

indicating the  $\text{Fe}^{\text{III}}$  piano-stool, cationic structure. They do not react with CO or other two-electron donors at 25 °C in  $\text{CH}_2\text{Cl}_2$ . Complexes 5 and 6 react with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  under 1 atm of CO at -70 °C to give  $[\text{FeCp}^*\text{P}_2(\text{CO})]^+ \text{BF}_4^-$  (and presumably methane) as a consequence of protonation of the metal center. Since the reaction shown in eq 4 does not work with larger ligands such as  $\text{PBu}_3$  and  $\text{P(OPh)}_3$ , one may conclude that adequate control of the steric bulk provides a route to both stable series of  $\text{Fe}^{\text{II}}\text{-CH}_3$  and  $\text{Fe}^{\text{III}}\text{-CH}_3$  complexes.

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**Registry No.** 1, 111004-92-3; 2, 111004-93-4; 3, 111004-94-5; 4, 94585-62-3; 5, 111004-95-6; 6, 111004-96-7; 7, 111004-97-8; 8, 111004-98-9;  $\text{FeCp}^*(\text{CO})_2(\text{CH}_3)$ , 52409-66-2;  $\text{Fe}(\text{acac})_2$ , 14024-17-0;  $\text{Cp}^*\text{H}$ , 4045-44-7.

### An Unusual Ring-Opening Reaction of (Tetrafluorobenzobicyclo[2.2.2]octatriene)tricarbonyliron

Jiabi Chen,\* Jlanguo Yin, and Weihua Xu

Shanghai Institute of Organic Chemistry  
Academia Sinica, 345 Lingling Lu  
Shanghai, China

Luhua Lal, Zeying Zhang, and Melcheng Shao

Department of Chemistry, Peking University  
Beijing, China

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**Summary:** Reaction of the title compound I with aryllithium reagents in ether at low temperature and subsequent alkylation of the acylmetalates formed with  $\text{Et}_3\text{OBF}_4$  leads to an unusual ring-opening reaction of the bicyclic diene ligand to generate novel chelated diallyldicarbonyliron complexes II-VII. Complex V belongs to the monoclinic space group  $C_{2h}^6$ — $C2/c$  with  $a = 16.870$  (4) Å,  $b = 13.707$  (4) Å,  $c = 19.361$  (4) Å,  $\beta = 107.92$  (2)°,  $V = 4259$  (1) Å<sup>3</sup>, and  $D_{\text{calcd}} = 1.51$  g/cm<sup>3</sup> for  $Z = 8$ . Least-squares refinement based on 2481 observed reflections led to a final  $R$  of 0.0409 and  $R_w$  of 0.0391.

Recently, we found that several cyclic polyene ligands such as cyclohexadiene,<sup>1</sup> cycloheptatriene,<sup>2</sup> and cyclooctatetraene<sup>3</sup> in (cyclopolyene)tricarbyliron complexes can be activated by the iron. A series of interesting isomerized olefin-metal carbene complexes were obtained by the reaction of the corresponding olefin-ligating metal carbonyl compounds with an aryllithium and subsequent alkylation with  $\text{Et}_3\text{OBF}_4$ . As an extension of our research in this field we have studied such reactions of a bicyclopolyene ligand, tetrafluorobenzobicyclo[2.2.2]octatriene. Herein we report an unusual ring-opening reaction of

tetrafluorobenzobicyclo[2.2.2]octatriene tricarbyliron (I)<sup>4</sup> with nucleophiles at low temperature, followed by alkylation with  $\text{Et}_3\text{OBF}_4$ , which led to the breaking of the tetrafluorobenzobicyclo[2.2.2]octatriene ring and the formation of novel chelated diallyldicarbonyliron complexes.

Reaction of I with about 20% excess of an aryllithium in ether at -60 °C and subsequent alkylation of the acylmetalates formed with  $\text{Et}_3\text{OBF}_4$  in aqueous solution at 0 °C leads to the isolation of orange-red chelated diallyldicarbonyliron complexes II-VII.<sup>5</sup> Elemental analyses and spectroscopic data<sup>6</sup> are consistent with their compositions and assigned structures. A possible reaction mechanism is proposed in Scheme I. The alkylation of acylmetalate intermediates a initially gives unstable olefin-coordinated alkoxycarbene complexes b<sup>7</sup> that are transformed into metallacyclobutane intermediates c prior to the formation of the transition state d. The latter gives new carbene-alkene complexes e upon opening of the ring. Subsequent hydrogen migration leads to the isomerized carbene complexes II-VII.

