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Carbon-Carbon Bond Formation at a Dinuclear Iron Center. 4. Synthesis of $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{OR})\text{H})(\mu\text{-CR}'=\text{CR}'\text{H})]^-$ Anions (R = Me, Et; R' = Ph, H) and the Subsequent Formation by Protonation of the Bridging Vinylcarbene Ligands $>\text{CHCR}'=\text{CR}'\text{H}$ or $>\text{CR}'\text{CH}=\text{CR}'\text{H}$, Depending on the Reaction Conditions

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The reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-COR})(\mu\text{-CR}'=\text{CR}'\text{H})$ (1a, R = Me, R' = Ph; 1b, R = Et, R' = Ph; 4, R = Et, R' = H) complexes with $[\text{Na}][\text{BH}_4]$ (R = Me, Et; R' = Ph) or $[\text{PPN}][\text{BH}_4]$ (R = Et; R' = H) leads to the formation of the $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{OR})\text{H})(\mu\text{-CR}'=\text{CR}'\text{H})]^-$ anions 2a, 2b, and 5, in good yield. The X-ray structure has been determined where R = Et, R' = Ph when associated with the $[\text{PPh}_4]^+$ cation. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell with $a = 15.006$ (3) Å, $b = 13.143$ (2) Å, $c = 11.868$ (2) Å, $\alpha = 100.20$ (2)°, $\beta = 74.97$ (2)°, $\gamma = 113.90$ (2)°. When R' = Ph, protonation leads to the formation of $\text{Fe}_2(\text{CO})_6(\mu\text{-COEtCPhCPH})$ (6). In the presence of L = PPh_3 or PMe_2Ph , protonation gives $\text{Fe}_2(\text{CO})_6\text{L}(\mu\text{-CPhCHCPhH})$ complexes 7 and 8. The latter result suggests that the intermediate formation of 1,3-diphenylcyclopropene arises from a [1 + 2] addition of the CH and CPhCPhH fragments.

Introduction

We have previously shown that the $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}'=\text{CR}'\text{H})]$ complexes, one of the products of the reaction of $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$ with alkynes,¹ were good starting materials for the synthesis of neutral $\text{Fe}_2(\text{CO})_6(\mu\text{-COR})(\mu\text{-CR}'=\text{CR}'\text{H})$ compounds upon reaction with alkylating agents.² These neutral complexes seemed good candidates for the study of their reactivity toward nucleophilic reagents as the two bridging ligands are electrophilic centers.

For instance, the reaction with hydride anion could occur either by nucleophilic attack on the ethenyl bridge to give

an anionic complex containing bridging carbene and carbyne ligands or by nucleophilic attack on the carbyne ligand to give an anionic complex with carbene and ethenyl bridges. The literature provides numerous examples of both types of reactivity.^{3,4}

In this paper we relate that only one type of reaction has been observed with $[\text{BH}_4]^-$ as the source of hydride anion, viz., the nucleophilic attack onto the alkoxycarbyne ligand leading to the formation of $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{OR})-$

(3) See, for instance: (a) Herrmann, W. A. *Adv. Organomet. Chem.* 1982, 20, 159, and references therein. (b) Casey, C. P.; Vosejka, P. C. *Organometallics* 1988, 7, 934.

(4) See, for instance: (a) Connelly, N. G.; Forrow, N. J.; Gracey, B. P.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1985, 14. (b) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* 1982, 1, 911. (c) Casey, C. P.; Fagan, P. J.; Day, V. W. *J. Am. Chem. Soc.* 1982, 104, 7360.

(1) Lourdichi, M.; Mathieu, R. *Nouv. J. Chim.* 1982, 6, 231.
(2) (a) Ros, J.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Organomet. Chem.* 1984, 260, C40. (b) Ros, J.; Commenges, G.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* 1985, 1087.

