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# Synthesis and Reactions of the $[(\mu\text{-}Ph_2P)Fe_2(CO)_6]^-$ Anion

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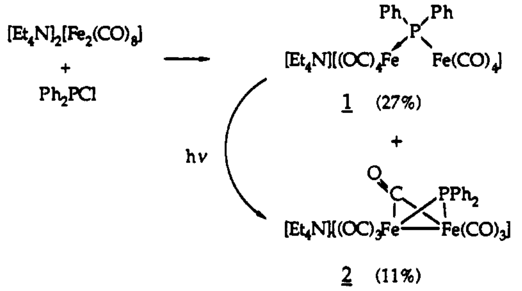
The action of 2 molar equiv of $LiBEt_3H$ on $(\mu\text{-}CH_3C{=}O)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ gives a reactive species which IR spectroscopic evidence suggests to be $Li[(\mu\text{-}Ph_2P)Fe_2(CO)_6]$. This species reacts with acid halides, $RC(O)Cl$, $Me_2NC(S)Cl$, $Me_2P(S)Cl$, and chlorophosphines; neutral products of type $(\mu\text{-}E)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ ($E = RC{=}O$, $Me_2NC{=}S$, $Me_2P{=}S$, $R_2P$) were obtained in good yield. Reaction with $CS_2$ and RNCS gave anionic products, $(\mu\text{-}\overset{-}{S}C{=}S)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ and $(\mu\text{-}R\overset{-}{N}C{=}S)(\mu\text{-}Ph_2P)Fe_2(CO)_6$. The $[(\mu\text{-}Ph_2P)Fe_2(CO)_6]^-$ reagent is much more reactive than the known $[(\mu\text{-}CO)(\mu\text{-}Ph_2P)Fe_2(CO)_6]^-$. The structure of $(\mu\text{-}(CH_3)_2P{=}S)(\mu\text{-}PhS)Fe_2(CO)_6$ (**18b**) has been determined by X-ray techniques. Compound **18b** crystallizes in the orthorhombic space group $P2_12_12_1$ with $a$ = 12.494 (2) Å, $b$ = 17.075 (2) Å, $c$ = 8.7909 (9) Å, $V$ = 1944.7 (7) Å$^3$, and $Z$ = 4. The two $Fe(CO)_3$ groups in the complex are bridged by the benzenethiolate and the dimethylphosphino sulfide groups, the latter of which is S-bound to one metal and P-bound to the other. Within the $SPMe_2$ ligand the P—S distance of 2.030 (2) Å lies intermediate between that of a single (2.18 Å) and a double (1.95 Å) bond.

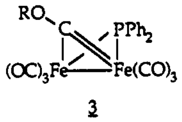
## Introduction

Recent investigations in these laboratories[1] have been devoted to a detailed study of the synthesis and reactivity of salts of anions of the type $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$. It was of interest to broaden this work to include salts of analogous phosphido-bridged anions, $[(\mu\text{-}CO)(\mu\text{-}R_2P)Fe_2(CO)_6]^-$. The simple route which served so well in the preparation of thiolate analogs, the reaction of an alkali metal or an ammonium alkane- or arenethiolate with $Fe_3(CO)_{12}$,[1a] proved not to be transferable to the reaction of $Ph_2PLi$ with $Fe_3(CO)_{12}$. However, a more complicated route to salts of the $[(\mu\text{-}CO)(\mu\text{-}R_2P)Fe_2(CO)_6]^-$ anions had been reported by Osterloh.[2] This synthesis is shown in Scheme I.

Scheme I



Salt **1** could be converted quantitatively to **2** by UV irradiation in THF solution. The structure of the anion in **2** was confirmed by an X-ray diffraction study of its tetraethylammonium salt.[2,3] This anion reacted with trimethyl- and triethyloxonium tetrafluoroborates as an O-nucleophile, giving a bridging alkoxymethylidyne complex, **3**. However, it did not react with alkyl iodides or acyl bromides, even in refluxing THF,[2] in marked contrast to the high reactivity of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions with acyl halides.[1a]



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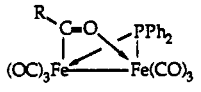
Reaction of salt **2** with acyl bromides would have been expected to give $\mu$-acyl complexes **4**. These were accessible by other routes, the reaction of $[Et_4N][(\mu\text{-}Ph_2P)Fe_2(CO)_8]$ with $[R_3O][BF_4]$ (R = Me, Et) or of $Na[(\mu\text{-}Ph_2P)Fe_2(CO)_8]$ with alkyl iodides and $CH_3OCH_2Cl$.[2,4] These reactions were not clean, giving other products as well, and the reactions with alkyl iodides were slow and the product yields were low (15–26%).[2] We found that the $(\mu\text{-}CH_3C{=}O)(\mu\text{-}R_2P)Fe_2(CO)_6$ (R = Ph, Et) complexes could be prepared more conveniently and in somewhat better yields (~40%) by adding first 1 molar equiv of iodomethane to a THF solution of $[Et_4N]_2[Fe_2(CO)_8]$ and then 1 equiv of diphenyl- or diethylchlorophosphine. A byproduct in the case of diphenylchlorophosphine was the unbridged acetyl complex **5**. The latter underwent decarbonylation in refluxing THF to give $(\mu\text{-}CH_3C{=}O)(\mu\text{-}Ph_2P)Fe_2(CO)_6$.



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During the course of our study of the reactivity of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions, we discovered an alter-

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[1] (a) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430. (b) Seyferth, D.; Womack, G. B.; Archer, C. M.; Fackler, J. P. Jr.; Marler, D. O. *Organometallics* **1989**, *8*, 443.

[2] Osterloh, W. T. Ph.D. Dissertation, University of Texas at Austin, 1982.

[3] (a) One-electron oxidation of the $[(\mu\text{-}CO)(\mu\text{-}PR_2)Fe_2(CO)_6]^-$ anions (R = Et, Ph, c-$C_6H_{11}$, $t$-Bu) with ferrocenium tetrafluoroborate results in the neutral radical $(\mu\text{-}R_2P)Fe_2(CO)_7$ whose ESR and IR spectra were studied: Baker, R. T.; Calabrese, J. C.; Krusic, P. J.; Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 8392. Krusic, P. J.; Baker, R. T.; Calabrese, J. C.; Morton, J. R.; Preston, K. F.; Le Page, Y. *J. Am. Chem. Soc.* **1989**, *111*, 1262. (b) Reina, R.; Rossell, O.; Seco, M. *J. Organomet. Chem.* **1990**, *398*, 285. (c) Walther, B.; Hartung, H.; Böttcher, H.-C.; Baumeister, U.; Böhland, U.; Reinhold, J.; Sieler, J.; Ladriere, J.; Schiebl, H.-M. *Polyhedron* **1991**, *10*, 2423. (d) Walther, B.; Hartung, H.; Reinhold, J.; Jones, P. G.; Mealli, C.; Böttcher, H.-C.; Baumeister, U.; Krug, A.; Möckel, A. *Organometallics* **1992**, *11*, 1542.

[4] Note also the preparation of $(\mu\text{-}CH_3C{=}O)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ by reaction of $[(\mu\text{-}Ph_2P)Fe_2(CO)_8]^+$ with $LiCu(CN)CH_3$ in $Et_2O$ at −78 °C: Witter, D. J.; Breckenridge, S. M.; Cherkas, A. A.; Randall, L. H.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1990**, *9*, 2636.

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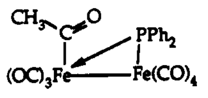
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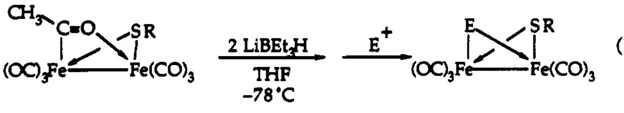
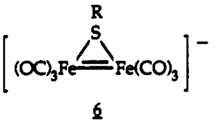
nate, albeit less practical, route to the neutral products usually derived from reactions of this anion which used $(\mu\text{-}CH_3C{=}O)(\mu\text{-}RS)Fe_2(CO)_6$ as the starting material (eq 1).[1a] The anionic intermediate in this reaction was presumed to be of the type **6**, i.e., one without a bridging CO ligand. A 2 molar equiv amount of the complex hydride



(1)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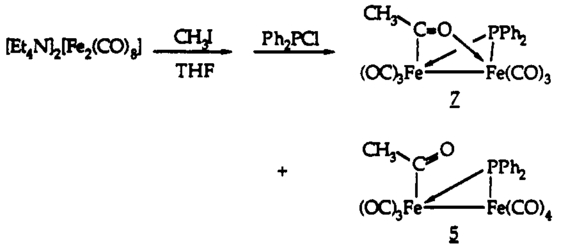
was required in reaction 1 since the reaction of $LiBEt_3H$ with the acetaldehyde released in its attack on the bridging acetyl complex was competitive with the desired reaction.

In this paper we report that this type of reaction can be applied to the synthesis of products of type $(\mu\text{-}E)(\mu\text{-}Ph_2P)Fe_2(CO)_6$.

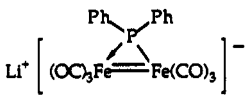
## Results and Discussion

The starting material required for the synthesis of the $(\mu\text{-}E)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ complexes is readily prepared by the sequence shown in eq 2. The reaction also gave the unbridged acetyl compound, **5**, as well in 10–15% yield. This product undergoes ready thermal decarbonylation in refluxing THF to give **7**, but usually it was not isolated in our synthesis of **7**.



7
5
(2)

The reaction of **7** with 2 molar equiv of $LiBEt_3H$ proceeded as expected. When the hydride solution (in THF) was added to an orange THF solution of **7** at −78 °C, a green-black solution resulted. We believe this solution to contain the coordinatively unsaturated anion **8** on the basis of an IR spectroscopic study. The IR spectrum of the green-black solution in THF showed five strong bands in the terminal CO region (2033 (s), 2000 (s), 1992 (s, broad), 1928 (vs), 1895 (vs) cm$^{-1}$) and only very weak bands at 1722, 1653, and 1581 cm$^{-1}$ (Figure 1a). Thus the absence of a bridging CO ligand is indicated. When, on the other hand, carbon monoxide was bubbled through such a green-black solution while it was being warmed to room temperature, a color change to red was observed and the IR spectrum now showed strong bands at 1737 (s) and 1665 (vs) cm$^{-1}$ (Figure 1b), in addition to terminal CO bands at 2056 (s), 2034 (vs), 2020 (vs), 2013 (s), and 1960–1880 (broad) cm$^{-1}$. This process was not reversible; purging the red solution with nitrogen did not regenerate the green anion (Figure 1c). It is likely that the red solution contains anion **9**. Osterloh[2] reported that $Li[(\mu\text{-}CO)(\mu\text{-}Ph_2P)Fe_2(CO)_6]$ showed bridging CO bands in the IR spectrum at 1664 and 1735 cm$^{-1}$, while the IR spectrum of $Li[(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ had such absorptions at 1670 and 1745 cm$^{-1}$.[1a] Attempts to obtain good, clear low-temperature NMR spectra ($^1H$, $^{13}C$, $^{31}P$, $^{11}B$) of the green-black solution were unsuccessful and repeated attempts to isolate a stable, crystalline salt of the $[(\mu\text{-}Ph_2P)Fe_2(CO)_6]^-$ anion ($Li^+$, $Et_4N^+$, $Ph_4P^+$, $PPN^+$ counterion) failed. All salts decomposed as the solution was allowed to warm from −78 to −20 °C. The $Et_4N^+$ salt of the anion present in the red solution could be isolated in 68% yield, and its $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were found to be identical with those reported by Osterloh for $[Et_4N][(\mu\text{-}CO)(\mu\text{-}Ph_2P)Fe_2(CO)_6]$.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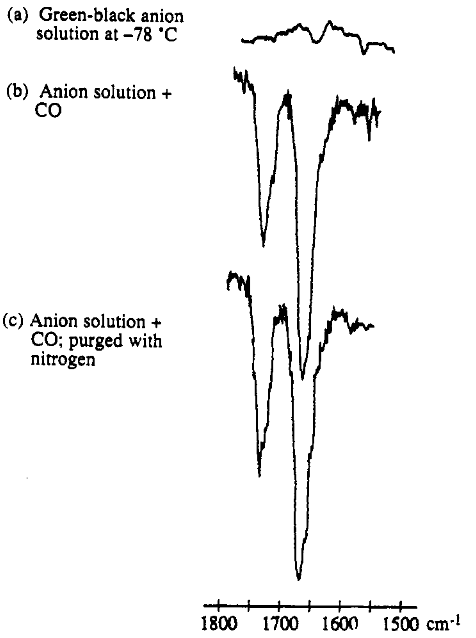
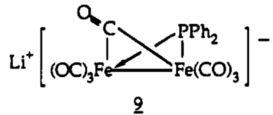


