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Selective Formation of One or Two C−C Bonds Promoted by Carbanion Addition to $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]^+$

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The reactions of $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]CF_3SO_3$ (**1**; cp = $\eta\text{-}C_5H_5$) with a variety of carbon nucleophiles result in C−C bond formation at different sites of the molecule. (allyl)MgCl (allyl = C_3H_5) undergoes cp addition to form $[Fe_2(cp)(\eta^4\text{-}C_5H_5\text{-allyl})(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]$ (**2**) and the alkylidene complex $[Fe_2(cp)(\eta\text{-}C_5H_4\text{-allyl})(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)H\}]$ (**3**), derived from cp to μ-C hydrogen migration. $Li_2Cu(CN)R_2$ adds at the μ-C atom to yield $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)R\}]$ (R = Ph, **4**; R = Me, **8**), $[Fe\overline{Fe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(S}Me)R\}]$ (R = Ph, **5**; R = Me, **9**), and $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ (**6**) or the vinylidene derivative $[Fe_2(cp)_2(CO)(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)]$ (**10**) in the case of phenyl or methyl organocuprate reagents, respectively. The latter complexes are the result of C−SMe bond breaking occurring, through different reaction paths, in **4** and **8.** Likewise, the formation of $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C{=}C(CN)_2\}]$ (**11**) from **1** and $NaCH(CN)_2$ occurs *via* a direct addition at the μ-C carbon followed by HSMe elimination. The nucleophilic attack at the terminal CO in **1** is achieved with LiC≡CPh, which forms two new C−C bonds in the alkylidene complex $[Fe\overline{Fe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(S}Me)C(O)CCPh\}]$ (**12**) after C(O)CCPh migration from Fe to the bridging carbene carbon. The analogous $[Fe\overline{Fe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(S}Me)C(O)(2\text{-th})\}]$ (**13;** 2-th = $2\text{-}C_4H_3S$) and $[Fe_2(cp)(\eta^4\text{-}C_5H_5\text{-}(2\text{-th})(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]$ (**14**) are obtained from **1** and Lith *via* addition at the CO and cp groups, respectively. The relevance of these reactions is discussed in terms of selective C−C bond formation that, if it occurs at the cp or CO terminal ligands, favors the hydrogen migration (*e.g.* formation of **3**) or the carbyne−carbonyl migratory coupling (*e.g.* formation of **12** and **13**), respectively. The X-ray structures of $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ (**6**) and $[Fe\overline{Fe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(S}Me)C(O)(2\text{-th})\}]$ (**13**) have revealed the peculiarity of the Ph and SMe group coordination to the iron. Their structural features are discussed in comparison with those of analogous complexes.

Introduction

Dinuclear or polynuclear transition-metal complexes containing bridging hydrocarbon ligands have been extensively studied as models of intermediates postulated in several important metal-catalyzed processes.[1] In particular, the study of reactions leading to the formation of C−C bonds in dinuclear compounds may result in a better understanding of surface-catalyzed hydrocarbon chain growth (Fischer−Tropsch reactions).[2] A number of reactions of carbon−carbon bond formation have recently been described. They are based upon the strong electrophilic character of the bridging carbyne ligand in diiron cationic complexes of the type $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CR)]^+$.[3] In contrast, the thiocarbyne analogue $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]CF_3SO_3$ (**1**)[4] exhibits an extensive chemistry toward nucleophiles[5] but undergoes only a few reactions generating new C−C bonds. These include the nucleophilic addition of CN^- at the μ-C carbon of **1** to form the corresponding μ-carbene derivative $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)CN\}]$[6] and the carbonyl−thiocarbyne coupling promoted by $LiHBEt_3$, which affords $[Fe\overline{Fe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(CHO)S}Me\}]$.[7] In addition to these reactions, which form a C−C bond at the μ-C carbyne carbon, we have

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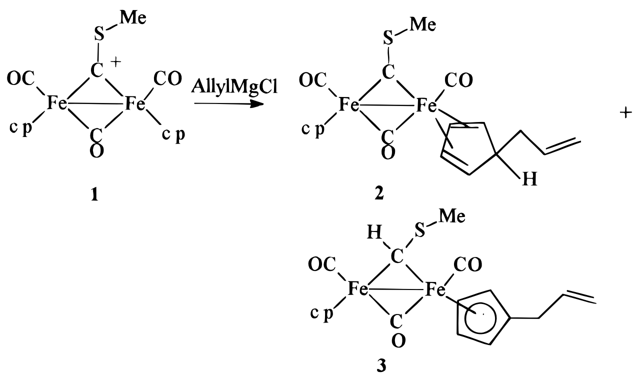
Scheme 1



recently found that Grignard reagents (RMgCl) add at one cp ring of **1**, yielding the corresponding cyclopentadiene (η^4-C_5H_5R) derivative.[8]

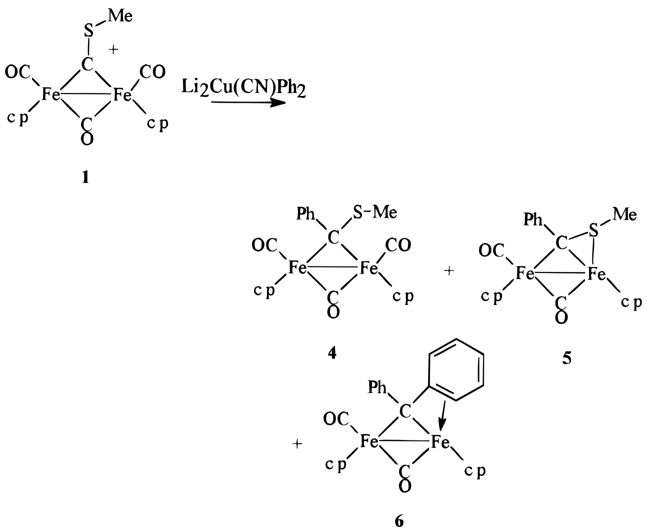
In the present paper we extend our studies to the reactions of **1** with carbon nucleophiles, including stabilized carbanions, organocopper, and organomagnesium reagents. All give addition reactions leading, however, to quite different product distributions, depending on the site of **1** (cp, CO, or μ-CSMe) involved. Unusual rearrangements, following the direct carbon−carbon bond formation, are also observed; some of these have been ascertained by X-ray crystallographic studies. The structures of two of these products, namely $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ and $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)C(O)(2\text{-}th)\}]$, are discussed.

Results

Addition at the cp Ligand. Reactions of 1 with Grignard Reagents. Allylmagnesium chloride reacts with **1**, as previously described[1] for other Grignard reagents RMgCl (R = phenyl, benzyl, isopropyl), to form the η^4-cyclopentadiene complex $[Fe_2(cp)(\eta^4\text{-}C_5H_5\text{-allyl})(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]$ (**2**) and the alkylidene complex $[Fe_2(cp)(\eta\text{-}C_5H_4\text{-allyl})(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)H\}]$ (**3**) (Scheme 1). Compound **2** is the result of direct C−C bond formation at the cp ligand of **1**; the allyl group addition occurs at the *exo* side of the cp ring, as indicated by the absence of the characteristic IR absorption of the cyclopentadiene H-*exo* atom around 2750 cm^{-1}.[9] The previously documented hydrogen migration from the C_5H_5R group to the μ-C carbyne carbon generates **3**.[8] Compounds **2** and **3** have been isolated from the reaction mixture in 7% and 74% yields, respectively, indicating that **2** is largely converted into **3**. In contrast, in the reported reactions of **1** with RMgX (R = Ph, Bz, *i*Pr)[2] the corresponding type **2** and **3** products have been obtained in about 40% and 20% yields, respectively, suggesting that the nature of the R group in the η^4-C_5H_5R ligand may influence the hydrogen migration process.