Table I. Selected Bond Lengths (angstroms) and Angles (degrees) with Estimated Standard Deviations in Parentheses for 2b

Fe(1)–Fe(2)	2.542 (2)	C(1)–C(2)	1.422 (9)
Fe(1)–C(1)	2.010 (9)	C(1)–C(11)	1.50 (1)
Fe(1)–C(3)	1.991 (9)	C(2)–C(21)	1.47 (1)
Fe(1)–C(101)	1.75 (1)	C(3)–O(3)	1.41 (1)
Fe(1)–C(102)	1.79 (1)	O(3)–C(4)	1.43 (1)
Fe(1)–C(103)	1.80 (1)	C(4)–C(5)	1.37 (3)
Fe(2)–C(1)	2.06 (1)	C(101)–O(101)	1.14 (1)
Fe(2)–C(2)	2.184 (9)	C(102)–O(102)	1.15 (2)
Fe(2)–C(3)	2.050 (9)	C(103)–O(103)	1.17 (1)
Fe(2)–C(201)	1.77 (1)	C(201)–O(201)	1.16 (1)
Fe(2)–C(202)	1.77 (1)	C(202)–O(202)	1.15 (1)
Fe(2)–C(203)	1.75 (1)	C(203)–O(203)	1.17 (1)
Fe(1)–C(1)–Fe(2)	77.3 (4)	Fe(1)–C(102)–O(102)	178 (1)
Fe(1)–C(1)–C(2)	120.1 (7)	Fe(1)–C(103)–O(103)	172.7 (9)
Fe(1)–C(1)–C(11)	118.1 (5)	Fe(2)–C(201)–O(201)	179 (1)
Fe(2)–C(1)–C(11)	127.5 (6)	Fe(2)–C(202)–O(202)	175 (1)
C(2)–C(1)–C(11)	120.9 (8)	Fe(2)–C(203)–O(203)	175.6 (8)
Fe(1)–C(3)–Fe(2)	78.0 (3)	Fe(2)–C(1)–C(2)	75.3 (5)
Fe(1)–C(3)–O(3)	118.0 (5)	Fe(2)–C(2)–C(1)	65.7 (5)
Fe(2)–C(3)–O(3)	121.0 (6)	Fe(2)–C(2)–C(21)	124.0 (5)
C(3)–O(3)–C(4)	114.9 (8)	C(21)–C(2)–C(1)	127.9 (8)
O(3)–C(4)–C(5)	115 (1)	C(2)–C(1)–C(11)	120.9 (8)
Fe(1)–C(101)–O(101)	178 (1)		

H)(μ -CR'H)]⁻ anions (R = Me, Et, R' = Ph; R = Et, R' = H).

The reactivity of these anionic complexes toward acid will also be presented.

Results

Synthesis of [Fe₂(CO)₆(μ -C(OR)H)(μ -CR'=CR'H)]⁻ Complexes. The dinuclear complexes Fe₂(CO)₆(μ -COR)(μ -CPh=CPhH) (**1a**, R = Me, and **1b**, R = Et) react in acetone solution with 1 equiv of NaBH₄ leading to the anionic complexes [Fe₂(CO)₆(μ -C(OR)H)(μ -CPhCPhH)]⁻ (**2a**, R = Me, and **2b**, R = Et). These complexes were isolated and purified as their tetraphenylphosphonium salts by metathesis. The infrared spectra in the ν (CO) stretching region of **2a** and **2b** indicate that only terminal carbonyl groups were present, while proton NMR data gave additional and more specific information about the nature of the products formed. In addition to the phenyl and R resonances, two signals are observed with an integrated intensity of one hydrogen each at 5.64 and 2.65 ppm for **2a**, and at 5.80 and 2.67 ppm for **2b**. This is consistent with an attack of the hydride anion onto the carbon of the alkoxy carbyne ligand and is corroborated by ¹³C NMR data. The ¹³C NMR spectrum of **2b** exhibits two doublets centered at 179.3 ($J_{\text{CH}} = 149.7$ Hz) and 79.8 ppm ($J_{\text{CH}} = 156$ Hz), which is consistent with the occurrence of bridging CH(OC₂H₅) and CPhCPhH ligands.

Confirmation of the proposed structures based on ¹H and ¹³C NMR data has been obtained by an X-ray structure determination of **2b**. The structure of the anionic part of **2b** is shown in Figure 1. Principal bond lengths and bond angles are gathered in Table I.

