

and hydroxo Fe(EHGS) in a 60:40 mixture and obtained the spectrum in Figure 7b. Spectrum 7a is from Fe(OTF) and is identical with spectrum 4d in ref 45. The 60:40 mixture was chosen to match the peaks at -4 mm/s. Comparison between the spectra in Figure 7 shows similarities and differences. The composite Fe(EHGS) spectrum reproduces fairly well the OTF peaks outside the region ± 2 mm/s. The central region is not reproduced as faithfully, but we do not reasonably expect to match all the features in the OTF spectrum. After all, simple addition of the EPR spectra from aquo and hydroxo Fe(EHGS) does not yield a composite that resembles the OTF EPR spectrum. Differences in and between Fe(EHGS) and OTF are expected to give rise to differences in the EPR spectra and to a mismatch between central regions in the Mössbauer spectra where the middle doublet contribution is most prominent. Nevertheless, our results seem to support a possibility suggested in ref 45, namely that both OTF iron sites exist in more than one conformation, resulting in different ligand fields and, hence, in different spin Hamiltonian parameters. On the basis of our present study of Fe(EHGS), we find it reasonable to identify these conformations in OTF with one that favors an aquo-like configuration at the iron and one that favors a hydroxo-like configuration.

The relative weight of each environment in the binding site will be governed by the conformations of the protein chain. Chaotropic agents such as perchlorate and thiocyanate have been known to perturb the native conformation/conformations by binding to several specific sites remote from the iron.⁴⁶ The EPR⁴⁷ and Mössbauer⁴⁸ spectra of transferrins reflect these perturbations, which indicates transmission of information to the iron sites. The model we propose for the binding site in these proteins provides

(46) Folastar, D. A.; Chasteen, N. D. *J. Am. Chem. Soc.* **1982**, *104*, 5775.

(47) Price, E. M.; Gibson, J. F. *J. Biol. Chem.* **1972**, *247*, 8031.

(48) Lang, G., unpublished results.

a simple way of perturbing the iron environment by altering the proton relay so as to favor either a hydroxo or an aquo environment.

Summary

We present a crystallographic determination of a novel Fe(III) complex with an open coordination site where solvent can bind. In aqueous solution the coordinated water can undergo hydrolysis at near neutral pH to yield a hydroxo complex. Interpretation of magnetic measurements on these complexes suggests that they may serve as models of the iron binding sites in the transferrins. Study of the models indicates that the nature of the sixth ligand (aquo/hydroxo) in the proteins is linked by a proton relay mechanism to the form of the obligate anion (carbonate/bicarbonate). We substantiate a previous suggestion⁴⁵ that two conformations of the iron binding site may coexist in ovotransferrin. The two conformations are distinguished by the presence of a water molecule or hydroxide as the sixth ligand of the iron. Extension of this model to other iron tyrosinate proteins is in progress.

Acknowledgment. Work at the University of Vermont was supported by Research Corporation grants to C.J.C. and K.S., for which we are grateful. We thank J. A. Bonadies and C. T. Bailey for their excellent technical assistance. Crystallographic work at the University of Wisconsin was partially supported by NIH Grant GM-17378 and by the College of Agricultural and Life Sciences, University of Wisconsin. A government of Indian fellowship to G.V.N.A.R. and an NIH postdoctoral fellowship to V.L.P. are gratefully acknowledged. We thank Prof. K. N. Raymond and Dr. P. Riley for prepublication release of the X-ray data on Na[VO(EHGS)].

Registry No. Fe(EHGS)H₂O, 90432-10-3; VO(EHGS), 89890-28-8; Fe(EHGS)MeOH, 94706-21-5.

Alkyne-Induced Carbyne-Carbyne Coupling in the Trinuclear Bis(carbyne) Iron Cluster Fe₃(CO)₉(μ₃-COC₂H₅)(μ₃-CCH₃). X-ray Structures of Fe₃(CO)₆(μ-CO)₂-μ₃-η⁴[C(OC₂H₅)C(CH₃)C(C₆H₅)C(C₆H₅)] and Fe₃(CO)₆(μ-CO)₂- μ₃-η⁴[C(CH₃)C(OC₂H₅)C(Si(CH₃)₃)C(Si(CH₃)₃)]

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Abstract: The reaction of alkynes R₁CCR₂ with the trinuclear bis(carbyne) iron cluster Fe₃(CO)₉(μ₃-COC₂H₅)(μ₃-CCH₃) produces complexes in which coupling of the entering alkynes with the carbyne ligands has occurred. X-ray structure determinations of the resulting Fe₃(CO)₆(μ-CO)₂(R₁CCR₂)(C(OC₂H₅)C(CH₃)) complexes in the cases where R₁ = R₂ = C₆H₅ or Si(CH₃)₃ show the presence of Fe-C(C₆H₅)-C(C₆H₅)-C(CH₃)-C-(OC₂H₅) and Fe-C(Si(CH₃)₃)-C(Si(CH₃)₃)-C(OC₂H₅)-C(CH₃) ferracyclopentadiene rings. Extension to other alkynes like acetylene and phenylacetylene or *tert*-butylacetylene revealed a third situation in which the ferracyclopentadiene rings result from the insertion of the alkynes between the two carbyne ligands. Spectroscopic data also suggest that in the case of phenyl- and *tert*-butylacetylene, the ferracyclopentadiene ring results from the carbon-carbon breaking of alkynes and coupling of the resulting carbyne fragments. Mechanisms for these observations are proposed and discussed.

The proposal that molecular metal clusters may be reasonable models for the interactions of organic molecules with metal surfaces¹ has induced in the past few years numerous works on the reactions between clusters and unsaturated organic molecules.²

(1) Muetterties, E. L.; Rhodin, N. T.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91-137.

The problem of chain growth in the Fischer-Tropsch reaction is specifically at the origin of numerous studies on the chemistry of polynuclear alkylidene complexes.³ However, the field of the

(2) Deeming, A. J. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; pp 391-469.

reactivity of carbon-carbon bond formation starting with clusters containing alkyldiyne ligands has been less developed, and only a few examples have been reported so far,⁴ possibly owing to the fact that these clusters are generally not easily available.

During the study of the reactivity of the cluster anion $\text{HFe}_3(\text{CO})_{11}^-$ toward alkynes, we found that it reacts readily with acetylene, leading to $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-CCH}_3)^-$ at room temperature.⁵ Moreover, due to the presence of a bridging CO in this anionic complex, it is easily transformed into the neutral bis(carbyne) cluster $\text{Fe}_3(\text{CO})_9(\mu_3\text{-COC}_2\text{H}_5)(\mu_3\text{-CCH}_3)$ by the action of triethyl oxonium tetrafluoroborate.⁶

Having in hand this easily obtainable bis(carbyne) cluster, we have undertaken the study of its reactivity, related to the problem of carbon-carbon bond formation starting with alkyldiyne ligands, and we report here the results of the reaction with alkynes.

Experimental Section

All reactions were performed under a nitrogen atmosphere. ^1H NMR spectra were recorded on a Bruker WH90 and ^{13}C NMR spectra on a Bruker WM250 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer in hexadecane solution in the ν_{CO} stretching region. Mass spectra were recorded on a Varian MAT 311-A by using 70-eV electron impact. Elemental analyses were performed at the laboratory by Magna.