The air-stable complex **3** exhibits the expected spectroscopic properties; the key feature in its ^1H NMR spectrum is the low-field resonance at 11.4 ppm due to the methylidene proton.

Scheme 2



Addition at the μ-CSMe Ligand. Reaction of 1 with Organocopper Reagents. The reaction of **1** with $Li_2Cu(CN)Ph_2$ in thf solution at −40 °C rapidly affords a mixture of products: $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)Ph\}]$ (**4**; 42%), $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)\text{-}Ph\}]$ (**5**; 18%), and $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ (**6**; 27%) (Scheme 2), which have been separated by alumina column chromatography and obtained as air-stable microcrystalline solids.

The thioalkylidene complex **4** shows in its IR spectrum the usual strong−weak−medium ν(CO) band pattern (at 1986, 1947, and 1780 cm^{-1} in CH_2Cl_2 solution) observed in the analogous μ-alkylidene complexes $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)X\}]$ (X = H, CN),[5a,6] adopting a *cis* configuration (facing CO and cp ligands, respectively). In accord with an idealized C_s symmetry, compound **4** has equivalent cp groups, reflected in the occurrence of one signal in both its ^1H and ^{13}C NMR spectra (at 4.99 and 91.6 ppm, respectively). The μ-alkylidene carbon in **4** displays, in its ^{13}C NMR spectrum, a low-field-shifted signal (193.7 ppm) within the characteristic range of μ-CR_2 ligands (140−200 ppm). Analogously to the (thiomethoxy)alkylidenes $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(SMe)X]$ (X = H, CN), complex **4** can be easily converted (61% yield) into the cyanoalkylidene $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Ph)(CN)\}]$ (**7**) by a two-step reaction consisting of: (i) S-methylation (with $MeSO_3CF_3$) and (ii) SMe_2 displacement by cyanide (NBu_4CN) addition.[10] Complex **7** has been identified by its spectroscopic data (see Experimental Section).

The greenish-brown complex $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)Ph\}]$ (**5**), in which the sulfur is coordinated to one Fe atom, is obviously generated from **4** (in about 18% yield) by intramolecular CO displacement. This

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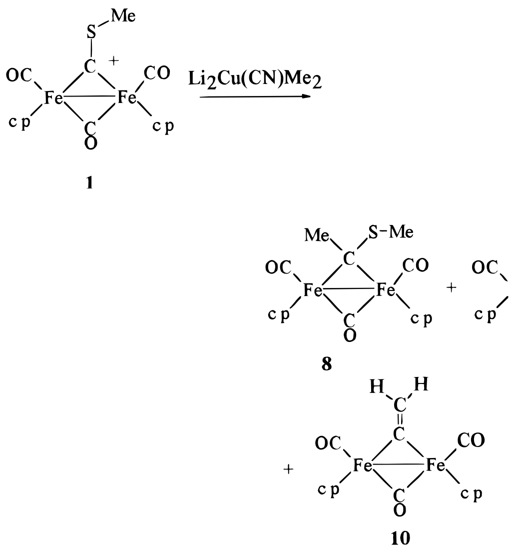
Scheme 3

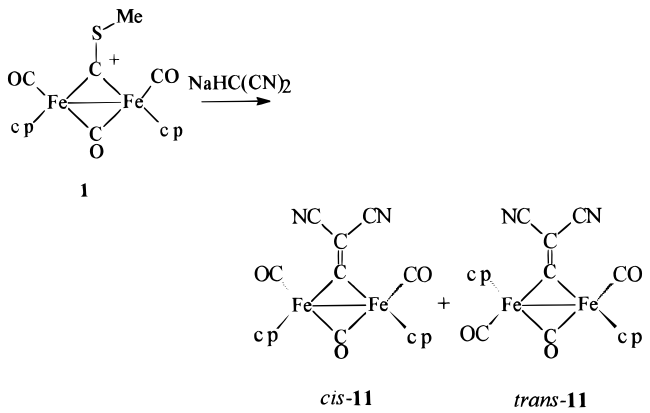


process occurs spontaneously at room temperature in chlorinated solvents. In fact, over a 12−14 h period, about 50% of **4** has been converted into **5**, as shown by NMR spectroscopy. The characterization of **5** is straightforward, since a number of strictly related dinuclear complexes containing the doubly coordinated μ-C(SMe)X (X = CN,[6,12] SR,[11] H[12]) ligands have previously been described. In their ^{1}H NMR spectra, the SMe resonances appear to be high-field-shifted compared to the corresponding uncoordinated SMe groups. Accordingly, the SMe signal in **5** is observed at 1.25 ppm, whereas the corresponding resonance in **4** occurs at 2.01 ppm. The ν(CO) band pattern of **5** consists of one terminal and one bridging carbonyl stretching at 1942 and 1759 cm^{-1} (CH_2Cl_2 solution).

The third derivative, isolated in about 27% yield from the reaction of **1** with $Li_2Cu(CN)Ph_2$, is [Fe_2(cp)$_2$(CO)(μ-CO){μ-C(η^2-Ph)Ph}] (**6**). Its nature has been elucidated by an X-ray diffraction study (Figure 1). In this molecule the bridging diphenylalkylidene ligand is further coordinated to one Fe atom through a double bond of one phenyl ring (see next section). The spectroscopic properties of complex **6** closely resemble those of the analogous ruthenium compound [Ru_2(cp)$_2$(CO)(μ-CO){μ-C(η^2-Ph)Ph}] obtained from [Ru_2(cp)$_2$(CO)(μ-CO){μ-C(O)C_2Ph_2}].[13] The resonance at 1.50 ppm observed in the ^{1}H NMR spectrum of **6** has been readily attributed to the proton of the C_6H_5 ring involved in the "olefinic bond". The resulting inequivalence of the cp groups gives rise to two unusually high-field shifted signals at 4.40 and 3.94 ppm, whereas the μ-alkylidene carbon resonance in the ^{13}C NMR spectrum at 184.3 ppm falls in the range expected for this class of complexes.

Treatment of **1** with $Li_2Cu(CN)Me_2$ in thf at −40 °C results in a mixture of products: [Fe_2(cp)$_2$(CO)$_2$(μ-CO){μ-C(SMe)Me}] (**8**; 64%), [FeFe(cp)$_2$(CO)(μ-CO){μ-C(SMe)Me}] (**9**; 12%), and the bridging vinylidene complex [Fe_2(cp)$_2$(CO)$_2$(μ-CO)(μ-C=CH_2)] (**10**; 17%) (Scheme 3).

Scheme 4



The most significant difference from the corresponding reaction with $Li_2Cu(CN)Ph_2$ is represented by the presence of **10** among the reaction products. Interestingly, the formation of **10** seems dependent on the nature of the organocopper reagent. Indeed, when **1** is treated with a large excess of the "low-order" cuprate LiCu(CN)Me (MeLi/CuCN = 1:1) the vinylidene derivative **10** is the most abundant product (73% yield). The spectroscopic characterization of **8** and **9** (Experimental Section) has been straightforward because of the analogy with **4** and **5,** respectively. The nature of **10** has been ascertained by comparing its spectroscopic properties with those reported.[14] In particular our method exclusively yields *cis*-**10**, which is also the only isomer obtained by deprotonation of [Fe_2(cp)$_2$(CO)$_2$(μ-CO)(μ-CCH_3)]$^+$.[14b]

Reaction of 1 with NaCH(CN)$_2$. Treatment of **1** with NaCH(CN)$_2$ (Scheme 4) affords the known bridging vinylidene complex [Fe_2(cp)$_2$(CO)$_2$(μ-CO){μ-C=C(CN)$_2$}] (**11**) in 53% yield. Unlike most of the related diiron bridging vinylidenes,[15] compound **11** consists of a mixture of the *cis* and *trans* isomers, which have been separated by column chromatography. Their spectroscopic properties are in agreement with those previously reported for the same isomers obtained in low yield (overall 3%) from [Fe(cp)(CO)$_2$]$^-$ and Cl_2C=C(CN)$_2$.[16] In addition, the ^{13}C NMR spectra show the bridging-vinylidene carbon signal in the usual range[15] (334.9 and 336.5 ppm for *cis*-**11** and *trans*-**11**, respectively) although shifted to low field compared to **10** (276.7 and 279.2 ppm) because of the presence of the CN groups.

