(5)	9.3337(4)	7.7994(4)
$c(\mathbf{A})$	17.4895(8)	25.6580(7)	25.7957(13)	21.3862(12)
α (deg)				
β (deg)	114.527(6)		106.165	
γ (deg)				103.533(6)
$V(Å^3)$	3733.8(3)	7041.6(3)	4423.6(4)	
Ζ	4	8	4	4
$\rho_{\rm calc} ({\rm Mg}{\rm mm}^{-3})$	1.575	1.562	1.328	1.315
$\mu (\mathrm{mm}^{-1})$	1.299	1.227	0.863	0.359
cryst size (mm)	$0.26 \times 0.13 \times 0.02$	0.25 imes 0.14 imes 0.11	0.18 imes 0.10 imes 0.05	0.39 imes 0.22 imes 0.08
range of θ (deg)	2.56-26.37	2.49-26.37	2.45-24.71	2.74 - 28.28
reflns measd	28 168	51 898	28 904	21 306
R _{int}	0.0634	0.0662	0.1154	0.0360
unique data/params	7619/441	7197/425	7526	6145/290
$R_1\left[I > 2\sigma(I)\right]$	0.0429	0.0344	0.0479	0.0427
R_1 (all data)	0.0896	0.0720	0.1248	0.0784
wR_2 (all data)	0.1022	0.0953	0.1065	0.1168
goodness of-fit on F^2	0.950	1.015	0.889	0.967
$\Delta \rho_{\rm max,} \Delta \rho_{\rm min} ({\rm e}{\rm \AA}^{-3})$	0.695, -0.569	0.633, -0.456	0.453, -0.333	0.600, -0.470

red crystals (yield: 280 mg, 65%). Data for **3**–**3**' are as follows. IR (CH₂Cl₂, cm⁻¹): ν (CO) 2032(s), 1980(s), 1969(sh). Major product (80%) ¹H NMR (CDCl₃, 25 °C): δ 7.92–7.23 (m, 20H, C₆H₅), ({4.58 (m, 1H), 3.97 (m, 1H), 3.56 (m, 1H), 2.96 (m, 1H)}, PCH₂NCH₂S), 2.70 (s, 3H, NCH₃). ³¹P{¹H} NMR (CDCl₃, 25 °C): δ 73.9 (d, *J* = 4.6 Hz), 60.0 (d, *J* = 4.6 Hz). Minor product (20%) ¹H NMR (CDCl₃, 25 °C): δ 7.92–7.23 (m, 20H, C₆H₅), ({4.75 (m, 1H), 3.99 (m, 1H), 3.55 (m, 1H), 2.90 (m, 1H)}, PCH₂NCH₂S), 2.50 (s, 3H, NCH₃). ³¹P{¹H} NMR (CDCl₃, 25 °C): δ 78.7 (d, *J* = 4.4 Hz), 56.5 (d, *J* = 4.4 Hz).

Reaction of 1 with $(Ph_2PCH_2)_2NCH_3$ in the Presence of *tBuNC*. A typical procedure was used: 300 mg $(0.87 \times 10^{-3} \text{ mol})$ of 1 was reacted with 1 equiv of PNP (480 mg) in CH₂Cl₂ (10 mL) in the presence of an excess of *tBuNC* (300 μ L, 4 equiv) for 3 h at room temperature. The solution was then evaporated to dryness under vacuum to give a red residue, which was analyzed without any further purification. Attempts to purify

products of the reaction were performed by crystallization in dichloromethane–hexane (1:1) and did not give satisfactory separation. Data for **5** are as follows. ¹H NMR (CDCl₃, 25 °C): δ 7.83–7.39 (m, 20H, C₆H₅), 4.03 (s, 4H, CH₂), 2.48 (s, 3H, NCH₃). ³¹P{¹H} NMR (CDCl₃, 25 °C): δ 35.6 (s).

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Supporting Information Available: CIF files and Figure 5. This material is available free of charge via the Internet at http://pubs.acs.org.