The structure of **2b** shows that hydride addition has occurred endo with respect to the ethenyl bridge, a position that implies lesser steric interactions between the ethoxy group and the ethenyl bridge. Comparison of the structure of **2b** with the structure of the closely related **1b** complex, Fe₂(CO)₆(μ -COEt)(μ -CPhCMeH) (**3**),⁵ shows that the most significant changes concern the bridging carbene ligands as expected. Especially, the transformation of the ethoxy carbyne to the ethoxy carbene ligand induces a notable lengthening of the C(3)–O(3) distance (1.41 (1) Å compared

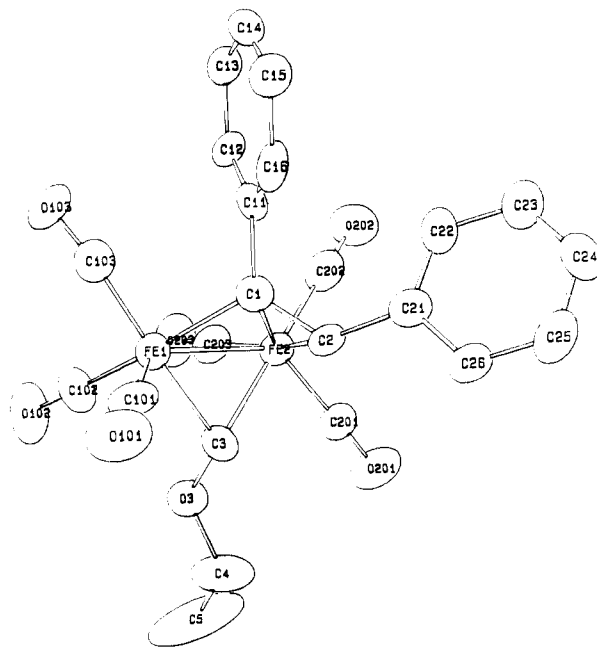


Figure 1. ORTEP view of complex **2b** showing the atomic numbering scheme.

to 1.29 (1) Å in **3**). This may be ascribed to the loss of multiple-bond character between these two atoms.⁶ The same phenomenon has been found in homo- and heterobimetallic μ -carbene complexes such as W₂(CO)₉[C-(OCH₃)C=CH(CH₂)₃CH₂]⁷ or (PMe₃)(CO)₄W[μ -C-(OCH₃)C₆H₄CH₃-4]Pt(PMe₃)₂.⁸

The ethoxy carbene ligand bridges the two iron centers asymmetrically. The shortest distance is associated with the iron atom σ -bonded to the ethenyl bridge. The iron-carbon distances are nevertheless similar to those found in μ -carbene complexes of iron.⁹

To summarize, the reaction of NaBH₄ with **1a** and **1b** has led to the nucleophilic addition of hydride to the ethoxy carbyne ligand.

To check whether this observation is the result of an electronic or steric effect, we have also studied the reactivity of Fe₂(CO)₆(μ -COEt)(μ -CHCH₂) (**4**) toward [BH₄]⁻. In the case of NaBH₄, no clean reaction was observed in acetone solution, whereas the reaction with [PPN][BH₄] in dichloromethane led to the isolation of [PPN][Fe₂(CO)₆(μ -C(OEt)H)(μ -CHCH₂)] (**5**) in 55% yield. This complex has an infrared spectrum very similar to those of **2a** and **2b**. Proton and ¹³C NMR spectra have given evidence that the hydride addition occurred at the ethoxy carbyne ligand. In accord, typical vinyl resonances are observed in the ¹³C NMR spectrum (see Experimental Section). Furthermore, the ¹H NMR spectrum exhibits a resonance at 5.55 ppm, which is attributed to the hydrogen of the ethoxy carbene bridge.

Protonation of 2a, 2b, and 5. Considering the anionic nature of these dinuclear bridging carbene complexes and the presence of an alkoxy group, we could expect that protonation would allow for the formation of the analogues

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of complexes **1** and **4** in which the bridging methylidyne group would replace the ethoxy carbyne ligand.^{4b,c} This would lead to more reactive molecules due to the greater reactivity of the CH group.¹⁰

Protonation of **2a** or **2b** affords the same complex **6** for which infrared spectroscopy gives evidence for the presence of only terminal carbonyl groups. Mass spectrometry and chemical analysis are consistent with the Fe₂(CO)₆(CHCPhCPhH) formulation. In the proton NMR spectra, in addition to phenyl resonances, a doublet and a doublet plus a multiplet at 4.87 ppm are observed, each signal having an intensity of 1 H. The latter result closely resembles the data obtained for Fe₂(CO)₆(μ-COEtCPhCPhH)^{2a} and Fe₂(CO)₆(μ-CMeCPhCPhH)¹¹ complexes. It has been shown for the first one that the X-ray structure consists of an Fe₂(CO)₆ unit bridged by the COEtCPhCPhH ligand where one of the double bonds of the phenyl bonded to the C_γ carbon is a π-bond with an iron atom. Moreover, the resonances of the aromatic hydrogen on the π-bond double bond of the aromatic cycle are respectively observed at 5.51 and 5.12 ppm. Therefore, we propose that **6** has the same type of structure.

