

**Reactions between Transition-Metal Alkynyl Complexes and Nucleophiles: Syntheses and Crystal Structures of  $[\text{Fe}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^3(\sigma)\text{-C}(\text{O})\text{C}_2(\text{CH}_3)[\text{C}(\text{O})\text{R}]\}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5(\text{R}')_5)]$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, n\text{-C}_4\text{H}_9$ ;  $\text{R}' = \text{H}, \text{CH}_3$ )**

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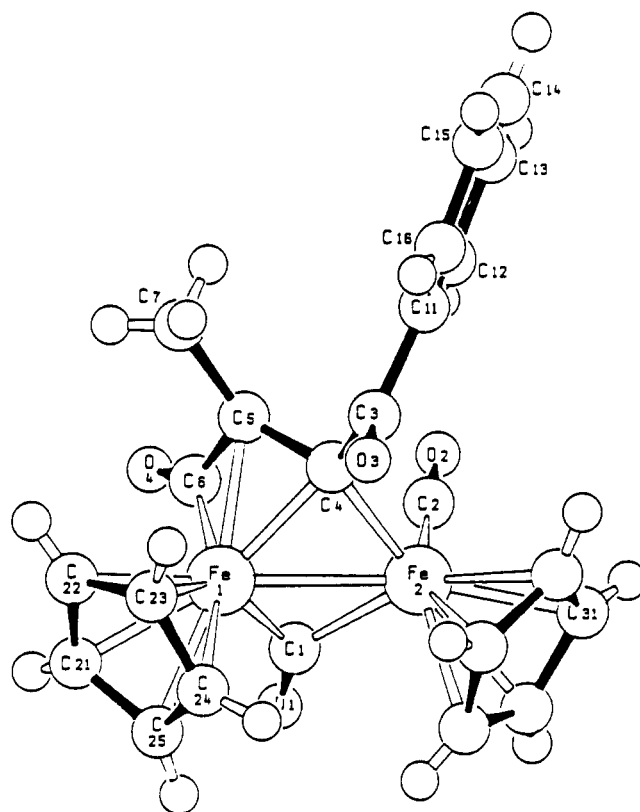
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**Summary:** Reaction between  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-\text{CH}_3$  (**1**) and  $\text{RLi}$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, n\text{-C}_4\text{H}_9$ ) at low temperature followed by  $(\eta^5\text{-C}_5\text{R}'_5)(\text{CO})_2\text{Fe}-\text{Cl}$  ( $\text{R}' = \text{H}, \text{CH}_3$ ) resulted in the isolation of  $[\text{Fe}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^3(\sigma)\text{-C}(\text{O})\text{C}_2(\text{CH}_3)[\text{C}(\text{O})\text{R}]\}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5(\text{R}')_5)]$  ( $\text{R}' = \text{H}, \text{R} = \text{CH}_3$  (**2a**),  $n\text{-C}_4\text{H}_9$  (**2b**),  $\text{C}_6\text{H}_5$  (**2c**);  $\text{R}' = \text{CH}_3, \text{R} = n\text{-C}_4\text{H}_9$  (**2b'**)). The structures of **2c** and **2b'** were confirmed by X-ray crystallographic data. The initial site of attack by the nucleophile  $\text{R}^-$  appeared to be the carbon of a carbonyl on **1**, on the basis of an experiment with a carbon-13-labeled sample of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(^*\text{CO})\text{Fe}-\text{C}\equiv\text{C}-\text{CH}_3$ .

