In further experiments, *cis*- and *trans*-propenyltrimethylsilane were separated by GLC (6 ft × 0.25 in. 20% by weight of a 14% $AgNO_3$ solution in tetraethylene glycol; F&M 700 gas chromatograph). Each isomer (3.6 and 2.6 mmol, respectively) was added separately to an argon-purged 5-mm NMR tube capped with a rubber septum, and then 15 μL of C_6D_6 (lock sample and reference sample for ^{13}C NMR) and 0.49 mmol of hexamethylsilirane (THF concentrate) were added by syringe. The NMR tubes were cooled, evacuated, sealed off, and heated for 17 h at 70 °C. After ^{1}H and ^{13}C NMR spectra had been obtained, 100 μL of MeOH was added to each tube (exothermic reaction). ^{1}H and ^{13}C NMR measurements were repeated. Subsequent GLC analysis of the solutions showed the presence of $Me_2(OMe)SiCH(Et)SiMe_3$ (GLC retention time and IR spectrum) in each case. The yield of this methoxysilane was 68% in the case of the *cis*-propenylsilane experiment and 55% in the case of the experiment with the trans isomer.

(f) *anti*-Bi-7-norcaranylidene, 6. A solution of 0.90 mmol of hexamethylsilirane (THF concentrate), 2.40 g (12.6 mmol) of *anti*-bi-7-norcaranylidene[17] and 5 mL of benzene was stirred and heated for 18 h at 73 °C. The solution was cooled to room temperature, and 0.5 mL of methanol was added (mild exotherm). An additional 5 mL of MeOH was added to precipitate most of the unreacted olefin. Filtration was followed by concentration of the filtrate at reduced pressure. GLC analysis of the residue indicated that one major product had been formed. This material was collected by GLC and identified ($n^{25}{}_D$ and IR) as the methanolysis product of silirane 4.[15] The yield of this product was 35%; tetramethylethylene was present in 76% yield.

Acknowledgment. We are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this work and to Dr. Michel Massol for a sample of *anti*-bi-7-norcaranylidene. We are indebted to a reviewer for very useful comments concerning the mechanistic aspects of this work.

Registry No. $Et_3SiSiMe_2H$, 31732-54-4; *i*-$PrMe_2SiSiMe_2H$, 58023-36-2; $HEt_2SiSiMe_2H$, 34202-97-6; $PhMe(OMe)SiSiMe_2OMe$, 82281-37-6; hexamethylsilirane, 55644-09-2; triethylsilane, 617-86-7; tetramethylethylene, 563-79-1; isopropyldimethylsilane, 18209-61-5; diethylsilane, 542-91-6; dimethyldimethoxysilane, 1112-39-6; 1,2-dimethoxytetramethyldisilane, 10124-62-6; methylphenyldimethoxysilane, 3027-21-2; methyltrimethoxysilane, 1185-55-3; 1,1,2-trimethyl-1,2,2-trimethoxydisilane, 18107-31-8; trimethylmethoxysilane, 1825-61-2; trimethylphenoxysilane, 1529-17-5; hexamethylcyclotrisiloxane, 541-05-9; 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxa-1,2,4,6-tetrasilacycloheptane, 17865-99-5; 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane, 7418-20-4; 2,2,3,3,6,6-hexamethyl-2,3,6-trisila-1-oxacyclohexane, 66977-50-2; *cis*-4-octene, 7642-15-1; 4-octyldimethylmethoxysilane, 61753-24-0; *trans*-4-octene, 14850-23-8; 2,3-dimethyl-2-pentane, 10574-37-5; 3-(3,4-dimethylpentyl)dimethylmethoxysilane, 61753-26-2; cyclooctene, 931-88-4; cyclooctyldimethylmethoxysilane, 61753-23-9; propenyltrimethylsilane, 17680-01-2; 1-(1-(trimethylsilyl)propyl)dimethylmethoxysilane, 61753-25-1; anti-bi-7-norcaranylidene, 18688-18-1; dimethylsilane, 1111-74-6.

Preparation and Properties of (μ_3-Thio)(μ_3-organophosphido)tris(tricarbonyliron)(*2Fe–Fe*) Complexes

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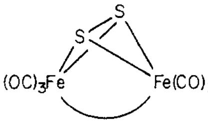
The reactions of $Fe_3(CO)_{12}$ with $RP(S)Cl_2$ gave $(\mu_3\text{-}S)(\mu_3\text{-}RP)Fe_3(CO)_9$ and not the desired $(\mu\text{-}RPS)Fe_2(CO)_6$ complexes.

Introduction

Our studies have shown that (μ-dithio)bis(tricarbonyliron),[1] 1, has a very reactive S–S bond.[2] The analogous selenium compound 2[1] shows similar reactivity,[3] and the tellurium analogue 3 recently has been isolated and characterized.[4] The RN, RP, RAs, and RSb moieties are isoelectronic with the corresponding chalcogen atoms, O, S, Se, and Te, respectively, and so it is not surprising that 4,[5] a group 5 analogue of complexes 1–3, and 5,[6] an analogous mixed group 5/group 6 complex, are known. It would be of interest to study in detail the chemistries of 4 and 5, but, unfortunately, the known preparative routes to these complexes are unsatisfactory, giving only very low yields. A $Fe_2(CO)_6$ complex of the group 5/group 6 bridge type which has not yet been reported is 6, and we report here concerning our attempts to prepare compounds of this type.