**Figure 1.** Infrared spectra of the $\mu\text{-}PPh_2$ anion solution in the range 1500–1800 cm$^{-1}$.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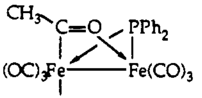
Our studies confirmed Osterloh's observation that the $[(\mu\text{-}CO)(\mu\text{-}Ph_2P)Fe_2(CO)_6]^-$ anion is a rather unreactive nucleophile. Addition of $C_2H_5C(O)Cl$, $Me_2NC(S)Cl$, or $Ph_2PCl$ to the red solution obtained by bubbling CO through the initially formed green-black anion solution resulted in formation of several low-yield products in addition to an appreciable amount of decomposition products that were immobile on column chromatography. However, we found that the reaction of the red anion, generated by Osterloh's procedure, with t-BuSCl, did give the expected product, $(\mu\text{-}t\text{-}BuS)(\mu\text{-}Ph_2P)Fe_2(CO)_6$, in 79% yield. The Osterloh red anion, as reported recently by other workers, reacts also with other more reactive electrophiles such as $L_nMHgCl$ complexes ($L_nM$ = $\eta\text{-}C_5H_5Mo(CO)_3$, $\eta\text{-}C_5H_5W(CO)_3$, $Mn(CO)_5$, $Co(CO)_4$, $\eta\text{-}C_5H_5Fe(CO)_2$,[3b] $Ph_3PMCl$ (M = Cu, Ag, Au),[3c] $RCO_2H$ (R = $CH_3$, $CF_3$),[3c] and $R_2PCl$.[3d] In any case, the red anion, whether generated by our procedure as the lithium salt or by Osterloh's procedure as the $Et_4N^+$ salt, is not an especially useful nucleophilic reagent in reactions with organic halides. On the other hand, the green-black anion **8** is a very reactive and generally useful reagent for the preparation of complexes of type $(\mu\text{-}E)(\mu\text{-}Ph_2P)Fe_2(CO)_6$. However, there is a limitation: it is stable in THF solution at −78 °C for only about 1 h and decomposes rapidly as the temperature is raised to room temperature. The obvious difference between the $[(\mu\text{-CO})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6]^-$ anions is the coordinatively unsaturated nature of the former. This should lead to a higher reactivity toward electrophiles, as has been observed.

It must be emphasized that *2* molar equiv of $\text{LiBEt}_3\text{H}$ are required for the high yield conversion of $(\mu\text{-CH}_3\text{C}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ to the $[(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6]^-$ anion. The reason for this probably is the same as that for the same requirement of stoichiometry in the case of $(\mu\text{-CH}_3\text{C}{=}\text{O})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$.[1a] This requirement was made clear in a reaction of $(\mu\text{-CH}_3\text{C}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ with only 1 molar equiv of $\text{LiBEt}_3\text{H}$ in THF at −78 °C, followed by addition of EtC(O)Cl. Two complexes were isolated: $(\mu\text{-CH}_3\text{C}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$, the starting material, in 51% yield, and the expected product, $(\mu\text{-EtC}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$, in 18% yield.

In our preparative experiments, the following general procedure served well: $(\mu\text{-CH}_3\text{C}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ and 2 molar equiv of $\text{LiBEt}_3\text{H}$ were allowed to react in THF solution at −78 °C during a period of 45–60 min. Then the electrophile was added and the reaction mixture was allowed to warm very slowly to room temperature. A reaction time of 18 h generally was used, although for some electrophiles a shorter reaction time sufficed.

Reactions of green-black anion **8** with acyl chlorides gave bridging acyl complexes, $(\mu\text{-RC}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ (R = Et, *i*-Pr, Ph, $\text{PhCH}_2$, PhCH=CH, $\text{CH}_3\text{CH}{=}\text{CH}$, $(\text{CH}_3)_2\text{C}{=}\text{CH}$) in good (40–91%) yield. No such product was formed with $(\text{CH}_3)_3\text{CC(O)Cl}$, presumably because attack at the carbonyl carbon atom of this bulky acyl chloride is hindered. The C=O stretching frequencies in the IR spectra of these products were observed between 1457 and 1458 $\text{cm}^{-1}$, in agreement with prior reports on similar complexes:



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$\nu(\text{CO}) = 1483\ \text{cm}^{-1}$
(ref. 5)

$(\mu\text{-CH}_3\text{OCH}_2\text{C}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$

11

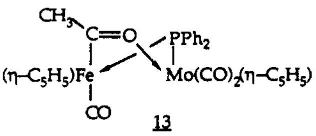
$\nu(\text{CO}) = 1515\ \text{cm}^{-1}$
(ref. 2)

$(\mu\text{-CH}_3\text{C}{=}\text{O})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$

12

$\nu(\text{CO}) = 1510\ \text{cm}^{-1}$
(ref. 1a)

The $^{13}\text{C}$ NMR resonances of the acyl carbon atoms of the products were found far downfield at around 300 ppm (range 291–306 ppm) which also is in agreement with literature data for similar complexes: **10**, $\delta_\text{C}$ = 299.6;[5] **11**, $\delta_\text{C}$ = 299.25;[2] **12**, $\delta_\text{C}$ = 307.6;[1a] **13**, $\delta_\text{C}$ = 324.4.[6] Furthermore,



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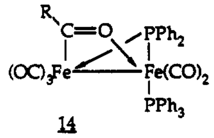
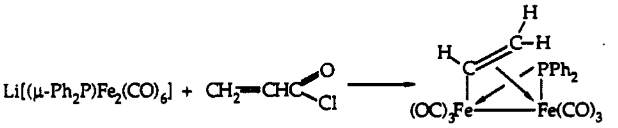
in the $^{13}\text{C}$ NMR spectra of $(\mu\text{-RC}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ the two-bond coupling $J_{(\text{RCO})-(\text{Ph}_2\text{P})}$ was around 20 Hz, which compares well with similar coupling found in the $^{13}\text{C}$ NMR spectra of **10** (20.5 Hz) and **11** (21.3 Hz). Some of our acyl products were isolated by column chromatography as oils from which the pentane eluent could not be removed completely. Some, but not all, of these could be converted to the solid mono(triphenylphosphine) substitution products **14**, which gave satisfactory C, H analyses.



14

The structure shown is based on the fact that their $^{13}\text{C}$ NMR spectra showed no additional $^2J_{\text{C-P}}$ coupling which would have been expected if substitution had occurred at the other iron atom.

The reaction of acryloyl chloride with anion **8** did not give a μ-acyl complex (eq 3). By analogy with our findings in the chemistry of $[(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]^-$ anions,[1] the



(3)

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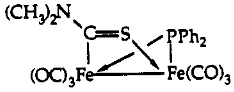
μ-acyl complex $(\mu\text{-CH}_2{=}\text{CHC}{=}\text{O})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ most likely was formed initially and underwent decarbonylation at room temperature, in solution or during the isolation procedure, to give the μ-σ,π-vinyl complex **15**.

As expected, *N,N*-dimethylthiocarbamoyl chloride reacted with a solution of anion **8** to give **16**. Dimethylthiophosphinic chloride, $(\text{CH}_3)_2\text{P(S)Cl}$, reacted with anion



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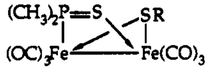
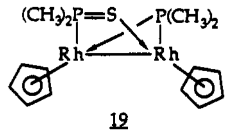
**8** in similar fashion, giving orange **17**. Since such a reaction of the analogous μ-thiolato anions had not been investigated, reactions of $(\text{CH}_3)_2\text{P(S)Cl}$ with $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]$ (R = Et, Ph) were carried out. In each case a dark red, crystalline product, **18**, was obtained. The structure of **18b** was confirmed by a single-crystal X-ray diffraction study (see below). A rhodium complex analogous to **17** was known, but this compound, **19**, had been prepared by reaction of $(\mu\text{-(CH}_3)_2\text{P)}_2\text{Rh}_2(\mu\text{-C}_5\text{H}_5)_2$ with elemental sulfur.[7]

17



18 a, R = Et
b, R = Ph



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Curiously, in processes whose course at the present time is obscure, the reactions of anion **8** with $(\text{CH}_3)_2\text{P(O)Cl}$ and

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[5] Yu, Y.-P.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

[6] Targos, T. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Organomet. Chem.* **1986**, *299*, 223.

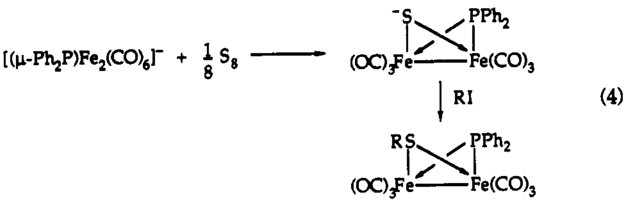
[7] Klingert, B.; Rheingold, A. L.; Werner, H. *Inorg. Chem.* **1988**, *27*, 1354.

$(CH_3)_2P(NR)Cl$ (R = *t*-Bu, Ph) gave simple bridging phosphido complexes **20a**,**b**, respectively. Complex **20b**

20 a, R = $CH_3$
b, R = Ph
c, R = Cl

also could be prepared by reaction of anion **8** with $Ph_2PCl$. When $PCl_3$ was used in place of $Ph_2PCl$ in a reaction with anion **8**, the complex (μ-$Cl_2P$)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**20c**) was isolated.