The chemistry of transition-metal alkynyl complexes has been studied extensively.<sup>1</sup> It has been well documented that alkynyl complexes containing electron-donating transition-metal fragments undergo  $\alpha$  attack by nucleophiles and  $\beta$  attack by electrophiles. However, in all known examples, attack by electrophiles always preceded attack by nucleophiles. For example, Selegue and Davidson used a sequence of four addition reactions (electrophile, nucleophile, electrophile, and nucleophile) to reduce an ethynyliron complex into a neopentyliron complex.<sup>2</sup> Gladysz and co-workers also demonstrated that chiral rhenium alkynyl complexes undergo stereospecific electrophilic attack at the  $\beta$ -carbon; the resulting cationic vinylidenes may subsequently react stereospecifically with a nucleophile in the  $\alpha$ -position.<sup>3</sup> To the best of our knowledge, an initial nucleophilic attack on a metal alkynyl complex has never been reported. We had previously shown that the terminal proton on  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{C}(\text{C}\equiv\text{C})_2\text{-H}$  may be deprotonated by  $n\text{-BuLi}$  at  $-78^\circ\text{C}$ . The reaction was sluggish and appeared to be complicated by side reactions, possibly with  $n\text{-BuLi}$  acting as a nucleophile.<sup>4</sup> To ascertain this possibility, we initiated a study to investigate the reactions between transition-metal alkynyl complexes and nucleophiles. In this paper, we report the first example of transition-metal alkynyl complexes reacting with nucleophiles. The product of this reaction may be trapped by  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{Cl}$  to form the dinuclear complexes  $[\text{Fe}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^3(\sigma)\text{-C}(\text{O})\text{C}_2(\text{CH}_3)[\text{C}(\text{O})\text{R}]\}(\eta^5\text{-C}_5\text{H}_5)_2]$  (**2a**,  $\text{R} = \text{CH}_3$ ; **2b**,  $\text{R} = n\text{-C}_4\text{H}_9$ ; **2c**,  $\text{R} = \text{C}_6\text{H}_5$ ).

In a typical reaction, 1.2 equiv of  $\text{RLi}$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, n\text{-C}_4\text{H}_9$ ) was added dropwise to a THF solution of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-\text{CH}_3$  (**1**) cooled at  $-78^\circ\text{C}$ . The



**Figure 1.** ORTEP drawing of  $[\text{Fe}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^3(\sigma)\text{-C}(\text{O})\text{C}_2(\text{CH}_3)[\text{C}(\text{O})\text{C}_6\text{H}_5]\}(\eta^5\text{-C}_5\text{H}_5)_2]$  (**2c**), showing the atomic labeling scheme.

reaction was stirred at  $-78^\circ\text{C}$  for 1 h, after which 1.2 equiv of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{Cl}$  dissolved in THF was added. The reaction mixture was allowed to react for an additional  $1/2$  h with concurrent warming to room temperature. Complexes **2<sup>b</sup>** may be isolated in 28–45% yields (based on **1**) as dark brown crystals after separation with silica gel column chromatography and recrystallization with  $\text{CH}_2\text{Cl}_2$