Preparation of $\text{Fe}_3(\text{CO})_8\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)$, 1. $\text{Fe}_3(\text{CO})_9(\text{CCH}_3)(\text{COC}_2\text{H}_5)$ (0.5 g) and $\text{C}_6\text{H}_5\text{CCC}_6\text{H}_5$ (0.180 g) (1:1 ratio) were dissolved in 30 mL of toluene. The solution was refluxed for 6 h. The product was purified by chromatography on Florisil. Elution with hexane/benzene mixture with increasing concentration of benzene gave successively a red band of the starting material, a yellow band of unidentified compounds, and a green band of 1. Evaporation of the solvent and crystallization in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ mixture gave 0.200 g of 1 (31% yield) as dark green crystals: mp 165 °C (dec); IR ν_{CO} 2057 (m), 2019 (s), 2015 (s), 1992 (m), 1976 (m), 1867 (m), 1858 cm^{-1} (m); ^1H NMR (CD_2Cl_2) ppm 7.84, 7.47, 6.86, 6.32 (C_6H_5), 3.03 (q, $J = 7.3$ Hz, OCH_2CH_3), 2.92 (CH_3), 0.94 (t, $J = 7.3$ Hz, OCH_2CH_3); ^{13}C NMR (CD_2Cl_2) (except phenyl resonances) ppm 207, 204 (CO), 132.8 (FeCX), 120.3 (FeCX), 118.8 (FeCX); 106.2 (q, $J = 6$ Hz, FeCCH₃), 72.8 (t, $J = 143$ Hz OCH_2), 18.1 (q, $J = 131$ Hz CCH₃), 14.6 (q, $J = 128$ Hz OCH_2CH_3); mass spectrum, m/e 654. Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{Fe}_3\text{O}_9$: C, 49.55; H, 2.75. Found: C, 49.52; H, 2.47.

Preparation of $\text{Fe}_3(\text{CO})_8\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{Si}(\text{CH}_3)_3)\text{C}(\text{Si}(\text{CH}_3)_3)$, 2. $\text{Fe}_3(\text{CO})_9(\text{CCH}_3)(\text{COC}_2\text{H}_5)$ (0.5 g) and $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ (1 g) (sixfold excess) were dissolved in methylcyclohexane, and the solution was refluxed for 5 h. The product was isolated following the same procedure as for 1 giving 0.250 g of 2 (40% yield) as green crystals: mp 130 °C (dec); IR ν_{CO} 2054 (m), 2017 (s), 2007 (s), 1988 (s), 1981 (m), 1965 (m), 1871 (m), 1855 cm^{-1} (m); ^1H NMR (CD_2Cl_2) ppm 4.26 (q, $J = 7.0$ Hz, OCH_2CH_3), 1.60 (t, $J = 7.0$ Hz, OCH_2CH_3), 1.06 (CH_3), 0.85, 0.0 ($\text{Si}(\text{CH}_3)_3$); ^{13}C NMR (CD_2Cl_2) ppm 205.6, 204.7 (CO), 143.8, 113.8, 109.9, 106.3 (FeCX), 75.9 (t, $J = 145.4$ Hz, OCH_2), 25.6 (q, $J = 129.5$ Hz, CH_3), 15.4 (q, $J = 125.6$ Hz, OCH_2CH_3), 5.70, 4.28 (q, $J = 118.4$ Hz, $\text{Si}(\text{CH}_3)_3$); mass spectrum, m/e 646. Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{Fe}_3\text{O}_9\text{Si}_2$: C, 40.0; H, 4.12. Found: C, 39.57; H, 4.11.

Preparation of $\text{Fe}_3(\text{CO})_8\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)$, 3. It was prepared as described for 2 except that crystallization was performed in hexane, giving 0.130 g of 3 (25% yield) as green crystals: mp 105 °C (dec); IR ν_{CO} 2054 (m), 2015 (s), 2011 (s), 1985 (m), 1974 (m), 1871 (m), 1861 cm^{-1} (m); ^1H NMR (CD_2Cl_2) ppm 3.22, 3.11 (CH_3), 2.85 (q, $J = 7.0$ Hz, OCH_2), 1.21 (CH_3), 0.97 (t, $J = 7.0$ Hz, OCH_2CH_3). Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{Fe}_3\text{O}_8$: C, 38.49; H, 2.64. Found: C, 39.1; H, 2.57.

(3) (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 160-263. (b) Dyke, A. F.; Finnimore, S. R.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Riding, G. M.; Taylor, G. E. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; Washington, DC, 1981; ACS. Symp. Ser. No. 155, pp 25-97 and references therein.

(4) (a) Dyke, A. F.; Guerschais, J. E.; Knox, S. A. R.; Roué, J.; Short, R. L.; Taylor, G. E.; Woodward, P. J. *Chem. Soc., Chem. Commun.* **1981**, 537-538. (b) Jeffrey, J. C.; Mead, K. A.; Razay, M.; Stone, F. G. A.; Went, M. J.; Woodward, P. J. *J. Chem. Soc., Chem. Commun.* **1981**, 867-868. (c) Beanan, R. L.; Rahman, Z. A.; Keister, J. B. *Organometallics* **1983**, *2*, 1062-1064. (d) Casey, P. C.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173-188. (e) Allison, N. T.; Fritch, J. R.; Vollhardt, K. P. C.; Walborsky, E. C. *J. Am. Chem. Soc.* **1983**, *105*, 1384-1386. (f) Vollhardt, K. P. C.; Walborsky, E. C. *J. Am. Chem. Soc.* **1983**, *105*, 5507-5509. (g) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 1151-1153.

(5) Lourdichi, M.; Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231-232.

(6) Lourdichi, M.; Mathieu, R., unpublished results.

Table I. Summary of Crystal and Intensity Collection Data

compound	Physical and Crystallographic Data	
	1	2
formula	$\text{C}_{27}\text{H}_{18}\text{O}_9\text{Fe}_3$	$\text{C}_{21}\text{H}_{26}\text{O}_9\text{Si}_2\text{Fe}_3$
fw	653.55	645.75
crystal system	triclinic	monoclinic
space group	$C_1^-P\bar{1}$	$C_{2h}^2-P2_1/c$
a, Å	10.344 (2)	17.945 (3)
b, Å	14.355 (2)	9.501 (1)
c, Å	10.053 (2)	17.139 (3)
α , deg	95.73 (1)	90
β , deg	113.73 (1)	109.45 (2)
γ , deg	74.34 (1)	90
V, Å ³	1315.8	2755.4
Z	2	4
F(000)	660	1320
D_c , g/cm ³	1.649	1.557
$\mu_{\text{MoK}\alpha}$, cm ⁻¹	16.8	16.9
radiation	Data Collection	
	Mo K α ($\lambda = 0.71069$ Å) from graphite monochromator	
temp, °C	20	20
takeoff angle, deg	4.25	3.30
detector window, mm	4 × 4	4 × 4
scan mode	$\omega - 2\theta$	ω
scan range, deg	$1.00 + 0.35 \tan \theta$	$0.95 + 0.35 \tan \theta$
2 θ limits, deg	56	50

Preparation of $\text{Fe}_3(\text{CO})_8\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{H})\text{C}(\text{H})$, 4. A solution of 0.5 g of $\text{Fe}_3(\text{CO})_9(\text{CCH}_3)(\text{COC}_2\text{H}_5)$ in toluene was saturated with acetylene and refluxed under an acetylene atmosphere for 1.5 h. Chromatography on Florisil and crystallization of the green fraction in pentane gave 0.05 g of 4 (10% yield) as green crystals: mp 98 °C; IR ν_{CO} 2064 (m), 2021 (s), 2015 (s), 2004 (m), 1990 (m), 1975 (s), 1874 (m), 1864 (m); ^1H NMR (CD_2Cl_2) ppm 6.83 (br, CH), 3.05 (q, $J = 7.1$ Hz, OCH_2), 0.88 (CH_3), 0.79 (t, $J = 7.1$ Hz, OCH_2CH_3); ^{13}C NMR (C_6D_6) ppm 6.04, 5.91 (d, $J = 2$ Hz, CH), 2.69 (q, $J = 7.04$ Hz, OCH_2), 0.61 (CH_3), 0.58 (t, $J = 7.04$ Hz, OCH_2CH_3); mass spectrum m/e 502. Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{Fe}_3\text{O}_9$: C, 35.85; H, 1.99. Found: C, 36.52; H, 1.62.

