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## Novel Ring-opening Reaction of Norbornadiene(tricarbonyl)iron: Synthesis and Crystal Structure of $C_7H_8(CO)_2FeC(OEt)Ar$

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Reaction of norbornadiene(tricarbonyl)iron with aryl-lithium reagents at low temperature, followed by alkylation of the intermediate acylmetallates with  $Et_3OBF_4$  in aqueous solution at 0 °C gives novel ring-opened diallyl complexes,  $C_7H_8(CO)_2FeC(OC_2H_5)Ar$ .

In continuation of work on diene co-ordinated metal carbene complexes, a series of isomerized butadiene- and isoprene-(dicarbonyl)[ethoxy(aryl)carbene]iron complexes<sup>1,2</sup> have been synthesized and identified. Cyclic polyenes such as cyclo-octatetraene<sup>3</sup> and cycloheptatriene<sup>4</sup> can also be activated by iron, and a series of interesting, isomerized products of olefin-metal-carbene complexes were obtained by the reaction of cyclo-octatetraene- and cycloheptatriene-(tricarbonyl)iron with aryl-lithium reagents at low temperature and subsequent alkylation with  $Et_3OBF_4$ , respectively. We have now extended our studies to the activation of nonconjugated cyclic polyene ligands like norbornadiene, and report a novel ring-opening reaction of norbornadiene(tricarbonyl)iron (1) with aryl-lithium at low temperature, followed by alkylation with  $Et_3OBF_4$ , which leads to cleavage of the norbornadiene ring and formation of a new C–C bond.



## Scheme 1

Reaction of (1) with equimolar quantities of aryl-lithium (ArLi; Ar = p-,o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) in ether at -60 °C and subsequent alkylation of the acylmetallates formed with Et<sub>3</sub>OBF<sub>4</sub> in aqueous solution at 0 °C gave orange-red crystalline complexes (2–4)† with compositions C<sub>7</sub>H<sub>8</sub>(CO)<sub>2</sub>FeC(OC<sub>2</sub>H<sub>5</sub>)Ar in moderate yield (Scheme 1).



Figure 1. ORTEP drawing of  $C_{19}H_{20}O_3Fe$  (3). Fe–C(1), 1.76(1); Fe–C(2), 1.78(1); Fe–C(10), 2.19(1); Fe–C(11), 2.03(1); Fe–C(12), 2.11(1); Fe–C(15), 2.19(1); Fe–C(16), 2.08(1); Fe–C(17), 2.23(1); C(10)–C(11), 1.41(1); C(11)–C(12), 1.42(1); C(12)–C(13), 1.50(1); C(13)–C(14), 1.53(1); C(13)–C(17), 1.52(1); C(14)–C(15), 1.50(1); C(15)–C(16), 1.44(1); C(16)–C(17), 1.38(1); C(10)–O(3), 1.41(1)Å. C(9)–C(10)–O(3), 115.1(5)°; C(9)–C(10)–C(11), 121.3(6)°; C(11)–C(10)–O(3), 117.8(6)°.



A possible mechanism for the formation of these novel complexes (Scheme 1) might involve an unstable alkoxycarbene complex (b) and a 16e metallacyclobutane intermediate (c) which on homolysis involving the  $\sigma$ -bond shown gives the 18e species, (2-4).

The complexes (2-4) are highly sensitive to air and temperature. Their structures were determined by elemental analyses, spectroscopic analyses and single-crystal X-ray diffraction of (3).