As result, it appears that protonation of **2a** and **2b** has induced the formation of the methylidyne ligand but that this ligand quickly reacts with the diphenylethenyl bridge to give a bridging vinyl carbene in which the phenyl groups are now in a trans position with one of the double bonds of the phenyl group attached to the C_γ carbon π-bonded to an iron atom. In the case of complex **1b** it was observed that this coupling reaction occurs only very slowly at room temperature.^{2a}

To avoid either the coupling of the bridging ligands or the complexation of a phenyl ring, the protonation has been conducted in the presence of triphenylphosphine or dimethylphenylphosphine. In both cases, new products Fe₂(CO)₆(PPh₃)(μ-CPhCHCPhH) (**7**) and Fe₂(CO)₆(PMe₂Ph)(μ-CPhCHCPhH) (**8**) have been formed, which have very similar infrared spectra in the ν(CO) stretching region although these resonances are shifted toward lower frequencies compared to **6**. Mass spectra and chemical analysis are consistent with the Fe₂(CO)₆L(CHCPhCPhH) formulation (L = PPh₃, PMe₂Ph).

¹³C NMR data gave no evidence for the presence of a bridging carbyne ligand and suggest that the presence of an added ligand has not prevented the coupling of the organic fragments.

Moreover, examination of proton NMR data shows that these fragments have a different structure than that observed for **6**. The most significant features come from the chemical shifts and coupling constants for the CH groups, especially the CH resonance originating from the methylidyne group, which is observed at 6.06 ppm for **7** and 5.90 ppm for **8**. Thus, the data show that this group is not in a bridging position between the two iron atoms. This situation, compared with the data obtained for Fe(CO)₆(L)(μ-CHCHCH₂)¹² (L = CO, PPh₃), is consistent with a CH group in a 2 position of a vinyl carbene bridge.

The position of the CH groups is corroborated by the ¹³C NMR data for **7**, which exhibit, except for the phenyl and CO resonances, two CH groups centered at 68 and 98.2 ppm. These two resonances are characteristic of the CHPh group and a CH group in a 2 position¹² of a vinyl carbene bridging ligand. A third resonance is observed at 156.9

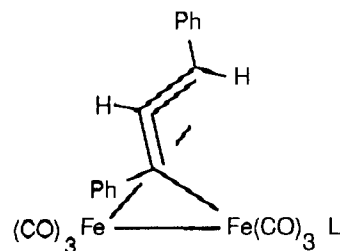
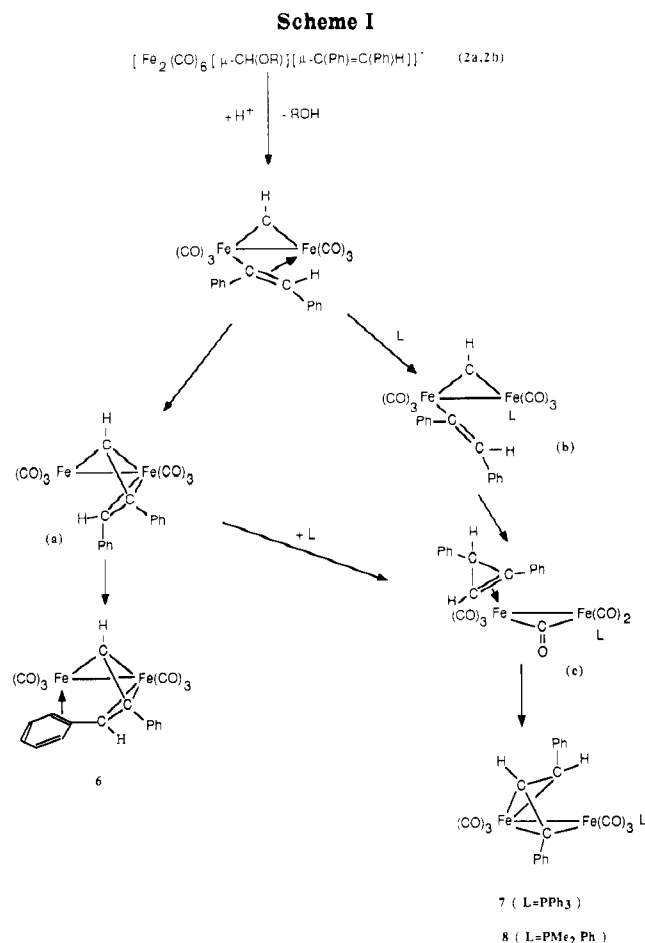


Figure 2. Structure of complex **7** (L = PPh₃) and **8** (L = PMe₂Ph).



ppm, and this is attributed to the C(Ph) carbon bridging the two iron atoms.