Complexes II-VII were readily soluble in polar solvents and moderately soluble in nonpolar solvents such as pentane and petroleum ether. Several day's exposure of II-VII in the solid state to air at room temperature showed little evidence of oxidative decomposition, whereas the acylmetalate intermediates (a) were highly sensitive to air and temperature. These new complexes were characterized by

(4) Tomlinson, A. J.; Massey, A. G. *J. Organomet. Chem.* 1967, 8, 321.

(5) Experimental Procedure. To a solution of 0.20 g (0.55 mmol) of I in 30 mL of ether was added dropwise 0.65 mmol of the appropriate aryllithium,  $\text{ArLi}$  ( $\text{Ar} = \text{C}_6\text{H}_5$ , *o*-, *m*-, or *p*- $\text{CH}_3\text{C}_6\text{H}_4$ , *p*- $\text{CH}_3\text{OC}_6\text{H}_4$ , *p*- $\text{ClC}_6\text{H}_4$ ), in 20 mL of ether at -65 °C. After being stirred at -60 to -40 °C for 3-4 h, the resulting orange solution was concentrated to dryness under vacuum at -40 °C. The residue was dissolved in 25 mL of  $\text{N}_2$ -saturated water at 0 °C to give an orange-red solution, to which was added immediately  $\text{Et}_3\text{OBF}_4$  in portions with vigorous stirring until the aqueous solution became acidic. The aqueous solution was extracted with petroleum ether (30-60 °C), and the combined extracts were concentrated under vacuum at -20 °C. Column chromatography of the residue on alumina at -20 °C followed (petroleum ether and then petroleum ether/ether (10/1)). The crude product was recrystallized from petroleum ether at -80 °C to give orange to red crystals of II-VII, respectively.