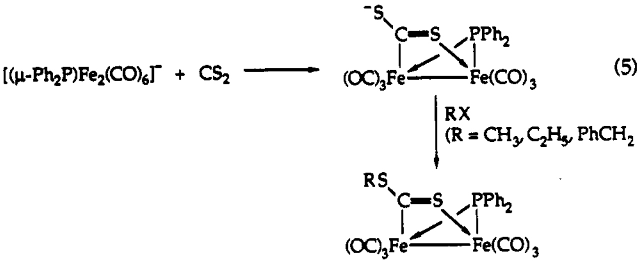
Some reactions of the green-black THF solution of the presumed anion **8** also were carried out with neutral electrophiles. These, as expected on the basis of known [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$ chemistry,[1b] gave anionic complexes as products which required a subsequent reaction with an electrophile to give a neutral product. Thus anion **8** reacted with sulfur as shown in eq 4. Complexes of type



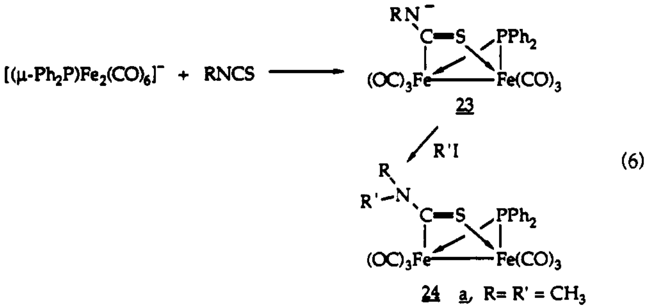
21 a, R = $CH_3$
b, R = $C_2H_5$

**21** had already been prepared by reaction of [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$ with $Ph_2PCl$[1] and of [(μ-$Ph_2P$)$Fe_2(CO)_6$]$^-$ with *t*-BuSCl (see above). Such μ-thiolato, μ-phosphido $Fe_2(CO)_6$ complexes, including P-functional complexes, will be the subject of a subsequent paper.

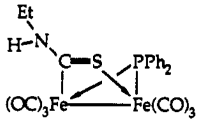
Reaction of anion **8** with carbon disulfide proceeded as shown in eq 5. Analogous (μ-RSC=S)(μ-R′S)$Fe_2(CO)_6$ complexes have been prepared similarly from [(μ-CO)(μ-R′S)$Fe_2(CO)_6$]$^-$.[1b] Alkyl isothiocyanates reacted similarly (eq 6). In the case where both R and R′ were $CH_3$, the product obtained was the same one, **16**, that had been obtained in the reaction of anion **8** with $(CH_3)_2NC(S)Cl$. The μ-thiolate anions, [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$, reacted in the same manner with isothiocyanates. In that case, however, the counterion was not $Li^+$ but $[Et_3NH]^+$ and the initially formed anionic product was sufficiently basic to deprotonase the triethylammonium ion, giving (μ-RNHC=S)(μ-R′S)$Fe_2(CO)_6$ as product. In line with this, treatment of the anionic product **23** (R = Et) with triethylammonium bromide resulted in formation of **25**.



22 a, R = $CH_3$
b, R = $C_2H_5$
c, R = $PhCH_2$



24 a, R = R′ = $CH_3$
b, R = R′ = $C_2H_5$
c, R = Ph, R′ = $CH_3$



25

Table I. $^{31}P$ NMR and IR Spectral Data for $Me_2P$=S Derivatives

| compd | $^{31}P$ NMR ($\delta_P$), ppm | $\nu$(P=), $cm^{-1}$ |
|---|---|---|
| $Me_2P(S)Cl$ | 85.7 | 615 |
| (μ-$Me_2P$=S)(μ-EtS)$Fe_2(CO)_6$ | 54.3 | 615 |
| (μ-$Me_2P$=S)(μ-PhS)$Fe_2(CO)_6$ | 56.7 | 615 |
| (μ-$Me_2P$=S)(μ-$Ph_2P$)$Fe_2(CO)_6$ | 36.8, 184.4 | 612 |
| η-$C_5H_5Fe(Me_2P$=S)$(CO)_2$[a] | not reported | 620 |
| η-$C_3F_7Fe$(μ-$Me_2P$=S)$(CO)_3I$[b] | 37.6 | 531 |
| (η-$C_5Me_5)_2Rh_2$(μ-$Me_2P$=S)(μ-$Me_2P$)[c] | 9.4, 118.3 | 550 |

[a] Lindner, E.; Krieg, C.-P. *J. Organomet. Chem.* **1984**, *269*, 65. Messbauer, B.; Meyer, H.; Walther, B.; Rahman, A. F. M. M.; Oliver, J. P. *Inorg. Chem.* **1983**, *22*, 272. [b] Reference 8. [c] Reference 7.

Most of our studies were carried out using (μ-$CH_3C$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ as starting material. A few reactions used (μ-$CH_3C$=O)(μ-$Et_2P$)$Fe_2(CO)_6$, and the observed chemistry was essentially the same. Treatment of this complex with 2 molar equiv of $LiBEt_3H$ in THF at −78 °C gave a green-black solution with IR bands at 2044 (m/w), 2012 (s), 1937 (vs, broad), 1910 (vs, broad), 1893 (vs, broad), 1734 (w), and 1660 (w) $cm^{-1}$. Bubbling CO into this solution at −78 °C while it was warming to room temperature resulted in a color change to brown-yellow. In addition to strong bands in the terminal CO region at 2065, 2050, 2020, 2018, and 1960–1890 $cm^{-1}$, the infrared spectrum of this solution showed absorptions in the bridging CO region at 1733 (m) and 1660 (s) $cm^{-1}$. Addition of $(CH_3)_2NC(S)Cl$ to a green-black solution that presumably contained the [(μ-$Et_2P$)$Fe_2(CO)_6$]$^-$ anion resulted in formation of (μ-$(CH_3)_2NC$=S)(μ-$Et_2P$)$Fe_2(CO)_6$ in 61% yield. In contrast, when $(CH_3)_2NC(S)Cl$ was added to a [(μ-$Et_2P$)$Fe_2(CO)_6$]$^-$ solution that had been treated with carbon monoxide as described above and presumably now contained the [(μ-CO)(μ-$Et_2P$)$Fe_2(CO)_6$]$^-$ anion, the same product was formed only in 17% yield.

This brief study has served to provide an entry to unsymmetrically bridged $Fe_2(CO)_6$ complexes of type (μ-E)(μ-$R_2P$)$Fe_2(CO)_6$. The μ-diphenylphosphido analog of the [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$ anions shows poor reactivity toward electrophiles that are sources of three-electron bridging groups. However, the coordinatively unsaturated [(μ-$R_2P$)$Fe_2(CO)_6$]$^-$ anions that are produced by the action of 2 molar equiv of $LiBEt_3H$ on (μ-$CH_3C$=O)(μ-$R_2P$)-$Fe_2(CO)_6$ complexes are very reactive and useful reagents. The scope of their application in the synthesis of (μ-E)-(μ-$R_2P$)$Fe_2(CO)_6$ complexes has been delineated in this investigation, but considering the more highly developed chemistry of the [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$ anion,[1] much more chemistry of the [(μ-$R_2P$)$Fe_2(CO)_6$]$^-$ anion should be possible.

**Characterization of (μ-$(CH_3)_2P$=S)(μ-$Ph_2P$)$Fe_2(CO)_6$ and (μ-$(CH_3)_2P$=S)(μ-RS)$Fe_2(CO)_6$ (R = Et, Ph): Spectroscopy and X-ray Diffraction (R = Ph).** Important spectral data are given in Table I. The $^{31}P$ NMR

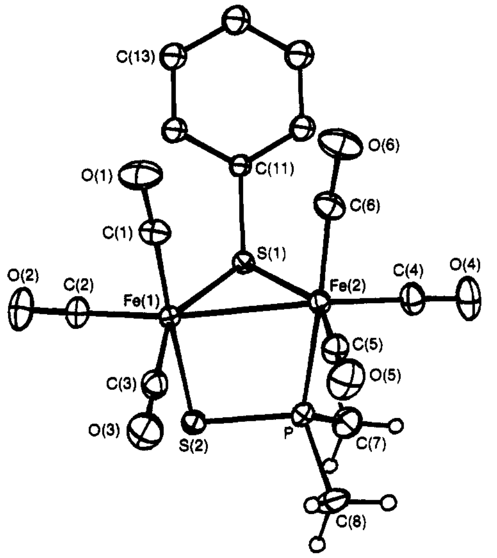


**Figure 2.** Molecular structure of ($\mu$-PhS)($\mu$-Me$_2$P=S)Fe$_2$(CO)$_6$ showing 20% probability ellipsoids.

**Table II. Bond Lengths in ($\mu$-SPh)($\mu$-Me$_2$P=S)(Fe$_2$(CO)$_6$, with Estimated Standard Deviations in the Least Significant Digit in Parentheses**

| bond | bond distance, Å | bond | bond distance, Å |
|---|---|---|---|
| Fe(1)–Fe(2) | 2.6408 (8) | P–C(8) | 1.815 (6) |
| Fe(1)–S(1) | 2.247 (1) | O(1)–C(1) | 1.133 (6) |
| Fe(1)–S(2) | 2.359 (1) | O(2)–C(2) | 1.120 (6) |
| Fe(1)–C(1) | 1.767 (5) | O(3)–C(3) | 1.133 (6) |
| Fe(1)–C(2) | 1.805 (5) | O(4)–C(4) | 1.133 (6) |
| Fe(1)–C(3) | 1.803 (5) | O(5)–C(5) | 1.130 (6) |
| Fe(2)–S(1) | 2.262 (1) | O(6)–C(6) | 1.130 (6) |
| Fe(2)–P | 2.260 (1) | C(11)–C(12) | 1.385 (6) |
| Fe(2)–C(4) | 1.797 (5) | C(11)–C(16) | 1.375 (7) |
| Fe(2)–C(5) | 1.788 (5) | C(12)–C(13) | 1.397 (7) |
| Fe(2)–C(6) | 1.819 (5) | C(13)–C(14) | 1.371 (8) |
| S(1)–C(11) | 1.799 (4) | C(14)–C(15) | 1.352 (8) |
| S(2)–P | 2.030 (2) | C(15)–C(16) | 1.399 (7) |
| P–C(7) | 1.814 (6) | | |

spectra of the new $\mu$-(CH$_3$)$_2$P=S complexes showed chemical shifts for the $\mu$-(CH$_3$)$_2$P=S ligand between 35 and 55 ppm in agreement with those of other $\mu$-thiophosphinito complexes. The upfield chemical shift of $\mu$-(CH$_3$)$_2$P=S from that of the free ligand has been noted for other thiophosphinito complexes.[8] The signal due to the bridging phosphido group of this complex was observed at 184 ppm, in the normal range for neutral ($\mu$-phosphido)diiron hexacarbonyl complexes (140–200 ppm). In the $^1$H NMR spectrum of **18a**,**b** and **17**, the methyl groups of the $\mu$-(CH$_3$)$_2$P=S ligand showed a $^2J_{H-P}$ of 10 Hz in accord with the coupling constant found for the thiophosphinito bridge of Cp*$_2$($\mu$-P(CH$_3$)$_2$)($\mu$-(CH$_3$)$_2$P=S)Rh$_2$.[8]

The $\nu$(P=S) stretch in the IR spectrum for this class of complexes has been assigned as a medium intensity band between 550 and 620 cm$^{-1}$.[9] The assignments for the new compounds, **17** and **18a**,**b**, are included in Table I. The free ligand has a $\nu$(P=S) stretch at 615 cm$^{-1}$ and this absorption is not significantly shifted upon coordination to the diiron core. This has also been noted for other $\mu$-(CH$_3$)$_2$P=S complexes[10] and has shown that the transition metal and the other ligands have only a small influence on the P=S bond.