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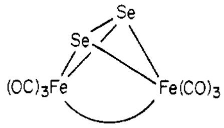

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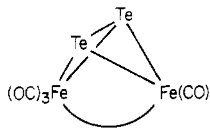

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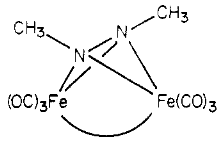

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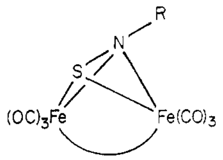

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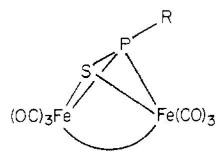

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Table I. The CO Stretching Bands in the IR Spectra of (μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$ and (μ_3-S)$_2Fe_3(CO)_9$ (cm^{-1} in CCl_4 solution)

(μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$	(μ_3-S)$_2Fe_3(CO)_9$
2085 w	2078 vw
2058 vs	2060 vs
2037 vs	2042 vs
2015 s	2020 s
2001 vw	2001 vw
1998 vw	1983 vw

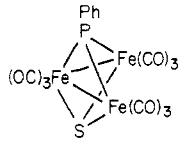
Results and Discussion

The approach to the preparation of complexes of type **6** which we chose to investigate was based on the trapping of a phosphinothioylidene, $R\ddot{P}{=}S$, by an iron carbonyl. Routes to such intermediates have been studied by Japanese workers[7] (eq 1). It is not certain that this reaction

$$RP({=}S)Cl_2 + Mg \xrightarrow{THF} R\ddot{P}{=}S \xrightarrow{EtSSEt} RP({=}S)(SEt)_2 \quad (1)$$

proceeds by way of a "free" phosphinothioylidene, but in any case, the active reagent, whatever its constitution, provides the elements of $R\ddot{P}{=}S$. Since the intermediate is highly reactive, it must be brought into reaction by the "in situ" technique.

Our first reaction was carried out between $PhP(S)Cl_2$ and metallic magnesium in THF in the presence of $Fe_3(CO)_{12}$, all in equimolar quantities. No reaction appeared to occur at room temperature, but when the mixture was heated to gentle reflux, the green $Fe_3(CO)_{12}$ was consumed. TLC analysis of the reaction mixture showed that a variety of products had been formed. Three iron carbonyl complexes which were soluble in organic solvents were isolated. The major product (17%) was **7**, (μ_3-thio)(μ_3-phenylphosphido)tris(tricarbonyliron)(*2Fe–Fe*). The two other products, **8** and **9**, were isolated in about 1% yield. The expected (μ-phenylphosphinothioylidene)bis(tricarbonyliron), **6**, was not present. Complexes **8**[2] and **9**[8] are known compounds and are isostructural; **7** has not been reported previously. The properties of (μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$ are similar to those of (μ_3-S)$_2Fe_3(CO)_9$ and (μ_3-PhP)$_2Fe_3(CO)_9$. It is air-stable, both in the solid state and in solution, readily soluble in hexane and benzene, more so in more polar solvents such as dichloromethane, THF, and acetone. The structure of **7** was assigned on the basis of its analysis, its mass spectrum, which showed the molecular ion and fragment ions corresponding to the successive loss of the nine CO ligands, and the similarity of its IR spectrum in the terminal CO region to that of (μ_3-S)$_2Fe_3(CO)_9$ (Figure 1 and Table I).



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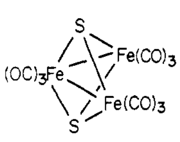

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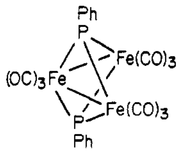

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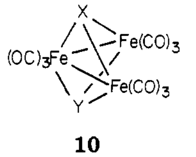

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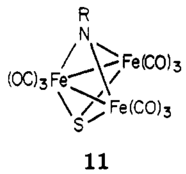

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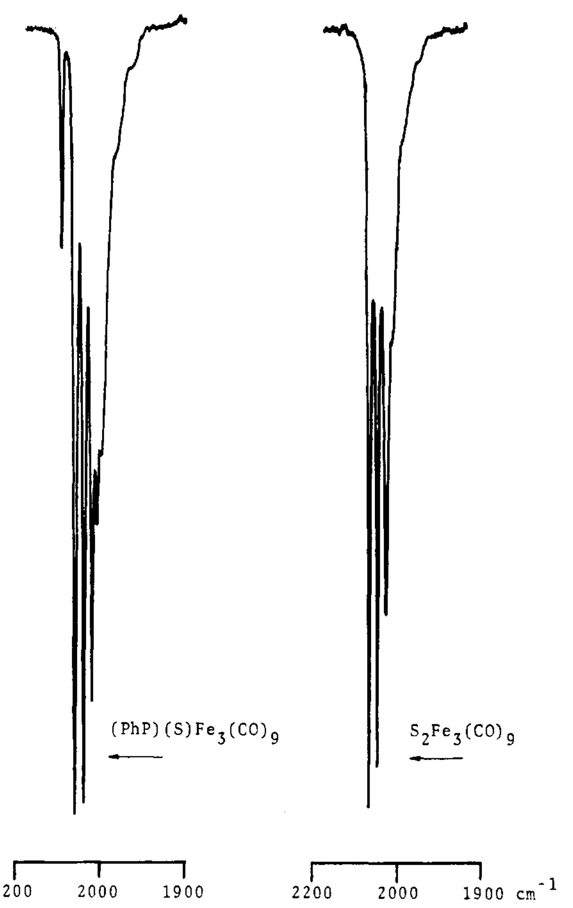

Figure 1. The IR spectra in the terminal CO region of (μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$ and (μ_3-S)$_2Fe_2(CO)_9$ (in CCl_4 solution).

Known complexes of type **10** are not restricted to those with X = Y = S, X = Y = PPh, and X = S, Y = PPh. Also reported have been those with X = Y = Se,[2] X = Y = Te,[2] X = Y = NMe,[5] X = Y = AsPh[9] and X = S, Y = NR (**11**).[6] The molecular structures of many of these complexes have been determined.