(5) Complex **2a**: IR (KBr,  $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ) 1980 (s), 1804 (s), 1751 (m), 1670 (m);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ,  $23^\circ\text{C}$ )  $\delta$  4.88 (s, 5 H, Cp), 4.83 (s, 5 H, Cp), 2.79 (s, 3 H,  $\text{CH}_3$ ), 1.55 (s, 3 H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ,  $23^\circ\text{C}$ )  $\delta$  259.0 ( $\mu\text{-CO}$ ), 230.5, 210.3, 209.2 (CO), 193.8 ( $=\text{C}$ ), 88.38, 87.78 (Cp), 31.54, 16.22 ( $\text{CH}_3$ ), 21.62 ( $=\text{C}$ ). Anal. Calcd for  $\text{C}_{18}\text{H}_{16}\text{Fe}_2\text{O}_4$ : C, 52.99; H, 3.95. Found: C, 53.12; H, 3.89. Complex **2b**: IR (KBr,  $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ) 1986 (s), 1803 (s), 1751 (m), 1667 (m);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ,  $23^\circ\text{C}$ )  $\delta$  4.87 (s, 5 H, Cp), 4.84 (s, 5 H, Cp), 3.23 (m, 1 H,  $\text{CH}_2\text{CH}_2$ ), 2.95 (m, 1 H,  $\text{CH}_2\text{CH}_2$ ), 1.89 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.52–1.40 (overlapping m, 5 H,  $\text{CH}_3$  and  $\text{CH}_2$ ), 1.05 (t, 3 H,  $\text{CH}_3\text{CH}_2$ );  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ,  $23^\circ\text{C}$ )  $\delta$  259.2 ( $\mu\text{-CO}$ ), 230.7, 212.0, 210.5 (CO), 193.9 ( $=\text{C}$ ), 88.37, 87.84 (Cp), 43.42, 26.40, 22.80, 14.12 ( $n\text{-Bu}$ ), 16.62 ( $\text{CH}_3$ ), 22.19 ( $=\text{C}$ ). Anal. Calcd for  $\text{C}_{21}\text{H}_{22}\text{Fe}_2\text{O}_4$ : C, 56.04; H, 4.93. Found: C, 56.21; H, 4.83. Complex **2c**: IR (KBr,  $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ) 1981 (s), 1802 (s), 1748 (m), 1641 (m);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ,  $23^\circ\text{C}$ )  $\delta$  8.21–8.25 (m, 2 H, Ph), 7.56–7.61 (m, 3 H, Ph), 4.93 (s, 5 H, Cp), 4.78 (s, 5 H, Cp), 1.42 (s, 3 H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ,  $23^\circ\text{C}$ )  $\delta$  259.0 ( $\mu\text{-CO}$ ), 230.6, 211.1, 201.2 (CO), 191.9 ( $=\text{C}$ ), 137.1, 132.9, 129.5, 129.0 (Ph), 88.72, 88.24 (Cp), 25.04 ( $=\text{C}$ ), 16.98 ( $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{23}\text{H}_{16}\text{Fe}_2\text{O}_4$ : C, 58.77; H, 3.86. Found: C, 58.35; H, 3.86.

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G.; *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* 1990, 9, 816 and references cited therein.

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(3) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* 1988, 110, 6096.

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**Table I. Selected Bond Distances (Å) and Angles (deg) for 2c**

Fe(1)–Fe(2)	2.5367 (13)	O(2)–C(2)	1.139 (5)
Fe(1)–C(1)	1.885 (4)	O(3)–C(3)	1.211 (5)
Fe(1)–C(4)	2.000 (4)	O(4)–C(6)	1.199 (5)
Fe(1)–C(5)	2.081 (4)	C(3)–C(4)	1.502 (5)
Fe(1)–C(6)	1.895 (4)	C(3)–C(11)	1.500 (6)
Fe(2)–C(1)	1.950 (4)	C(4)–C(5)	1.412 (5)
Fe(2)–C(2)	1.759 (4)	C(5)–C(6)	1.435 (5)
Fe(2)–C(4)	1.963 (4)	C(5)–C(7)	1.510 (6)
O(1)–C(1)	1.172 (5)		
Fe(2)–Fe(1)–C(1)	49.69 (12)	Fe(1)–C(5)–C(4)	66.71 (20)
Fe(2)–Fe(1)–C(4)	49.55 (11)	Fe(1)–C(5)–C(6)	62.04 (20)
Fe(2)–Fe(1)–C(5)	79.44 (11)	Fe(1)–C(5)–C(7)	126.9 (3)
Fe(2)–Fe(1)–C(6)	89.73 (12)	C(4)–C(5)–C(6)	114.5 (3)
C(1)–Fe(1)–C(4)	94.27 (17)	C(4)–C(5)–C(7)	125.0 (4)
C(1)–Fe(1)–C(5)	103.67 (16)	C(6)–C(5)–C(7)	117.8 (3)
C(1)–Fe(1)–C(6)	79.90 (17)	Fe(1)–C(6)–O(4)	143.2 (3)
C(4)–Fe(1)–C(5)	40.43 (14)	Fe(1)–C(6)–C(5)	75.98 (22)
C(4)–Fe(1)–C(6)	75.81 (15)		