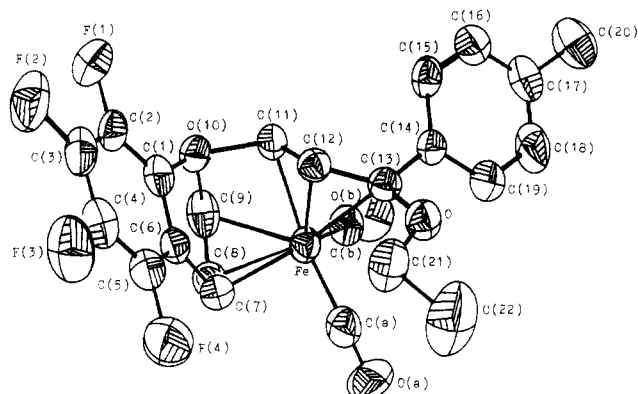
(6) II: yield 75%; mp 96-97 °C dec. Anal. Calcd for  $\text{C}_{23}\text{H}_{16}\text{O}_3\text{F}_4\text{Fe}$ : C, 58.50; H, 3.42. Found: C, 58.95; H, 3.90. IR ( $\nu_{\text{CO}}$ , hexane): 1992 (vs), 1943 (vs)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 7.30 (m, 5 H), 4.90 (t, 1 H), 4.65 (t, 1 H), 3.84 (m, 1 H), 3.52 (m, 1 H), 3.40 (m, 2 H), 1.64 (m, 1 H), 1.24 (t, 3 H), 0.86 (m, 1 H). MS:  $m/e$  (relative intensity) 472 ( $\text{M}^+$ , 10.7), 444 ( $(\text{M} - \text{CO})^+$ , 7.7), 416 ( $(\text{M} - 2\text{CO})^+$ , 100). III: yield 78%; mp 122 °C dec. Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_3\text{F}_4\text{Fe}$ : C, 59.28; H, 3.73. Found: C, 59.52; H, 3.54. IR ( $\nu_{\text{CO}}$ , hexane): 1985 (vs), 1938 (vs)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\delta$ , acetone- $d_6$ ): 7.24 (m, 4 H), 5.20 (br, 1 H), 4.84 (br, 1 H), 3.86 (br, 2 H), 3.50 (m, 2 H), 2.60 (s, 3 H), 1.62 (m, 1 H), 1.24 (m, 3 H), 0.90 (m, 1 H). MS:  $m/e$  (relative intensity) 486 ( $\text{M}^+$ , 2.3), 458 ( $(\text{M} - \text{CO})^+$ , 3.7), 430 ( $(\text{M} - 2\text{CO})^+$ , 24.7). IV: yield 57%; mp 114-116 °C dec. Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_3\text{F}_4\text{Fe}$ : C, 59.28; H, 3.73. Found: C, 59.51; H, 3.92. IR ( $\nu_{\text{CO}}$ , hexane): 1990 (vs), 1943 (vs)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\delta$ , acetone- $d_6$ ): 7.20 (m, 4 H), 4.90 (m, 1 H), 4.64 (m, 1 H), 3.84 (m, 1 H), 3.52 (m, 1 H), 3.40 (m, 2 H), 2.36 (s, 3 H), 1.60 (m, 1 H), 1.24 (m, 3 H), 0.88 (m, 1 H). MS:  $m/e$  (relative intensity) 486 ( $\text{M}^+$ , 2.3), 458 ( $(\text{M} - \text{CO})^+$ , 3.3), 430 ( $(\text{M} - 2\text{CO})^+$ , 7.1). V: yield 62%; mp 116-118 °C dec. Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_3\text{F}_4\text{Fe}$ : C, 59.28; H, 3.73. Found: C, 58.98; H, 3.66. IR ( $\nu_{\text{CO}}$ , hexane): 1989 (vs), 1935 (vs)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\delta$ , acetone- $d_6$ ): 7.38 (d, 2 H), 7.10 (d, 2 H), 5.10 (t, 1 H), 4.82 (t, 1 H), 3.82 (m, 2 H), 3.50 (q, 2 H), 2.28 (s, 3 H), 1.82 (m, 1 H), 1.24 (t, 3 H), 0.92 (m, 1 H). MS:  $m/e$  (relative intensity) 486 ( $\text{M}^+$ , 27.0), 458 ( $(\text{M} - \text{CO})^+$ , 22.8), 430 ( $(\text{M} - 2\text{CO})^+$ , 100). VI: yield 29%; mp 124-126 °C dec. Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_3\text{F}_4\text{Fe}$ : C, 57.38; H, 3.61. Found: C, 57.35; H, 3.42. IR ( $\nu_{\text{CO}}$ , hexane): 1982 (vs), 1931 (vs)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\delta$ , acetone- $d_6$ ): 7.42 (d, 2 H), 6.88 (d, 2 H), 5.08 (t, 1 H), 4.83 (t, 1 H), 3.74 (m, 2 H), 3.66 (s, 3 H), 3.42 (q, 2 H), 1.76 (m, 1 H), 1.18 (t, 3 H), 0.92 (m, 1 H). MS:  $m/e$  (relative intensity) 502 ( $\text{M}^+$ , 2.8), 474 ( $(\text{M} - \text{CO})^+$ , 1.8), 446 ( $(\text{M} - 2\text{CO})^+$ , 30.6). VII: yield 23%; mp 127-129 °C dec. Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{O}_3\text{ClF}_4\text{Fe}$ : C, 54.51; H, 2.98. Found: C, 54.35; H, 2.62. IR ( $\nu_{\text{CO}}$ , hexane): 1993 (vs), 1945 (vs)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\delta$ , acetone- $d_6$ ): 7.30 (dd, 4 H), 5.10 (t, 1 H), 4.82 (t, 1 H), 3.88 (m, 2 H), 3.50 (q, 2 H), 1.84 (m, 1 H), 1.18 (t, 3 H), 0.92 (m, 1 H). MS:  $m/e$  (relative intensity) 506 ( $\text{M}^+$ , 4.1), 478 ( $(\text{M} - \text{CO})^+$ , 5.8), 450 ( $(\text{M} - 2\text{CO})^+$ , 21.5).