The H-H coupling constants of 9.3 Hz are consistent with the two hydrogens in a trans position.^{2b} All these data allow us to propose for **7** and **8** the structure shown in Figure 2. In this structure, the phosphine ligand is bonded to the iron which is σ-bonded to the vinyl carbene bridge, taking into account the fact that there is no apparent coupling of the phosphine with the CH group.

To summarize, although the presence of added ligands during the protonation of **2a** and **2b** has not prevented coupling of the generated methylidyne ligand with the ethenyl group, it has induced an unexpected phenomenon, i.e., the breaking of the carbon-carbon double bond and the insertion of the methylidyne group between these two fragments.

To check if this transformation could result from the reaction of **6** with phosphine ligands, we have reacted **6** with PPh₃. No reaction occurs at room temperature, even in refluxing benzene. As a result, **7** or **8** are obtained by an independent route. From these observations we propose the mechanism shown in Scheme I for the formation of **6**, **7**, or **8**.

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The protonation of **1a** or **1b** would generate $\text{Fe}_2(\text{CO})_6(\mu\text{-CH})(\mu\text{-CPhCPhH})$, which in the absence of added phosphine would evolve to the formation of **6** by coupling of the methylidyne and the alkenyl ligands through an intermediate (a) in which an iron center has 16 valence electrons. The cis-trans isomerization for the phenyl groups would be induced by the coordination of a double bond of the phenyl ring to the unsaturated iron center. This isomerization closely resembles the isomerization of the η^3 -coordinated allylic group.¹³ In the presence of phosphine, the phosphine coordination to iron would be allowed by the opening of the iron-ethenyl π -bond, giving the intermediate (b). Next, the transient formation of 1,3-diphenylcyclopropene by [1 + 2] addition of the CH and the CPhCPhH fragment would occur, leading to intermediate (c). Another way to the intermediate (c) should be also the addition of the phosphine on the intermediate (a). Finally, ring opening of the cyclopropene ring would give the end products **7** or **8**. The ring opening of the cyclopropene rings is a well-known reaction with iron carbonyl.¹⁴ Furthermore, in the case of dinuclear molybdenum complexes, it has been shown that it leads to dinuclear compounds containing bridging vinyl carbene ligands.¹⁵

It has to be noted that like in the case of mononuclear complexes of iron,¹⁴ the ring opening is observed for the most sterically hindered single bond.

In the case of complex **5**, protonation with or without added phosphorus ligand does not lead to isolable products. This result is quite surprising considering that the $\text{Fe}_2(\text{CO})_6\text{L}(\mu\text{-CHCHCH}_2)$ complexes (L = CO, PPh₃) have been obtained through independent routes.¹²

Experimental Section

General Data. All reactions were performed under nitrogen by using standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer in hexane or dichloromethane solutions. ¹H NMR spectra were obtained with a Bruker WH90 and ¹³C NMR spectra on a Bruker WM250 spectrometer. Mass spectra were obtained on a Varian Mat 311A. PPNBH₄ was prepared according to a published procedure,¹⁶ and the complexes $\text{Fe}_2(\text{CO})_6(\mu\text{-COR})(\mu\text{-CPhCPhH})^{2a}$ (R = Me, Et) and $\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-CHCH}_2)^{2b}$ were prepared as previously described.

Synthesis of [PPh₄][Fe₂(CO)₆(μ-C(OR)(μ-CPhCPhH)) Complexes 2a (R = Me) and 2b (R = Et). To 1 g of **1a** or **1b** dissolved in acetone was added 0.1 g of NaBH₄. The solution was stirred for 0.5 h, then filtered, and evaporated to dryness. Addition of a slight excess of PPh₄Br, dissolved in methanol, to the residue induced the precipitation of red crystals. These crystals were filtered, washed with methanol and ether, and dried in vacuo. Recrystallization in methanol/dichloromethane at -20 °C gave **2a** and **2b**.