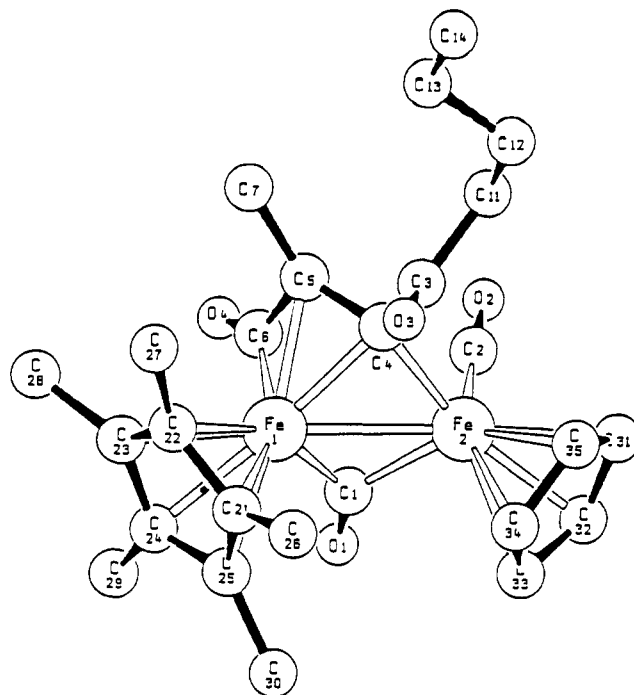
**Table II. Selected Bond Distances (Å) and Angles (deg) for 2b'**

Fe(1)–C(1)	1.886 (3)	O(2)–C(2)	1.144 (3)
Fe(1)–C(4)	2.027 (3)	O(3)–C(3)	1.206 (3)
Fe(1)–C(5)	2.092 (3)	O(4)–C(6)	1.200 (3)
Fe(1)–C(6)	1.888 (3)	C(3)–C(4)	1.492 (4)
Fe(2)–C(1)	1.961 (3)	C(3)–C(11)	1.516 (4)
Fe(2)–C(2)	1.757 (3)	C(4)–C(5)	1.409 (4)
Fe(2)–C(4)	1.962 (2)	C(5)–C(6)	1.449 (4)
O(1)–C(1)	1.173 (3)	C(5)–C(7)	1.519 (4)
C(1)–Fe(1)–C(4)	93.63 (11)	Fe(1)–C(1)–F(2)	84.31 (10)
C(1)–Fe(1)–C(5)	103.05 (11)	Fe(1)–C(4)–Fe(2)	80.69 (9)
C(1)–Fe(1)–C(6)	80.02 (11)	Fe(1)–C(4)–C(3)	132.04 (17)
C(4)–Fe(1)–C(5)	39.98 (10)	Fe(1)–C(4)–C(5)	72.52 (15)
C(4)–Fe(1)–C(6)	75.58 (11)	Fe(2)–C(4)–C(3)	117.74 (17)
C(5)–Fe(1)–C(6)	42.30 (11)	Fe(2)–C(4)–C(5)	121.51 (17)
C(1)–Fe(2)–C(2)	87.92 (12)	C(3)–C(4)–C(5)	118.90 (21)
C(1)–Fe(2)–C(4)	93.38 (10)	C(4)–C(5)–C(6)	115.10 (21)
C(2)–Fe(2)–C(4)	89.41 (11)		

and hexane. The diiron dimer  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2$  and  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-R}$  were also formed (total yield up to 45%) as a result of the reaction between the excess RLi and  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-Cl}$ .