Preparation of $\text{Fe}_3(\text{CO})_8\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{t-Bu})\text{C}(\text{H})$ (5) and $\text{Fe}_3(\text{CO})_8\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{H})$, 6. They were prepared as described for 2 and 3. Crystallization in hexane gave two fractions with different infrared spectra, 5a and b and 6a and b.

5a: green crystals; IR ν_{CO} 2051 (m), 2013 (s), 2007 (s), 1987 (m), 1965 (m), 1867 (m), 1857 cm^{-1} (m); ^1H NMR (CD_2Cl_2) ppm 5.39 (q, $J = 1.2$ Hz, CH), 3.72 (q, $J = 7.04$ Hz, OCH_2), 1.87 ($\text{C}(\text{CH}_3)_3$), 1.43 (d, $J = 1.2$ Hz, CH₃), 1.14 (t, $J = 7.04$ Hz, OCH_2CH_3).

5b: green crystals; IR ν_{CO} 2057 (m), 2016 (s), 2013 (s), 1992 (m), 1975 (m), 1942 (w), 1868 (m), 1858 cm^{-1} (m); ^1H NMR (CD_2Cl_2) ppm 2.97 (CH_3), 2.83 (q, $J = 7.0$ Hz, OCH_2), 2.81 (CH), 1.86 ($\text{C}(\text{CH}_3)_3$), 0.97 (t, $J = 7.0$ Hz, OCH_2CH_3). Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{Fe}_3\text{O}_9$: C, 40.86; H, 3.22. Found: C, 40.66; H, 3.15.

6a: green crystals; mp 84 °C; IR ν_{CO} 2061 (m), 2022 (s), 2013 (s), 1997 (m), 1985 (sh), 1981 (m), 1970 (m), 1875 (m), 1861 cm^{-1} (m); ^1H NMR (CD_2Cl_2) 6a-1 (major compound) ppm 8.18, 7.80, 7.58, 7.42 (C_6H_5), 4.47 (q, $J = 7.05$ Hz, OCH_2), 2.36 (CH), 1.49 (t, $J = 7.05$ Hz, OCH_2CH_3), 1.03 (CH_3), 6a-2 (same phenyl resonances) 3.44 (q, $J = 7.05$ Hz, OCH_2), 2.13 (CH), 1.27 (CH_3), 1.16 (t, $J = 7.05$ Hz, OCH_2CH_3).

6b: green crystals; mp 103 °C; IR ν_{CO} 2057 (m), 2020 (s), 2017 (s), 1991.7 (s), 1980 (m), 1870 (m), 1868 (sh), 1860 cm^{-1} (m); ^1H NMR (CD_2Cl_2) 6b-1 ppm 8.17, 8.04, 7.53 (C_6H_5), 3.12 (CH_3), 2.92 (q, $J = 7.05$ Hz, OCH_2), 2.73 (CH), 1.05 (t, $J = 7.05$ Hz, OCH_2CH_3), 6b-2 (same phenyl resonances) 2.90 (q, $J = 7.03$ Hz, OCH_2), 1.19 (CH_3), 0.94 (t, $J = 7.03$ Hz, OCH_2CH_3) (the CH resonance is probably obscured by phenyl resonances); mass spectra for 6a and 6b, m/e 578. Anal. Calcd for $\text{C}_{21}\text{H}_{14}\text{Fe}_3\text{O}_9$: C, 43.6; H, 2.42. Found: C, 43.75; H, 2.51.

X-ray Data Collection and Reduction. $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)$, 1. Preliminary Weissenberg photographs failed to reveal any symmetry. Crystals belong to the triclinic system, space groups $P1$ or $P\bar{1}$. The structure was solved in the $C_1^-P\bar{1}$ space group. The selected crystal was dark green parallelepiped with dimensions $0.250 \times 0.125 \times 0.10$ mm. The crystal was sealed on a glass fiber and mounted on a Nonius-CAD4 diffractometer. Cell constants were obtained from a least-square fit of the setting angles of 25 reflections. Delaunay reduction did not show any higher symmetry. The summary

Table II. Final Least-Squares Atomic Coordinates with Estimated Standard Deviations in Parentheses for Complex 1

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Fe(1)	0.28931 (4)	0.29188 (3)	0.04621 (5)
Fe(2)	0.43272 (5)	0.38518 (3)	0.23752 (5)
Fe(3)	0.40653 (5)	0.15373 (3)	0.21336 (5)
C(1)	0.3003 (3)	0.4326 (2)	0.0538 (3)
O(1)	0.2437 (3)	0.4989 (2)	-0.0247 (3)
C(2)	0.2615 (4)	0.1530 (2)	0.0304 (4)
O(2)	0.1841 (3)	0.1119 (2)	-0.0565 (3)
C(3)	0.2993 (3)	0.2786 (2)	-0.1291 (4)
O(3)	0.2996 (3)	0.2715 (2)	-0.2419 (3)
C(4)	0.0960 (4)	0.3322 (2)	-0.0470 (4)
O(4)	-0.0252 (3)	0.3579 (2)	-0.1181 (3)
C(5)	0.3638 (4)	0.4817 (2)	0.3342 (4)
O(5)	0.3180 (3)	0.5441 (2)	0.3947 (3)
C(6)	0.5627 (4)	0.4477 (2)	0.2502 (4)
O(6)	0.6397 (3)	0.4949 (2)	0.2602 (3)
C(7)	0.5155 (4)	0.0365 (3)	0.2034 (4)
O(7)	0.5783 (3)	-0.0412 (2)	0.1961 (4)
C(8)	0.3286 (5)	0.1008 (3)	0.3029 (5)
O(8)	0.2794 (5)	0.0667 (3)	0.3629 (5)
C(9)	0.5119 (3)	0.2468 (2)	0.1594 (3)
C(10)	0.5685 (3)	0.2382 (2)	0.3153 (3)
C(11)	0.4563 (3)	0.2673 (2)	0.3719 (3)
C(12)	0.3120 (3)	0.2969 (2)	0.2591 (3)
C(13)	0.6145 (3)	0.2243 (2)	0.0820 (3)
C(14)	0.6166 (3)	0.2950 (2)	-0.0010 (4)
C(15)	0.7132 (4)	0.2768 (3)	-0.0710 (4)
C(16)	0.8072 (4)	0.1866 (3)	-0.0583 (5)
C(17)	0.8057 (4)	0.1154 (3)	0.0221 (5)
C(18)	0.7095 (4)	0.1342 (2)	0.0918 (4)
C(19)	0.7262 (3)	0.2035 (2)	0.4118 (3)
C(20)	0.7712 (4)	0.1258 (3)	0.5044 (4)
C(21)	0.9173 (4)	0.0920 (3)	0.5937 (4)
C(22)	1.0190 (4)	0.1353 (3)	0.5903 (5)
C(23)	0.9761 (4)	0.2111 (3)	0.4965 (5)
C(24)	0.8302 (4)	0.2456 (3)	0.4087 (4)
C(25)	0.4835 (4)	0.2702 (3)	0.5314 (4)
O(9)	0.2067 (2)	0.3219 (2)	0.3156 (2)
C(26)	0.0687 (4)	0.3870 (3)	0.2381 (4)
C(27)	0.0170 (4)	0.4425 (3)	0.3503 (4)

of crystal and intensity collection data is given in Table I. Independent reflections (5835) were recorded out to $2\theta(\text{Mo}) = 56^\circ$ by procedures described elsewhere.⁷ Intensity standards, recorded periodically, showed only random, statistical fluctuations. Data reduction was then performed. No absorption corrections were made. Reflections having $F_0^2 > 4\sigma(F_0^2)$ (3584) were used in subsequent calculations.