In our initial experiment, 50% of the magnesium charged was recovered unchanged. In view of this, and also, because iron carbonyls are known to be very effective dehalogenation agents,[10] we repeated the experiment in the absence of magnesium. Such a reaction between $PhP(S)Cl_2$ and $Fe_3(CO)_{12}$ in refluxing THF did indeed give **7** in 20% yield, together with minor amounts of **8** and **9**. Several experiments were performed in order to try to understand why the yields were so low and in order to improve the yields. The thermal stability of **7** was examined in refluxing THF solution, in both the absence and the presence of the other starting reagents. Heating a solution of **7** in THF at reflux for 4 h resulted in no appreciable decomposition; **7** was recovered in 80% yield. Heating **7** under the same conditions in the presence of 1 equiv of $PhP(S)Cl_2$ for 5 h also resulted in little decomposition or formation of other products (80% recovery of **7**). However, heating **7** in the same fashion in the presence of $Fe_3(CO)_{12}$ (1 equiv) for 4 h led to complete decomposition of $Fe_3(CO)_{12}$, 70% decomposition of (μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$, and the formation of small amounts of (μ_3-S)$_2Fe_3(CO)_9$. The presence of $Fe_3(CO)_{12}$ under these conditions thus appears to be detrimental to **7**. Very likely, the process responsible for the consumption of **7** is the

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Table II. Synthesis of (μ_3-RP)(μ_3-S)Fe$_3$(CO)$_9$ Complexes

RP(S)Cl$_2$ (mmol)	(μ_3-RP)(μ_3-S)Fe$_3$(CO)$_9$ (mmol)	% yield
p-CH$_3$C$_6$H$_4$P(S)Cl$_2$ (2.0)	(μ_3-*p*-CH$_3$C$_6$H$_4$P)-(μ_3-S)Fe$_3$(CO)$_9$ (0.3)	15
t-BuP(S)Cl$_2$ (2.0)	(μ_3-*t*-BuP)-(μ_3-S)Fe$_3$(CO)$_9$ (0.2)	10
PhP(S)Cl$_2$ (1.0)	(μ_3-PhP)-(μ_3-S)Fe$_3$(CO)$_9$ (0.2)	20

decomposition of Fe$_3$(CO)$_{12}$ on heating to give reactive fragments which then attack 7. The solvent was found to play a key role in the formation of 7. The reaction of PhP(S)Cl$_2$ with Fe$_3$(CO)$_{12}$ in refluxing hexane proceeded slowly. After 25 h of heating, a trace of Fe$_3$(CO)$_{12}$ still remained and a 21% yield of 7 was obtained. In benzene, a 4-h reaction time at 80 °C was necessary for complete consumption of the iron carbonyl, but, in this case, a 21% yield of (μ_3-S)$_2$Fe$_3$(CO)$_9$ resulted and only neglibible amounts of 7 were formed. This curious result lacks a ready explanation.

Further studies were performed to see what stoichiometry gives the best results. An excess of Fe$_3$(CO)$_{12}$, generally 1.5–2-fold, was found to give the best yields and the cleanest reaction in THF. If equimolar amounts of Fe$_3$(CO)$_{12}$ and PhP(S)Cl$_2$ (or an excess of the latter) were used, the yields of 7 were lower and 7 was obtained as an impure oil which contained unconverted PhP(S)Cl$_2$.

Since Fe$_3$(CO)$_{12}$ in refluxing THF appeared to react with the desired product, yet elevated temperatures also were required for product formation, a different reaction procedure was tried. A slurry of Fe$_3$(CO)$_{12}$ in THF was added slowly to a solution of PhP(S)Cl$_2$ in refluxing THF so that there was at no time an excess of the iron carbonyl present. However, the formation of 7 was not observed under these conditions and only decomposition resulted.

Of the three neutral iron carbonyls, Fe(CO)$_5$, Fe$_2$(CO)$_9$, and Fe$_3$(CO)$_{12}$, only the last gave useful yields of 7 under the best conditions. In this reaction, the thermal decomposition of Fe$_3$(CO)$_{12}$, accelerated by a coordinating solvent such as THF to give unstable, coordinatively unsaturated Fe(CO)$_3$·2THF, may be the primary process.[11] Although the mechanism of the formation of 7 in the reaction of PhP(S)Cl$_2$ with Fe$_3$(CO)$_{12}$ is not known, we suggest that the desired 6 is indeed the first product and that it reacts further with Fe$_3$(CO)$_{12}$ or Fe$_3$(CO)$_{12}$-derived species to give 7. A similar conversion of (μ-S$_2$)Fe$_2$(CO)$_6$ to (μ_3-S)$_2$Fe$_3$(CO)$_9$ by reaction with Fe$_3$(CO)$_{12}$ has been reported by Russian workers.[12]

Upon completion of these studies of the reaction conditions, other complexes analogous to 7 were prepared by using the reaction of Fe$_3$(CO)$_{12}$ with the appropriate RP(S)Cl$_2$ in refluxing THF. Table II summarizes the new complexes thus prepared.

The *tert*-butylphosphido derivative could be prepared in only 10% yield. The phenylphosphido derivatives proved to be the easiest to prepare and isolate. The *tert*-butylphosphido complex appeared to be somewhat less stable that the arylphosphido derivatives during storage as the solid in air.

Reactions of iron carbonyl anions with PhP(S)Cl$_2$ offered another, but less useful, route to the (μ_3-S)(μ_3-PhP)Fe$_3$(CO)$_9$ complex. Reactions of Na$_2$Fe$_2$(CO)$_8$·*x*THF or Na$_2$Fe(CO)$_4$·1.5dioxane with PhP(S)Cl$_2$ at room temperature gave 7 in yields of 5.3 and 1%, respectively. The reactions did not proceed at −78 °C. In contrast, the reaction of S$_2$Cl$_2$ with Na$_2$Fe$_2$(CO)$_8$·*x*THF at 0 °C produced (μ_3-S)$_2$Fe$_3$(CO)$_9$ in 30% yield.

Table III. ^{31}P NMR Data for (μ_3-S)(μ_3-RP)Fe$_3$(CO)$_9$ Complexes and (μ_3-PhP)$_2$Fe$_3$(CO)$_9$

complex	solvent	^{31}P NMR,[a] ppm
(μ_3-S)(μ_3-PhP)Fe$_3$(CO)$_9$	C$_6$H$_6$	359
(μ_3-S)(μ_3-PhP)Fe$_3$(CO)$_9$	CH$_2$Cl$_2$	360
(μ_3-S)(μ_3-p-MeC$_6$H$_4$P)Fe$_3$(CO)$_9$	C$_6$H$_6$	360
(μ_3-S)(μ_3-Me$_3$CP)Fe$_3$(CO)$_9$	C$_6$H$_6$	437
(μ_3-PhP)$_2$Fe$_3$(CO)$_9$	C$_6$H$_6$	318 (317[b])

[a] Downfield from external 85% aqueous H$_3$PO$_4$. [b] From [b] From Huntsman, J. R. *Diss. Abstr. Int. B* **1974**, *34*, 4897 4897.