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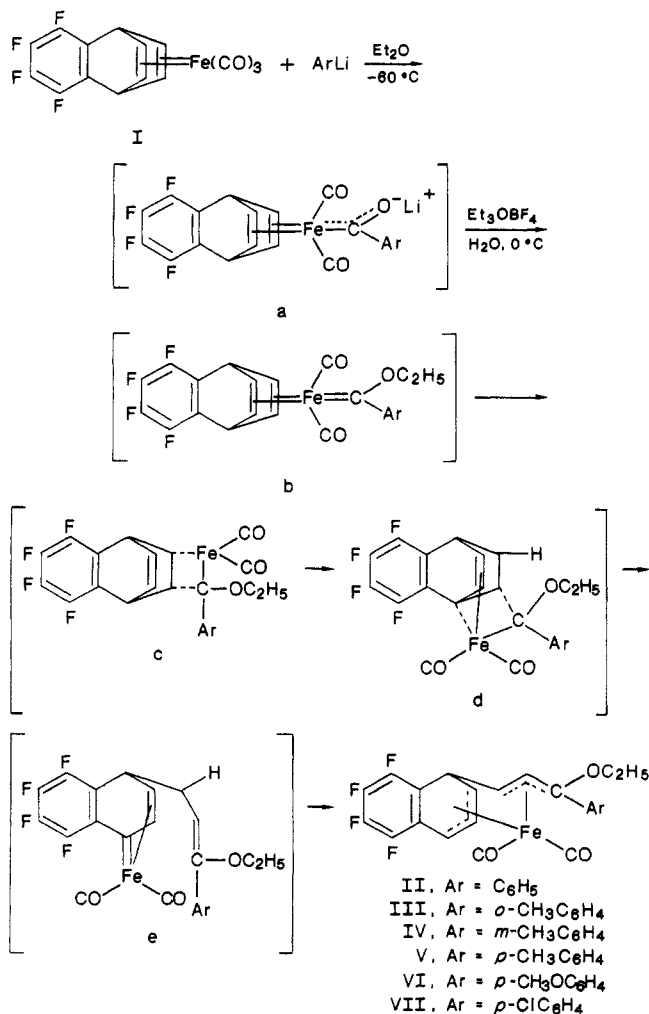
(2) Chen, J.-B.; Lei, G.-X.; Pan, Z.-H.; Zhang, S.-W.; Tang, Y.-Q. *J. Chem. Soc., Chem. Commun.* 1987, 1273.

(3) Chen, J.-B.; Lei, G.-X.; Xu, W.-H.; Pan, Z.-H.; Zhang, S.-W.; Zhang, Z.-Y.; Jin, X.-L.; Shao, M.-C.; Tang, Y.-Q. *Organometallics*, in press.



**Figure 1.** A drawing of  $C_{24}H_{18}O_3F_3Fe$  (V) showing the molecular structure and atom numbering. Selected bond lengths (Å) and angles (deg) include the following: Fe-C(a), 1.764 (4); Fe-C(b), 1.769 (4); Fe-C(7), 2.191 (4); Fe-C(8), 2.061 (4); Fe-C(9), 2.239 (3); F-C(11), 2.110 (3); Fe-C(12), 2.063 (3); Fe-C(13), 2.253 (3); C(7)-C(8), 1.409 (6); C(8)-C(9), 1.379 (6); C(9)-C(10), 1.528 (5); C(10)-C(11), 1.526 (4); C(11)-C(12), 1.405 (4); C(12)-C(13), 1.410 (4); C(1)-C(6), 1.398 (5); C(6)-C(7), 1.464 (5); C(13)-C(14), 1.472 (5); C(13)-O, 1.388 (4); C(14)-C(13)-O, 107.8 (2); C(12)-C(13)-C(14), 126.2 (3); C(12)-C(13)-O, 120.5 (3); C(6)-C(7)-C(8), 117.1 (3); C(7)-C(8)-C(9), 116.8 (3); C(8)-C(9)-C(10), 119.8 (4); C(9)-C(10)-C(1), 112.3 (3); C(10)-C(1)-C(6), 116.4 (3); C(1)-C(6)-C(7), 119.0 (3); C(9)-C(10)-C(11), 94.6 (3); C(10)-C(11)-C(12), 122.3 (3); C(11)-C(12)-C(13), 121.8 (3).