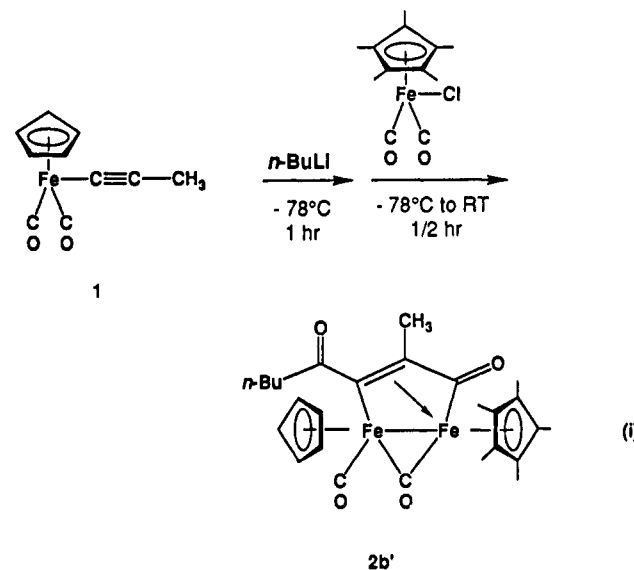
NMR data for complexes 2 revealed the presence of R groups and two inequivalent cyclopentadienyl ligands, indicating that the two iron fragments and R' groups have combined. IR spectra showed the characteristic terminal and bridging CO's. In addition, bands more typical of ketonic CO were observed. For example, complex 2a has absorptions at 1980 (s), 1804 (s), 1751 (m), and 1670 (m)  $\text{cm}^{-1}$ , further suggesting that the coupling of the alkynyl ligand and CO has taken place. To unambiguously assign the structures of 2, an X-ray diffraction study was performed, and the structure of 2c is shown in Figure 1. Interatomic distances and bond angles are given in Table I.<sup>6</sup>

The molecule is based on two iron atoms at a single-bond distance (2.537 Å), bridged symmetrically by a carbonyl group. Also bridging the diiron centers is a species derived from the linking of the propynyl ligand and two CO's. The bonding of this ligand is best represented as the dimetallacyclopentenone ring Fe(1)–C(6)–C(5)–C(4)–Fe(2), in which the ethylenic bond C(5)–C(6) is itself  $\eta^2$ -bonded to Fe(1).



**Figure 2.** ORTEP drawing of  $[\text{Fe}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^3(\sigma)\text{-C}(\text{O})\text{C}_2\text{-}(\text{CH}_3)\}[\text{C}(\text{O})\text{-}n\text{-C}_4\text{H}_9]\}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5(\text{CH}_3)_5)]$  (**2b'**), showing the atomic labeling scheme.

Complexes 2 are similar to a series of complexes formed by the photolysis of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2$  with  $\text{RC}\equiv\text{CR}'$ . These reactions were postulated to involve the initial photoassisted cleavage of the Fe–Fe bond to form an  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  radical.<sup>7</sup> The mechanism that led to the formation of 2, however, appeared to be quite different, on the basis of the following experiments. Reaction between *n*-BuLi and 1 followed by  $(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{Fe-Cl}$  resulted in the formation of 2b'<sup>8</sup> (reaction i), the structure



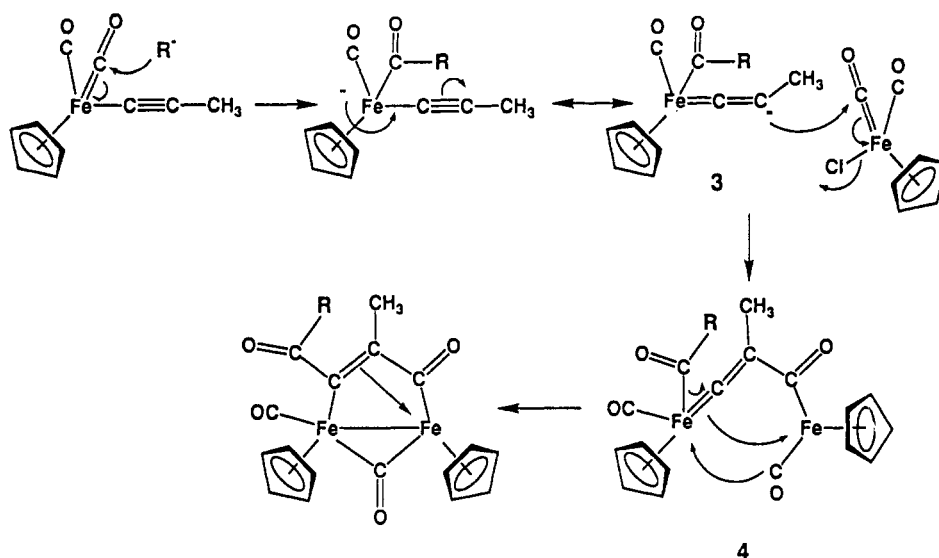
of which was confirmed by X-ray crystallographic data (Figure 2 and Table II).<sup>9</sup> Furthermore, the only iron dimer

