

(0.33 mm sec<sup>-1</sup>, 77°K; 0.27, 298°K) and quadrupole splitting  $\Delta E_Q$  (2.18 mm sec<sup>-1</sup>, 77°K; 1.90, 298°K) from those found for our diamagnetic dioxygen complex **1**.<sup>1</sup> The major difference between the Mössbauer parameters was the larger  $\Delta E_Q$  values found for **6**.

Single crystals of **2** were treated with pure O<sub>2</sub> (1 atm, 24 hr) affording **6**. X-Ray analysis showed the complex to retain its crystallinity during oxygenation—the crystals of **2** and **6** having the same cell constants within experimental error ( $a = 18.74$ ,  $b = 19.12$ ,  $c = 18.69$  Å,  $\beta = 91.6^\circ$ ,  $d_{\text{measd}} = 1.22$ ,  $Z = 4$ ,  $M_{\text{calcd}} = 1240$ ,  $M_{\text{found}} = 1228$ ). Full crystallographic analyses of the series **2**, **6**, and **7** are planned.

The nature of dioxygen coordination and the role of the two THF groups in the paramagnetic dioxygen complex **6** remains to be clarified by structural analysis and more detailed physical measurements. The structure and physical properties of **6** are of potential significance as they may be related to the dioxygen binding site in the P<sub>450</sub> cytochrome based monohydroxylases. The latter is thought to have a sulfur base rather than an imidazole as the axial base.<sup>10</sup> Further, these porous crystalline lattices may prove better models for the active hemoprotein sites, in contrast to solution studies, as solvent effects which are not important in the natural systems are eliminated with these solids.

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## Iron Carbonyl Complexes from Vinylcyclopropane<sup>1</sup>

Sir:

Polycyclic<sup>2a</sup> and bicyclic<sup>2b</sup> hydrocarbons containing vinylcyclopropane systems react with iron carbonyl to give both iron carbonyl complexes possessing an intact cyclopropane ring<sup>2b,3</sup> and compounds resulting from cleavage of a C–C bond of the cyclopropane ring.<sup>2,3</sup> The thermally unstable iron carbonyl compounds derived from parent vinylcyclopropane (**I**) in which rotation at the C<sup>3</sup>–C<sup>4</sup> bond is possible have so far escaped synthesis. I wish to report the synthesis and successful isolation of these compounds using low temperature techniques. Irradiation of a 1% ether solution of vinylcyclopropane (**I**) and two equivalents of iron pentacarbonyl with a high-pressure mercury lamp (125 W, 4 hr, filter of Duran glass) at  $-50^\circ$  results in the formation of a 10:1 mixture of 4,5- $\eta$ -vinylcyclopropaneiron

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(2) (a) R. Aumann, *Angew. Chem.*, **83**, 175, 176, 177 (1971); **84**, 583 (1972); *Angew. Chem., Int. Ed. Engl.*, **10**, 188, 189, 190 (1971); **11**, 522 (1972); R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **93**, 6709 (1971); (b) R. Aumann, *J. Organometal. Chem.*, **47**, C29 (1973).

(3) R. Aumann, *J. Organometal. Chem.*, in press.

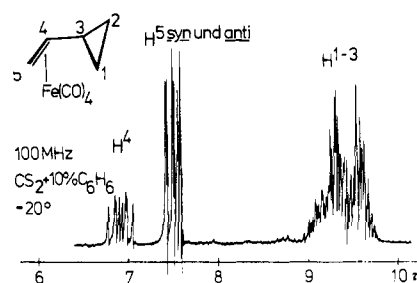


Figure 1. The 100-MHz spectrum of II.