Addition at the CO Ligand. Reaction of 1 with LiC≡CPh. Treatment of **1** with LiC≡CPh in thf at −20 °C gives the alkylidene complex [FeFe(cp)$_2$(CO)(μ-CO){μ-C(SMe)C(O)CCPh}] (**12**), which has been isolated by column chromatography in about 50% yield (Scheme 5). The IR spectrum of the moderately air stable **12**, in CH_2Cl_2 solution, shows terminal and bridging carbonyl absorptions (at 1956 and 1784 cm^{-1}) and bands attributable to ν(C≡C) and ν{C(=O)R} at 2187 and 1573 cm^{-1}, respectively. The NMR spectra exhibit nonequivalent C_5H_5 signals at 4.79, 4.75 (^{1}H) and 85.7, 84.2

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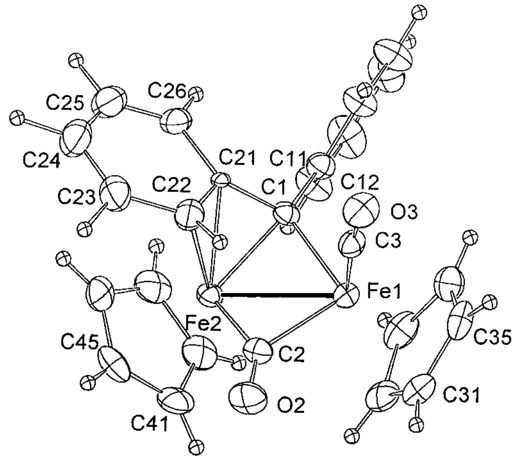
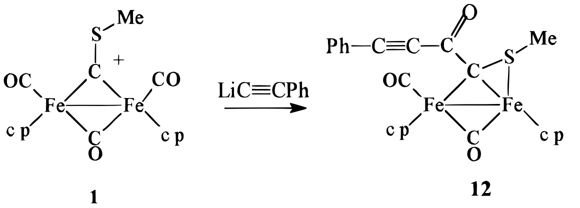


Figure 1. ORTEP drawing of $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ (**6**) showing the η^2 coordination of one phenyl ring. Thermal ellipsoids are drawn at 40% probability.

Scheme 5



ppm (^{13}C). Furthermore, in the ^{13}C NMR spectrum the bridging ligand {C(SMe)C(O)C≡CPh} gives rise to resonances at 161.5 and 189.8 ppm, attributable to the alkylidene and ketone carbons, respectively, and at 93.0 and 88.7 ppm due to the −C≡C− moiety. In addition, the resonance observed in the ^1H NMR for the SMe protons at 1.72 ppm is indicative of a direct S−Fe interaction.

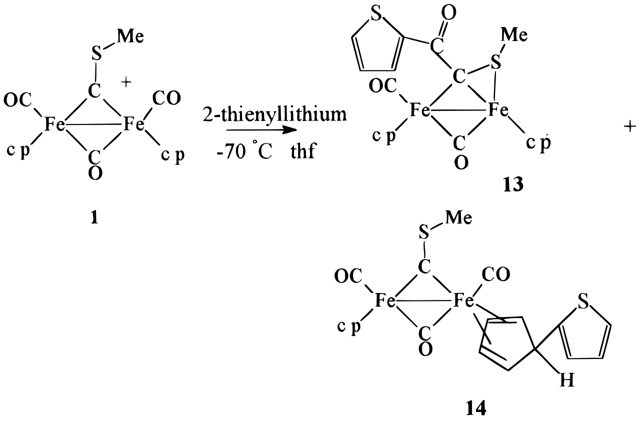
Reaction of 1 with 2-Thienyllithium. Treatment of **1** with Lith in thf at −70 °C rapidly forms a mixture of the complexes $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)C(O)\text{-}(2\text{-}th)\}]$ (**13**; 19%) and $[Fe_2(cp)(C_5H_5\text{-}(2\text{-}th))(CO)_2(\mu\text{-}CO)\text{-}(\mu\text{-}CSMe)]$ (**14**; 40%) resulting from the 2-thienyl carbanion addition at the carbonyl and cyclopentadienyl ligands, respectively (Scheme 6). These complexes have been separated by column chromatography and purified by crystallization. The spectroscopic properties of **13** are similar to those of the analogous complex **12**, and its molecular structure has been determined by an X-ray structural study (Figure 2). The IR spectrum of **14** exhibits a ν(CO) pattern consistent with two terminal and one bridging *cis*-CO (1983, 1949, 1792 cm^{-1}). A single resonance for the cp group is observed in both the ^1H and ^{13}C NMR spectra. The presence of the η^4-C_5H_5-(2-th) moiety is confirmed by the ^{13}C NMR spectrum that shows nine distinct signals due to the diastereotopic ring carbons at 154.1, 123.6, 122.5, 121.4 (2-th) and 91.4, 87.6, 72.1, 69.2, 56.1 ppm (C_5H_5-(2-Th)). As for type **2** complexes, the absence in the IR spectrum of the $C-H_{exo}$ band at about 2750 cm^{-1} suggests that the nucleophilic attack at one cp ring has occurred at the *exo* position.

In contrast with the results reported above on the addition of Grignard reagents to **1**, the reaction with 2-thienyllithium forms **14** but not the alkylidene complex $[Fe_2(cp)(C_5H_4th)(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)SMe)]$, in which one hydrogen would migrate from the C_5H_5R ring to the μ-carbyne carbon. Complex **14** does not exhibit any hydrogen rearrangement upon standing in CH_2Cl_2 solution or by treatment with silica gel.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ (6)

Fe(1)−Fe(2)	2.525(2	C(1)−C(11)	1.505(5)
Fe(1)−C(1)	1.972(5)	C(1)−C(21)	1.520(6)
Fe(1)−C(2)	1.968(5)	C(2)−O(2)	1.169(7)
Fe(1)−C(3)	1.742(6)	C(3)−O(3)	1.153(7)
Fe(2)−C(1)	1.976(5)	C(21)−C(22)	1.356(8)
Fe(2)−C(2)	1.872(6)	C(21)−C(26)	1.496(7)
Fe(1)−$C(cp)_{av}$	2.123	C(22)−C(23)	1.439(9)
Fe(2)−$C(cp)_{av}$	2.095	C(23)−C(24)	1.372(11)
Fe(2)−C(21)	2.124(4)	C(24)−C(25)	1.435(12)
Fe(2)−C(22)	2.232(6)	C(25)−C(26)	1.309(10)
C(3)−Fe(1)−C(2)	90.6(2)	C(11)−C(1)−Fe(2)	137.1(3)
C(3)−Fe(1)−C(1)	90.4(2)	C(21)−C(1)−Fe(2)	73.5(2)
C(2)−Fe(1)−C(1)	93.7(2)	Fe(1)−C(1)−Fe(2)	79.5(2)
C(3)−Fe(1)−C(35)	87.3(2)	Fe(2)−C(2)−Fe(1)	82.2(2)
C(3)−Fe(1)−Fe(2)	106.3(2)	C(12)−C(11)−C(1)	123.2(3)
C(2)−Fe(1)−Fe(2)	47.3(2)	C(16)−C(11)−C(1)	116.8(3)
C(1)−Fe(1)−Fe(2)	50.3(1)	C(22)−C(21)−C(26)	118.7(5)
C(2)−Fe(2)−C(1)	96.6(2)	C(22)−C(21)−C(1)	122.2(4)
C(2)−Fe(2)−C(21)	104.5(2)	C(26)−C(21)−C(1)	116.3(4)
C(1)−Fe(2)−C(21)	43.3(2)	C(22)−C(21)−Fe(2)	76.3(3)
C(2)−Fe(2)−C(22)	82.1(2)	C(26)−C(21)−Fe(2)	118.2(3)
C(1)−Fe(2)−C(22)	73.2(2)	C(1)−C(21)−Fe(2)	63.2(2)
C(21)−Fe(2)−C(22)	36.2(2)	C(21)−C(22)−C(23)	120.2(6)
C(2)−Fe(2)−Fe(1)	50.5(2)	C(21)−C(22)−Fe(2)	67.6(3)
C(1)−Fe(2)−Fe(1)	50.1(1)	C(23)−C(22)−Fe(2)	123.8(4)
C(21)−Fe(2)−Fe(1)	80.9(1)	C(24)−C(23)−C(22)	120.4(7)
C(22)−Fe(2)−Fe(1)	87.7(2)	C(23)−C(24)−C(25)	118.8(7)
C(11)−C(1)−C(21)	117.3(4)	C(26)−C(25)−C(24)	122.5(7)
C(11)−C(1)−Fe(1)	119.0(3)	C(25)−C(26)−C(21)	119.3(6)
C(21)−C(1)−Fe(1)	120.1(3)		