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(8) Complex 2b': IR (KBr,  $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ) 1986 (s), 1803 (s), 1751 (m), 1667 (m); <sup>1</sup>H NMR (200 MHz,  $\text{CDCl}_3$ , 23 °C)  $\delta$  4.84 (s, 5 H, Cp), 3.24 (m, 1 H,  $\text{CH}_2\text{CH}_2$ ), 2.97 (m, 1 H,  $\text{CH}_2\text{CH}_2$ ), 1.98 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.75 (s, 15 H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.51–1.46 (overlapping m, 5 H,  $\text{CH}_3$  and  $\text{CH}_2$ ), 1.04 (t, 3 H,  $\text{CH}_3\text{CH}_2$ ). <sup>13</sup>C NMR (50 MHz,  $\text{CDCl}_3$ , 3 °C)  $\delta$  262.7 ( $\mu\text{-CO}$ ), 235.5, 212.7, 211.2 (CO), 191.3 (=C), 98.60 ( $\text{C}_5(\text{CH}_3)_5$ ), 87.31 (Cp), 43.58, 26.69, 22.85, 14.12 (*n*-Bu), 11.62 ( $\text{CH}_3$ ), 22.85 (=C), 9.25 ( $\text{C}_5(\text{CH}_3)_5$ ).

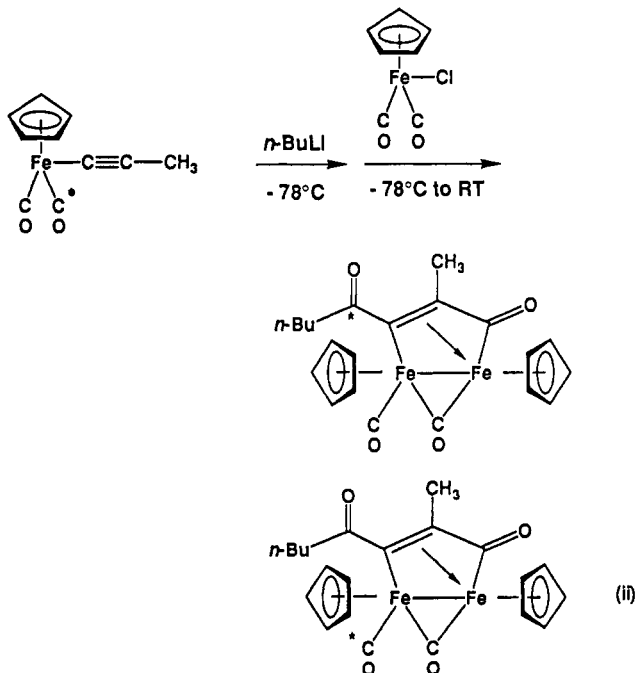
(6) Crystal data for 2c:  $\text{C}_{27}\text{H}_{18}\text{Fe}_2\text{O}_4$ ,  $M_r = 469.92$ , orthorhombic, space group *Pbca*;  $a = 9.065$  (4) Å,  $b = 18.560$  (3) Å,  $c = 22.873$  (6) Å,  $V = 3848.1$  (2) Å<sup>3</sup>;  $Z = 8$ ,  $F(000) = 1919.67$ ,  $d_{\text{calc}} = 1.623$  g/cm<sup>3</sup>; Nonius CAD-4 data, Mo radiation,  $\lambda = 0.7093$  Å,  $\mu = 1.53$  mm<sup>-1</sup>. Minimum and maximum transmission factors are 0.968 and 0.999.  $R = 0.029$ ,  $R_w = 0.031$ , and GOF = 1.24 with 47 atoms and 335 parameters for 2107 out of 3385 measured reflections, cut off with  $I > 2.5\sigma(I)$ .