**Scheme I**



elemental analyses and IR,  $^1H$  NMR, and mass spectroscopic measurements. The structure of V was verified by a single-crystal X-ray structure determination.

The molecular structure of V (Figure 1)<sup>8</sup> shows that a six-membered ring of the tetrafluorobenzobicyclo[2.2.2]octatriene ligand is opened with breaking of an original  $\sigma$  bond corresponding to C(7)-C(12) in the tetrafluorobenzobicyclo[2.2.2]octatriene moiety. The carbon atom C(12) is now bonded to the "carbene" carbon atom C(13) forming a new  $\sigma$  bond. In addition, two  $\pi$ -allyl groups composed of C(7)-C(8)-C(9) and C(11)-C(12)-C(13), respectively, are bonded side-on to the orbitals of the central iron atom to satisfy the 18-electron rule. More interestingly, the six-membered ring containing a  $\pi$ -allyl ligand adopts a twisted boat conformation.

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**Registry No.** I, 12130-08-4; II, 110718-70-2; III, 110718-71-3; IV, 110718-72-4; V, 110718-73-5; VI, 110718-74-6; VII, 110718-75-7;  $C_6H_5Li$ , 591-51-5;  $o-CH_3C_6H_4Li$ , 6699-93-0;  $m-CH_3C_6H_4Li$ , 10325-82-3;  $p-CH_3C_6H_4Li$ , 2417-95-0;  $p-CH_3OC_6H_4Li$ , 14774-77-7;  $p-ClC_6H_4Li$ , 14774-78-8.

**Supplementary Material Available:** General procedures for the preparations of complexes II-VII and tables of crystallographic data, final fractional atomic coordinates and thermal parameters, bond lengths and angles, and least-squares plane for V (8 pages); a listing of structure factors for complex V (15 pages). Ordering information is given on any current masthead page.

(8)  $C_{24}H_{18}O_3F_3Fe$ : monoclinic,  $C_{2h}^2-C2/c$ ,  $a = 16.870$  (4) Å,  $b = 13.707$  (4) Å,  $c = 19.361$  (4) Å,  $\beta = 107.92$  (2)°,  $V = 4259$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_{calcd} = 1.51$  g/cm<sup>3</sup>,  $\mu = 7.9$  cm<sup>3</sup> (Mo K $\alpha$ ). A total of 4068 unique reflections were collected within the range of  $3^\circ \leq 2\theta \leq 50^\circ$  in the conventional  $\theta/2\theta$  scan mode, of which 2481 observed reflections ( $I > 3\sigma(I)$ ) were used in the structure solution (Patterson method and differential Fourier synthesis) and refinement (block-matrix least-squares method) to give final  $R = 0.0409$  and  $R_w = 0.0391$ .

## The Mechanism of the Wacker Process. Corroborative Evidence for Distal Addition of Water and Palladium

Björn Åkermark\* and Björn C. Söderberg

Department of Organic Chemistry  
 Royal Institute of Technology  
 S-100 44 Stockholm, Sweden

Stan S. Hall

Department of Chemistry, Olson Laboratories  
 Rutgers University, Newark, New Jersey 07102

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**Summary:** Water adds to 1,2-dimethyl-1,4-cyclohexadiene in the presence of bis(acetonitrile)palladium dichloride in aqueous acetone to afford predominately *trans*-bis(5-hydroxy-1,2-dimethyl-1- $\eta^3$ -cyclohexenyl)-palladium chloride (2), as well as the Wacker oxidation product 3,4-dimethyl-3-cyclohexen-1-one (3). The *trans* stereochemistry of the ( $\eta^3$ -allyl)palladium complex 2 confirms distal addition of water and palladium to the less substituted double bond of the cyclohexadiene.

The Wacker process for oxidation of ethylene to acetaldehyde is one of the first examples of the successful industrial application of homogeneous catalysis. As a consequence its mechanism has been extensively studied and the reaction is a classic example of transition-metal-promoted nucleophilic addition to unactivated alkenes.<sup>1</sup>