**Table III. Bond Angles in ($\mu$-SPh)($\mu$-Me$_2$P=S)Fe$_2$(CO)$_6$, with Estimated Standard Deviations in the Least Significant Digit in Parentheses**

| | bond angle, deg | bond | bond angle, deg |
|---|---|---|---|
| Fe(2)–Fe(1)–S(1) | 54.41 (3) | C(4)–Fe(2)–C(5) | 103.6 (2) |
| Fe(2)–Fe(1)–S(2) | 86.65 (4) | C(4)–Fe(2)–C(6) | 92.9 (3) |
| Fe(2)–Fe(1)–C(1) | 91.0 (2) | C(5)–Fe(2)–C(6) | 89.6 (2) |
| Fe(2)–Fe(1)–C(2) | 160.6 (2) | Fe(1)–S(1)–Fe(2) | 71.72 (4) |
| Fe(2)–Fe(1)–C(3) | 97.3 (2) | Fe(1)–S(1)–C(11) | 115.6 (1) |
| S(1)–Fe(1)–S(2) | 84.04 (5) | Fe(2)–S(1)–C(11) | 111.2 (1) |
| S(1)–Fe(1)–C(1) | 95.5 (2) | Fe(1)–S(2)–P | 88.48 (5) |
| S(1)–Fe(1)–C(2) | 106.3 (2) | Fe(2)–P–S(2) | 106.35 (6) |
| S(1)–Fe(1)–C(3) | 150.6 (2) | Fe(2)–P–C(7) | 116.2 (2) |
| S(2)–Fe(1)–C(1) | 177.5 (2) | Fe(2)–P–C(8) | 116.2 (2) |
| S(2)–Fe(1)–C(2) | 89.8 (2) | S(2)–P–C(7) | 107.3 (2) |
| S(2)–Fe(1)–C(3) | 86.5 (2) | S(2)–P–C(8) | 108.1 (2) |
| C(1)–Fe(1)–C(2) | 92.7 (2) | C(7)–P–C(8) | 102.2 (3) |
| C(1)–Fe(1)–C(3) | 92.8 (2) | Fe(1)–C(1)–O(1) | 176.3 (5) |
| C(2)–Fe(1)–C(3) | 101.5 (2) | Fe(1)–C(2)–O(2) | 177.6 (5) |
| Fe(1)–Fe(2)–S(1) | 53.89 (3) | Fe(1)–C(3)–O(3) | 179.1 (5) |
| Fe(1)–Fe(2)–P | 77.17 (4) | Fe(2)–C(4)–O(4) | 178.5 (6) |
| Fe(1)–Fe(2)–C(4) | 157.1 (2) | Fe(2)–C(5)–O(5) | 178.5 (5) |
| Fe(1)–Fe(2)–C(5) | 95.4 (2) | Fe(2)–C(6)–O(6) | 176.5 (5) |
| Fe(1)–Fe(2)–C(6) | 100.0 (2) | S(1)–C(11)–C(12) | 120.0 (3) |
| S(1)–Fe(2)–P | 84.63 (5) | S(1)–C(11)–C(16) | 119.4 (3) |
| S(1)–Fe(2)–C(4) | 106.9 (2) | C(12)–C(11)–C(16) | 120.5 (4) |
| S(1)–Fe(2)–C(5) | 149.2 (2) | C(11)–C(12)–C(13) | 119.2 (5) |
| S(1)–Fe(2)–C(6) | 93.4 (2) | C(12)–C(13)–C(14) | 120.1 (5) |
| P–Fe(2)–C(4) | 89.7 (2) | C(13)–C(14)–C(15) | 120.5 (5) |
| P–Fe(2)–C(5) | 91.0 (2) | C(14)–C(15)–C(16) | 120.7 (5) |
| P–Fe(2)–C(6) | 177.2 (2) | C(11)–C(16)–C(15) | 119.2 (5) |
| | Torsion Angles | | |
| S(2)–Fe(1)–Fe(2)–P | −7.64 (5) | | |
| C(1)–Fe(1)–Fe(2)–C(6) | −9.0 (2) | | |
| C(3)–Fe(1)–Fe(2)–C(5) | −11.4 (2) | | |

The molecular structure of ($\mu$-CH$_3$)$_2$P=S)($\mu$-PhS)Fe$_2$(CO)$_6$ (**18b**) is shown in Figure 2 with the bond distances and bond angles for the complex listed in Tables II and III. The structure reveals the expected butterfly structure of doubly-bridged diiron hexacarbonyl complexes, in which each metal has a distorted-octahedral geometry, comprising the Fe—Fe bond, the two bridging groups, and the three terminal carbonyls. Distortion from an idealized geometry results primarily from the strain imposed by the bridging thiolate group, leaving rather acute S(1)—Fe—Fe angles of ca. 54°. Otherwise the parameters involving the thiolate bridge and the Fe$_2$(CO)$_6$ core are as expected. The Fe—Fe bond (2.6408 (8) Å) lies within the range previously noted for single bonds (2.43–2.88 Å),[11] and the thiolate ligand bridges symmetrically, with Fe—S distances (2.247 (1), 2.262 (1) Å) in agreement with those of other $\mu$-SR diiron complexes.[1,12] The acute Fe(1)—S(1)—Fe(2) angle (71.72 (4)°) is as expected in the presence of a metal–metal bond.

The thiophosphinito ligand binds as an $\eta^2$ bridge, with the sulfur bound to one metal and phosphorus to the other, much as has been observed in other structures containing bridging SPR$_2$ groups.[13-15] The Fe(1)-S(2) bond, at 2.359 (1) Å, is longer than the Fe–S bonds involving the thiolate bridge but is still normal for such an interaction. This lengthening may result from the strain imposed by the four-membered Fe(1)-Fe(2)-P-S(2) ring. Although the Fe(2)-P-S(2) angle is normal (106.35 (6)°), the comparable angle at S(2) (i.e., Fe(1)-S(2)-P) is rather acute, at 88.48

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(5)°. This strain has previously been observed in complexes in which a thiophosphinito group bridges a metal–metal bond, resulting in analogous angles at sulfur of between ca. 81 and 87° and angles at phosphorus of between ca. 108 and 114°.[13,14] By contrast, in a thiophosphinito-bridged complex in which there is no metal–metal bond, the angle at sulfur opens up to 108°,[15] and in an even less strained environment, in which a thiophosphinato group is $\eta^1$-bound through sulfur, the angle at sulfur is almost 123°,[16] as expected if sulfur utilizes one of its lone pairs for binding to the metal. In spite of the apparent strain at S(2), the complex is not twisted significantly about the Fe–Fe bond, with relevant torsion angles less than 11.4° (see Table III). The Fe(2)–P bond length (2.260 (1) Å) is also somewhat longer than the Fe–P single bond of a phosphido bridge (2.18–2.20 Å).[17] The P–S(2) bond distance (2.030 (2) Å) lies between the extremes typical of double (1.95 Å) and single (2.18 Å) bonds,[18] consistent with significant multiple-bond character. This value compares well to the P–S distances, of ca. 2.0 Å, observed in a number of thiophosphinito complexes,[8,13–16,19] irrespective of the coordination modes observed.

## Experimental Section

**General Comments.** All reactions were carried out under an inert atmosphere of prepurified nitrogen or argon. Solvents (THF, $Et_2O$) were purified by standard methods and purged with inert gas prior to use. Diphenylchlorophosphine was distilled and stored at room temperature under an inert atmosphere. Lithium triethylborohydride (1 M solution in THF) was obtained from Aldrich and kept refrigerated under an inert atmosphere. Diiron nonacarbonyl was obtained from Strem Chemical Co. and stored cold in the drybox. $[NEt_4]_2[Fe_2(CO)_8]$ was prepared by the literature procedure.[20] All other reagents were distilled whenever appropriate and degassed with inert gas prior to use.

The progress of all reactions was monitored by thin-layer chromatography (Baker Flex-Silica Gel IB-F). Purification of the compounds was effected by filtration chromatography in which the reaction products, after removal of the solvent by trap-to-trap distillation, were dissolved in pentane/methylene chloride and chromatographed on a bed of 200 mL of silicic acid (100–300 mesh, Sigma or Mallinkrodt) in a 350-mL glass fritted funnel. In some cases, further purification was effected by medium-pressure column chromatography using a 450- × 25-mm gravity column with Sigma 230–400-mesh silica gel. All chromatographic separations were carried out without the exclusion of atmospheric oxygen and moisture. Solid products were recrystallized from deoxygenated pentane/methylene chloride at −20 °C.

Infrared spectra (NaCl solution cells) were obtained using a Perkin-Elmer Model 1430 double-beam grating infrared spectrometer and were referenced with polystyrene film. Proton NMR spectra were recorded on either a Jeol FX90-Q, Bruker WM-250, or Varian XL-300 spectrometer operating at 90, 250, or 300 MHz, respectively. $^{31}P\{^1H\}$ NMR spectra were recorded on either a Jeol FX90-Q or a Varian XL-300 spectrometer operating at 36.2 or 121.64 MHz, respectively, using an external standard of 85% aqueous $H_3PO_4$ as a reference. $^{13}C$ NMR spectra were recorded on either a Bruker WM-270 or a Varian XL-300 spectrometer operating at 67.9 or 75.4 MHz, respectively. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Masses were correlated using the following isotopes: $^1H$, $^{12}C$, $^{14}N$, $^{16}O$, $^{31}P$, $^{32}S$, $^{35}Cl$, and $^{56}Fe$. Melting points of analytically pure crystalline and solid products were determined in air using a Büchi melting point apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory in Herlev, Denmark.

Table IV gives $^1H$ and $^{31}P$ NMR data for all new compounds and $^{13}C$ NMR data for bridging C=O and C=S moieties.

**Preparation of $(\mu\text{-}CH_3C{=}O)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ (7).** A 200-mL Schlenk flask equipped with a magnetic stir-bar and a rubber septum was charged with 3.20 g (5.37 mmol) of $[Et_4N]_2[Fe_2(CO)_8]$ and 100 mL of THF. Iodomethane (0.75 g, 5.37 mmol) was added, and the resulting solution was stirred at room temperature for 3–4 h. A color change from red to brown was noted. Diphenylchlorophosphine (0.96 mL, 5.37 mmol) was added dropwise by syringe, causing gas evolution and the formation of a precipitate. The reaction mixture was stirred for 18 h. Subsequently, the solvent was removed at reduced pressure, leaving an orange-brown solid residue. The latter was dissolved in pentane and purified by filtration chromatography (silicic acid). Elution with $CH_2Cl_2$/pentane (1/4 v/v) gave 1.11 g (41%) of 7, an orange solid, mp 116–117 °C (from pentane). Anal. Calcd for $C_{20}H_{13}O_7PFe_2$: C, 47.29; H, 2.58. Found: C, 47.55; H, 2.67. IR ($CHCl_3$): $\nu$(C=O) 1473, terminal CO, 2058 (s), 2018 (vs), 1991 (vs), 1978 (s), 1959 (sh) $cm^{-1}$.