Fe₃(CO)₆(μ-CO)₂[C(CH₃)C(OC₂H₅)C(Si(CH₃)₃)C(Si(CH₃)₃)]₂. Preliminary Weissenberg photographs indicated the crystal to be monoclinic, with systematic absences, $h0l, l = 2n + 1, 0k0, k = 2n + 1$, corresponding to the space group $C_{2h}^2-P2_1/c$. The selected crystal was a dark-green rhomb with dimensions 0.70 mm (edge) and 0.15 mm (thickness). Cell constants were obtained as for 1. Details of crystal and intensity data collection appear in Table I. Independent reflections (4838) were recorded out to $2\theta(\text{Mo}) = 45^\circ$. Intensity standards showed no fluctuation greater than 3%. Intensity data were then reduced. No absorption corrections were made. Reflections having $F_0^2 > 4\sigma(F_0^2)$ (3829) were used in subsequent calculations.

Structure Solution and Refinement. **Fe₃(CO)₆(μ-CO)₂[C(CH₃)C(OC₂H₅)C(C₆H₅)C(C₆H₅)]₂, 1.** The structure was solved by the heavy-atom method.⁸ The positions of the iron atoms were revealed from a Patterson map. Subsequent Fourier maps revealed the positions of all non-hydrogen atoms which were refined anisotropically.

The hydrogen atoms were located on a difference Fourier map and introduced in calculations in idealized positions (C-H = 0.95 Å, H-C-H = 120° for phenyls and 109.5° for ethyl and methyls) with temperature factors kept fixed, $U_H = 0.07 \text{ \AA}^2$.

The atomic scattering factors used were those proposed by Cromer and Waber⁹ with anomalous dispersion effects.¹⁰ Scattering factors for the

Table III. Final Least-Squares Atomic Coordinates with Estimated Standard Deviations in Parentheses for Complex 2

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Fe(1)	0.18206 (3)	0.62298 (5)	0.62186 (3)
Fe(2)	0.19714 (3)	0.38694 (5)	0.67908 (3)
Fe(3)	0.21658 (3)	0.70927 (5)	0.76353 (3)
C(1)	0.1624 (2)	0.4242 (4)	0.5670 (2)
O(1)	0.1398 (2)	0.3855 (3)	0.4992 (2)
C(2)	0.1955 (2)	0.8193 (4)	0.6671 (2)
O(2)	0.1895 (2)	-0.9338 (3)	0.6410 (2)
C(3)	0.2311 (2)	0.6614 (5)	0.5494 (2)
O(3)	0.2565 (2)	0.6827 (4)	0.4981 (2)
C(4)	0.0914 (2)	0.6750 (4)	0.5457 (2)
O(4)	0.0346 (2)	0.7074 (4)	0.4958 (2)
C(5)	0.1266 (2)	0.2542 (4)	0.6773 (3)
O(5)	0.0809 (2)	0.1728 (4)	0.6787 (2)
C(6)	0.2640 (2)	0.2545 (4)	0.6715 (3)
O(6)	0.3063 (2)	0.1690 (4)	0.6636 (3)
C(7)	0.2965 (2)	0.8102 (4)	0.8263 (3)
O(7)	0.3484 (2)	0.8776 (4)	0.8663 (2)
C(8)	0.1558 (2)	0.8141 (4)	0.8036 (2)
O(8)	0.1172 (2)	0.8857 (4)	0.8267 (2)
C(9)	0.2800 (2)	0.5559 (3)	0.7234 (2)
C(10)	0.2625 (2)	0.4903 (4)	0.7927 (2)
C(11)	0.1775 (2)	0.4983 (4)	0.7788 (2)
C(12)	0.1293 (2)	0.5575 (4)	0.7022 (2)
Si(1)	0.38088 (6)	0.5989 (1)	0.71655 (6)
C(13)	0.4064 (3)	0.4720 (5)	0.6462 (3)
C(14)	0.4630 (2)	0.6045 (5)	0.8173 (3)
C(15)	0.3839 (2)	0.7814 (4)	0.6769 (3)
Si(2)	0.32793 (7)	0.3833 (2)	0.88543 (7)
C(16)	0.4052 (3)	0.2841 (5)	0.8578 (3)
C(17)	0.2695 (3)	0.2033 (7)	0.9115 (5)
C(18)	0.3699 (4)	0.5018 (8)	0.9734 (3)
O(9)	0.1451 (2)	0.4378 (3)	0.8326 (2)
C(19)	0.1239 (3)	0.5246 (5)	0.8896 (3)
C(20)	0.0756 (3)	0.4439 (6)	0.9275 (3)
C(21)	0.0412 (2)	0.5610 (5)	0.6840 (2)

hydrogen atoms were those of Stewart et al.¹¹

The final full-matrix least-squares refinement converged to $R = \sum ||F_0| - |F_c|| / \sum |F_0| = 0.029$ and $R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2} = 0.036$ with 3584 observations and 352 variables. The weighting scheme used in the minimization of the function $\sum w(|F_0| - |F_c|)^2$ is defined as $w = [\sigma^2(F_0) + (pF_0)^2]^{-1}$ where $p = 0.025$ is the factor to prevent over-weighting of strong reflections. An analysis of variance according to F_0 and $(\sin \theta/\lambda)$ showed satisfactory consistency. A final difference Fourier map showed no excursion of electron density greater than 0.3 e/Å³.

Fe₃(CO)₆(μ-CO)₂[C(CH₃)C(OC₂H₅)C(Si(CH₃)₃)C(Si(CH₃)₃)]₂, 2. The structure was solved by automatic centrosymmetric direct methods.⁸ Iron and silicon atoms were introduced in subsequent Fourier maps which revealed the positions of all non-hydrogen atoms. There were important residuals around one of the trimethylsilane atoms. In the first stage, they were considered as disordered atoms and refined with occupancy factors allowed to vary. There was no significant R factor improvement and the distances between "disordered" atoms were less than 0.3 Å. Thus, the disordered phenomenon was ignored. All non-hydrogen atoms were then refined anisotropically. Residuals disappeared and were included in thermal agitation.

Most hydrogen atoms were located on a difference Fourier map. All of them were introduced in calculations with constrained geometry (C-H = 0.95 Å and H-C-H = 109.5°) with fixed U_H temperature factors, 0.10 Å² for Si(2) methyls and 0.08 Å² for all other hydrogens.

Atomic scattering factors were those from ref 9-11.

The final full-matrix least-squares refinement converged to values of $R = 0.039$ and $R_w = 0.048$ with 3829 observations and 316 variables. The weighting scheme used in the minimization of the function $\sum w(|F_0| - |F_c|)^2$ was $w = [\sigma^2(F_0) + (0.012F_0)^2]^{-1}$. An analysis of variance showed no unusual trends. The largest peaks on the final difference Fourier map, 0.7 e/Å³ height, are located at 0.9-1.0 Å from iron atoms.

The final atomic coordinates with their estimated standard deviations as derived from the inverse matrix of the last cycle of least-squares refinement for 1 and 2 are given in Tables II and III, respectively. Ortep

(7) Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B* 1977, B33, 2639-2644.

(8) Program for crystal structure determination: Sheldrick, G. M. "Shelx 76"; University of Cambridge: Cambridge, England, 1976.

(9) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 72-79.

(10) Cromer, D. T. ref 9, Table 2.3.1, p 149.

(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175-3187.