Scheme 6



X-ray Molecular Structures of $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ (6) and $[FeFe(cp)_2(CO)(\mu\text{-}CO)\text{-}\{\mu\text{-}C(SMe)C(O)(2\text{-}th)\}]$ (13). The solid-state structure of **6** is illustrated in Figure 1. It contains, as expected, the $Fe_2(cp)_2$ unit with the cp ligands in a *cis* configuration. The Fe−Fe bond is bridged by a CO and a diphenylcarbene ligand. A peculiarity of the molecule is that one of the phenyl rings is η^2-coordinated to Fe-(2), taking the place of a terminal CO ligand. The molecule is therefore asymmetric, and the crystal contains the racemic mixture generated by the coordination of either face of the phenyl ring, depending on which terminal CO ligand in the precursor **1** has been eliminated.

The iron−iron distance (2.525(2) Å) is in the range of those found in this family of compounds, and the bridging carbene atom (C(1)) exhibits strictly equivalent μ-C—Fe interactions (1.972, 1.976(5) Å), in spite of the distortions introduced by the η^2 coordination of one phenyl group. The μ-C—C(phenyl) distances are substantially equivalent (C(1)—C(11), 1.505(5) Å; C(1)—C(21), 1.520(6) Å) and consistent with single bonds. The phenyl carbons coordinated to Fe are asymmetrically bonded (Fe(2)—C(21), 2.124(4) Å; Fe(2)—C(22), 2.232(6) Å), and the coordination generates some π-electron localization, resulting in a cyclohexatriene type structure (mean C—C bond distances 1.35 and 1.46 Å). The actual structure is the one that allows improved donation to the metal. In conclusion, the diphenylcarbene ligand is η^1-bonded to Fe(1) and η^3-bonded to Fe(2); however, the geometric evidence (C(1)—C(21) and C(21)—C(22) separations 1.520(6) and 1.36(1) Å, respectively) suggests a description of this nonclassical bonding system as a vinylalkylidene group, *i.e.* the sum of η^2 and η^1 bonds. Few examples of arylalkylidene dinuclear complexes with η^2 attachment of the aryl ring to a metal are known: *e.g.* $[Mo_2(cp)_2(CO)_4\{C(p\text{-}MeC_6H_4)_2\}]$[17] and $[PtW\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(cp)][BF_4]$.[18] In these molecules, as opposed to the case under discussion, the μ-C—C(ring)—C(ring) distances exhibit substantially equal values and have been described as allylic groups.

The nonequivalence of the iron atoms is pointed out by a slight asymmetry of the bridging CO ligand (Fe(1)—C(2), 1.968(5) Å; Fe(2)—C(2), 1.872(6) Å), the shorter distance being from the iron bearing the coordinated phenyl. The same effect has been observed in related molecules containing a coordinated C=C double bond, *i.e.* $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^3(\sigma)\text{-}C(O)C_2(CH_3)[C(O)C_6H_5]\}]$ and $[Fe_2(cp)(cp^*)(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^3(\sigma)\text{-}C(O)C_2(CH_3)[C(O)\text{-}n\text{-}C_4H_9]\}]$.[19] The shortening effect can be explained by different σ−π bonding contributions of CO and olefinic ligands. The same kind of asymmetries for the bridging CO have been observed in molecules such as $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(CHO)SEt\}]$, $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(COOMe)SMe\}]$,[7] and **13** (see later), in which the S atoms are coordinated in the place of a terminal CO group. As the sulfur atom is a better donor than carbon monoxide, the coincidence of shorter Fe—(μ-CO) distances observed on the side of the coordinated sulfur or phenyl groups is indicative of a more consistent π-back-donation to the bridging carbonyl.

The molecular structure of **13** is illustrated in Figure 2. The stereogeometry is comparable, in a broad sense, to that just described for **6**. The $Fe_2(\mu\text{-}CO)(cp)_2$ moieties are strictly equivalent in the two species, and the μ-alkylidene group, μ-C{C(O)(2-th)}(SMe), in spite of the different substituents, exhibits coordination of the sulfur atom to the iron atom, paralleling the η^2 coordination of the phenyl group in **6**. As a consequence the same kind of asymmetry is present in the two molecules and the bridging CO ligand is distorted (Fe(1)—C(2), 1.846(4) Å; Fe(2)—C(2), 2.046(4) Å), in accord with what was discussed above. The bridging carbene atom is slightly asymmetric (Fe(1)—C(1), 1.904(4) Å; Fe(2)—C(1), 1.957(3) Å), and the same rationalization applies to it. In fact in the bis(carbene) species $[Fe_2(cp)_2\{\mu\text{-}C(CN)SMe\}_2]$,[12] in which two iron-coordinated sulfur atoms make the iron atoms equivalent, a slight asymmetry in the opposite sense is present; *i.e.*, the Fe—C interaction spanned by the sulfur is longer (1.952(3) *vs* 1.929(3) Å).

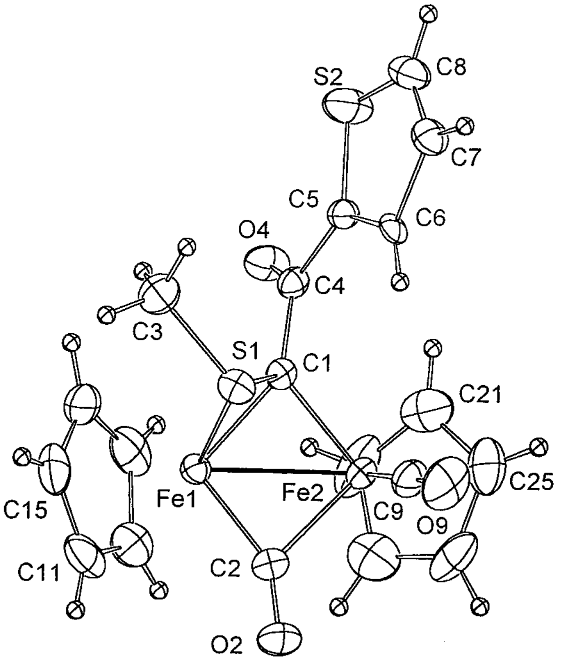


Figure 2. ORTEP drawing of $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)C(O)(2\text{-}th)\}]$ (**13**). Thermal ellipsoids are drawn at 30% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)C(O)(2\text{-}th)\}]$ (13)