A second, dark orange band was eluted with $CH_2Cl_2$/pentane (2/3 v/v) to give a low (6%) yield of a red-orange solid, 5, mp 112–114 °C dec (pentane). Anal. Calcd for $C_{21}H_{13}O_8PFe_2$: C, 47.06; H, 2.44. Found: C, 47.20; H, 2.52. IR ($CHCl_3$): $\nu$(C=O) 1654 (s), terminal CO, 2080 (s), 2020 (vs), 2008 (vs), 1997 (sh), 1914 (m) $cm^{-1}$.

The preparation usually was carried out on a 17-mmol scale (10.2 g of $[Et_4N][Fe_2(CO)_8]$, 2.43 g of $CH_3I$, and 3.77 g of $Ph_2PCl$) and gave, on the average, a 52% yield (4.34 g) of 7 on filtration chromatography with 1/4 (v/v) $CH_2Cl_2$/pentane on silica gel. Byproduct 5 was not isolated.

**Derivatives. i. $(\mu\text{-}CH_3C{=}O)(\mu\text{-}Ph_2P)Fe_2(CO)_5(PPh_3)$ (14, R = $CH_3$).** A solution of 7 (1.53 g, 3.0 mmol) and 0.79 g (3.0 mmol) of $Ph_3P$ in 100 mL of THF was heated at reflux for 22 h. Removal of the solvent at reduced pressure left a brown-orange, oily residue that was purified by filtration chromatography. Elution with 1/9 $CH_2Cl_2$/pentane afforded an orange solid (starting material, 40% recovery); further elution with 4/5 $CH_2Cl_2$/pentane gave 1.27 g (57%) of the dark red-orange mono(triphenylphosphine) substitution product, mp 179–180 °C. Anal. Calcd for $C_{37}H_{28}O_6P_2Fe_2$: C, 59.87; H, 3.80. Found: C, 59.51; H, 3.93. IR ($CHCl_3$): $\nu$(C=O) 1497, terminal CO, 2036 (s), 1985 (vs), 1947 (s), 1928 (m) $cm^{-1}$.

**ii. $(\mu\text{-}CH_3C{=}O)(\mu\text{-}Ph_2P)Fe_2(CO)_4(Ph_2PCH_2CH_2PPh_2)$.** A similar procedure was used in the reaction of 1.97 g (4.94 mmol) of $Ph_2PCH_2CH_2PPh_2$ (Strem) and 2.50 g (4.93 mmol) of 7 in 100 mL of THF. The brown-orange product was purified by filtration chromatography (4/6 $CH_2Cl_2$/pentane) and preparative TLC (3/7 $CH_2Cl_2$/pentane). The first band to elute decomposed; the second gave 1.52 g (36%) of deep red solid which was recrystallized from $CH_2Cl_2$ to give pure product, mp 135–140 °C dec (with gas evolution); resulting solid, mp 165–166 °C. Anal. Calcd for $C_{44}H_{37}O_5P_3Fe_2$: C, 62.15; H, 4.39. Found: C, 62.10; H, 4.62. IR ($CHCl_3$) (terminal CO): 1987 (s), 1984 (vs), 1916 (s), 1896 (s).

**Preparation of $(\mu\text{-}CH_3C{=}O)(\mu\text{-}Et_2P)Fe_2(CO)_6$.** The same procedure was used in the reaction of 10.00 g (16.77 mmol) of 1, 1.05 mL (16.86 mmol) of $CH_3I$, and 2.09 g (16.79 mmol) of $Et_2PCl$ in THF. Filtration chromatography (1/9 v/v $CH_2Cl_2$/pentane) gave 2.49 g (36%) of the product as an orange oil.

A satisfactory analysis could not be obtained, so the mono(triphenylphosphine) substitution product, $(\mu\text{-}CH_3C{=}O)(\mu\text{-}Et_2P)Fe_2(CO)_5(PPh_3)$, mp 133–134 °C, was prepared. Anal. Calcd for $C_{29}H_{28}O_6P_2Fe_2$: C, 53.90; H, 4.37. Found: C, 54.50; H, 4.55.

**Generation of a Solution Containing the $[(\mu\text{-}Ph_2P)Fe_2(CO)_6]^-$ Anion.** A 100-mL Schlenk flask equipped with a stir-bar and a rubber septum was charged with 7 (typically, 0.51 g, 1.0 mmol) and degassed using three evacuation/inert gas back-fill cycles. THF (30 mL) was added by syringe, and the solution was cooled to −78 °C (dry ice/acetone). A 2 molar equiv amount of a 1.0 M solution of $LiBEt_3H$ in THF was added. The initially clear orange solution immediately darkened to green-black. The resulting solution was stirred at −78 °C for 45–60 min, and then 2 molar equiv (usually a slight excess) of the electrophile was added at −78 °C. Upon completion of the addition, the reaction mixture

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**Table IV. NMR Spectral Data**

| compd | $^1$H ($\delta$), ppm[a] (solvent used was CD$_2$Cl$_2$ unless otherwise specified) | $^{31}$P ($\delta_P$), ppm (solvent used was CDCl$_3$ unless otherwise specified | $^{13}$C [bridging $\delta_{C=O}$ or $\delta_{C=S}$], ppm ($^2J_{C\text{-}P}$, Hz) |
|---|---|---|---|
| (μ-CH$_3$C=O)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**7**) | 2.00 (s, 3 H, CH$_3$) | 182.4 | 301.4 (22.0) |
| (CH$_3$C=O)(μ-Ph$_2$P)Fe$_2$(CO)$_7$ (**5**) | 2.97 (s, 3 H, CH$_3$) | 154.5 | 298.08 (19.5) |
| (μ-CH$_3$C=O)(μ-Ph$_2$P)Fe$_2$(CO)$_5$(PPh$_3$) (**14**, R = CH$_3$) | 1.63 (s, 3 H, CH$_3$) | 59.3 (d, $J_{P-P}$ = 67.5 Hz, Ph$_3$P)<br>175.1 (broad s) | |
| (μ-CH$_3$C=O)(μ-Ph$_2$P)Fe$_2$(CO)$_4$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) | (CDCl$_3$)<br>1.45 (s, 3 H, CH$_3$)<br>2.20–2.60 (m, CH$_2$) | 50.4 (d, $^2J_{P-P}$ = 121.0 hz)<br>56.6 (d, $^2J_{P-P}$ = 65.0 Hz)<br>183.6 (dd, $^2J_{P-P}$ = 65.0 Hz, $^2J_{P-P}$ = 121.0 Hz) | 312.14 |
| (μ-CH$_3$C=O)(μ-Et$_2$P)Fe$_2$(CO)$_6$ | 1.28–1.47 (m, 6 H, CH$_3$ of Et)<br>1.82–1.94 (complex overlapping dq, 4 H, CH$_2$ of Et)<br>2.26 (s, 3 H, CH$_3$CO) | 193.5 | 301.36 (4.6) |
| (μ-CH$_3$C=O)(μ-Et$_2$P)Fe$_2$(CO)$_5$(PPh$_3$) | | 58.7 (d, $^2J_{P-P}$ = 47.7 Hz, Ph$_3$P)<br>183.8 (broad s, Et$_2$P) | 292.88 (19.8) |
| (μ-C$_2$H$_5$C=O)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**4a**) | 0.32 (t, $J$ = 7.3 Hz, 3 H, C$H_3$CH$_2$C=O)<br>2.54 (dq, $J_{H-H}$ = 7.3 Hz, $^4J_{H-P}$ = 17.8 Hz, 1 H, CH$_3$C$H_2$C=O)<br>2.20 (dq, $J_{H-H}$ = 7.3 Hz, $^4J_{H-P}$ = 17.8 Hz, 1 H, CH$_3$C$H_2$C=O) | 181.8 | 302.13 (22.0) |
| (μ-(CH$_3$)$_2$CHC=O)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**4b**) | 0.15 (d, $J$ = 7.9 Hz, 3 H, CH$_3$)<br>0.88 (d, $J$ = 7.1 Hz, 3 H, CH$_3$)<br>2.64 (m, 1 H, CH) | 183.1 | 305.98 (20.2) |
| (μ-(CH$_3$)$_2$CHC=O)(μ-Ph$_2$P)Fe$_2$(CO)$_5$(PPh$_3$) (**4b′**) | | 58.8 (d, $J_{P-P}$ = 29.3 Hz, Ph$_3$P)<br>165.2 (d, $J_{P-P}$ = 29.4 Hz) | |
| (μ-PhC=O)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**4c**) | | 186.8 | 291.59 (19.5) |
| (μ-PhC=O)(μ-Ph$_2$P)Fe$_2$(CO)$_5$(PPh$_3$) (**4c′**) | | 58.4 (d, $J_{P-P}$ = 29.3 Hz)<br>168.4 (d, $J_{P-P}$ = 29.3 Hz) | 289.29 (15.7) |
| (μ-PhCH$_2$C=O)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**4d**) | 3.41 (d, $J$ = 16.2 Hz, 1 H of PhC$H_2$)<br>3.95 (d, $J$ = 16.2 Hz, 1 H of PhC$H_2$) | 182.4 | 298.68 (19.6) |
| (μ-PhCH=CHC=O)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (trans isomer) (**4e**) | 6.56 (d, $J$ = 15.9 Hz, 1 H, CHC=O)<br>7.02 (d, $J$ = 15.9 Hz, 1 H, PhCH) | 185.7 | 286.26 (23.9) |
| (μ-CH$_3$CH=CHCO)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (trans isomer) (**4f**) | 1.77 (d, $J$ = 6.6 Hz, 3 H, CH$_3$)<br>5.88 (d, $J$ = 15.3 Hz, 1 H, CHC=O)<br>6.47 (m, 1 H, CH$_3$C$H$) | 184.8 | 286.83 (19.0) |
| (μ-(CH$_3$)$_2$C=CHC=O)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**4g**) | 1.06 (s, 3 H, CH$_3$ cis to H)<br>1.60 (s, 3 H, CH$_3$ trans to H)<br>6.37 (s, 1 H, =CH) | 184.1 | 285.43 (12.3) |
| (μ-σ,π-CH$_2$=CH)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**15**) | 2.59 (ddd, $J_{H-H}$ = 13.4 Hz, $^2J_{H-P}$ = 2.1 Hz, 1 H, FeCH)<br>3.47 (m, 1 H, H cis to Fe)<br>8.65 (m, 1 H, H trans to Fe) | 175.5 | |
| (μ-(CH$_3$)$_2$NC=S)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**16**) | 2.84 (s, 3 H, CH$_3$N)<br>3.56 (s, 3 H, CH$_3$N) | 191.0 | 242.23 (13.6) |
| (μ-(CH$_3$)$_2$P=S)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**17**) | (acetone-$d_6$)<br>0.93 (d, $^2J_{H-P}$ = 10.0 Hz, 3 H, CH$_3$)<br>1.92 (d, $^2J_{H-P}$ = 10.0 Hz, 3 H, CH$_3$) | 36.8 (d, $^2J_{P-P}$ = 31.0 Hz, Me$_2$PS)<br>184.4 (d, $^3J_{P-P}$ = 31.0 Hz) | |
| (μ-(CH$_3$)$_2$P)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**20a**) | 0.75 (d, $^2J_{H-P}$ = 12.2 Hz, 3 H, CH$_3$)<br>1.91 (d, $^2J_{H-P}$ = 12.2 Hz, 3 H, CH$_3$) | 111.1 (d, $J_{P-P}$ = 154.8 Hz, Me$_2$P)<br>149.9 (d, $J_{P-P}$ = 154.8 Hz, Ph$_2$P) | |
| (μ-Cl$_2$P)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**20c**) | | 126.2 (d, $^2J_{P-P}$ = 125.0 Hz, Ph$_2$P)<br>322.8 (d, $^2J_{P-P}$ = 125.0 Hz, Cl$_2$P) | |
| (μ-CH$_3$SC=S)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**22a**) | 2.19 (s, 3 H, CH$_3$) | 192.2 | 302.72 (7.9) |
| (μ-CH$_3$CH$_2$SC=S)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**22b**) | 0.86 (t, $J_{H-H}$ = 7.6 Hz, 3 H, CH$_3$)<br>2.67, 2.92 (complex dq, 1 H, diastereotopic CH$_2$)<br>7.30–7.8 (m, 10 H, Ph) | 192.7 | 302.14 (not observed) |
| (μ-PhCH$_2$SC=S)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**22c**) | 3.98 (s, 2 H, CH$_2$) | 193.0 | 301.08 (10.7) |
| (μ-C$_2$H$_5$NHC=S)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**25**) | 0.85 (t, $J_{H-H}$ = 7.3 Hz, 3 H, CH$_3$)<br>3.15 (m, 2 H, CH$_2$)<br>(NH not observed) | 189.6 | 246.75 (10.7) |
| (μ-(C$_2$H$_5$)$_2$NC=S)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**24b**) | 0.54 (t, $J_{H-H}$ = 7.51 Hz, 3 H, CH$_3$)<br>1.39 (t, $J_{H-H}$ = 7.15 Hz, 3 H, CH$_3$)<br>3.39, 3.82 (m, 2 H each, CH$_2$) | 190.5 | 238.61 (6.61) |
| (μ-Ph(CH$_3$)NC=S)(μ-Ph$_2$P)-Fe$_2$(CO)$_6$ (**24c**) | 3.12 (s, 2.46 H, CH$_3$)<br>3.81 (s, 0.54 H, CH$_3$) | 189.3 (major)<br>191.5 | 248.03 (10.9) |
| (μ-CH$_3$S)(μ-Ph$_2$P)Fe$_2$(CO)$_6$ (**21a**) | 2.13 (d, $^4J_{P-H}$ = 1.8 Hz, 3 H, CH$_3$) | 142.3 | |
| (μ-(CH$_3$)$_2$NC=S)(μ-Et$_2$P)Fe$_2$(CO)$_6$ (**26**) | (CDCl$_3$)<br>1.38 (m, 6 H, CH$_3$ of Et)<br>2.11, 2.26 (m, 4 H, CH$_2$ of Et)<br>3.21 (s, 3 H, NCH$_3$)<br>3.47 (s, 3 H, NCH$_3$) | 200.1 | 242.69 (12.5) |
| (μ-(CH$_3$)$_2$P=S)(μ-EtS)Fe$_2$(CO)$_6$ (**18a**) | (CDCl$_3$)<br>1.51 (d, $^2J_{P-H}$ = 10.4 Hz, 3 H, PCH$_3$)<br>1.57 (t, $J_{H-H}$ = 7.3 Hz, 3 H, CH$_3$ of equatorial Et) | 54.3 (t, $J_{P-H}$ = 10.1 Hz) | |