<sup>†</sup> Satisfactory elemental analyses were obtained for the compounds described. (2): m.p. 99 °C (dec.); i.r. ( $\nu_{CO}$ , cm<sup>-1</sup>): 1970vs, 1906vs (CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H n.m.r (δ, CD<sub>3</sub>COCD<sub>3</sub>): 7.32, 7.10 (m, 4H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 4.46 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 3.90 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.64 (m, 1H, C<sub>7</sub>H<sub>8</sub>),  $3.18 (m, 1H, C_7H_8), 2.98 (m, 1H C_7H_8), 2.76 (m, 1H, C_7H_8), 2.28 (s, 1)$ 3H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 1.32 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.16 (s, 2, C<sub>7</sub>H<sub>8</sub>), 0.96 (m, 1H, C<sub>7</sub>H<sub>8</sub>); m/z 352( $M^+$ ). (3): m.p. 105–106 °C (decomp.); i.r.( $\nu_{CO}$ , cm<sup>-1</sup>): 1972vs, 1915vs (CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H n.m.r.(δ, CD<sub>3</sub>COCD<sub>3</sub>): 7.20, 7.08 (m, 4H,  $C_6H_4CH_3$ ), 4.52 (m, 1H,  $C_7H_8$ ), 3.84 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.60 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 3.20 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 2.96 (m, 1H,  $C_7H_8$ ), 2.78 (m, 1H,  $C_7H_8$ ), 2.58 (s, 3H,  $CH_3C_6H_4$ ), 1.30 (t, 3H,  $OCH_2CH_3$ ), 1.18 (s, 2H,  $C_7H_8$ ), 0.95 (m, 1H,  $C_7H_8$ ); m/z 352( $M^+$ ). (4): m.p. 90–91 °C (decomp), i.r.( $v_{CO}$ , cm<sup>-1</sup>): 1973vs, 1912vs (CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H n.m.r.(δ, CD<sub>3</sub>COCD<sub>3</sub>): 7.60 (m, 4H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 4.50 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 3.92 (q, 2H OCH<sub>2</sub>CH<sub>3</sub>), 3.26–3.18 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 3.12-3.08 (m, 2H,  $C_7H_8$ ), 2.95 (m, 1H,  $C_7H_8$ ), 1.33 (t, 3H,  $OCH_2CH_3$ , 1.20 (s, 2H, C<sub>7</sub>H<sub>8</sub>), 0.95 (m, 1H, C<sub>7</sub>H<sub>8</sub>); m/z 406( $M^+$ ). (5): m.p. 91.5–92 °C; i.r.( $v_{CO}$ , cm<sup>-1</sup>): 2046vs, 1975vs, br (CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H n.m.r. ( $\delta$ , CD<sub>3</sub>COCD<sub>3</sub>): 7.76, 7.66 (m, 4*H*, C<sub>6</sub>*H*<sub>4</sub>CF<sub>3</sub>), 6.46 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 5.80 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 5.60 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 5.40 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 3.98 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.94(m, 1H, C<sub>7</sub>H<sub>8</sub>), 2.32 (t, 1H, C<sub>7</sub>H<sub>8</sub>), 1.83 (m, 1H, C<sub>7</sub>H<sub>8</sub>), 1.35 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 0.82 (m, 1H,  $C_7H_8$ ; m/z 434( $M^+$ ).

The X-ray structure of (3) (Figure 1)‡ shows that a five-membered ring of the norbornadiene ligand is opened with breaking of the  $\sigma$ -bond in the norbornadiene moiety corresponding to C(11)-C(15), and carbon atom C(11) is now linked to the carbene carbon atom C(10) forming a new  $\sigma$ -bond C(11)-C(10). Along with the formation of the new  $\sigma$ -bond, the atomic chains C(15)-C(16)-C(17) and C(10)-C(11)-C(12) are co-ordinated to the orbitals of the iron atom in an  $\eta^3$  allyl-type  $\pi$ -bonding to satisfy the 18-electron rule.

When an orange-red benzene solution of (4) was heated in a sealed tube at 95–99 °C for 75 h, a new acyclic 1,3-diene-tricarbonyliron complex (5)† and an unidentified polymer (practically insoluble in all organic solvents) were obtained (Scheme 2).

‡ (3): C<sub>19</sub>H<sub>20</sub>O<sub>3</sub>Fe, triclinic,  $P\overline{1}$ , a = 7.824(3), b = 8.229(3), c = 13.597(4) Å,  $\alpha = 83.18(3)$ ,  $\beta = 87.12(3)$ ,  $\gamma = 71.79(3)^\circ$ , V = 825.52 Å<sup>3</sup>, Z = 2,  $D_c = 1.42$  g/cm<sup>3</sup>. Of 2154 unique reflections, 1822 [ $I \ge 3\sigma(I)$ ] were observed, collected within the range 0° ≤ 20 ≤ 45° (radiation Mo- $K_{\alpha}$ : 0.71069 Å), and used in structural analysis by Patterson-Fourier method and refinement to R = 0.0652 and  $R_w = 0.0646$ . (5): C<sub>20</sub>H<sub>17</sub>O<sub>4</sub>F<sub>3</sub>Fe, monoclinic,  $C_{2n}^2 - P2_1/n$ , a = 10.804(5), b = 12.044(9), c = 15.056(9) Å,  $\beta = 98.91^\circ$ ; V = 1959.10 Å<sup>3</sup>, Z = 4,  $D_c = 1.47$  g/cm<sup>3</sup>. Of 3843 unique reflections, 1755 [ $I \ge 3\sigma(I)$ ] were observed, collected within the range 3° ≤ 20 ≤ 50°, and used in the structure solution (direct methods) and refinement (block-diagonal matrix least-squares) to R = 0.129 and  $R_w = 0.108$ . For both structures, atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic

The structure of (5) has also been characterized by X-ray analysis.<sup>‡</sup> Because the crystal of (5) is too small to get good reflection data we have obtained just a preliminary structure with R = 0.129 and  $R_w = 0.108$ . However, it is clear that on heating of (4), another five-membered ring of the norbornadiene ligand was opened with breaking of the C-C  $\sigma$ -bond and formation of an  $\eta^4 \pi$ -bond with the iron atom. To satisfy the 18-electron rule, one CO generated by thermal decomposition of (4) is co-ordinated to the iron atom.

The reaction described above implies that the  $\sigma$ -bonds of a cyclic polyene ligand in this kind of complex can be activated by the iron atom, resulting in the breaking of a C–C  $\sigma$ -bond and formation of a new one.

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