Fe(1)−Fe(2)	2.517(1)	C(1)−S(1)	1.777(4)
Fe(1)−C(1)	1.904(4)	S(1)−C(3)	1.813(5)
Fe(1)−C(2)	1.846(4)	C(1)−C(4)	1.476(5)
Fe(1)−S(1)	2.246(1)	C(4)−O(4)	1.234(4)
Fe(2)−C(1)	1.957(3)	C(4)−C(5)	1.484(5)
Fe(2)−C(2)	2.046(4)	C(5)−C(6)	1.503(5)
Fe(2)−C(9)	1.756(4)	C(6)−C(7)	1.494(5)
Fe(1)−C(cp)$_{av}$	2.096	C(7)−C(8)	1.317(7)
Fe(2)−C(cp)$_{av}$	2.110	C(8)−S(2)	1.669(5)
C(2)−O(2)	1.169(5)	C(5)−S(2)	1.702(4)
C(9)−O(9)	1.144(5)		

C(2)−Fe(1)−C(1)	97.4(2)	C(4)−C(1)−S(1)	119.8(2)
C(2)−Fe(1)−S(1)	94.0(1)	C(4)−C(1)−Fe(1)	136.0(2)
C(1)−Fe(1)−S(1)	49.9(1)	S(1)−C(1)−Fe(1)	75.1(1)
S(1)−Fe(1)−Fe(2)	80.98(4)	C(4)−C(1)−Fe(2)	121.1(2)
C(9)−Fe(2)−C(1)	94.2(2)	S(1)−C(1)−Fe(2)	112.1(2)
C(9)−Fe(2)−C(2)	86.1(2)	C(1)−S(1)−C(3)	105.3(2)
C(1)−Fe(2)−C(2)	89.4(2)	C(1)−S(1)−Fe(1)	55.02(1)
C(9)−Fe(2)−Fe(1)	107.5(2)	C(3)−S(1)−Fe(1)	108.7(2)
C(1)−Fe(2)−Fe(1)	48.4(1)	O(4)−C(4)−C(1)	122.2(3)
C(2)−Fe(2)−Fe(1)	46.3(1)	O(4)−C(4)−C(5)	118.8(3)
Fe(1)−C(1)−Fe(2)	81.4(1)	C(1)−C(4)−C(5)	118.9(3)
Fe(1)−C(2)−Fe(2)	80.4(2)	C(4)−C(5)−C(6)	127.1(3)
O(2)−C(2)−Fe(1)	149.0(4)	C(4)−C(5)−S(2)	119.3(3)
O(2)−C(2)−Fe(2)	130.2(3)	C(6)−C(5)−S(2)	113.7(3)
O(9)−C(9)−Fe(2)	176.2(4)		

The $C(O)(C_4H_3S)$ substituent is characterized by the two dihedral angles of the planar group C(4)—C(1)—O(4)—C(15) with the dimetallacyclopropane ring Fe(1)—Fe(2)—C(1) (76.8°) and thienyl ring (8.8°). These angles, together with the bond distances around C(4)

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(C(4)–C(1), 1.476(5) Å; C(4)–C(5), 1.484(5) Å; C(4)–O(4), 1.234(5) Å), indicate that the p_z orbital of C(4) is primarily involved in the π bond to O(4) and little π-electron delocalization involving C(1), C(4), and the thienyl ring is evidenced. Other acyl substituents at the μ-carbene atom are present in $[Fe_2(cp)_2(CO)(\mu\text{-}CO)(\mu\text{-}CHCOPh)]$,[20] $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^3(\sigma)\text{-}C(O)C_2(CH_3)[C(O)C_6H_5]\}]$, $[Fe_2(cp)(cp^*)(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^3(\sigma)\text{-}C(O)C_2(CH_3)[C(O)\text{-}n\text{-}C_4H_9]\}]$,[19] $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SEt)\{C(O)H\}\}]$, and $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)\{C(O)OMe\}\}]$,[7] and their geometries have been found comparable to that of **13**.

Discussion

The formation of C–C bonds at the diiron thiocarbyne complex **1** has been carried out *via* selective addition at all of its electrophilic sites, resulting in a number of reaction pathways. These include ring addition (reactions with RMgX, Scheme 1), CO addition (th and phenylacetylide reagents), and nucleophilic attack at the μ-carbyne carbon (reactions with organocopper and $NaHC(CN)_2$). In spite of the considerable efforts aimed at determining the factors influencing regio- and stereochemical control in the reactions of nucleophiles with metal carbonyl complexes,[21] the nature of the products obtained from **1** and carbon nucleophiles remains largely unpredictable. However, previous findings show that the soft organocuprate reagents can be conveniently utilized to form C–C bonds at the μ-alkylidyne carbon of $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)(\mu\text{-}CR)]^+$.[3d] This observation suggests that the alkylidyne is a softer site compared to CO or cp. Further support for this idea comes from the previously reported reactions of **1** with CN^-, which give selective cyanide addition at the μ-C atom. In view of these facts, it seems plausible that under comparable experimental conditions, $Li_2Cu(CN)R_2$ species selectively attack the μ-carbyne carbon of **1,** affording the alkylidenes $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)R\}]$ (R = Ph, **4**; **R** = Me, **8**) (Schemes 2 and 3). These complexes are the precursors of $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)R\}]$ (R = Ph, **5**; R = Me, **9**), generated *via* intramolecular CO displacement by the S atom. The other products observed, $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ (**6**) and $[Fe_2(cp)_2(CO)(\mu\text{-}CO)(\mu\text{-}CCH_2)]$ (**10**), are rather unexpected because their formation requires μ-C–SMe bond breaking at some stage of the reaction paths. Desulfurization and nucleophilic replacement of the SMe moiety in $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)X\}]$ (X= CN, H, Ph) is usually achieved only by converting SMe into SMe_2, which is a better leaving group. However, since the C–S cleavage has been observed in the reactions of **1** with NCO^{-} [5c] and NHR_2[5a] and proposed to occur *via* nucleophilic addition at the bridging carbon atom, it is feasible that complex **4** is the intermediate in the formation of $[Fe_2(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(\eta^2\text{-}Ph)Ph\}]$ (**6**), although no direct evidence has been found. It is worth mentioning that the additional coordination of the C_6H_5 ring to the Fe atom contributes to the stability of the complex because of the entropic gain determined by the elimination of a CO molecule. Complex **10** may arise from $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)Me\}]$ **(8)** (Scheme 3). In this case, however, deprotonation of the hydrogen on the carbon α to the μ-C atom and C–S bond cleavage are required steps in order to explain the formation of the vinylidene. The fact that the acidic α-hydrogen in the bridging C(SMe)Me ligand plays a pivotal role in promoting the μ-vinylidene formation is further supported by the observation that reaction of **1** with $NaCH(CN)_2$ directly leads to the formation of the known *cis*- and *trans*-vinylidene complexes $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{=}C(CN)_2\}]$ (**11**) in yields higher than those obtained by the published method.[16] Although no alkylidene intermediate of the type $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)CH(CN)_2\}]$ has been detected, it seems obvious that the reaction proceeds *via* addition of $[CH(CN)_2]^-$ at the bridging carbon atom of **1**.

The addition of RMgX, NaCCPh, and Lith occurs at the cp or CO groups of **1**. Despite the different product distributions, a common feature of these reactions is the intramolecular rearrangement which follows the attack. In fact, as previously reported[8] and shown in Scheme 1, hydrogen migration from the C_5H_5R ring to μ-C must occur in order to explain the formation of complex **3**. This rearrangement is probably favored by the net energy gain of the aromatization and subsequent η^5 coordination of the C_5H_5R ring. However, other factors, including steric crowding, may be responsible for the transformation of **2** into **3**, since in the case of $[Fe_2(cp)(C_5H_5\text{-}(2\text{-}th))(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]$ (**14**) no detectable amount of the rearranged product has been observed.