An attempt was made to prepare (μ_3-S)(μ_3-PhP)Fe$_3$(CO)$_9$ by the reaction of Fe$_3$(CO)$_{12}$ with (PhPS)$_4$. Equimolar amounts of the iron carbonyl and "PhPS" were heated together in refluxing THF for several hours. The desired product was formed but was isolated in only 8% yield.

A different approach to the synthesis of (μ-PhPS)Fe$_2$(CO)$_6$ by the reaction of (μ_3-PhP)$_2$Fe$_3$(CO)$_9$ with elemental sulfur was examined briefly. We have found that (μ_3-S)$_2$Fe$_3$(CO)$_9$ could be converted to (μ-S$_2$)Fe$_2$(CO)$_6$ in 39% yield by reaction with S$_8$ in refluxing THF. However, (μ_3-PhP)$_2$Fe$_3$(CO)$_9$ did not react with elemental sulfur under those conditions.

The ^{31}P NMR spectra of the three new (μ_3-S)(μ_3-RP)Fe$_3$(CO)$_9$ complexes have been measured (Table III). The phosphorus resonances observed agree well with the values reported for other phosphido complexes,[13] especially the very similar (μ_3-PhP)$_2$Fe$_3$(CO)$_9$ complex. The large downfield shift for the *tert*-butylphosphido derivative is not out of the ordinary; shifts as far downfield as 739 ppm have been reported for the triply bridging phosphido complex [η^5-C$_5$H$_5$(CO)$_2$MnP]$_2$Fe$_3$(CO)$_9$.[14]

A structure determination of one of the (μ_3-S)(μ_3-RP)Fe$_3$(CO)$_9$ complexes would be of interest in view of the comparison between the structures of (μ_3-S)$_2$Fe$_3$(CO)$_9$ (S···S = 2.885 Å)[15] and (μ_3-PhP)$_2$Fe$_3$(CO)$_9$ (P···P = 2.592 Å).[16] On the basis of these observed distances, there must be an attractive interligand attraction in the phosphorus derivative, one considerably stronger than any in the sulfur compound. It may be expected that (μ_3-S)(μ_3-RP)Fe$_3$(CO)$_9$ complexes will have a P···S distance intermediate between the P···P and S···S distances in the symmetrical complexes. Unfortunately, an attempted determination of the structure of (μ_3-S)-(μ_3-PhP)Fe$_3$(CO)$_9$ by X-ray diffraction was not successful.

Experimental Section

General Comments. All reactions were carried out in flame-dried flasks under an atmosphere of prepurified nitrogen unless indicated otherwise. Air- and/or moisture-sensitive materials were handled either in a Vacuum Atmospheres HE-43 Dri-Lab glovebox or by using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl. Reagent-grade dichloromethane (Mallinckrodt) was deoxygenated by purging it with nitrogen for

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15 min. Hexane was distilled under nitrogen from sodium metal. All other solvents were dried by the appropriate method and distilled under nitrogen. All solvents were stored under a positive pressure of nitrogen. Thin-layer chromatography (TLC) was used to monitor the progress of the reaction being studied (Eastman or J.T. Baker silica gel plates). The intense colors of the compounds involved made further treatment of the TLC plate unnecessary. Mixtures of reaction products were, in general, separated by column chromatography or filtration chromatography using hexane, pentane, or a pentane/dichloromethane (95/5) mixture as eluents.

Triiron dodecacarbonyl[11] and (μ_3-phenylphosphido)tris(tricarbonyliron)[8] were prepared according to the published procedures. Phenylphosphonothioic dichloride was purchased from Alfa/Ventron, distilled at reduced pressure, and stored under nitrogen. All other specific reagents were prepared and purified prior to use as indicated and referenced in the detailed experimental procedure of each reaction.

Proton nuclear magnetic resonance spectra were recorded on either a Varian Assoc. T-60 or Hitachi-Perkin-Elmer R-24B spectrometer operating at 60 MHz. Chemical shifts are reported in δ units, parts per million downfield from internal tetramethylsilane. Phosphorus-31 NMR spectra were recorded on a JEOL FX-90Q spectrometer operating at 36.2 MHz in the Fourier transform mode. The ^{31}P chemical shifts are reported in δ_P units, parts per million downfield from 85% aqueous H_3PO_4 using external triphenylphosphine (in the same solvent as the sample) as the reference signal at −6 ppm. Infrared spectra were obtained by using a Perkin-Elmer Model 457A double-beam grating spectrophotomer. Solution samples were contained in 0.1-mm path-length sodium chloride solution cells. Mass spectra were recorded on a Varian MAT-44 mass spectrometer operating at 70 eV. Melting points were determined by using analytically pure samples, which were sealed in evacuated or nitrogen-filled capillaries, on a Büchi melting point apparatus and are uncorrected.

Reaction of Triiron Dodecacarbonyl with Phenylphosphonothioic Dichloride in the Presence of Magnesium. A 100-mL three-necked, round-bottomed flask equipped with a mechanical stirring unit, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and no-air stoppers was charged with 0.10 g (4.1 mmol) of Mg chips (Alfa/Ventron M4N grade) and stirred overnight under nitrogen to activate the chips.[17] $Fe_3(CO)_{12}$ (2.0 g, 4.0 mmol) was added against a counterflow of nitrogen, and then PhP(S)Cl_2 (0.61 mL, 4.0 mmol and THF (40 mL) were added by syringe. After 20 min of stirring at room temperature no reaction was observed by TLC (pentane and dichloromethane). CH_3I (0.02 mL, 0.3 mmol, Eastman, as received) was added to try and initiate the reaction. After 25 min more, no reaction was observed, only the green, streaking band of $Fe_3(CO)_{12}$ eluting with pentane. The reaction mixture was gently heated to reflux, and after 15 min, red, orange, and yellow bands eluted respectively with pentane. The reaction mixture was heated at reflux until all of the $Fe_3(CO)_{12}$ had been consumed (~45 min). The cooled reaction mixture, now colored brown-red, was filtered to obtain 0.049 g (2.0 mmol) of Mg. The filtrate was evaporated on a rotary evaporator to yield a brown oily residue. This residue was extracted with 3 × 40-mL portions of a 20% dichloromethane/80% pentane mixture and filtered, and the solvent was evaporated on a rotary evaporator to give a dark red semi-solid material which was chromatographed by using the standard column. Elution with a 5% dichloromethane/95% pentane mixture separated three products. In order of their elution these were the following.

