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

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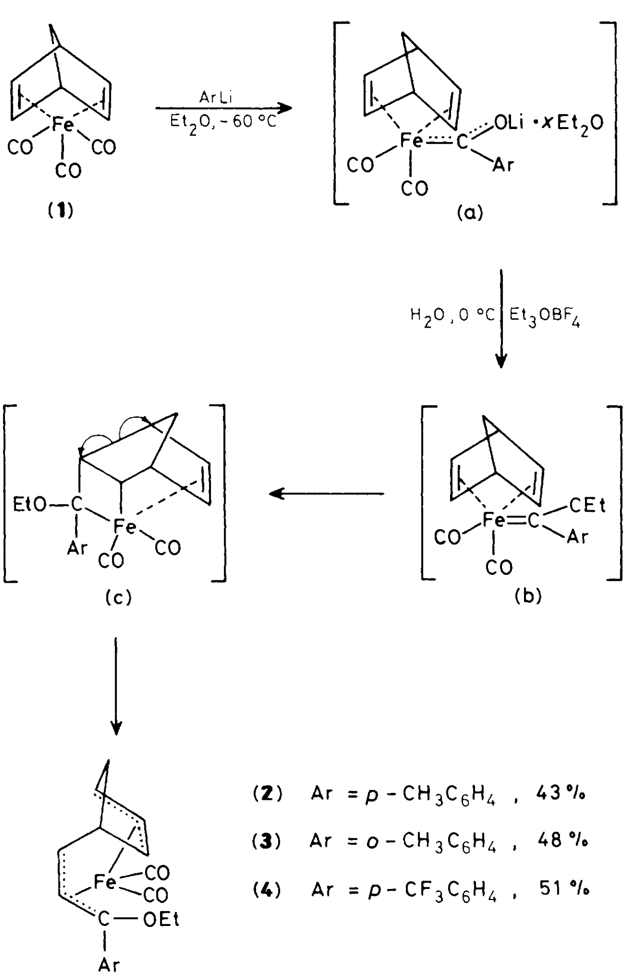
Reaction of norbornadiene(tricarbonyl)iron with aryl-lithium reagents at low temperature, followed by alkylation of the intermediate acylmetallates with Et_3OBF_4 in aqueous solution at 0 °C gives novel ring-opened diallyl complexes, $C_7H_8(CO)_2FeC(OC_2H_5)Ar$.

In continuation of work on diene co-ordinated metal carbene complexes, a series of isomerized butadiene- and isoprene-(dicarbonyl)[ethoxy(aryl)carbene]iron complexes[1,2] have been synthesized and identified. Cyclic polyenes such as cyclo-octatetraene[3] and cycloheptatriene[4] 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-$CH_3C_6H_4$, p-$CF_3C_6H_4$) in ether at −60 °C and subsequent alkylation of the acylmetallates formed with Et_3OBF_4 in aqueous solution at 0 °C gave orange-red crystalline complexes (**2**—**4**)† with compositions $C_7H_8(CO)_2FeC(OC_2H_5)Ar$ in moderate yield (Scheme 1).

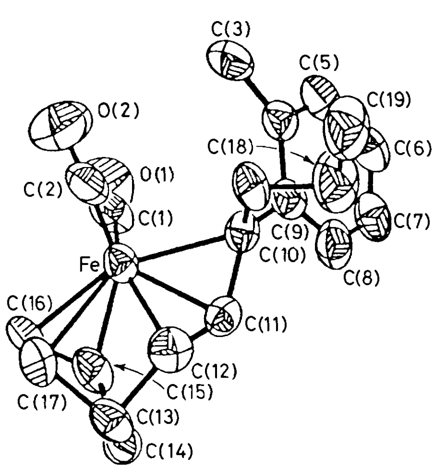
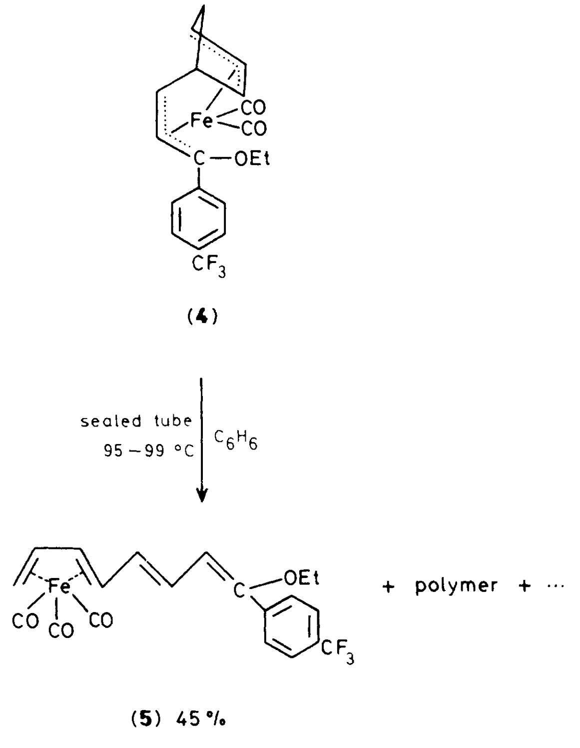


Figure 1. ORTEP drawing of $C_{19}H_{20}O_3Fe$ (**3**). Fe–C(1), 1.76(1); Fe–C(2), 1.78(1); Fe–C(10), 2.19(1); Fe–C(11), 2.03(1); Fe–C(12), 2.11(1); Fe–C(15), 2.19(1); Fe–C(16), 2.08(1); Fe–C(17), 2.23(1); C(10)–C(11), 1.41(1); C(11)–C(12), 1.42(1); C(12)–C(13), 1.50(1); C(13)–C(14), 1.53(1); C(13)–C(17), 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)°.