The alkylidene complexes $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)C(O)R\}]$ (R = CCPh, **12**; R = 2-Th, **13**) are very likely formed *via* nucleophilic attack at the terminal CO followed by COR migration from the iron center to the bridging carbyne carbon. This path resembles that observed for the analogous complexes $[FeFe(cp)_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(SMe)C(O)R\}]$ (R = H, OR) obtained by treatment of **1** with $HBEt_3^-$ or RO^-. Indeed in the case of the RO^- addition, the alkoxycarbonyl intermediate $[Fe_2(cp)_2(CO)(COOR)(\mu\text{-}CO)(\mu\text{-}CSR)]$ has been isolated and fully characterized.[7] It should be noted that two C–C bonds are generated in the reactions forming **12** and **13**: the first arises from direct attack at the coordinated CO and the second from CO μ-carbyne coupling. The nucleophile induced carbonyl-carbyne coupling, recognized as a possible key step in Fischer–Tropsch chemistry, has been largely explored since the discovery of Kreissl in 1976.[22] Another example is the carbonyl-thiocarbyne coupling reported by Angelici.[23] This latter study is somewhat related to our systems, although it involves mononuclear complexes. Notwithstanding this, similar reactions have never been observed in dinuclear systems. Therefore, **1** provides a unique example of a complex which selectively ac-

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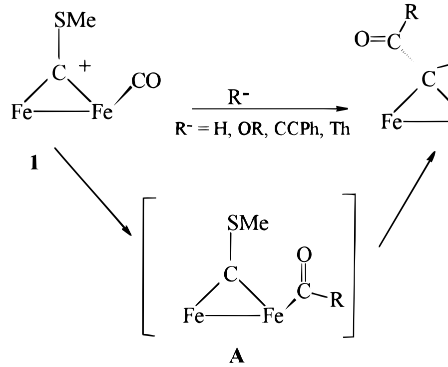
complishes the one-step nucleophilically promoted transformation of a coordinated CO into aldehyde, ester, or ketone functional groups anchored at two metal centers:



The intramolecular rearrangement A→B is driven by a favorable enthalpic balance of the bonds formed (Fe—S and μ-C—C(O)R) and cleaved (Fe—C(O)R). It should be pointed out that the nucleophilic attack at the terminal CO or cp ligands unbalances the electron counting on the iron atoms. Therefore, the observed migration may be due to the need to saturate the formal one-electron vacancy on the Fe atom bearing the transformed cp or CO ligands. The CO—μ-C nucleophilically promoted migratory coupling implies the same stereochemical modification occurring in the **1**→B conversion. The crystal structure of **13** shows that, as in [FeFe(cp)$_2$(CO)(μ-CO){μ-C(SR)C(O)X}] (X = OR, H),[7] the migrated C(O)th occupies a *trans* position with respect to the remaining CO group, despite the mutual *cis* positions of the carbonyl ligands in the precursor **1**. The observed stereochemistry is not easily explainable; however, it may arise from the bridge-opening mechanism common to all these diiron complexes.

Experimental Section

General Procedures. All reactions were routinely carried out under nitrogen by standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Glassware was oven-dried before use. Instruments employed: IR, Perkin Elmer 983-G; NMR, Varian Gemini 300. The ^{1}H and ^{13}C NMR spectra were referenced to SiMe$_4$. The compound [Fe$_2$(cp)$_2$(CO)$_2$(μ-CO)(μ-CSMe)]SO$_3$CF$_3$ was synthesized according to published methods.[4] Li$_2$Cu(CN)R$_2$ species were prepared from CuCN and the appropriate organolithium reagent according to the literature.[24]

Reaction of 1 with (allyl)MgCl To Give 2 and 3. Freshly prepared (allyl)MgBr (0.45 mmol) in thf solution was added to a stirred suspension of **1** (0.21 g, 0.39 mmol) in thf (15 mL) cooled to 0 °C with an external ice bath. The mixture, which rapidly turned brownish green, was stirred for about 90 min, warmed to room temperature, and then filtered on an alumina pad. The solution was evaporated under reduced pressure, and the residue was chromatographed on an alumina column with a CH$_2$Cl$_2$−hexane mixture (1:4, v/v) as eluent. A green fraction was collected and evaporated to dryness, yielding [Fe$_2$(cp)(C$_5$H$_5$-allyl)(CO)$_2$(μ-CO)(μ-CSMe)] (**2**; 12 mg, 7%). IR (CH$_2$Cl$_2$): ν(CO) 1981 s, 1942 w, 1785 m cm^{-1}. Further elution with CH$_2$Cl$_2$−hexane (1:1, v/v) gave a red fraction which yielded, by crystallization from CH$_2$Cl$_2$ layered with pentane at −20 °C, [Fe$_2$(cp)(C$_5$H$_4$-allyl)(CO)$_2$(μ-CO){μ-C(SMe)H}] (**3**; 123 mg, 74%). Anal. Calcd for C$_{18}$H$_{18}$Fe$_2$O$_3$S: C, 55.74; H, 4.26. Found: C, 55.68; H, 4.33. IR (CH$_2$Cl$_2$): ν(CO) 1981 s, 1943 w, 1780 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ_{H} 11.38 (1 H, s, μ-CH), 6.02 (m, 1 H, C*H*=CH$_2$), 5.22−5.08 (m, 2 H; CH=C*H*$_2$) 4.74 (s, 5 H, cp), 4.57, 4.36, 4.32 (m, 4 H, C$_5$*H*$_4$R), 3.24 (d, 2 H, -C*H*$_2$−, J_{H-H} = 6 Hz), 2.82 (s, 3 H, SMe).

Reaction of 1 with Li$_2$Cu(CN)Ph$_2$ To Give 4−6. Phenyllithium (1.0 mmol) was added to a stirred suspension of CuCN (45 mg, 0.5 mmol) in thf (10 mL) at −78 °C. The resulting Li$_2$Cu(CN)Ph$_2$ solution was warmed to −40 °C and transferred by cannula into a solution of [Fe$_2$(cp)$_2$(CO)$_2$(μ-CO)(μ-CSMe)] CF$_3$SO$_3$ (**1**; 238 mg, 0.446 mmol) in thf (10 mL) at −40°C. The mixture was warmed to room temperature, stirred for an additional 30 min, and filtered on a Celite pad. Evaporation of the solvent and crystallization from CH$_2$Cl$_2$ layered with pentane at −20 °C gave dark red crystals of [Fe$_2$(cp)$_2$(CO)$_2$(μ-CO){μ-C(SMe)Ph}] (**4**; 87 mg, 42%), which were collected from the solution. Anal. Calcd for C$_{21}$H$_{18}$Fe$_2$O$_3$S: C, 54.58; H, 3.93. Found: C, 55.01; H, 4.13. IR (CH$_2$Cl$_2$): ν(CO) 1986 s, 1947 w, 1780 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ_{H} 7.51−7.00 (m, 5 H, Ph), 4.99 (s, 10 H, cp), 2.01 (s, 3 H, SMe). ^{13}C NMR (CDCl$_3$): δ_{C} 273.7 (μ-CO), 212.5 (CO), 193.7 (μ-C), 125.3, 126.6, 132.1, 164.7 (Ph), 91.6 (cp), 23.8 (SMe).