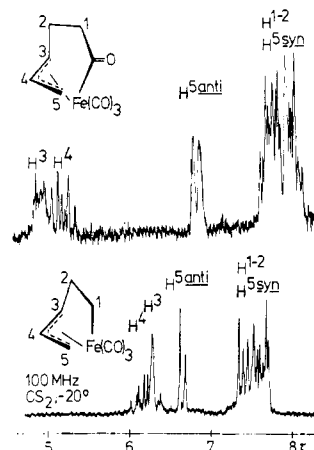
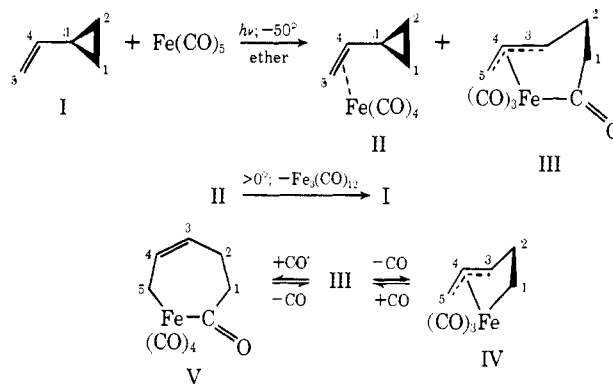


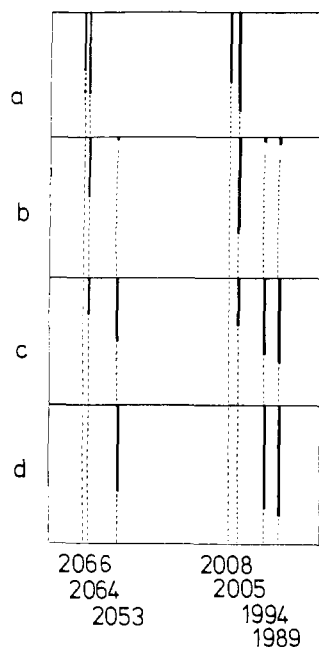
Figure 2. The 100-MHz spectra of III and IV.



tetracarbonyl (**II**) and 3,4,5,6- $\eta$ -hex-4-en-3,6-yl-6-one-iron tricarbonyl (**III**) (total yield 89%). **II** and **III** were separated by chromatography under nitrogen atmosphere on a short silica (Woelm neutral) column at  $-20^\circ$  using pentane to elute **II** (80%; yellow oil; decomposition  $T > 0^\circ$  to **I** and  $\text{Fe}_3(\text{CO})_{12}$ ;  $m/e$  236; ir ( $\nu(\text{M})-\text{C}\equiv\text{O}$ ) 2080, 1999, 1986  $\text{cm}^{-1}$ ; nmr<sup>4</sup> (Figure 1,  $\text{CS}_2 + 10\% \text{C}_6\text{H}_6$ ,  $-20^\circ$ )  $\delta$  3.10 (m, H-4), 2.6–2.4 (m, H-5 syn, H-5 anti), 1.0–0.3 (m, H-1, H-2, H-3). *Anal.* Calcd for  $\text{C}_9\text{H}_8\text{FeO}_4$ : C, 45.80; H, 3.42. Found: C, 45.92; H, 3.55.) and ether to elute **III** (9%; yellow crystals; gradual decomposition on warming;  $m/e$  236; ir ( $\nu(\text{M})-\text{C}\equiv\text{O}$  (hexane) 2064, 2005  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{O})$  ( $\text{CH}_2\text{Cl}_2$ ) 1665  $\text{cm}^{-1}$ ; nmr<sup>4</sup> (Figure 2,  $\text{CS}_2$ ,  $-20^\circ$ )  $\delta$  5.15 (m, H-3), 4.89 (ddd,  $J = 8.5, 8.5, 12.5$  Hz; H-4), 3.25 (d, H-5 syn), 2.5–2.1 (m, H-5 anti, H-1, H-2). *Anal.* Calcd for  $\text{C}_9\text{H}_8\text{FeO}_4$ : C, 45.80; H, 3.42. Found: C, 45.69; H, 3.50.)