Scheme 2

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 σ-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**).

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† Satisfactory elemental analyses were obtained for the compounds described. (**2**): m.p. 99 °C (dec.); i.r. (ν_{CO}, cm^{-1}): 1970vs, 1906vs (CH_2Cl_2); ^1H n.m.r (δ, CD_3COCD_3): 7.32, 7.10 (m, 4H, $C_6H_4CH_3$), 4.46 (m, 1H, C_7H_8), 3.90 (q, 2H, OCH_2CH_3), 3.64 (m, 1H, C_7H_8), 3.18 (m, 1H, C_7H_8), 2.98 (m, 1H C_7H_8), 2.76 (m, 1H, C_7H_8), 2.28 (s, 3H, $CH_3C_6H_4$), 1.32 (t, 3H, OCH_2CH_3), 1.16 (s, 2, C_7H_8), 0.96 (m, 1H, C_7H_8); m/z 352(M^+). (**3**): m.p. 105—106 °C (decomp.); i.r.(ν_{CO}, cm^{-1}): 1972vs, 1915vs (CH_2Cl_2); ^1H n.m.r.(δ, CD_3COCD_3): 7.20, 7.08 (m, 4H, $C_6H_4CH_3$), 4.52 (m, 1H, C_7H_8), 3.84 (q, 2H, OCH_2CH_3), 3.60 (m, 1H, C_7H_8), 3.20 (m, 1H, C_7H_8), 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.(ν_{CO}, cm^{-1}): 1973vs, 1912vs (CH_2Cl_2); ^1H n.m.r.(δ, CD_3COCD_3): 7.60 (m, 4H, $C_6H_4CH_3$), 4.50 (m, 1H, C_7H_8), 3.92 (q, 2H OCH_2CH_3), 3.26—3.18 (m, 1H, C_7H_8), 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_7H_8), 0.95 (m, 1H, C_7H_8); m/z 406(M^+). (**5**): m.p. 91.5—92 °C; i.r.(ν_{CO}, cm^{-1}): 2046vs, 1975vs, br (CH_2Cl_2); ^1H n.m.r. (δ, CD_3COCD_3): 7.76, 7.66 (m, 4H, $C_6H_4CF_3$), 6.46 (m, 1H, C_7H_8), 5.80 (m, 1H, C_7H_8), 5.60 (m, 1H, C_7H_8), 5.40 (m, 1H, C_7H_8), 3.98 (q, 2H, OCH_2CH_3), 2.94(m, 1H, C_7H_8), 2.32 (t, 1H, C_7H_8), 1.83 (m, 1H, C_7H_8), 1.35 (t, 3H, OCH_2CH_3), 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 σ-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 σ-bond C(11)–C(10). Along with the formation of the new σ-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 η^3 allyl-type π-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).

The structure of (**5**) has also been characterized by *X*-ray analysis.‡ 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 σ-bond and formation of an η^4 π-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 σ-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 σ-bond and formation of a new one.

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‡ (**3**): $C_{19}H_{20}O_3Fe$, triclinic, $P\bar{1}$, $a = 7.824(3)$, $b = 8.229(3)$, $c = 13.597(4)$ Å, $\alpha = 83.18(3)$, $\beta = 87.12(3)$, $\gamma = 71.79(3)°$, $V = 825.52$ Å^3, $Z = 2$, $D_c = 1.42$ g/cm^3. Of 2154 unique reflections, 1822 [$I \geqslant 3\sigma(I)$] were observed, collected within the range $0° \leqslant 2\theta \leqslant 45°$ (radiation Mo-K_α: 0.71069 Å), and used in structural analysis by Patterson–Fourier method and refinement to $R = 0.0652$ and $R_w = 0.0646$. (**5**): $C_{20}H_{17}O_4F_3Fe$, monoclinic, C_{2h}^5–$P2_1/n$, $a = 10.804(5)$, $b = 12.044(9)$, $c = 15.056(9)$ Å, $\beta = 98.91°$; $V = 1959.10$ Å^3, $Z = 4$, $D_c = 1.47$ g/cm^3. Of 3843 unique reflections, 1755 [$I \geqslant 3\sigma(I)$] were observed, collected within the range $3° \leqslant 2\theta \leqslant 50°$, 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 Data Centre. See Notice to Authors, Issue 1.