2a: red crystals in 55% yield; IR $\nu(\text{CO})$ (CH_2Cl_2 solution) 2016 (m), 1977 vs. 1929 cm^{-1} ; ¹H NMR ((CD_3)₂CO solution) 8.1 m (20 H), 6.79 m (10 H), 5.64 s (1 H), 3.47 s (3 H), 2.65 s (1 H) ppm. Anal. Calcd for C₄₆H₃₅O₇PF₂: C, 65.86; H, 4.16. Found: C, 65.56; H, 4.19.

2b: red crystals in 60% yield; IR $\nu(\text{CO})$ (CH_2Cl_2 solution) 2014 (m), 1976 vs. 1929 cm^{-1} ; ¹H NMR ((CD_3)₂CO solution) 8.1 m (20 H), 6.78 m (10 H), 5.80 s (1 H), 3.66 m (2 H), 2.67 s (1 H), 1.18 t ($J = 7.0$ Hz, 3 H) ppm; ¹³C NMR (CDCl_2 solution) (except phenyl resonances) 220.4 (CO), 179.3 (d, $J = 149$ Hz, CH(OCH₃)),

Table II. Crystal Data and Data Collection Details for 2b

formula	C ₂₃ H ₁₇ O ₇ Fe ₂ (C ₂₄ H ₂₀ P)
fw	856.5
cryst syst	triclinic
space group	P1
a, Å	15.006 (3)
b, Å	13.143 (2)
c, Å	11.868 (2)
α, deg	100.20 (2)
β, deg	74.97 (2)
γ, deg	113.90 (2)
V, Å ³	2060 (2)
Z	2
d _{calc} , g·cm ⁻³	1.380
F(000)	884
diffractometer	Philips PW-1100
radiatn	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα), cm ⁻¹	8.15
scan mode	ω
scan range, deg	2-25
reflectns measd	2786
reflections with I ≥ 2.5σ(I)	2663
final R	0.053

Table III. Fractional Atomic Coordinates (×10 000) with Estimated Standard Deviations in Parentheses for 2b

	x/a	y/b	z/c
Fe(1)	2186 (1)	1591 (1)	3233 (1)
Fe(2)	1497 (1)	-65 (1)	1804 (1)
C(1)	2256 (6)	75 (7)	3077 (7)
C(2)	1367 (5)	-887 (6)	3319 (7)
C(11)	3258 (6)	14 (6)	2907 (7)
C(12)	4017 (6)	368 (7)	1937 (8)
C(13)	4941 (7)	319 (7)	1844 (9)
C(14)	5105 (7)	-115 (8)	2730 (10)
C(15)	4382 (7)	-451 (7)	3698 (10)
C(16)	3461 (7)	-382 (7)	3799 (8)
C(21)	1271 (6)	-2052 (7)	3265 (7)
C(22)	1942 (6)	-2509 (7)	2576 (7)
C(23)	1777 (7)	-3639 (8)	2562 (8)
C(24)	942 (8)	-4330 (7)	3255 (9)
C(25)	268 (7)	-3906 (8)	3951 (9)
C(26)	415 (6)	-2794 (8)	3968 (8)
C(3)	776 (6)	777 (7)	3073 (8)
O(3)	289 (4)	1380 (5)	2779 (5)
C(4)	-770 (7)	924 (10)	3128 (10)
C(5)	-1247 (9)	1443 (16)	2738 (18)
C(101)	1780 (6)	1696 (8)	4759 (9)
O(101)	1495 (5)	1773 (7)	5746 (6)
C(102)	2185 (7)	2848 (8)	2857 (9)
O(102)	2198 (6)	3671 (6)	2643 (7)
C(103)	3507 (7)	2300 (8)	3164 (8)
O(103)	4335 (5)	2847 (5)	3201 (6)
C(201)	279 (7)	-871 (8)	1566 (8)
O(201)	-516 (5)	-1378 (6)	1403 (7)
C(202)	2132 (7)	-801 (8)	733 (8)
O(202)	2503 (5)	-1272 (6)	-15 (6)
C(203)	1922 (7)	1013 (8)	880 (9)
O(203)	2195 (6)	1678 (6)	206 (6)

173.7 (CPh), 79.8 (CPhH), 71.4 (t, $J = 140$ Hz, OCH₂), 14.8 (q, $J = 126$ Hz, CH₃). Anal. Calcd for C₄₇H₃₇O₇PF₂: C, 65.91; H, 4.33. Found: C, 65.89; H, 4.33.