Table IV (Continued)

| compd | $^1$H (δ), ppm$^a$ (solvent used was $CD_2Cl_2$ unless otherwise specified) | $^{31}$P ($δ_P$), ppm (solvent used was $CDCl_3$ unless otherwise specified | $^{13}$C [bridging $δ_{C=O}$ or $δ_{C=S}$], ppm ($^2J_{C-P}$, Hz) |
|---|---|---|---|
| (μ-$(CH_3)_2P$=S)(μ-EtS)$Fe_2(CO)_6$ (**18a**) | 1.76 (d, $^2J_{P-H}$ = 9.1 Hz, 3 H, $PCH_3$)<br>2.73 (q, $J_{H-H}$ = 7.3 Hz, 2 H, $CH_2$ of Et) | | |
| (μ-$(CH_3)_2P$=S)(μ-PhS)$Fe_2(CO)_6$ (**18b**) | 1.62 (d, $^2J_{P-H}$ = 10.3 Hz, 3 H, $PCH_3$)<br>1.85 (d, $^2J_{P-H}$ = 9.0 Hz, 3 H, $PCH_3$) | 56.7 | |

$^a$Ph C—H resonances not listed; complete $^1$H NMR spectra are in supplementary material.

was allowed to warm slowly to room temperature. During this time the mixture changed slowly from green-black to orange. Subsequently, solvent and other volatiles were removed by trap-to-trap distillation (room temperature, high vacuum, −78 or −196 °C trap). The residue was purified by filtration chromatography (silicic acid).

**Reactions of the [(μ-$Ph_2P$)$Fe_2(CO)_6$]$^-$ Anion with Electrophiles. (a) Propionyl Chloride.** Filtration chromatography (silicic acid, 1/9 v/v $CH_2Cl_2$/pentane) gave (μ-$C_2H_5C$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**4a**) as an orange solid, mp 98.0–99.0 °C (from $CH_2Cl_2$/pentane) in 72% yield. Anal. Calcd for $C_{21}H_{15}O_7PFe_2$: C, 48.32; H, 2.90. Found: C, 48.27; H, 3.05.

**(b) Isobutyryl Chloride.** Filtration chromatography (1/20 v/v $CH_2Cl_2$/pentane) gave (μ-$(CH_3)_2CHC$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**4b**) as an orange oil, in 77% yield, and the mono(triphenylphosphine) substitution product (μ-$(CH_3)_2CHC$=O)(μ-$Ph_2P$)-$Fe_2(CO)_5(PPh_3)$ (**4b′**) was prepared as a red-orange solid, mp 168–169 °C dec. Anal. Calcd for $C_{39}H_{32}O_6P_2Fe_2$: C, 60.81; H, 4.19. Found: C, 61.13; H, 4.51.

**(c) Benzoyl Chloride.** Filtration chromatography (1/9 v/v $CH_2Cl_2$/pentane) gave an orange oil in 85% yield which, according to its NMR spectra, was (μ-PhC=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**4c**), and the mono(triphenylphosphine) substitution product (μ-PhC=O)(μ-$Ph_2P$)$Fe_2(CO)_5(PPh_3)$ (**4c′**) was prepared as a red-orange solid, mp 174-176 °C dec. Anal. Calcd for $C_{42}H_{30}O_6P_2Fe_2$: C, 62.72; H, 3.76. Found: C, 62.32; H, 3.98.

**(d) Phenylacetyl Chloride.** Filtration chromatography (1/9 v/v $CH_2Cl_2$/pentane) gave the product (μ-$PhCH_2C$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**4d**) as an orange oil in 45% yield. This compound had been prepared by Osterloh.[2]

**(e) *trans*-Cinnamoyl Chloride.** Filtration chromatography (1/9 v/v $CH_2Cl_2$/pentane) gave an orange oil in 50% yield, whose NMR spectra were consistent with its formulation as (μ-*trans*-PhCH=CHC=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**4e**), although a satisfactory analysis could not be obtained. Attempted reaction of the oil with $Ph_3P$ in refluxing THF resulted in decomposition. A figure of the $^1$H NMR spectrum of the orange oil showing the presence of pentane can be found in the supplementary material.

**(f) *trans*-Crotonyl Chloride.** Filtration chromatography (1/9 v/v $CH_2Cl_2$/pentane) gave an orange oil which was purified further by column chromatography. The resulting orange oil (39% yield) held traces of pentane tenaciously (a figure of the $^1$H NMR spectrum is in the supplementary material) and did not give a satisfactory C, H analysis. Attempts to prepare a mono(triphenylphosphine) substitution product resulted in decomposition.

**(g) 3,3-Dimethylacryloyl Chloride.** Purification was carried out as in (f) above. The resulting, slightly air-sensitive orange oil (84% yield) was kept in high vacuum for 2 days, but pentane still was present (a figure of the $^1$H NMR spectrum is in the supplementary material). A red-orange, solid mono(triphenylphosphine) substitution product could be prepared, (μ-$(CH_3)_2C$=CHC=O)(μ-$Ph_2P$)$Fe(CO)_5(PPh_3)$ (**4g′**). Anal. Calcd for $C_{40}H_{32}O_6P_2Fe_2$: C, 61.41; H, 4.12. Found: C, 60.93; H, 4.32.

**(h) Acryloyl Chloride.** Filtration chromatography (1/20 v/v $CH_2Cl_2$/pentane) gave an orange-red solid, mp 128–129 °C ($CH_2Cl_2$/pentane), (μ-σ,π-$CH_2$=CH)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**15**) in 52% yield. Anal. Calcd for $C_{20}H_{13}O_6PFe_2$: C, 48.83; H, 2.66. Found: C, 48.69; H, 2.81.

**(i) *N,N*-Dimethylthiocarbamoyl Chloride.** Reaction of the green-black anion solution obtained by adding 2.0 mmol of $LiBEt_3H$ (1 M in THF) to 0.97 mmol of (μ-$CH_3C$=O)(μ-$Ph_2P$)-$Fe_2(CO)_6$ at −78 °C with 0.25 g (2.03 mmol) of $Me_2NC(S)Cl$ in THF gave, after warming to room temperature, an orange solution. Trap-to-trap distillation and filtration chromatography of the residue (1/9 v/v $CH_2Cl_2$/pentane) afforded 0.48 g (89% yield) of an orange solid, (μ-$(CH_3)_2NC$=S)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**16**), mp 139–140 °C dec (to a red solid which melted at 149–150 °C) ($CH_2Cl_2$/pentane). Anal. Calcd for $C_{21}H_{16}O_6SNPFe_2$: C, 45.60; H, 2.92. Found: C, 45.62; H, 3.19.

**(j) Dimethylthiophosphinic Chloride.** Using the standard procedure, 0.19 g (1.49 mmol) of $(CH_3)_2P(S)Cl$[21] was added, at −78 °C, to a green-black solution of the anion prepared from 0.64 mmol of (μ-$CH_3C$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ and 1.29 mmol of $LiBEt_3H$. Slow warming to room temperature was followed by stirring for 18 h, trap-to-trap distillation, and filtration chromatography (1/4 v/v $CH_2Cl_2$/pentane). An orange solid, mp 145–146 °C (red melt) ($CH_2Cl_2$/pentane), (μ-$(CH_3)_2P$=S)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**17**), was obtained in 36% yield. Anal. Calcd for $C_{20}H_{16}O_6SP_2Fe_2$: C, 43.05; H, 2.89. Found: C, 43.01; H, 2.95.

**(k) Dimethylphosphinic Chloride.** The same procedure was used in the reaction of the green-black anion solution (from 0.85 mmol of (μ-$CH_3C$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ and 1.69 mmol of $LiBEt_3H$) with 0.19 g (1.69 mmol) of $(CH_3)_2P(O)Cl$. Filtration chromatography (1/9 v/v $CH_2Cl_2$/pentane) of the reaction residue gave 0.35 g, 76%) of (μ-$Me_2P$)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**20a**), an orange solid, mp 122–123 °C. Anal. Calcd for $C_{20}H_{16}O_6P_2Fe_2$: C, 45.67; H, 3.07. Found: C, 45.82; H, 3.16.