(1) Red-purple solution, which upon removal of the solvent on a rotary evaporator, yielded 0.023 g (0.05 mmol, 1%) of a black solid identified as bis(μ_3-thio)tris(tricarbonyliron), $S_2Fe_3(CO)_9$, mp 110–113 °C (lit.[18] 114 °C), by comparison of its IR spectrum to that reported[18] and by its mass spectrum (observed $M^+ - 1CO$ and consecutive loss of eight CO's, *m/e* 456–232).

(2) Orange-red solution, which upon removal of the solvent on a rotary evaporator, yielded 0.408 g (0.7 mmol, 17%) of an orange-red oil that slowly crystallized on standing. After subsequent recrystallization from pentane at −30 °C to give dark red nuggets, it was identified as (μ_3-phenylphosphido)(μ_3-thio)tris(tricarbonyliron), (μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$: mp 93–94.5 °C (constant melting point after three recrystallizations); IR (CCl_4) 3060 (w), 2955 (w), 2930 (w), 2870 (w), 1475 (w), 1439 (s), 1433 (s), 1379 (w), 1330 (w), 1301 (w), 1180 (w), 1099 (s), 998 (w), 710 (sh), 693 (vs), 586 (vs) cm^{-1}, carbonyl region, 2085 (w), 2058 (vs), 2037 (vs), 2015 (s), 2001 (vw), 1998 (vw) cm^{-1}; ^{1}H NMR(C_6D_6) δ 6.66–7.65 (m); ^{31}P{^{1}H}NMR(C_6H_6) δ_P +359 (s); mass spectrum, *m/e* 560 (M^+, <1), 532 ($M^+ - 1CO$, 10), 504 ($M^+ - 2CO$, 8), 448 ($M^+ - 4CO$, 6), 420 ($M^+ - 5CO$, 8), 392 ($M^+ - 6CO$, 18), 364 ($M^+ - 7CO$, 12), 336 ($M^+ - 8CO$, 20), 308 ($M^+ - 9CO$, 100). Anal. Calcd for $C_{15}H_5Fe_3O_9PS$ (559.78): C, 32.18; H, 0.90. Found: C, 32.20; H, 0.97.

(3) Yellow-orange solution, which upon removal of the solvent on a rotary evaporator, yielded 0.032 g (0.05 mmol, 1%) of a yellow solid identified as bis(μ_3-phenylphosphido)tris(tricarbonyliron), $(PhP)_2Fe_3(CO)_9$, mp 128–131 °C (lit.[8] 130–135 °C), by comparison of its IR spectrum to that of an authentic sample and by its mass spectrum (observed *m/e* 608 ($M^+ - 1CO$, 12.2%), 524 ($M^+ - 3CO$, 14.3), 496 ($M^+ - 4CO$, 18.4), 468 ($M^+ - 5CO$ 20.4), 440 ($M^+ - 6CO$, 16.3), 412 ($M^+ - 7CO$, 12.2), 384 ($M^+ - 8CO$, 100.0); scanning from *m/e* 650 to 250).

Reaction of Triiron Dodecacarbonyl with Phenylphosphonothioic Dichloride in the Absence of Magnesium. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and two no-air stoppers was charged with 2.0 g (4.0 mmol) of $Fe_3(CO)_{12}$, evacuated, and refilled with nitrogen. PhP(S)Cl_2 (0.61 mL, 4.0 mmol) and 40 mL of THF were added by syringe. The reaction mixture was heated at a gentle reflux until all the $Fe_3(CO)_{12}$ had been consumed (~2.5 h by TLC monitoring). The cooled reaction mixture was filtered and the filtrate evaporated on a rotary evaporator to give a brown oil. The oil was extracted with 100 mL of hexane and filtered and the solvent removed on a rotary evaporator to give a dark red oil. This was chromatographed as in the previous experiment, eluting with a 95% pentane/5% dichloromethane mixture. A red-purple band eluted first, which upon removal of the solvent, yielded 0.041 g (0.08 mmol, 2%) of $S_2Fe_3(CO)_9$ identified by its infrared spectrum. Next, an orange-red band eluted, which upon removal of the solvent, yielded 0.467 g (0.8 mmol, 20%) of (μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$, mp 91–94 °C, identified by comparison of its infrared and mass spectra to those of an authentic sample. No $(PhP)_2Fe_3(CO)_9$ was isolated from the column.

Studies of the Effect of Stoichiometry and Solvent on the Yield of (μ_3-Phenylphosphido)(μ_3-thio)tris(tricarbonyliron). A description of the standard apparatus and procedure is as follows. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and two no-air stoppers was charged with $Fe_3(CO)_{12}$, evacuated, and refilled with nitrogen. The solvent and PhP(S)Cl_2 were added by syringe and the mixture heated at reflux while being stirred. TLC was used to follow the progress of the reaction. Upon completion of the reaction, the solvent was removed on a rotary evaporator and the resulting residue extracted with hexane. Evaporation of the solvent from the extract gave an oil. Filtration chromatography eluting with pentane was used to isolate the products from this oil.

A. Reaction of Triiron Dodecacarbonyl with Two Equivalents of Phenylphosphonothioic Dichloride in THF. Following the standard procedure, a reaction was carried out between 1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$ and 0.603 mL (3.97 mmol) of PhP(S)Cl_2 in 40 mL of THF. After a reflux period of 2.5 h, all the $Fe_3(CO)_{12}$ had been consumed and product formation was evident. The standard workup was used to isolate 0.032 g (0.07 mmol, 4%) of $S_2Fe_3(CO)_9$ as black crystals and 0.338 g of (μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$ as an orange oil with the distinct odor of PhP(S)Cl_2. An attempt made to remove the PhP(S)Cl_2 by hydrolysis with 15% aqueous NaOH resulted in the isolation of 0.262 g (0.5 mmol, 25%) of (μ_3-S)(μ_3-PhP)$Fe_3(CO)_9$, again as an orange oil which could not be crystallized.