**III** can be recrystallized from pentane at  $-70^\circ$  and is

(4) Assignments deduced from decoupling experiments and comparison of chemical shifts of related compounds, ref 2 and 3.



**Figure 3.** Ir spectra (hexane solution;  $\nu(\text{M})-\text{C}\equiv\text{O}$ ) absorptions in  $\text{cm}^{-1}$  of compounds III and V (a), III (b), III and IV (c) and IV (d).

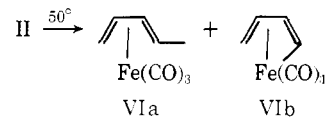
stable at  $25^\circ$  for several hours in hexane solution saturated with CO but decomposes by loss of CO at  $25^\circ$  within 1 hr if isolated in crystalline form to give 1,3,4,5- $\eta$ -pent-4-ene-3,1-yliron tricarbonyl (IV). Flash distillation ( $15^\circ$ ; 0.001 Torr) of III gives IV (almost quantitative; yellow oil;  $m/e$  208; ir (hexane)  $\nu(\text{M})-\text{C}\equiv\text{O}$ ) 2053, 1994, 1989  $\text{cm}^{-1}$ ; nmr<sup>4</sup> (Figure 2,  $\text{CS}_2$ ;  $-20^\circ$ )  $\delta$  3.9 (m, H-4), 3.7 (m, H-3), 3.50 (d, H-5 syn), 2.6–2.2 (m, H-5 anti, H-1, H-2). *Anal.* Calcd for  $\text{C}_8\text{H}_8\text{FeO}_3$ : C, 46.20; H, 3.88. Found: C, 46.37; H, 3.99.)

Interconversion of III and IV can be followed by ir (Figure 3). The two carbonyl absorptions at 2064 and 2005  $\text{cm}^{-1}$  typical<sup>2b</sup> of III disappear within seconds, if nitrogen is bubbled through a hexane solution of III at  $25^\circ$ , while three new absorptions appear at 2053, 1994, and 1989  $\text{cm}^{-1}$  typical<sup>2b</sup> of IV (Figure 3, spectra b  $\rightarrow$  c  $\rightarrow$  d). If CO is bubbled through the hexane solution of IV for a few seconds, the original spectrum of III can be observed again. Solutions of III treated for at least 20 sec with a stream of CO show absorptions at 2066 and 2008  $\text{cm}^{-1}$  in addition to those of III. These absorptions are due to a new compound, for which structure V is assumed. V may be formed by the equilibrium  $\text{III} + \text{CO} \rightleftharpoons \text{V}$  suggesting, that an Fe-olefin bond in III is replaced by an Fe-CO bond in V. Attempts to isolate this compound have been unsuccessful so far.

Solutions of III decompose to 2-cyclohexenone<sup>2b,5</sup> (80%) under the influence of air or if a positive pressure of CO (20 atm) is applied. II on warming in a sealed ampoule (benzene,  $50^\circ$ , 24 hr) gives a 3:1 mixture (nmr analysis) of pentadi-1,3-ene-iron tricarbonyl complexes<sup>6</sup> VIa and VIb in 76% yield.

(5) Cyclohexenones have been obtained also by Sarel on the light induced reaction of vinylcyclopropanes with  $\text{Fe}(\text{CO})_5$ : R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Lett.*, 4253 (1970).

(6) G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964); 1,3-diene- $\text{Fe}(\text{CO})_5$  complexes have been isolated by Sarel, *et al.*, on reaction of vinylcyclopropane with  $\text{Fe}(\text{CO})_5$  (ref 5).



II does not rearrange to III on low temperature photolysis. We suggest<sup>3</sup> that II and III are formed by competing reactions of I with different iron carbonyl species generated on photolysis of  $\text{Fe}(\text{CO})_5$ <sup>7</sup> in ether.

(7) E. Koerner von Gustorf and F.-W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 379 (1969); E. Koerner von Gustorf, private communication.