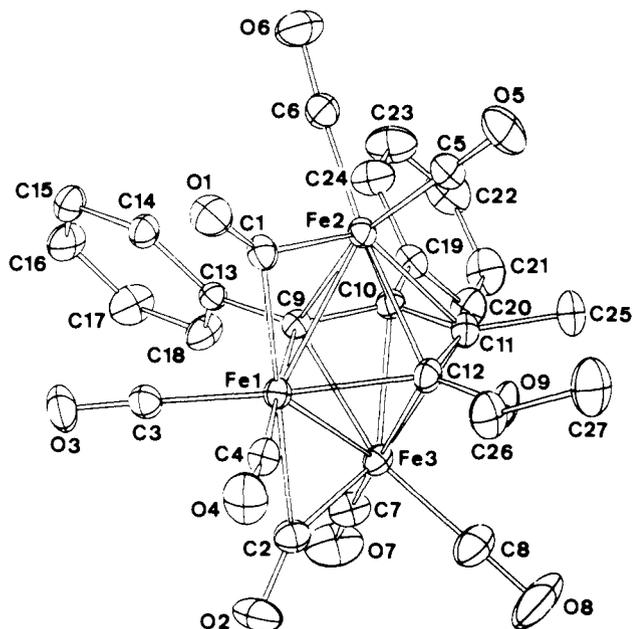


Figure 1. Structure of complex 1 showing the atomic numbering scheme with the ellipsoids at 40% probability level.

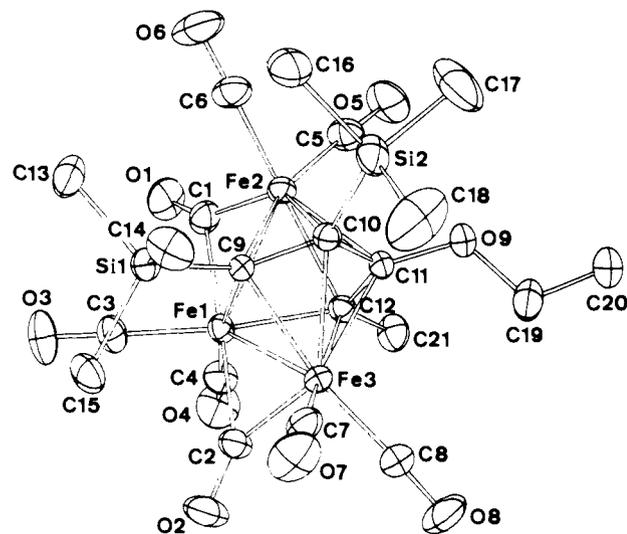


Figure 2. Structure of complex 2 showing the atomic numbering scheme with the ellipsoids at 40% probability level.

plots of 1 and 2 with atomic labeling scheme are shown in Figures 1 and 2, respectively.

Results and Discussion

The alkynes RCCR used in this study react quite readily with $\text{Fe}_3(\text{CO})_9(\mu_3\text{-COC}_2\text{H}_5)(\mu_3\text{-CCH}_3)$. Nevertheless, the yield of the isolated green derivatives is generally low, apparently for several reasons: (i) depending on the nature of alkynes, the use of stoichiometric amounts of reactants leads to low yield which suggest that some part of the alkynes is oligomerized; (ii) the use of an excess of alkyne in order to improve the yield increases the amount of mixtures of yellow complexes which have not been fully characterized. Nevertheless, in one case ($\text{R} = \text{CH}_3$), one of the yellow complexes has been isolated and has been identified by mass spectroscopy as $\text{Fe}_2(\text{CO})_6(\text{CH}_3\text{CCCH}_3)_2$. This indicates that the yellow complexes observed in all these reactions are of the well-known "ferrole" family.¹² We first studied the case of diphenylacetylene and have obtained a dark green compound, 1,

Table IV. Intramolecular Bond Distances (Å) with Estimated Standard Deviations in Parentheses for

$\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2[\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)]$, 1, and $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2[\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{Si}(\text{CH}_3)_3)\text{C}(\text{Si}(\text{CH}_3)_3)]$, 2

	1	2
Fe(1)-Fe(2)	2.4403 (7)	2.4264 (7)
Fe(1)-Fe(3)	2.4401 (7)	2.4392 (8)
Fe(2)-Fe(3)	3.3827 (8)	3.3554 (7)
Fe(1)-C(1)	2.046 (4)	2.087 (4)
Fe(2)-C(1)	1.861 (3)	1.845 (4)
C(1)-O(1)	1.161 (4)	1.157 (5)
Fe(1)-C(2)	2.072 (4)	2.004 (4)
Fe(3)-C(2)	1.849 (3)	1.885 (4)
C(2)-O(2)	1.157 (4)	1.168 (5)
Fe(1)-C(3)	1.795 (4)	1.782 (5)
C(3)-O(3)	1.130 (5)	1.135 (6)
Fe(1)-C(4)	1.785 (3)	1.784 (4)
C(4)-O(4)	1.141 (4)	1.133 (5)
Fe(2)-C(5)	1.768 (4)	1.779 (4)
C(5)-O(5)	1.137 (5)	1.134 (6)
Fe(2)-C(6)	1.767 (4)	1.773 (5)
C(6)-O(6)	1.147 (6)	1.150 (6)
Fe(3)-C(7)	1.774 (4)	1.763 (4)
C(7)-O(7)	1.142 (4)	1.150 (5)
Fe(3)-C(8)	1.758 (6)	1.777 (5)
C(8)-O(8)	1.141 (8)	1.131 (6)
Fe(1)-C(9)	2.061 (3)	2.118 (3)
Fe(2)-C(9)	2.136 (3)	2.147 (3)
Fe(3)-C(9)	2.162 (4)	2.100 (4)
Fe(2)-C(10)	2.209 (3)	2.148 (3)
Fe(3)-C(10)	2.190 (3)	2.232 (3)
Fe(2)-C(11)	2.172 (4)	2.136 (4)
Fe(3)-C(11)	2.176 (3)	2.168 (4)
Fe(1)-C(12)	2.053 (4)	2.011 (4)
Fe(2)-C(12)	2.083 (4)	2.142 (4)
Fe(3)-C(12)	2.116 (3)	2.131 (3)
C(9)-C(10)	1.440 (5)	1.464 (5)
C(10)-C(11)	1.439 (6)	1.465 (5)
C(11)-C(12)	1.444 (4)	1.426 (4)
C(9)-C(13)	1.505 (5)	C(9)-Si(1) 1.898 (4)
C(10)-C(19)	1.495 (5)	C(10)-Si(2) 1.922 (3)
C(11)-C(25)	1.510 (5)	C(12)-C(21) 1.506 (5)
C(12)-O(9)	1.373 (5)	C(11)-O(9) 1.369 (5)
O(9)-C(26)	1.431 (4)	O(9)-C(19) 1.425 (7)
C(26)-C(27)	1.506 (6)	C(19)-C(20) 1.462 (9)

in reasonable yield. In the ν_{CO} stretching region, this compound shows five infrared active bands in the terminal CO stretching region and two bands in the bridging carbonyl stretching region. Proton NMR gives evidence that the organic part of the molecule contains the diphenylacetylene and the $\text{C}(\text{CH}_3)$ and $\text{C}(\text{OC}_2\text{H}_5)$ fragments. Furthermore, the ^{13}C NMR spectrum indicates that the mode of bonding of the latter fragments is strongly modified: there are no signals in the area expected for the carbon of alkyldiene groups μ_2 - or μ_3 -bonded to iron, but four signals appear in the 150–100 ppm area where carbons of π -bonded olefins are generally found.¹³

As the mass spectrum shows a parent ion at m/e 654 with the successive loss of eight carbon monoxides, this is in favor of a $\text{Fe}_3(\text{CO})_8\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)$ formulation. All these spectroscopic data strongly suggest that the product 1 has a structure similar to that of the trinuclear complex which results from the action of $\text{Fe}_3(\text{CO})_{12}$ with diphenylacetylene, $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2\text{C}(\text{C}_6\text{H}_5)_4$, which contains a ferracyclopentadiene ring.¹⁴ Nevertheless, spectroscopic data are not sufficient to determine the precise nature of the ferracyclopentadiene ring. In order to solve this problem and to confirm firmly our hypothesis, X-ray structure determination of 1 has been performed.