B. Reaction of Two Equivalents of Triiron Dodecacarbonyl with Phenylphosphonothioic Dichloride in THF. Following the standard procedure, a reaction was carried out between 1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$ and 0.152 mL (1.00 mmol) of PhP(S)Cl_2 in 35 mL of THF. After 2 h at reflux, all the

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$Fe_3(CO)_{12}$ has been consumed and product formation was at a maximum. The standard workup was used to isolate 0.101 g 0.2 mmol, 20%) of $(\mu_3\text{-S})(\mu_3\text{-PhP})Fe_3(CO)_9$ as a red-brown solid directly from the filtration chromatography pad. An unisolable amount of $S_2Fe_3(CO)_9$ was observed.

C. Reaction of Triiron Dodecacarbonyl with Phenylphosphonothioic Dichloride in Hexane. Following the standard procedure a reaction was carried out between 1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$ and 0.228 mL (1.50 mmol) of $PhP(S)Cl_2$ in 40 mL of hexane. After 7 h at reflux, the reaction mixture still contained a substantial amount of $Fe_3(CO)_{12}$. After 10 h more of heating, some $Fe_3(CO)_{12}$ still remained and product formation was observed. After a total of 23 h at reflux, product formation appeared to be at a maximum and nearly all the $Fe_3(CO)_{12}$ had been consumed. The standard workup yielded 0.108 g (0.22 mmol, 7%) of $S_2Fe_3(CO)_9$ as a black solid and 0.180 g (0.32 mmol, 21%) of $(\mu_3\text{-S})(\mu_3\text{-PhP})Fe_3(CO)_9$ as a red-brown solid.

D. Reaction of Triiron Dodecacarbonyl with Phenylphosphonothioic Dichloride in Benzene. Following the standard procedure a reaction was carried out between 1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$ and 0.228 mL (1.50 mmol) of $PhP(S)Cl_2$ in 40 mL of benzene (distilled from sodium/benzophenone ketyl under nitrogen prior to use). After 4 h at reflux, product formation was evident and most of the $Fe_3(CO)_{12}$ had been consumed. Since the progress of the reaction appeared slow, more $PhP(S)Cl_2$ (0.05 mL, 0.3 mmol) was added and the reaction mixture heated at reflux for 1 h more. Product formation was evident but not substantial. Only $S_2Fe_3(CO)_9$ appeared to be the major product and as such was isolated by using the standard workup to give 0.079 g (0.16 mmol, 21%). Only a negligible amount of $(\mu_3\text{-S})(\mu_3\text{-PhP})Fe_3(CO)_9$ was observed during chromatography and not quantified.

Reaction of Triiron Dodecacarbonyl with *p*-Tolylphosphonothioic Dichloride. $p\text{-}CH_3C_6H_4P(S)Cl_2$ was prepared by using a two-step procedure starting with $(p\text{-}CH_3C_6H_4)_2Hg$. The reaction of $(p\text{-}CH_3C_6H_4)_2Hg$ with PCl_3 to give $p\text{-}CH_3C_6H_4PCl_2$ was carried out according to the method of Michaelis and Paneck.[19] The $AlCl_3$-catalyzed oxidation of $p\text{-}CH_3C_6H_4PCl_2$ to give $p\text{-}CH_3C_6H_4P(S)Cl_2$ as a colorless liquid [bp 85–90 °C (0.12 mm) (lit.[20] 85–87 °C (0.05 mm); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P 75.9 (s) (lit.[20] δ_P 74.1 (s, solvent not specified)] in the presence of sulfur was carried out by the method of Jenson.[21] The $p\text{-}CH_3C_6H_4P(S)Cl_2$ was handled and stored under an inert atmosphere.

Following the standard procedure described in part B of the previous section, a reaction was carried out between 2.00 g (3.96 mmol) of $Fe_3(CO)_{12}$ and 0.45 g (2.00 mmol) of $p\text{-}CH_3C_6H_4P(S)Cl_2$ in 50 mL of THF. The green reaction mixture was heated at reflux for about 50 min at which point all the $Fe_3(CO)_{12}$ had been consumed and the color was red-brown. Product formation was evident by TLC. The standard workup using a 20% dichloromethane/80% pentane mixture as the extraction solvent was employed. Filtration chromatography separated, in order of their elution with pentane: (1) a faint yellow band [$Fe(CO)_5$, not quantified], (2) a purple band [$S_2Fe_3(CO)_9$, not quantified], (3) an orange band (the desired product), (4) a faint yellow band [$(CH_3C_6H_4P)_2Fe_3(CO)_9$, not quantified], and (5) a green band (not identified). Removal of the solvent on a rotary evaporator from fraction 3 yielded, after subsequent recrystallization from pentane at −30 °C, 0.169 g (0.29 mmol, 15%) of dark red cubes, identified as (μ_3-*p*-tolylphosphido)(μ_3-thio)tris(gtricarbonyliron), $(\mu_3\text{-S})(\mu_3\text{-p-MeC}_6H_4P)Fe_3(CO)_9$: mp 124–126 °C; IR ($CCl_4$) 3057 (vw), 3010 (w), 2942 (vw), 2912 (w), 2851 (vw), 2473 (w, br), 1597 (m), 1498 (m), 1450 (w), 1401 (m), 1193 (m), 1101 (s), 1126 (w), 1022 (m), 650 (s), 582 (s, br) cm^{-1}, carbonyl region, 2081 (m), 2053 (vs), 2032 (vs), 2011 (s), 1995 (w) cm^{-1}; ^1H NMR (CCl_4) δ 2.45 (s, 3 H, CH_3), 7.20–7.65 (m, 4 H, Ph); $^{31}P\{^1H\}$ NMR (C_6H_6) δ_P +360 (s); mass spectrum, *m/e* 575 (M^+, 0.5), 547 ($M^+ - 1CO$, 9.4), 519 ($M^+ - 2CO$, 10.2), 491 ($M^+ - 3CO$, 5.3), 463 ($M^+ - 4CO$, 7.9), 435 ($M^+ - 5CO$, 9.5), 407 ($M^+ - 6CO$, 29.8), 379 ($M^+ - 7CO$, 27.0), 351 ($M^+ - 8CO$, 24.3), 323 ($M^+ - 9CO$, 65.6). Anal. Calcd for $C_{16}H_7Fe_3O_9PS$ (573.81): .C, 33.49; H, 1.23. Found: C, 33.29; H, 1.32.