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### Electroreduction of Cobaltocene. Evidence for a Metallocene Anion

Sir:

Except for the report of a Ni(IV) species formed by dioxidation of nickelocene,<sup>1,2</sup> no unusual redox properties have been reported for di- $\pi$ -cyclopentadienyl-metal complexes<sup>3,4</sup> (the "metallocenes,"  $(\pi\text{-Cp})_2\text{M}$ ). In particular, no claims of unusually highly reduced metallocenes or metallocene anions have appeared.<sup>5,6</sup> Indeed, attempts to reduce neutral ferrocene, nickelocene, and chromocene with potassium in liquid ammonia have led to complete disruption of the organometallic species.<sup>7</sup> Since complexes in lower metal oxidation states in this class would be of interest as possible model systems for electrophilic attack at metallocenes, we wish to report the results of experiments in which we have successfully generated by electrochemical methods stable dimethoxyethane solutions of the cobaltocene anion,  $\text{Cp}_2\text{Co}^-$ . This species, the first reported metallocene anion, is the third member of the electron-transfer series consisting of  $\text{Cp}_2\text{Co}^+$ ,  $\text{Cp}_2\text{Co}$ , and  $\text{Cp}_2\text{Co}^-$ . These compounds possess respectively the formal  $d^6$ ,  $d^7$ , and  $d^8$  electron configurations, iso-

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(2) R. P. Van Duyne and C. N. Reilly, *Anal. Chem.*, **44**, 158 (1972).

(3) For a recent review see E. G. Perevalova and T. V. Nikitina, *Organometal. React.*, **4**, 163 (1972).

(4) Representative papers concerned with metallocene redox processes are (a) T. Kuwana, D. E. Bublitz, and G. Hoh, *J. Amer. Chem. Soc.*, **82**, 5811 (1960); S. P. Gubin, S. A. Smirnova, L. I. Denisovich, and A. A. Lubovich, *J. Organometal. Chem.*, **30**, 243 (1971) (Fe, Ru, Os); (b) A. A. Vlcek, *Collect. Czech. Chem. Commun.*, **30**, 952 (1965); S. P. Gubin, S. A. Smirnova, and L. I. Denisovich, *J. Organometal. Chem.*, **30**, 257 (1971) (Co); (c) F. A. Cotton, R. O. Whipple, and G. Wilkinson, *J. Amer. Chem. Soc.*, **75**, 3586 (1953) (Rh, Ir); (d) G. Wilkinson and J. M. Birmingham, *ibid.*, **76**, 4281 (1954) (V, Nb).

(5) Several papers have appeared in which the reduction of substituted (e.g., nitrophenyl) ferrocenes have yielded stable anions. However, esr studies have shown that these species should be considered as organic anion radicals with a ferrocenyl substituent: (a) Ch. Elschenbroich and M. Cais, *J. Organometal. Chem.*, **18**, 135 (1969); (b) G. P. Underwood, D. Jurkowitz, and S. C. Dickerman, *J. Phys. Chem.*, **74**, 544 (1970); (c) G. Bigam, J. Hooz, S. Linke, R. E. D. McClung, M. W. Mosher, and D. D. Tanner, *Can. J. Chem.*, **50**, 1825 (1972). Ferrocene itself is not reduced electrochemically.

(6) Recently some excellent work has been reported on the reduction of mixed  $\pi$ -sandwich complexes of chromium: see Ch. Elschenbroich and F. Gerson, *J. Organometal. Chem.*, **49**, 445 (1973); Ch. Elschenbroich, F. Gerson, and F. Stohler, *J. Amer. Chem. Soc.*, **95**, 6956 (1973).

(7) G. W. Watt and L. J. Baye, *J. Inorg. Nucl. Chem.*, **26**, 2099 (1964); L. J. Baye, *Diss. Abstr.*, **24**, 3968 (1964).