**(l) Diphenylchlorophosphine.** To the standard green-black anion solution (from 0.98 mmol of (μ-$CH_3C$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ and 1.96 mmol of $LiBEt_3H$) was added at −78 °C 0.43 g (1.95 mmol) of $Ph_2PCl$. The usual workup gave (μ-$Ph_2P$)$_2Fe_2(CO)_6$ (**20b**), a yellow solid, mp 186–188 °C, in 72% yield. Its spectroscopic properties were in good agreement with those reported for this compound.[20]

This product also was formed in 44% yield in the reaction of the green-black anion solution with $Ph_2P(Cl)$=NPh.

**(m) Phosphorus Trichloride.** Upon addition, at −78 °C, of 0.24 g (1.72 mmol) of $PCl_3$ to the green-black anion solution from 0.70 mmol of (μ-$CH_3C$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ and 1.40 mmol of $LiBEt_3H$ there occurred an immediate color change to orange. The orange oil which remained after solvent removal gave, on filtration chromatography (1/9 v/v $CH_2Cl_2$/pentane), 0.24 g (62%) of yellow, crystalline (μ-$Cl_2P$)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**20c**) mp 135–136 °C. Anal. Calcd for $C_{18}H_{10}Cl_2O_6P_2Fe_2$: C, 38.14; H, 1.78. Found: C, 38.48; H, 1.84.

**(n) Carbon Disulfide. (i) Iodomethane Quench.** To the standard green-black anion solution (from 0.98 mmol of (μ-$CH_3C$=O)(μ-$Ph_2P$)$Fe_2(CO)_6$ and 1.97 mmol of $LiBEt_3H$) was added, at −78 °C, 0.32 g (4.16 mmol) of $CS_2$. The reaction mixture was stirred at 0 °C, during which time it became red-brown in color. Then 0.57 g (4.12 mmol) of $CH_3I$ was added and the resulting solution was stirred at room temperature for 18 h. The usual workup, including filtration chromatography (1/9 v/v $CH_2Cl_2$/pentane), gave 0.45 g (82%) of light orange crystals, mp 134–135 °C (pentane), of (μ-$CH_3SC$=S)(μ-$Ph_2P$)$Fe_2(CO)_6$ (**22a**). Anal. Calcd for $C_{20}H_{13}O_6PS_2Fe_2$: C, 43.20; H, 2.36. Found: C, 43.27; H, 2.60.

**(ii) Iodoethane Quench.** A similar reaction was carried out in which $C_2H_5I$ was added to the red-brown anion solution. Filtration chromatography (1/20 v/v $CH_2Cl_2$/pentane) gave an orange oil, **22b**, in about 50% yield which retained pentane in spite of high-vacuum (room-temperature) treatment for 2 days. The $^1$H NMR spectrum (figure in supplementary material) and the C, H analysis showed this. Anal. Calcd for $C_{22}H_{15}O_6S_2PFe_2$: C, 45.39; H, 2.60. Found: C, 49.46; H, 3.59.

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[21] Maier, L. *Chem. Ber.* **1961**, *94*, 3051.

Attempted reaction of this product with Ph$_3$P in refluxing THF resulted in decomposition.

**(iii) Benzyl Chloride.** The same problem was encountered in the synthesis and isolation of ($\mu$-PhCH$_2$SC=S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ (**22c**) when benzyl chloride was added to the red-brown anion solution. The orange oil that was isolated in about 75% yield retained pentane tenaciously and decomposed when treated with Ph$_3$P in refluxing THF.

**(o) Methyl Isothiocyanate.** To the green-black anion solution prepared by reaction of 0.97 mmol of ($\mu$-CH$_3$C=O)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ and 1.93 mmol of LiBEt$_3$H in THF at −78 °C was added 0.15 g (2.05 mmol) of CH$_3$NCS in 5 mol of THF. Within 15 min at −78 °C the solution became red-brown in color. Iodomethane (0.46 g, 3.2 mmol) was added. The reaction mixture was warmed slowly to room temperature and stirred for 18 h. Filtration chromatography after removal of solvent (1/9 v/v CH$_2$Cl$_2$/pentane) gave 0.42 g (79%) of light orange solid ($\mu$-(CH$_3$)$_2$NC=S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$, which was identical in all respects with the product of the reaction of the green-black anion solution with (CH$_3$)$_2$NC(S)Cl (**16**).

**(p) Ethyl Isothiocyanate. (i) Triethylammonium Bromide Quench.** The same procedure was used in the formation and reaction of the [($\mu$-C$_2$H$_5$NC=S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$]$^-$ anion solution (from 1.0 mmol of ($\mu$-CH$_3$C=O)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ and 2.01 mmol of LiBEt$_3$H, followed by 0.18 g (2.06 mmol) of C$_2$H$_5$NCS) with 0.39 g (2.13 mmol) of [Et$_3$NH]Br as a slurry in 10 mL of THF. Filtration chromatography, after removal of solvent, gave an orange oil which was subjected to column chromatography. The product, ($\mu$-C$_2$H$_5$NHC=S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ (**25**), obtained in about 80% yield, retained pentane tenaciously even after 4 days in vacuum. Attempted reaction with Ph$_3$P in refluxing THF resulted in decomposition.

**(ii) Iodoethane Quench.** Addition of C$_2$H$_5$I to the red-brown [($\mu$-C$_2$H$_5$NC=S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$]$^-$ anion solution gave ($\mu$-(C$_2$H$_5$)$_2$NC=S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ (**24b**) as an orange, oily solid in about 65% yield which presented the same problems of isolation and purification.

**(q) Phenyl Isothiocyanate.** Using the above procedure, 0.25 g (1.85 mmol) of PhNCS was added to the green-black anion solution prepared from 0.923 mmol of ($\mu$-CH$_3$C=O)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ and 1.85 mmol of LiBEt$_3$H. To the resulting red-brown solution was added 1.85 mmol of CH$_3$I. After a reaction time of 18 h at room temperature, solvent removal and filtration chromatography (1/9 v/v CH$_2$Cl$_2$/pentane) gave 0.28 g (50%) of an orange solid, ($\mu$-Ph(CH$_3$)NC=S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ (**24c**), mp 159–160 °C. Anal. Calcd for C$_{26}$H$_{18}$O$_6$NSPFe$_2$: C, 50.76; H, 2.95; N, 2.28. Found: C, 51.09; H, 3.28; N, 2.28.

**(r) Elemental Sulfur. (i) Iodomethane Quench.** To the green-black anion solution in THF at −78 °C (from 0.51 mmol of ($\mu$-CH$_3$C=O)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ and 1.01 mmol of LiBEt$_3$H) was added 0.04 g (1.18 mmol as "S") of sublimed S$_8$ as a THF slurry. The solution was stirred at 0 °C for 30 min, during which time the color changed to clear emerald green. Iodomethane (1.12 mmol) was added, and the reaction mixture was stirred for 18 h at room temperature. Removal of solvent left an orange oil which was purified by filtration chromatography (3/7 v/v CH$_2$Cl$_2$/pentane). The product, ($\mu$-CH$_3$S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$ (**21a**), mp 133–134 °C (CH$_2$Cl$_2$/pentane), an orange solid, was isolated in 77% yield. Anal. Calcd for C$_{19}$H$_{13}$O$_6$SPFe$_2$: C, 44.57; H, 2.56. Found: C, 44.64; H, 2.74.

**(ii) Iodoethane Quench.** The same general procedure was used, except that C$_2$H$_5$I was used in place of CH$_3$I. The product, ($\mu$-C$_2$H$_5$S)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$, an orange solid, was obtained in 54% yield. Its $^1$H and $^{31}$P NMR spectra were in agreement with literature data.[22]

**Reaction of Li[($\mu$-Et$_2$P)Fe$_2$(CO)$_6$] with *N*,*N*-Dimethylthiocarbamoyl Chloride.** Using the usual procedure, 3.18 mL of 1M LiBEt$_3$H in THF (3.18 mmol) was added, at −78 °C, to 0.66 g (1.59 mmol) of ($\mu$-CH$_3$C=O)($\mu$-Et$_2$P)Fe$_2$(CO)$_6$ in 40 mL of THF. After 45 min, 0.39 g (3.18 mmol) of (CH$_3$)$_2$NC(S)Cl in 5 mL of THF was added (at −78 °C). After a reaction time of 18 h at room temperature, solvent removal and filtration chromatography (1/20 v/v CH$_2$Cl$_2$/pentane) gave 0.44 g (61%) of orange-yellow ($\mu$-(CH$_3$)$_2$NC=S)($\mu$-Et$_2$P)Fe$_2$(CO)$_6$ (**26**), mp 109–110 °C (pentane). Anal. Calcd for C$_{13}$H$_{16}$O$_6$SPFe$_2$: C, 34.17; H, 3.53; N, 3.06. Found: C, 34.28; H, 3.60; N, 3.06.

In another experiment, CO was bubbled into the Li[($\mu$-Et$_2$P)Fe$_2$(CO)$_6$] green-black solution at −78 °C to give a clear brown-yellow solution. This solution was warmed to room temperature, and 0.29 g (2.34 mmol) of (CH$_3$)$_2$NC(S)Cl in 3 mL of THF was added. Further processing was as above. Column chromatography served to separate the major product, ($\mu$-(CH$_3$)$_2$NC=S)($\mu$-Et$_2$P)Fe$_2$(CO)$_6$, in 17% yield from several very minor products.

**Reaction of [Et$_4$N][($\mu$-CO)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$] with *tert*-Butanesulfenyl Chloride.** *tert*-Butanesulfenyl chloride (prepared by addition of 0.13 g (0.10 mmol) of SO$_2$Cl$_2$ to 0.21 g (0.93 mmol) of di-*tert*-butyl disulfide at −78 °C)[23] was added at −78 °C to a THF solution of 0.47 g (0.76 mmol) of [Et$_4$N][($\mu$-CO)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$] prepared by the method of Osterloh.[2] The solution darkened to brown-orange. It was warmed slowly to room temperature and stirred for 18 h. After removal of solvent, filtration chromatography (1/9 v/v CH$_2$Cl$_2$/pentane) gave ($\mu$-*t*-BuS)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$, an orange solid, whose spectra agreed with those in the literature.[24]

**Reaction of [Et$_3$NH][($\mu$-CO)($\mu$-EtS)Fe$_2$(CO)$_6$] with Dimethylthiophosphinic Chloride.** A 100-mL Schlenk flask was charged with 3.00 g (5.96 mmol) of Fe$_3$(CO)$_{12}$ and evacuated/argon back-filled three times. THF (40 mL) was added by cannula, and then 0.60 g (5.96 mmol) of triethylamine and 0.37 g (5.96 mmol) of C$_2$H$_5$SH were added. Within 45 min at room temperature the initially green solution had turned red, indicating the formation of [Et$_3$NH][($\mu$-CO)($\mu$-EtS)Fe$_2$(CO)$_6$].[1a] Upon addition of (CH$_3$)$_2$P(S)Cl (0.80 g, 6.23 mmol) no immediate reaction was apparent, but during a reaction time of 18 h at room temperature TLC indicated the formation of a single orange-red product. Removal of solvent in vacuo left a red-brown residue which was purified by filtration chromatography (1/4 v/v CH$_2$Cl$_2$/pentane) to give 2.24 g (87%) of red, crystalline ($\mu$-(CH$_3$)$_2$P=S)($\mu$-EtS)Fe$_2$(CO)$_6$ (**18a**), mp 60–61 °C (CH$_2$Cl$_2$/pentane). Anal. Calcd for C$_{10}$H$_{11}$O$_6$S$_2$PFe$_2$: C, 27.68; H, 2.55. Found: C, 27.70; H, 2.58.