Synthesis of [PPN][Fe₂(CO)₆(μ-C(OEt)H)(μ-CHCH₂)] (5). To $\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-CHCH}_2)$ freshly prepared from $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_6(\mu\text{-CHCH}_2)]$ (1 g) dissolved in dichloromethane was added [PPN][BH₄] (0.08 g). The solution was stirred for 0.5 h, filtered, and evaporated to dryness. Crystallization at -20 °C in dichloromethane/methanol afforded **5** as orange crystals (55% yield); IR $\nu(\text{CO})$ (CH_2Cl_2 solution) 2020 m, 1973 vs. 1920 cm^{-1} ; ¹H NMR ((CD_3)₂CO solution) 8.0 (30 H), 7.66 (dd ($J_1 = 12.3$ Hz, $J_2 = 8.8$ Hz, 1 H), 5.55 s (1 H), 3.54 m (2 H), 2.84 d ($J_2 = 8.8$ Hz, 1 H), 1.92 d ($J_1 = 12.3$ Hz, 1 H, 1.18 t ($J = 7$ Hz, 3 H)); ¹³C NMR (CD_2Cl_2 solution) (except phenyl resonances) 220.4 (CO), 180.9 (d, $J = 149$ Hz, CH(OC₂H₅)), 153.5 (d, $J = 148$ Hz, CH), 70.9 (t, $J = 141$ Hz, OCH₂), 65.8 (dd, $J_1 = 151$ Hz, $J_2 = 158$ Hz, CH₂), 14.8 (q, $J = 125$ Hz, CH₃). Anal. Calcd for C₄₇H₃₉NO₆P₂Fe₂:

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C, 63.58; H, 4.39; N, 1.57. Found: C, 63.43; H, 4.36; N, 1.46.

Reaction of $\text{HBF}_4/\text{Et}_2\text{O}$ with **2a or **2b**. A. Without Added Phosphine: Synthesis of $\text{Fe}_2(\text{CO})_6(\mu\text{-CHCPhPhH})$ (**6**). To 1 g of **2a** or **2b** in dichloromethane solution at 0 °C was added a slight excess of $\text{HBF}_4/\text{Et}_2\text{O}$. The solution turned dark red and was evaporated to dryness. Extraction of the residue with pentane (3 × 10 mL), concentration, and cooling to -20 °C gave **6** as dark red crystals in 30% yield; IR $\nu(\text{CO})$ (hexane solution) 2060 s, 2020 vs, 1994 vs, 1985 vs, 1970 m, 1962 m cm^{-1} ; ^1H NMR (CDCl_3 solution) 8.36 (d ($J = 2.4$ Hz, 1 H), 7.28 m (9 H), 4.87 d ($J = 2.4$ Hz) + m (2 H). Anal. Calcd for $\text{C}_{21}\text{H}_{12}\text{O}_6\text{Fe}_2$: C, 53.38; H, 2.54. Found: C, 53.53; H, 2.67. Mass spectrum, $m/z = 472$.**

B. With Added Phosphine. To a solution of 1 g of **2b** and 0.3 g of PPh_3 (or 17 μL of PMe_2Ph) in dichloromethane at 0 °C was added a slight excess of $\text{HBF}_4/\text{Et}_2\text{O}$. The solution was evaporated to dryness. Extraction of the residue with pentane and crystallization at -20 °C gave the following:

(i) With PPh_3 , **7** as orange crystals in 50% yield; IR $\nu(\text{CO})$ (hexane solution) 2059 m, 2018 s, 1994 m cm^{-1} ; ^1H NMR (CDCl_3 solution) 7.33 m (25 H), 6.06 d ($J = 9.4$, 1 H), 3.90 d ($J = 9.4$, 1 H); ^{13}C NMR (CDCl_3 solution) (except phenyl resonances) 215.2 d ($J_{\text{PC}} = 19$ Hz, CO), 212.7 s (CO), 156.9 s (CPh), 98.2 d ($J = 157$ Hz, CH), 68 d ($J = 157.4$, CHPh). Anal. Calcd for $\text{C}_{39}\text{H}_{27}\text{O}_6\text{PFe}_2$: C, 63.76; H, 3.68. Found: C, 63.52; H, 3.76. Mass spectrum, $m/z = 626$.