Reaction of Triiron Dodecacarbonyl with *tert*-Butylphosphonothioic Dichloride. $t\text{-}BuP(S)Cl_2$ was prepared by a two-step procedure. The first step involved the synthesis of $t\text{-}BuPCl_2$ by the reaction of $t\text{-}BuMgCl$[22] with PCl_3 according to the method of Isbell et al.[23] The second step was the $AlCl_3$-catalyzed oxidation of $t\text{-}BuPCl_2$ in the presence of sulfur to give $t\text{-}BuP(S)Cl_2$ as a waxy white solid [mp 168–171 °C (lit.[24] 172.5–175 °C); $^{31}P\{^1H\}$ NMR (C_6H_6) δ_P 116.5 (s)], modeled after the method of Jenson.[21] The $t\text{-}BuP(S)Cl_2$ was stored, weighed, and transferred in the glovebox.

Following the standard procedure, a reaction was carried out between 2.00 g (3.96 mmol) of $Fe_3(CO)_{12}$ and 0.38 g (2.00 mmol) of $t\text{-}BuP(S)Cl_2$ in 50 mL of THF. After 1.25 h at reflux, all the $Fe_3(CO)_{12}$ had been consumed and product formation was observed. The standard workup was followed, and, thus, filtration chromatography eluting with pentane removed a faint purple band, presumably $S_2Fe_3(CO)_9$, but it was not identified. *Immediately* following the first band was the orange band of the desired product. Removal of the solvent on a rotary evaporator and subsequent recrystallization from pentane at −30 °C yielded 0.10 g (0.2 mmol, 10%) of flaky red crystals, identified as (μ_3-*tert*-butylphosphido)(μ_3-thio)tris(tricarbonyliron), $(\mu_3\text{-S})(\mu_3\text{-Me}_3CP)Fe_3(CO)_9$: mp 169–171 °C (with gas evolution); IR ($CDCl_3$) 2990 (m), 2958 (m), 2919 (m), 2885 (w), 1467 (m), 1400 (w), 1374 (m), 1254 (w), 1201 (w), 1172 (m), 1028 (m), 868 (m), 820 (m), 590 (vs) cm^{-1}, carbonyl region, 2080 (m), 2055 (vs), 2030 (vs), 2007 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (d, J_{P-H} = 17 Hz, *t*-Bu); $^{31}P\{^1H\}$ NMR(C_6H_6) δ_P +437 (s); mass spectrum, *m/e* 541 (M^+, 1.3), 513 ($M^+ - 1CO$, 10.5), 485 ($M^+ - 3CO$, 8.6), 457 ($M^+ - 4CO$, 11.0), 429 ($M^+ - 5CO$, 12.8), 401 ($M^+ - 6CO$, 14.3), 373 ($M^+ - 7CO$, 14.7), 345 ($M^+ - 8CO$, 9.9), 317 ($M^+ - 9CO$, 10.0). Anal. Calcd for $C_{13}H_9Fe_3O_9PS$ (539.80): C, 28.92; H, 1.68. Found: C, 28.46; H, 1.76.

Reaction of Triiron Dodecacarbonyl with Tetraphenylcyclotetraphosphine–Tetrasulfide. $[PhPS]_4$ was prepared by the reaction of $PhPH_2$ with 2 equiv of sulfur according to the procedure of Maier.[25] $[PhPS]_4$ was isolated as white microcrystals, mp 153–155 °C (lit.[26] 150.5 °C), and stored under normal laboratory atmosphere.

Following the standard procedure, a reaction was carried out between 2.52 g (5.0 mmol) of $Fe_3(CO)_{12}$ and 0.70 g (1.66 mmol, 4.98 equiv of "PhPS") of $[PhPS]_4$ in 40 mL of THF. The reaction mixture was heated to reflux, and after 30 min at reflux, TLC indicated product formation. After 3 h at reflux some unconverted $Fe_3(CO)_{12}$ was still present, so 0.387 g (0.92 mmol, 2.76 equiv of "PhPS") of $[PhPS]_4$ was added. After 15 min more, all the $Fe_3(CO)_{12}$ had been consumed. The solvent was removed in vacuo to give a black-brown oily residue, which was extracted by 100 mL of hexane. Filtration chromatography, eluting with pentane, removed first a red-purple band, which upon removal of the solvent, yielded 0.016 g (0.03 mmol, 0.6%) of a black solid identified as $S_2Fe_3(CO)_9$ on the basis of its IR spectrum. Eluted next was an orange band, which upon removal of the solvent, yielded 0.241 g (0.4 mmol, 8%) of an oily red solid identified as $(\mu_3\text{-S})(\mu_3\text{-PhP})Fe_3(CO)_9$ on the basis of its IR spectrum.