In another experiment, (CH$_3$)$_2$P(S)Cl (6.23 mmol) was added to a THF solution of [Et$_3$NH][($\mu$-CO)($\mu$-PhS)Fe$_2$(CO)$_6$ (from 5.96 mmol each of Fe$_3$(CO)$_{12}$, triethylamine, and benzenethiol). The same general procedure gave first ($\mu$-PhS)$_2$Fe$_2$(CO)$_6$ (16.5%) on elution with pentane. Further elution with 1/4 v/v CH$_2$Cl$_2$/pentane gave ($\mu$-(CH$_3$)$_2$P=S)($\mu$-PhS)Fe$_2$(CO)$_6$ (**18b**), orange-red crystals, mp 139–140 °C (pentane/CH$_2$Cl$_2$), in 62% yield. Anal. Calcd for C$_{14}$H$_{11}$O$_6$S$_2$PFe$_2$: C, 34.88; H, 2.30. Found: C, 34.94; H, 2.41.

**Crystallization of the Tetraethylammonium Salt of the "Red-CO Anion".** Carbon monoxide was bubbled for 5 min through the green-black anion solution (generated from 0.98 mmol of 7 and 1.96 mmol of LiBEt$_3$H in THF) at −78 °C under argon. While the CO stream was continued, the now red solution was allowed to warm slowly to room temperature. The CO stream was continued for 30 min more. The solvent was removed at reduced pressure, leaving an oily red residue which was redissolved in 5 mL of CH$_2$Cl$_2$. A slurry of 0.25 g (1.53 mmol) of [Et$_4$N]Cl in THF/Et$_2$O was added. A red-orange powder precipitated as the solution was cooled at −30 °C overnight. The solid was recrystallized from CH$_2$Cl$_2$/pentane giving 0.42 g (68%) of [Et$_4$N][($\mu$-CO)($\mu$-Ph$_2$P)Fe$_2$(CO)$_6$]. $^1$H NMR (acetone-$d_6$, 300 MHz): $\delta$ 1.38 (t, 12 H, $J$ = 7.4 Hz, 12 H, CH$_3$), 3.48 (q, $J$ = 7.4 Hz, 8 H, CH$_2$), 7.26 and 7.62 (m, 10 H, C$_6$H$_5$). $^{13}$C NMR (DMSO, 75.4 MHz): $\delta_C$ 7.2 (q, $J_{C\text{-}H}$ = 129.4 Hz, CH$_3$), 51.5 (t, $J_{C\text{-}H}$ = 143.5 Hz, CH$_2$), 126.7–140.5 (m, C$_6$H$_5$), 225.8 ($J_{C\text{-}P}$ = 11.3 Hz) (all CO's). $^{31}$P NMR (CD$_2$Cl$_2$, 121.6 MHz): $\delta_P$ 124.0 (s). [Osterloh reports:[2] $^1$H NMR (acetone-$d_6$, 90 MHz) $\delta$ 1.32 (t, 12 H), 3.40 (q, 8 H), 7.20 and 7.60 (m, 10 H); $^{13}$C NMR (CD$_2$Cl$_2$, 50.3 MHz) $\delta_C$ 7.8 (CH$_3$), 53.1 (t, CH$_2$), 127.8–141.1 (m, C$_6$H$_5$), 227 (d, $J_{C\text{-}P}$ = 11.9 Hz) (all CO's); $^{31}$P NMR (CD$_2$Cl$_2$, 36.4 MHz) $\delta_P$ 124.8 (s).]

**X-ray Crystallography. X-ray Data Collection.** Suitable crystals of ($\mu$-(CH$_3$)$_2$P=S)($\mu$-PhS)Fe$_2$(CO)$_6$ were grown from

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[22] Archer, C. M. Ph.D. Dissertation, MIT, 1986. Manuscript in preparation.

[23] Still, I. W. J.; Kutney, G. W.; McLean, D. *J. Org. Chem.* **1982**, *47*, 560.

[24] Womack, G. B. Ph.D. Dissertation, MIT, 1984. Manuscript in preparation.

**Table V. Crystallographic Data**

| | |
|---|---|
| compd | $(\mu\text{-}(CH_3)_2P{=}S)(\mu\text{-}PhS)[Fe_2(CO)_6]$ |
| formula | $Fe_2S_2PO_6C_{14}H_{11}$ |
| fw | 482.04 |
| cryst shape | plate |
| cryst dimens, mm | 0.65 × 0.08 × 0.39 |
| space group | $P2_12_12_1$ |
| temp, °C | 21 |
| radiation (λ, Å) | graphite-monochromated Mo K$\alpha$ (0.71069) |
| cell params | |
| $a$, Å | 12.494 (2) |
| $b$, Å | 17.705 (2) |
| $c$, Å | 8.7909 (9) |
| $V$, Å$^3$ | 1944.7 (7) |
| $Z$ | 4 |
| $\rho$(calcd), g cm$^{-3}$ | 1.646 |
| linear abs coefft | 18.037 |
| range of transm factors | 0.807–1.712 |
| detector aperture, mm | (3.00 + tan $\theta$) wide × 4.00 high |
| takeoff angle, deg | 3.0 |
| max 2$\theta$, deg | 54.0 |
| crystal–detector distance, mm | 173 |
| scan type | $\theta/2\theta$ |
| scan rate, deg min$^{-1}$ | 1.05–6.67 |
| scan width, deg | 0.50 + 0.347 tan $\theta$ |
| total no. of unique reflections | 2442 ($h,k,l$) |
| total no. of obsns (NO) | 1981 |
| final no. of params varied (NV) | 196 |
| error in obs of unit wt (GOF)[a] | 1.327 |
| $R$[b] | 0.0325 |
| $R_w$[c] | 0.0407 |

[a] $GOF = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$. [b] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

pentane/$CH_2Cl_2$ solution at −20 °C. Data were collected on an Enraf-Nonius CAD4 diffractometer with use of Mo K$\alpha$ radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range 18.0° ≤ $2\theta$ ≤ 25.0°. The diffraction symmetry and the systematic absences $h00$ ($h$ = odd), $0k0$ ($k$ = odd), $00l$ ($l$ = odd) were consistent with the space group $P2_12_12_1$. Diffraction data were collected to a maximum $2\theta$ = 54°, and background counts were obtained by extending the scan 25% on each side of the peaks. Three reflections were chosen as intensity standards and were remeasured at 120-min intervals of X-ray exposure. There was no significant variation in the intensities of these standards, so no correction was applied. Absorption corrections were applied to the data by using the method of Walker and Stuart.[25] See Table V for a summary of crystal data and X-ray collection information.

**Structure Solution and Refinement.** The structure was solved by use of MULTAN,[26] which succeeded in locating the $Fe_2S_2P$ core atoms. Subsequent least-squares refinements[27] and difference Fourier Syntheses led to the location of all remaining atoms. Atomic scattering factors[28] and anomalous dispersion terms[29] were taken from the usual tabulations. Although hydrogen atoms were located, they were not refined but were input in their idealized positions and assigned isotropic thermal parameters of 20% greater than that of the attached carbon. Refinement of the other enantiomorph led to significantly higher residuals, establishing the original hand as correct. On the final difference Fourier map no residual was higher than 0.38 e/Å$^3$. The final positional and isotropic thermal parameters for the non-hydrogen atoms are given in Table VI.

**Table VI. Positional and Thermal Parameters for the Non-Hydrogen Atoms of $[Fe_2(CO)_6(\mu\text{-}SPMe_2)(\mu\text{-}SPh)]$**

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Fe(1) | 0.27675 (5) | 0.19983 (4) | 0.16810 (7) | 2.66 (1) |
| Fe(2) | 0.15187 (5) | 0.23622 (4) | 0.39910 (7) | 2.87 (1) |
| S(1) | 0.32724 (8) | 0.26549 (7) | 0.3747 (1) | 2.76 (2) |
| S(2) | 0.3290 (1) | 0.09402 (7) | 0.3132 (2) | 3.76 (2) |
| P | 0.2127 (1) | 0.12059 (7) | 0.4652 (1) | 3.41 (2) |
| O(1) | 0.2072 (4) | 0.3290 (2) | −0.0088 (5) | 6.1 (1) |
| O(2) | 0.4663 (4) | 0.1835 (3) | −0.0239 (5) | 7.3 (1) |
| O(3) | 0.1262 (3) | 0.0975 (3) | 0.0154 (5) | 6.0 (1) |
| O(4) | 0.0943 (3) | 0.2629 (3) | 0.7176 (5) | 6.8 (1) |
| O(5) | −0.0427 (3) | 0.1719 (3) | 0.2690 (6) | 5.9 (1) |
| O(6) | 0.0759 (3) | 0.3868 (2) | 0.3057 (6) | 6.5 (1) |
| C(1) | 0.2324 (4) | 0.2793 (3) | 0.0641 (6) | 3.7 (1) |
| C(2) | 0.3951 (4) | 0.1893 (3) | 0.0523 (6) | 4.2 (1) |
| C(3) | 0.1845 (4) | 0.1372 93) | 0.0733 (6) | 3.9 (1) |
| C(4) | 0.1163 (4) | 0.2536 (3) | 0.5904 (6) | 4.5 (1) |
| C(5) | 0.0331 (4) | 0.1959 93) | 0.3199 (6) | 3.7 (1) |
| C(6) | 0.1075 (4) | 0.3292 (3) | 0.3381 (7) | 4.2 (1) |
| C(7) | 0.2706 (6) | 0.1123 (4) | 0.6537 (7) | 6.4 (2) |
| C(8) | 0.1147 (5) | 0.0449 (3) | 0.4647 (9) | 6.0 (2) |
| C(11) | 0.3456 (4) | 0.3653 (3) | 0.3463 (5) | 2.89 (8)* |
| C(12) | 0.4004 (4) | 0.3912 (3) | 0.2197 (6) | 3.8 (1)* |
| C(13) | 0.4191 (4) | 0.4686 (3) | 0.2042 (6) | 4.4 (1)* |
| C(14) | 0.3817 95) | 0.5180 (3) | 0.3121 (7) | 4.8 (1)* |
| C(15) | 0.3296 (5) | 0.4922 (4) | 0.4365 (7) | 5.1 (1)* |
| C(16) | 0.3109 (4) | 0.4149 (3) | 0.4559 (6) | 4.0 (1)* |

[a] Starred values refer to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

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**Supplementary Material Available:** A listing of characterization data (melting points and IR, $^1H$, $^{13}C$, and $^{31}P$ NMR, and 70-eV EI mass spectra) for all new compounds, tables of anisotropic and isotropic thermal parameters and hydrogen atom parameters for compound **18b**, and figures of $^1H$ NMR spectra of product oils that retained pentane (33 pages). Ordering information is given on any current masthead page.

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