The mother liquor was evaporated under vacuum, giving a dark red solid residue which was chromatographed on an alumina column with a CH$_2$Cl$_2$−hexane mixture (1:2 v/v) as eluent. A first red fraction was collected, evaporated to dryness, and recrystallized from CH$_2$Cl$_2$ layered with pentane at −20 °C, affording red crystals of [Fe$_2$(cp)$_2$(CO)(μ-CO){μ-C)-(η^2-Ph)Ph}] (**6**; 56 mg, 27%). Anal. Calcd for C$_{25}$H$_{20}$Fe$_2$O$_2$: C, 64.70; H, 4.34. Found: C, 64.66; H, 4.35. IR (CH$_2$Cl$_2$): ν(CO) 1945 s, 1764 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ_{H} 8.45−6.70 (m, 9 H, Ph), 4.40 (s, 5 H, cp), 3.94 (s, 5 H, cp), 1.05 (m, 1 H, Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ_{C} 277.4 (μ-CO), 217.2 (CO), 184.3 (μ-C), 123.6, 125.4, 126.7, 128.4, 128.7, 129.2, 130.1, 130.4, 138.2, 158.9 (Ph), 84.4, 89.4 (cp). Finally, a second green fraction was collected and evaporated under reduced pressure, giving a solid residue of [FeFe(cp)$_2$(CO)(μ-CO){μ-C(SMe)Ph}] (**5**; 36 mg, 18%). Anal. Calcd for C$_{20}$H$_{18}$Fe$_2$O$_2$S: C, 55.34; H, 4.18. Found: C, 55.34; H, 4.26. IR (CH$_2$Cl$_2$): ν(CO) 1942 s, 1759 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ_{H} 8.0−7.2 (m, 5 H, Ph), 4.66 (s, 5 H, cp), 4.35 (s, 5 H, cp), 1.25 (s, 3 H, SMe). ^{13}C NMR (CD$_2$Cl$_2$): δ_{C} 276.1 (μ-CO), 218.3 (CO), 184.3 (μ-C), 155.4, 129.9, 129.5, 128.2 (Ph), 87.1, 83.4 (cp), 26.2 (SMe).

Reaction of 1 with Li$_2$Cu(CN)Me$_2$ To Give 8−10. A solution of Li$_2$Cu(CN)Me$_2$ prepared from dry CuCN (45 mg, 0.5 mmol) and LiMe (1.0 mmol) in thf (10 mL) at −80 °C was added to [Fe$_2$(cp)$_2$(CO)$_2$(μ-CO)(μ-CSMe)]CF$_3$SO$_3$ (**1**; 285 mg, 0.534 mmol) in thf (15 mL) at −40 °C. The mixture was warmed to room temperature, stirred for an additional 30 min, and filtered on an alumina pad. Evaporation of the solvent gave a dark red solid residue which was chromatographed on an alumina column with CH$_2$Cl$_2$−hexane (1:3 v/v) as eluent. A first red fraction contained [Fe$_2$(cp)$_2$(CO)$_2$(μ-CO)(μ-C=CH$_2$)] (**10**; 32 mg, 17%) that was identified by comparison of its spectroscopic properties with those reported in the literature.[14] Further elution with CH$_2$Cl$_2$−hexane (1:1 v/v) gave a second red fraction, which was collected, evaporated to dryness, and recrystallized from CH$_2$Cl$_2$ layered with pentane, affording red crystals of [Fe$_2$(cp)$_2$(CO)$_2$(μ-CO){μ-C(SMe)Me}] (**8**; 137 mg, 64%). Anal. Calcd for C$_{16}$H$_{16}$Fe$_2$O$_3$S: C, 48.04; H, 4.03. Found: C, 47.99; H, 4.05. IR (CH$_2$Cl$_2$): ν(CO) 1981 s, 1942 m, 1780 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ_{H} 4.75 (s, 10 H, cp), 3.38 (s, 3 H, CH$_3$), 2.73 (s, 3 H, CH$_3$). Finally a third green fraction gave, after crystallization, [FeFe(cp)$_2$(CO)(μ-CO){μ-C(SMe)Ph} (**9**; 24 mg, 12%). IR (CH$_2$Cl$_2$): ν(CO) 1935 s, 1757 m cm^{-1}.

Synthesis of [Fe$_2$(cp)$_2$(CO)$_2$(μ-CO){μ-C(Ph)CN}] (7). To a solution of **4** (209 mg, 0.45 mmol) in CH$_2$Cl$_2$ (10 mL) were added CH$_3$SO$_3$CF$_3$ (0.08 mL, 0.71 mmol) and, after 20 min of

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(24) (a) Lipshutz, B. H. in *Organometallics in Synthesis*; Scholsser, M., Ed.; Wiley: New York, 1994. (b) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

Table 3. Crystallographic Data for Complexes 6 and 13

	6	**13**
chem formula	$C_{25}H_20Fe_2O_2$	$C_{19}H_{16}Fe_2O_3S_2$
fw	464.11	468.14
temp, K	293(2)	293(2)
wavelength, Å	0.710 69	0.710 69
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	*Pbca* (No. 61)
a, Å	9.203(6)	8.135(1)
b, Å	17.253(7)	15.840(6)
c, Å	12.465(7)	28.710(9)
β, deg	93.61(5)	90
V, Å^3	1975(2)	3700(2)
Z	4	8
d_{calcd}, Mg/m^3	1.561	1.681
abs coeff, mm^{-1}	1.487	1.810
F(000)	952	1904
cryst dimens, mm	0.32 × 0.38 × 0.050	0.075 × 0.175 × 0.20
θ range, deg	2−25	2.5−30
scan type	ω	ω
no. of rflns collected	7052 ($\pm h$, $\pm k$, $\pm l$)	5373 ($+h$,$+k$,$+l$)
no. of unique obsd rflns ($F_o > 4\sigma(F_o)$)	3431	3043
goodness of fit (GOF) on F^2	1.093	1.023
R1(*F*),[a] wR2(F^2)[b]	0.0399, 0.1090	0.0444, 0.1209
weighting scheme	$a = 0.0612$, $b = 1.8022$[b]	$a = 0.0807$, $b = 2.4994$[b]

[a] $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

stirring, NBu_4CN (193 mg, 0.72 mmol). The mixture was stirred for an additional 30 min; then the volatile material was removed under vacuum. The residue was chromatographed on an alumina column (3 × 8 cm), with a CH_2Cl_2−hexane mixture (1:1, v/v) as eluent. A red fraction was collected and evaporated to dryness, and the solid residue was recrystallized from CH_2Cl_2 layered with pentane at −20 °C, giving red crystals of **7** (121 mg, 61%). Anal. Calcd for $C_{21}H_{15}Fe_2NO_3$: C, 57.19; H, 3.43. Found: C, 57.26; H, 3.44. IR (CH_2Cl_2): ν(CO) 2003 s, 1966 w, 1803 m, ν(CN) 2150 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ_H 7.53−7.21 (m, 5 H, Ph), 5.00 (s, 10 H, cp).

Reaction of [$Fe_2(cp)_2(CO)_2(\mu$-CO)(μ-CSMe)]CF_3SO_3 (1) with $NaCH(CN)_2$ To Give 11. A thf solution (10 mL) of $NaCH(CN)_2$, obtained by reacting $CH_2(CN)_2$ (46 mg, 0.70 mmol) with equimolar amounts of NaH, was transferred by cannula into a stirred solution of **1** (320 mg, 0.60 mmol) in thf (15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 60 min. The resulting greenish brown solution was filtered on an alumina pad; then the solvent was removed under vacuum. The residue, redissolved in CH_2Cl_2, was chromatographed on an alumina column with a CH_2Cl_2−hexane mixture (1:1, v/v) as eluent. A first red fraction containing some [$Fe_2(cp)_2(CO)_4$] was discharged. The second red-violet fraction was collected and crystallized from a CH_2Cl_2−pentane mixture, affording *trans*-[$Fe_2(cp)_2(CO)_2(\mu$-CO){μ-C═C(CN)$_2$}] (*trans*-**11**; 68 mg, 28%). A third orange fraction was finally collected with CH_2Cl_2 as eluent; crystallization from CH_2Cl_2−Et_2O gave *cis*-[$Fe_2(cp)_2(CO)_2(\mu$-CO){μ-C═C-(CN)$_2$}] (*cis*-**11**; 61 mg; 25%). Compounds *trans*-**11** and *cis*-**11** were identified by comparison of their spectroscopic properties with those reported in the literature;[16] moreover, ^{13}C NMR data were obtained. *trans*-**11** δ_C (CD_2Cl_2): 336.5 (μ-C), 259.8 (μ-CO), 209.2 (CO), 116.2 (CN), 98.1 {*C*(CN)$_2$}, 92.1 (cp). *cis*-**11** δ_C (CD_2Cl_2): 334.9 (μ-C), 260.0 (μ-CO), 208.7 (CO), 116.2 (CN), 98.0 {*C*(CN)$_2$}, 90.1 (cp).