(ii) With PMe_2Ph , **8**, as orange crystals (30% yield); IR $\nu(\text{CO})$ (hexane solution) 2040 m, 2000 s, 1963 m cm^{-1} ; ^1H NMR (CDCl_3 solution) 7.34 (15 H), 5.90 dd ($J_1 = 9.3$ Hz, $J_2 = 2.4$ Hz), 3.77 d ($J = 9.3$ Hz, 1 H), 1.87 d ($J = 9.1$ Hz, 3 H), 1.86 d ($J = 9.1$ Hz, 3 H). Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{O}_6\text{PFe}_2$: C, 57.04; H, 3.77. Found: C, 56.64; H, 3.89. Mass spectrum, $m/z = 610$.

X-ray Structure Analysis of $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{OEt})\text{-H})(\mu\text{-CPhPhH})]$ (2b**).** Crystals belong to the triclinic system, space group $\bar{P}1$. The crystal was sealed on a glass fiber and mounted on a Philips PW-1100 diffractometer. Unit-cell pa-

rameters were determined from 25 reflections ($4 \leq \theta \leq 12^\circ$) and refined by least-squares technique. A summary of crystal and intensity collection data is given in Table II. Three reflections were measured every 2-h as orientation and intensity control. Significant intensity decay was not observed. A total of 2786 reflections were measured in the range $2 \leq \theta \leq 25^\circ$, 2663 of which were assumed as observed applying the condition $I \geq 2.5\sigma(I)$. Lorentz-polarization corrections were made, but not absorption corrections.

The Fe atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms from a subsequent weighted Fourier synthesis. The structure was refined by least-squares method using the SHELX-76 computer program.¹⁷ The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = (\sigma^2|F_o| + 0.0054|F_o|^2)^{-1}$. The final R value was 0.053 ($R_w = 0.056$) for all observed reflections. The fractional atomic coordinates of the non-hydrogen atoms are listed in Table III.

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Registry No. **1a**, 125050-88-6; **1b**, 125134-34-1; **2a**, 125050-80-8; **2b**, 125050-82-0; **4**, 98814-91-6; **5**, 125050-84-2; **6**, 125050-85-3; **7**, 125050-86-4; **8**, 125050-87-5.

Supplementary Material Available: A table of anisotropic thermal parameters for $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CH}(\text{OEt}))(\mu\text{-CPhPhH})]$ (**2b**) (1 page); a table of structure factors for **2b** (12 pages). Ordering information is given on any current masthead page.

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Reaction of $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$ with Alkylphosphines: Formation and Isolation of η^1 -Fluorenyl Complexes

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Reaction of $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$ with $\text{L} = \text{PEt}_3$ or PBu_3 leads to formation of $(\eta^1\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3\text{L}_2$. The $\text{L} = \text{PEt}_3$ complex was isolated analytically pure in moderate yield and characterized as the trans-meridional isomer by ^1H , ^{31}P , and ^{13}C NMR and IR spectroscopies. $(\eta^1\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3\text{L}_2$ decomposes via Mn-C bond homolysis to the C_{13}H_9 radical and $\text{Mn}(\text{CO})_3\text{L}_2^{\cdot}$, which reacts further to yield $\text{HMn}(\text{CO})_3\text{L}_2$. $(\eta^1\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3\text{L}_2$ can also be prepared by reacting L with $(\eta^6\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$, apparently via a novel η^6 to η^1 shift.

Introduction

The ability of $\eta^5\text{-Cp}$ and related ligands to undergo haptotropic shifts to η^3 or η^1 coordination, facilitating substitution reactions, is well established and has recently been reviewed by O'Connor and Casey.² In particular, the greater reactivity of indenyl and fluorenyl complexes compared to that of Cp complexes has stimulated interest in their application to synthesis and catalysis.³ At the start of this work, the number of well-characterized η^1 -cyclopentadienyl and η^1 -indenyl complexes formed by ring slippage of η^5 complexes was quite limited, and there were

no well-documented examples of η^1 -fluorenyl complexes. Our interest in the reactivity of such complexes led us to attempt to isolate new examples of η^1 -indenyl and fluorenyl complexes.

In 1984, Ji, Rerek, and Basolo⁴ reported on the reaction of $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$ (**I**) with $\text{L} = \text{PBu}_3$ ($\text{Bu} = n\text{-butyl}$ throughout this report). At low PBu_3 concentrations, the reaction proceeded cleanly to the monosubstituted complex $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_2\text{L}$ (**IIa**, $\text{L} = \text{PBu}_3$), by second-order kinetics, presumably via an unobserved η^3 -fluorenyl intermediate, $(\eta^3\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3\text{PBu}_3$. However, at higher concentrations of PBu_3 , a long-lived green intermediate and a different, yellow final product were observed. The

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