A view of the $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)$ molecule with the numbering of atoms is shown in Figure 1. Bond distances and angles of interest are gathered

(12) Fehlamer, W. P.; Stolzenberg, H. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 4, pp 548–555.

(13) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* 1984, 79–85.

(14) Hübel, W. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Interscience: New York, 1968; Vol. 1, pp 273–342.

Table V. Bond Angles (deg) with Estimated Standard Deviations in Parentheses for

$\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2[\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)]$, **1**, and
 $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2[\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{Si}(\text{CH}_3)_3)\text{C}(\text{Si}(\text{CH}_3)_3)]$, **2**

1		2	
Fe(2)–Fe(1)–Fe(3)	87.76 (2)		87.20 (2)
Fe(1)–C(1)–O(1)	136.1 (2)		133.7 (3)
Fe(2)–C(1)–O(1)	146.7 (3)		150.4 (4)
Fe(1)–C(1)–Fe(2)	77.2 (1)		75.9 (1)
Fe(1)–C(2)–O(2)	134.6 (3)		137.3 (3)
Fe(3)–C(2)–O(2)	148.6 (3)		145.0 (3)
Fe(1)–C(2)–Fe(3)	76.7 (1)		77.6 (1)
Fe(1)–C(3)–O(3)	177.2 (3)		174.1 (3)
Fe(1)–C(4)–O(4)	173.6 (4)		178.3 (4)
C(3)–Fe(1)–C(4)	87.1 (2)		88.6 (2)
Fe(2)–C(5)–O(5)	179.1 (3)		177.1 (5)
Fe(2)–C(6)–O(6)	174.6 (3)		177.6 (4)
C(5)–Fe(2)–C(6)	87.3 (2)		89.5 (2)
Fe(3)–C(7)–O(7)	175.6 (4)		178.9 (4)
Fe(3)–C(8)–O(8)	179.0 (4)		176.8 (4)
C(7)–Fe(3)–C(8)	87.8 (2)		86.5 (2)
C(1)–Fe(1)–C(2)	175.7 (1)		175.9 (1)
C(3)–Fe(1)–C(9)	94.5 (1)		99.6 (2)
C(4)–Fe(1)–C(12)	101.7 (2)		93.7 (2)
Fe(1)–C(9)–C(10)	118.7 (3)		116.9 (2)
C(9)–C(10)–C(11)	112.9 (2)		109.7 (3)
C(10)–C(11)–C(12)	112.6 (3)		116.8 (3)
C(9)–Fe(1)–C(12)	76.7 (1)		78.2 (1)
Fe(1)–C(12)–C(11)	119.1 (3)		118.2 (3)
Fe(1)–C(9)–C(13)	121.1 (2)	Fe(1)–C(9)–Si(1)	115.6 (2)
C(10)–C(9)–C(13)	120.2 (2)	C(10)–C(9)–Si(1)	127.4 (2)
C(11)–C(10)–C(19)	122.0 (3)	C(11)–C(10)–Si(2)	118.6 (3)
C(12)–C(11)–C(25)	122.7 (3)	C(12)–C(11)–O(9)	121.5 (3)
Fe(1)–C(12)–O(9)	129.4 (2)	Fe(1)–C(12)–C(21)	123.5 (2)
C(12)–O(9)–C(26)	120.4 (3)	C(11)–O(9)–C(19)	119.3 (3)
O(9)–C(26)–C(27)	106.9 (3)	O(9)–C(19)–C(20)	109.6 (4)

in Tables IV and V. This structure is in agreement with an hypothesis based on spectroscopic data.

The most important feature revealed by this structure is that the ferracyclopentadiene ring results from the intramolecular coupling of the two carbyne ligands and coupling of the formed C_2 fragment with diphenylacetylene. This is the second example of such induced intramolecular coupling of the carbyne ligand. However, in the first case reported,^{4c} carbyne–carbyne coupling induced by sulfur was accompanied by destruction of the starting trinuclear cobalt cluster into a mononuclear cobalt complex. In our case, even though one iron–iron bond had been broken, the trinuclear unit was preserved.

A closer examination of the structure shows that in the ferracyclopentadiene ring, the $\text{C}(\text{OC}_2\text{H}_5)$ group is bonded to Fe(1) and to the $\text{C}(\text{CH}_3)$ group, the $\text{C}(\text{CH}_3)$ group being bonded to the diphenylacetylene part of the ring. Carbon–carbon distances in the ring are nearly equal and indicate extensive delocalization. The Fe(1), C(9), C(11), and C(12) atoms are nearly planar while the C(13), C(19), C(25), and O(9) atoms tilt out from this plane by a maximum of 0.082 Å. The overall structure is very similar to that of $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2\text{C}(\text{C}_6\text{H}_5)_4$,¹⁵ with the Fe(2) and Fe(3) atoms π -bonded to the ferracyclopentadiene ring at nonbonding distances. Moreover, the Fe–CO bridge linkages are asymmetric.

At this stage, we tried to trap some intermediates of the reaction in order to have a better insight into its mechanism. Attempts at room temperature to induce CO departure by lowering the reaction temperature or by using photochemical activation or trimethylamine oxide have failed. In a second approach, we thought of using a more bulky alkyne like bis(trimethylsilyl)acetylene.

This alkyne reacts in the same conditions as diphenylacetylene, and a dark green complex **2** has been isolated. The infrared spectra of this compound presents little difference with **1** except a greater splitting of the bands around 2015 cm^{-1} . Proton NMR

Table VI. Proton Chemical Shifts (ppm) in CD_2Cl_2 for the OC_2H_5 , CCH_3 , and CH Groups of the Isolated

$\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)\text{CHCR}$ Complexes

	C(CH ₃)		COCH ₂		COCH ₂ -CH ₃		CH	
	α^a	β	α	β	α	β	α	β
1		2.93	3.03		0.94			
2	1.06			4.26		1.60		
4	0.88		3.05		0.79			6.83
5a	1.43			3.72		1.14		5.39
5b		2.97	2.83		0.97		2.81	
6a-1	1.03			4.47		1.49		2.36
6a-2	1.27			3.44		1.16		2.13
6b-1		3.12	2.92		1.05			2.73
6b-2	1.19		2.90		0.94			

^a α and β refer to the position of the group related to the iron of the ferracyclopentadiene ring.

gives further evidence that the initial carbyne ligands and the entering alkyne are present in **2**, but examination of δ values shows a large shift of the CCH_3 and COC_2H_5 resonances: 1.23 ppm toward higher frequencies for the OCH_2 group, 1.86 ppm toward lower frequencies for the CCH_3 group.

Even though the similarities of the infrared spectra of **1** and **2** suggest a similar structure, the great difference in the proton chemical shifts of the carbyne groups indicates a different mode of bonding of the organic fragments. X-ray structure determination of **2** has been performed to elucidate this problem.

A view of the $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2\text{C}(\text{CH}_3)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{Si}(\text{CH}_3)_3)\text{C}(\text{Si}(\text{CH}_3)_3)$ molecule with the numbering of atoms is shown in Figure 2. Bond distances and angles of interest are gathered in Tables IV and V.

This structure shows that **2** is of the same family as **1**, with the major difference that the positions of $\text{C}(\text{CH}_3)$ and $\text{C}(\text{OC}_2\text{H}_5)$ have been exchanged: the $\text{C}(\text{CH}_3)$ group is presently bonded to Fe(1) in the ferracyclopentadiene ring. This change seems to be the result of the bulkiness of $\text{Si}(\text{CH}_3)_3$: it is bonded to the $\text{C}(\text{OC}_2\text{H}_5)$ group which is less overcrowded than the $\text{C}(\text{CH}_3)$ group. The consequence of the bulkiness of the $\text{Si}(\text{CH}_3)_3$ group is further apparent on the geometry around Fe(1): the C(3)Fe(1)C(9) angle is greater in **2** than in **1**, resulting in the C(4)Fe(1)C(12) angle being smaller in **2** than in **1**, with the C(3)Fe(1)C(4) angle nearly unchanged. It should be further noted that the Fe–Fe distances are slightly shorter in **2** than in **1** and that there are no significant changes in the carbon–carbon distances of the ferracyclopentadiene ring which is also nearly planar.