Reaction of [$Fe_2(cp)_2(CO)_2(\mu$-CO)(μ-CSMe)]CF_3SO_3 (1) with LiC≡CPh To Give 12. To a stirred solution of **1** (300 mg; 0.56 mmol) in thf (20 mL) at −20 °C was added LiC≡CPh (0.60 mmol), freshly prepared from HC≡CPh and LiBu in thf solution. The mixture, which immediately turned brown, was stirred for 10 min and warmed to room temperature. Evaporation of the solvent under reduced pressure and chromatography of the residue on an alumina column (8 × 3 cm) with a CH_2Cl_2−hexane mixture (1:1, v/v) as eluent gave a brown fraction, which was collected and evaporated to dryness. Crystallization from CH_2Cl_2 layered with pentane at −20 °C yielded [FeFe(cp)$_2$(CO)(μ-CO){μ-C(C(O)C≡CPh)(SMe)}] (**12**; 136 mg, 50%). Anal. Calcd for $C_{23}H_{18}Fe_2O_3S$: C, 56.82; H, 3.73. Found: C, 56.67; H, 3.74. IR (CH_2Cl_2): ν(CO) 1956 s, 1784 m, 1573 w; ν(C≡C) 2187 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ_H 7.68−7.44 (m, 5 H, Ph), 4.79 (s, 5 H, cp), 4.75 (s, 5 H, cp), 1.72 (s, 3 H, SMe). ^{13}C NMR (CD_2Cl_2): δ_C 267.9 (μ-CO), 217.1 (CO), 189.8 {*C*(O)CCPh}, 161.5 (μ-*C*), 133.1, 131.0, 129.6, 121.6 (Ph), 85.7, 84.2 (cp), 93.0, 88.7 (*C*≡*C*), 28.0 (SMe).

Reaction of [$Fe_2(cp)_2(CO)_2(\mu$-CO)(μ-CSMe)]CF_3SO_3 (1) with 2-thienyllithium To Give 13 and 14. To a stirred solution of **1** (200 mg, 0.37 mmol) in thf (15 mL) at −70 °C was added a slight excess of 2-thienyllithium (0.40 mL, 0.40 mmol of a 1.0 M solution in thf). The mixture, which rapidly turned brownish green, was stirred for 10 min, warmed to room temperature, and then filtered on an alumina pad. The solution was evaporated under reduced pressure and the residue chromatographed on an alumina column with a CH_2Cl_2−petroleum ether (40−70 °C) mixture (1:3, v/v) as eluent. A first greenish yellow fraction was collected and evaporated to dryness and the residue crystallized from CH_2Cl_2 layered with pentane at −20 °C, yielding [Fe_2(cp)(C_5H_5-(2-th))(CO)$_2$(μ-CO)(μ-CSMe)] (**14**; 69 mg, 40%). Anal. Calcd for $C_{19}H_{16}Fe_2O_3S_2$: C, 48.75; H, 3.44; S, 13.70. Found: C, 48.95; H, 3.39; S, 13.58. IR (CH_2Cl_2): ν(CO) 1983 s, 1949 m, 1792 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ_H 7.02, 6.84, 6.63 (m, 3 H, th), 4.77 (s, 5 H, cp), 4.89, 4.73, 4.21, 3.91 (m, 5 H, (C_5H_5-(2-th)), 3.16 (s, 3 H, SMe). ^{13}C NMR (CD_2Cl_2): δ_C 256.7 (μ-CO), 221.7, 213.1 (CO), 154.1, 123.6, 122.5, 121.4 (th), 91.4, 87.6, 72.1, 69.2, 56.1 ((C_5H_5-(2-th)), 87.0 (cp), 34.0 (SMe).

A second green fraction was then collected, affording, after crystallization from CH_2Cl_2 layered with pentane at −20 °C, green crystals of [FeFe(cp)$_2$(CO)(μ-CO){μ-C(SMe)C(O)(2-th)}] (**13**) (33 mg, 19%). Anal. Calcd for $C_{19}H_{16}Fe_2O_3S_2$: C, 48.75; H, 3.44; S, 13.70. Found: C, 48.95; H, 3.39; S, 13.58. IR (thf): ν(CO) 1944 s, 1789 m, 1601 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ_H 8.11, 7.67, 7.19 (m, 3 H, th), 4.75 (s, 5 H, cp), 4.47 (s, 5 H, cp), 1.44 (s, 3 H, SMe).

Crystallography. Crystal data and details of the data collection for complexes **6** and **13** are given in Table 3. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The unit cell parameters were determined by a least-squares fitting procedure using 25 reflections. Data were corrected for Lorentz and polarization effects. No decay correction was necessary.

(a) [Fe$_2$(cp)$_2$(CO)(μ-CO){μ-C)(η^2-Ph)Ph}] (6). An empirical absorption correction was applied by using the azimuthal scan method.[25] The positions of the metal atoms were found by direct methods using the SHELXS 86 program[26] and all the non-hydrogen atoms located from difference Fourier syntheses. The cyclopentadienyl rings and the uncoordinated phenyl ring (C(11)−C(16)) were treated as rigid groups (C−C = 1.42, 1.39 Å, respectively) and their hydrogen atoms were included at calculated positions (C−H = 0.96 Å). The hydrogen atoms of the η^2-coordinated phenyl ring were located from difference-Fourier maps and their positional parameters were refined. The final refinement on F^2 proceeded by full-matrix least-squares calculations (SHELXL 93)[27] using anisotropic thermal parameters for all the non-hydrogen atoms. The cyclopentadienyl and the phenyl H atoms were assigned an isotropic thermal parameter 1.2 times the U_{eq} values of the carbon atoms to which they were attached. In the final difference Fourier synthesis, the electron density was found in the range −0.36 to +0.53 e Å^{-3}.

(b) [FeFe(cp)$_2$(CO)(μ-CO){μ-C(SMe)C(O)(2-th)}] (13). No absorption correction was applied. The structure was solved by direct methods using the SHELX86 program,[26] and all the non-hydrogen atoms were located from difference Fourier maps. The cyclopentadienyl rings were treated as rigid groups, and their hydrogen atoms were included in calculated positions and treated using a riding model constraint with fixed isotropic displacement parameters as for **6**. The hydrogen atoms of the thienyl ring and the methyl hydrogen atoms were located in the difference Fourier map, but calculated positions were used. The final refinement on F^2 (SHELXL 93)[27] proceeded by full-matrix least-squares calculations, thermal motion being treated anisotropically for all non-hydrogen atoms. The cyclopentadienyl, thienyl, and methyl H atoms were assigned isotropic thermal parameters 1.2 times those of the attached atoms and were constrained to ride on the attached atoms. The final difference-Fourier map showed peaks in the range −0.63 to +0.88 e Å^{-3}.

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Supporting Information Available: Tables of X-ray crystallographic data, positional and thermal parameters, and bond lengths and angles for **6** and **13** (16 pages). Ordering information is given on any current masthead page.

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