Scheme I



formed was  $[(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{Fe}]_2$ ; no  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2$  or  $(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{Fe}-\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$  was observed. This is consistent with our earlier assertion that iron dimer was formed from the reaction between RLi and  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{Cl}$ .<sup>10</sup>

To ascertain the initial site of attack by RLi, a carbon-13-labeled sample of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(^*\text{CO})\text{Fe}-\text{C}\equiv\text{C}-\text{CH}_3$  (**1a\***)<sup>11</sup> was used to react with *n*-BuLi and  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{Cl}$ . The result is shown in reaction ii. From



(9) Crystal data for **2b'**:  $\text{C}_{26}\text{H}_{32}\text{Fe}_2\text{O}_4$ ,  $M_r = 520.23$ , triclinic, space group  $P\bar{1}$ ;  $a = 8.749$  (2) Å,  $b = 8.780$  (5) Å,  $c = 17.588$  (3) Å,  $\alpha = 99.76$  (3)°,  $\beta = 88.76$  (2)°,  $\gamma = 114.61$  (3)°,  $V = 1208.7$  (7) Å<sup>3</sup>;  $Z = 2$ ,  $F(000)$ , 543.91,  $d_{\text{calc}} = 1.429$  g/cm<sup>3</sup>; Nonius CAD-4 data, Mo radiation,  $\lambda = 0.7093$  Å,  $\mu = 1.23$  mm<sup>-1</sup>. Minimum and maximum transmission factors are 0.972 and 1.000.  $R = 0.027$ ,  $R_w = 0.034$ , and GOF = 1.67 with 64 atoms and 417 parameters for 3506 out of 4254 measured reflections, cut off with  $I > 2\sigma(I)$ .

(10) This is also good evidence that the main reaction pathway does not involve radicals. We have also performed experiments between RLi and **1** without the addition of any  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{Cl}$ . In these cases no Cp-containing fragments were observed.

(11) Complex **1a\*** was prepared by reacting **1** in toluene with 1 atm of  $^{13}\text{C}$  in a sealed tube at 90 °C for 4 days. An IR spectrum showed that **1a\*** was approximately 50% enriched.

an analysis of the products formed from the reaction, it appeared that an attack of the  $\text{R}^-$  group on the carbon of a carbonyl on **1** had occurred. A transition-metal alkynyl complex such as  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-\text{H}$ , in principle, has at least three reactive sites toward a nucleophile: the terminal proton may be removed or the  $\alpha$ -carbon on the alkynyl ligand or the carbon of a coordinated CO may be attacked. Kostic and Fenske had concluded from a molecular orbital calculation that the LUMO in  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-\text{H}$  is such that a nucleophile would preferentially add to the carbonyl carbon rather than to the alkynyl ligand.<sup>12</sup> This is consistent with the results we obtained.

On the basis of these experiments, we suggest that the formation of **2** may evolve by the pathway shown in Scheme I. Although unprecedented for metal alkynyl complexes, there are many examples of nucleophiles attacking a coordinated carbon monoxide.<sup>13</sup> Complex **4** has a coordinatively unsaturated iron center and may rearrange to form **2**.<sup>14</sup> The migration of an acyl group to a coordinated carbon fragment has also been demonstrated recently.<sup>15</sup> We are currently probing the generality of these reactions by using other nucleophiles and metal halides.

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**Supplementary Material Available:** Listings of crystal data and refinement details, fractional coordinates, thermal parameters, bond lengths, bond angles, and torsional angles for **2c** and **2b'** (20 pages); listings of structure factors (37 pages). Ordering information is given on any current masthead page.

(12) Kostic, N. M.; Fenske, R. F. *Organometallics* 1982, 1, 974.

(13) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Chapters 31, 37, and 50.

(14) An alternative mechanism involves the addition of **3** to the iron of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{Cl}$  directly, followed by migratory insertion to form **4**. This is less likely than the step we proposed, however, since the product of such a step would be an 18-electron species and would be unlikely to undergo migratory insertion under the reaction conditions.

(15) (a) Pouilhes, A.; Thomas, S. E. *Tetrahedron Lett.* 1989, 30, 2285. (b) Butler, I. R.; Gill, U.; LePage, Y.; Lindsell, W. E.; Preston, P. N. *Organometallics* 1990, 9, 1964.