As the proton chemical shifts of the $\text{C}(\text{CH}_3)$ and $\text{C}(\text{OC}_2\text{H}_5)$ groups are very sensitive to their position in the ferracyclopentadienyl ring, it seemed possible to deduce easily from proton NMR data how other alkynes react with $\text{Fe}_3(\text{CO})_9(\mu_3\text{-COC}_2\text{H}_5)(\mu_3\text{-CCH}_3)$. The alkynes selected for this study have been chosen with the aim of varying their steric crowding. They are acetylene, *tert*-butylacetylene, and phenylacetylene.

For the sake of clarity, we have gathered in Table VI proton NMR chemical shifts for the isolated compounds for $\text{C}(\text{CH}_3)$, $\text{C}(\text{OC}_2\text{H}_5)$, and CH groups.

In the case of acetylene, even though infrared spectra in the ν_{CO} stretching region of the reaction mixture indicate the presence of several isomers, only one product, **4**, has been isolated. The proton chemical shifts of the $\text{C}(\text{CH}_3)$ and $\text{C}(\text{OC}_2\text{H}_5)$ groups are in favor of a structure in which both of these groups are bonded to iron. Furthermore, the two protons of acetylene are not equivalent and in benzene as the solvent give an AB spin system with $J_{\text{AB}} = 2$ Hz. Thus, the reaction of acetylene illustrates a third possibility which was not met for **1** and **2**: a ferracyclopentadiene ring resulting from the insertion of the alkyne between the two carbyne groups (Figure 3C).

With *tert*-butylacetylene, two fractions have been separated. In one of these (**5b**), the proton NMR spectrum allows the assignment of an α position relative to iron for the $\text{C}(\text{OC}_2\text{H}_5)$ group and a β position for the $\text{C}(\text{CH}_3)$ group. By comparison with the chemical shift of the CH group in **4**, the value of the chemical

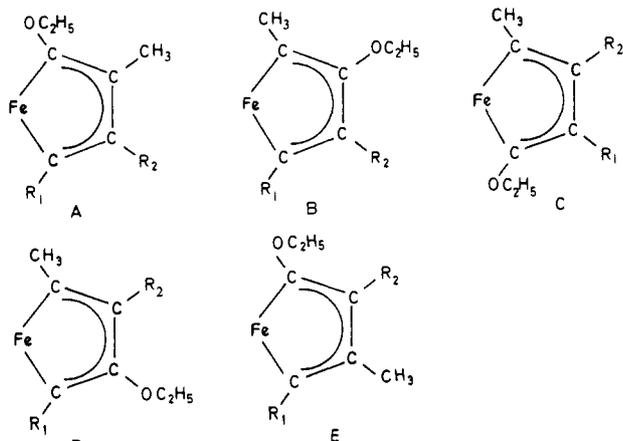


Figure 3. Different structures found for the ferracyclopentadiene ring in $\text{Fe}_3(\text{CO})_8[\text{C}(\text{R}_1)\text{C}(\text{R}_2)\text{C}(\text{OC}_2\text{H}_5)\text{C}(\text{CH}_3)]$ complexes.

shift of the CH group in **5** suggests that this group is in an α position toward iron. From these results, the two structures of type A and E with $\text{R}_1 = \text{H}$ are possible for **5b**.

For the other fraction, **5a**, the situation is more puzzling. From the chemical shift of the $\text{C}(\text{CH}_3)$ group, it can be deduced that this group is in an α position toward iron in the ferracyclopentadiene ring. Furthermore, the proton NMR parameters of the CH group indicate that this group is β -bonded to iron in the ring and that the proton of the CH group is coupled to the protons of the methyl group. The value of the coupling constant (1.2 Hz) strongly suggests that the CH group is bonded to the $\text{C}(\text{CH}_3)$ group, but we cannot exclude that these two groups are separated by a $\text{C}(\text{OC}_2\text{H}_5)$ or a $\text{C}(t\text{-Bu})$ group. For the $\text{C}(\text{OC}_2\text{H}_5)$ group, the situation is not clear either, as the chemical shift of the OCH_2 part suggests a situation in which this group is in a β position toward iron, but the chemical shift of the CH_3 part of this group is similar to the case in which this group is in an α position toward iron.

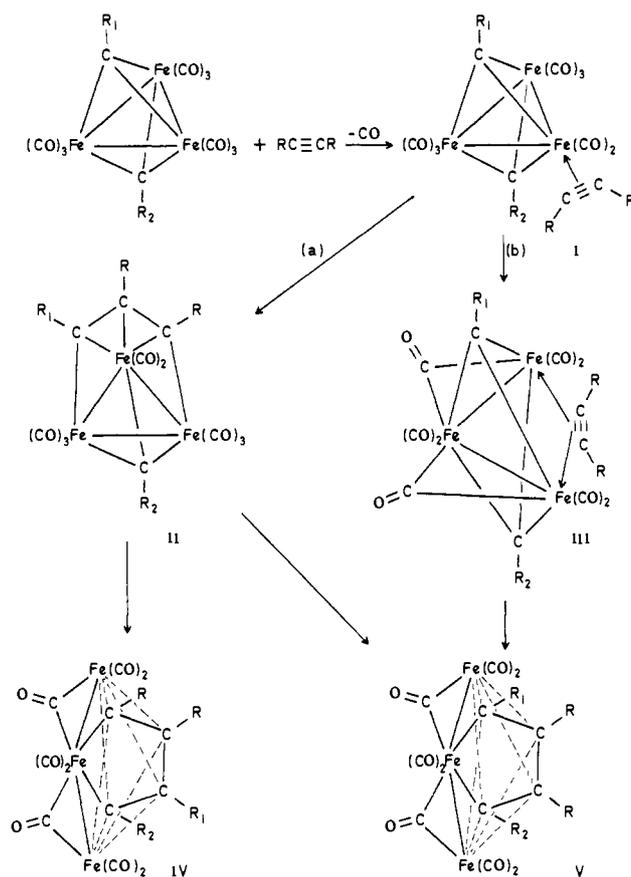
It is consequently difficult to choose between possibilities B, C, and D when $\text{R}_2 = \text{H}$ and type C when $\text{R}_1 = \text{H}$. Nevertheless, the fact that the proton of the CH group is coupled to the proton of the methyl group seems to favor possibilities C and D when $\text{R}_2 = \text{H}$. Case D implies carbon-carbon bond breaking for the alkyne, but this situation has been met for the $\text{FeW}(\mu_2\text{-C}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5))(\text{CO})_5(\text{C}_5\text{H}_5)$ complex which occurs in solution as two isomers with $\text{C}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{C}(\text{C}_6\text{H}_5)\text{-C}(\text{C}_6\text{H}_5)$ and $\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})\text{C}(\text{C}_6\text{H}_5)$ fragments.^{4b} Unfortunately, we have not obtained so far crystals of **5a** suitable for checking our hypothesis by an X-ray structure determination.

In the case of phenylacetylene, the reaction is still more complex. Two fractions have been crystallized, each containing two isomers. In fraction **6b**, two isomers are present in nearly the same amount. For **6b-1**, proton NMR data indicate a structure of type A or E in which $\text{R}_1 = \text{H}$ with the same arguments as for **5b**. For **6b-2**, the CH group has not been detected by proton NMR and its resonance is certainly obscured by the phenyl resonances. The fact that the phenyl resonances of **6b-1** and **6b-2** are not separated prevents from detecting securely the CH group by integration. A structure of type C is proposed in which R_1 could be either H or C_6H_5 . We have thus a second example in which the ferracyclopentadiene ring results from the insertion of the alkyne between the two carbyne groups.