Reaction of Disodium Octacarbonyl Diferrate with Sulfur Monochloride. $Na_2Fe_2(CO)_8 \cdot x$THF was prepared as described[27] from 3.45 g (10.0 mmol) of $Na_2Fe(CO)_4 \cdot 1.5$dioxane and 1.37 mL (10.0 mmol) of $Fe(CO)_5$ in 50 mL of THF. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, a gas inlet tube leading to a Schlenk manifold, a pressure-equilizing dropping funnel, and no-air stoppers was used as the apparatus. The orange $Na_2Fe_2(CO)_8$/THF slurry was cooled to 0 °C. The dropping funnel was charged with 0.8 mL (10.0mmol) of S_2Cl_2 (Aldrich, freshly disdtilled) and 10 mL of THF. This red solution was added dropwise to the cooled iron complex over

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10 min. Gas evolution occurred and the orange iron complex dissolved. Upon completion of the addition, the mixture was allowed to warm to room temperature and stirred for 30 min. TLC indicated a single purple band eluting with pentane. The mixture was filtered through a Celite pad with difficulty and the filtrate evaporated to dryness on a rotary evaporator. The resulting residue was extracted with a 20% dichloromethane/80% hexane mixture and filtered, and the solvent was removed on a rotary evaporator. This gave a black solid, which upon recrylstallization from pentane at −30 °C, yielded 0.962 g (2.0 mmol, 30%) of $S_2Fe_3(CO)_9$ as black needles, mp 112–115 °C (lit.[18] °C), identified by comparison of its IR spectrum with that of an authentic sample.

Conversion of Bis(μ_3-thio)tris(tricarbonyliron) to (μ-Dithio)bis(tricarbonyliron) by Treatment with Sulfur in Refluxing THF. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and no-air stoppers was charged with 0.344 g (0.7 mmol) of $S_2Fe_3(CO)_9$ and 0.069 g (1.4 mmol) of sulfur, then evacuated, and refilled with nitrogen. THF (30 mL) was added by syringe, and carbon monoxide was bubbled through the purple solution for 10 min by using a syringe needle. The reaction mixture was heated at reflux for 24 h with CO slowly bubbling through it. TLC indicated an orange band preceding a purple band eluting with pentane. More sulfur (0.035 g, 0.7mmol) was added against a counterflow of CO and the mixture heated for another hour. No change in the amounts of the two bands was observed by TLC. The cooled reaction mixture was filtered and the solvent removed on a rotary evaporator. Filtration chromatography eluting with pentane was used to isolate the 2 fractions. The orange fraction was identified as $S_2Fe_2(CO)_6$ (0.152 g, 0.4 mmol, 44% based on unrecovered $S_2Fe_3(CO)_9$) by comparison of its melting point and IR spectrum with those of an authentic sample. The purple fraction was identified as unconverted $S_2Fe_3(CO)_9$ (0.044 g, 0.09 mmol, 13% recovery) on the basis of its melting point and IR spectrum.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No. (μ_3-PhP)(μ_3-S)$Fe_3(CO)_9$, 82614-06-0; (μ_3-*p*-$CH_3C_6H_4P$)(μ_3-S)$Fe_3(CO_9)$, 82614-07-1; (μ_3-*t*-BuP)(μ_3-S)$Fe_3(CO_9)$, 82614-08-2; $Fe_3(CO)_{12}$, 17685-52-8; $PhP(S)Cl_2$, 3497-00-5; *p*-$CH_3C_6H_4P(S)Cl_2$, 6588-16-5; *t*-$BuP(S)Cl_2$, 21187-18-8; $(PhPS)_4$, 1447-25-2; Fe, 7439-89-6.

Dimetalated Olefins

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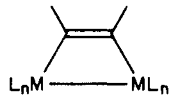
Extended Hückel calculations are performed on the subclass of transition-metal binuclear bridging acetylene complexes, $L_nM(\mu\text{-acetylene})ML_n$, that can be viewed as dimetalated olefins. The ethylene analogy is established and a clear bonding picture for the dimetalated olefins emerges once it is recognized that an isolobal analogy exists between the ML_n pieces of the known organometallic complexes and organic R or H. The simple arguments developed provide a basis for speculation on as yet unknown complexes in this class of molecules.

Passages of the mind between organic and inorganic chemistry serve not only to make us feel comfortable about unusual structural types but may in fact suggest new chemistry. In the course of a study of binuclear transition-metal acetylene complexes[1] we had occasion to look at the electronic structure of a number of "parallel" complexes of type 1. In some of these molecules no metal–metal bond is forced by molecular orbital reasoning or 18-electron rule considerations nor is much bonding to be inferred from the observed long metal–metal separations. Examples are the complexes $Au_2(PPh_3)_2(\mu\text{-}C_2(CF_3)_2)$, $Pd_2Cl_2(\mu\text{-dpm})_2(\mu\text{-}C_2(CF_3)_2)$ (dpm = $Ph_2PCH_2PPh_2$), $Fe_2(CO)_6(\mu\text{-}SCF_3)_2(\mu\text{-}C_2(CF_3)_2)$, and $Rh_2Cl_2(\mu\text{-CO})(\mu\text{-dpm})_2(\mu\text{-}C_2(CO_2Me)_2)$, 2–5, respectively.[2] As is evident here, the substituent on the acetylene carbon is most often CF_3, sometimes CO_2R. We have left it unspecified in the drawings, indicated only by a line. A possible reason for the common acceptor substitution in the known complexes has been discussed in ref 1.[3]



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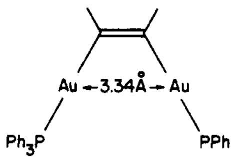

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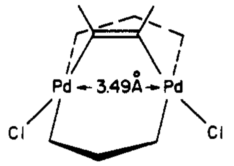

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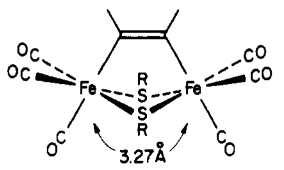

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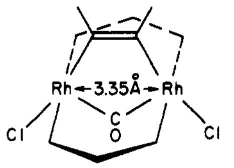

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The basic acetylene-containing structural unit in these may be summarized as 6, which can be viewed as a dimetalated olefin. This paper traces in detail the analogy

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[3] There are parallel bonded acetylene complexes in which the acetylene does *not* have CF_3 or CO_2R substituents. See the following: (a) Rossell, O.; Sales, J. *Inorg. Chim. Acta* **1981**, *64*, L43–L44. (b) Staal, L. H.; von Koten, G.; Vrieze, K.; Ploeger, F.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 1830–1835. (c) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 7870–7876. (d) Bennett, M. J.; Graham, W. A. G.; Stewart, Jr., R. P.; Tuggle, R. M. *Inorg. Chem.* **1973**, *12*, 2944–2947.

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