Eighty percent of fraction **6a** is the isomer **6a-1**, for which proton NMR data are in favor of a structure of type B or D in which $\text{R}_1 = \text{H}$. For the minor isomer **6a-2**, proton NMR data strongly suggest that the iron of the ferracyclopentadienyl ring is bonded to the $\text{C}(\text{CH}_3)$ and CH groups. Here again structures of type B or D in which $\text{R}_1 = \text{H}$ are suggested. This indicates that either **6a-1** or **6a-2** must result from a carbon-carbon bond breaking from the alkyne.

To summarize, extension of our study to alkynes with various steric crowding has revealed a new situation in which the ferra-

Scheme I



cyclopentadiene results from the insertion of the alkyne between the two carbyne groups (type C) (case of acetylene and phenylacetylene) and suggests a situation in which the ferracyclopentadiene ring should result from the carbon-carbon bond breaking of the alkyne (type D or E) (case of *tert*-butylacetylene and phenylacetylene).

We propose the mechanism presented in Scheme I to rationalize our observations.

The first step is the loss of one molecule of carbon monoxide and the substitution by the alkyne ligand leading to intermediate I. From this intermediate, two paths may be considered. In path a, insertion of the alkyne occurs into one of the iron-carbon bonds of one of the carbyne groups to give II, containing a dimetallaallyl group μ_3 -bonded and the other carbyne group. In the subsequent step, coupling between these two groups lead to IV or V, depending on the steric crowding of the R groups.

An alternative is path b in which the alkyne becomes μ - η bonded in a first step with simultaneous breaking of the iron-iron bond bridged by this alkyne. This assumption seems reasonable, as this mode of bonding is common for alkynes in dinuclear complexes.¹⁶ Furthermore, it has been already met in one of the products of the reaction of $\text{Fe}_2\text{W}(\mu\text{-CC}_6\text{H}_4\text{CH}_3\text{-4})(\mu\text{-CO})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)$ with bis(trimethylsilyl)acetylene.^{4b} Moreover, in intermediate III, application of the 18-electron rule gives a situation in which the iron frame is bonded to carbonyl ligands in the same way as in the final product. Coupling with the carbyne ligands then leads to the final product in which the ferracyclopentadiene ring has a structure of type C. This hypothesis seems substantiated by the occurrence of products of type C restricted to acetylene and monosubstituted alkynes only, for which the less encumbered CH group allows direct coupling to carbyne fragments.

Even though the carbon-carbon breaking of the alkynes *t*- $\text{BuC}\equiv\text{CH}$ and $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ is not firmly established, if we as-

(16) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323-377.

sume that step a of our mechanism is reversible, the carbon-carbon bond breaking of the entering alkyne is allowed to be a possible reaction.¹⁷

Registry No. 1, 94570-76-0; 2, 94596-67-5; 3, 94570-77-1; 4, 94570-78-2; 5, 94570-79-3; 6, 94570-80-6; Fe₃(CO)₉(CCH₃)(COC₂H₅),

88055-72-5; Fe₂(CO)₆(CH₃CCCH₃)₂, 12212-46-3; C₆H₅C≡CC₆H₅, 501-65-5; (CH₃)₃SiC≡CSi(CH₃)₃, 14630-40-1; CH₃C≡CCH₃, 503-17-3; HC≡CH, 74-86-2; *tert*-butylacetylene, 917-92-0; phenylacetylene, 536-74-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, structure factors, hydrogen parameters, and least-squares planes (43 pages). Ordering information is given on any current masthead page.

(17) We thank one of the referees for this suggestion.

Cobalt-Mediated Synthesis of Tricyclic Dienes Incorporating Fused Four-Membered Rings. Unprecedented Rearrangements and Structural Characterization of a Cobalt-Diene Complex by Two-Dimensional NMR Spectroscopy

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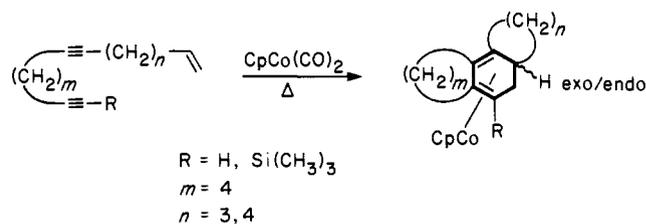
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Abstract: The CpCo(CO)₂-mediated intramolecular (2 + 2 + 2) cycloaddition of enediynes **6** and **9** leads to two tricyclic diene systems **13** and **21** incorporating four-membered rings, a novel transformation. Both cyclizations give unprecedented and unexpected products, the former catalytically and by intra-ring diene rearrangement, the latter stoichiometrically but involving an inter-ring diene shift. A sequence of 2D NMR experiments in conjunction with labeling experiments has pinpointed both structural and mechanistic details.

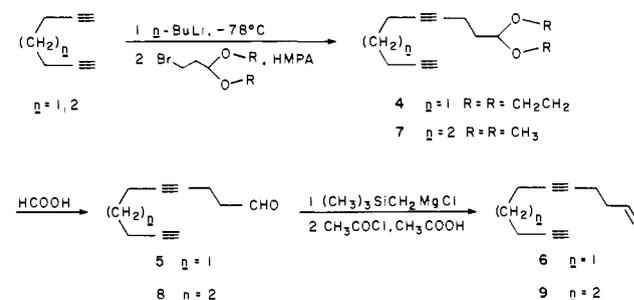
Constructing complex organic compounds in a chemo-, regio-, stereospecific, and expeditious manner is the synthetic organic chemist's most important goal. Elucidating the structure of such products in a rapid and inexpensive manner is the goal of structural chemists. We have shown that metal-mediated (2 + 2 + 2) cycloadditions provide a powerful, selective, and rapid entry into complex structures.¹ In this connection, we have recently employed (cyclopentadienyl)cobalt-promoted intramolecular (2 + 2 + 2) cycloadditions of α,δ,ω -enediynes to give novel steroids.² In these, as well as model transformations,^{1,3} the ring size was restricted to five and six members (Scheme I).

In order to explore further the potential of this transformation, it was of interest to investigate whether systems incorporating four-membered rings could also be constructed in this manner. Such products might be valuable synthetic intermediates by virtue of their built-in strain and also because of their rare topology. For example, the hydrocyclobuta[*a*]naphthalene nucleus **1** has been generated in studies aimed at developing new fragrant terpenes of the norlabdane type.⁴ In addition, the hydrocyclobutandane

Scheme I



Scheme II



framework occurs in various fungal antibacterial metabolites, as exemplified by the sesquiterpene alcohol punctatin A, **2**.⁵ We

(1) For reviews, see: (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Idem In "Chemistry for the Future"; Grünewald, H., Ed.; Pergamon Press: New York, 1984; p 181. (c) Chang, C.-A.; Francisco, C. G.; Gadek, T. R.; King, J. A. Jr.; Sternberg, E. D.; Vollhardt, K. P. C. In "Organic Synthesis. Today and Tomorrow"; Trost, B. W., Hutchinson, C. R., Eds.; Pergamon Press: New York, 1981; p 71.

(2) (a) Sternberg, E. D.; Vollhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 1574. (b) Clinet, J. C.; Duñach, E.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 6710. (c) Sternberg, E. D.; Vollhardt, K. P. C. *J. Org. Chem.* **1982**, *47*, 3447.

(3) Sternberg, E. D., Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 4839; *J. Org. Chem.* **1984**, *49*, 1564.

(4) (a) Ohloff, G.; Vial, C.; Wolf, H. R.; Jeger, O. *Helv. Chim. Acta* **1976**, *59*, 75. (b) Berger, J.; Yoshioka, M.; Zink, M. P.; Wolf, H. R.; Jeger, O. *Ibid.* **1980**, *63*, 154.