Novel ring-opened reaction of μ-(1–3-η : 4–7-η-cycloheptatrienyl)-tricarbonylirontricarbonylmanganese with aryllithium reagents

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The reactions of μ-(1–3-η : 4–7-cycloheptatrienyl)tricarbonylirontricarbonylmanganese $[Mn(CO)_3Fe(CO)_3(C_7H_7)]$ 1, with aryllithium reagents, ArLi (Ar = Ph, *o*-, *m*-, *p*-MeC_6H_4), in ether at low temperature, followed by alkylation of the acylmetalate intermediates with Et_3OBF_4 in aqueous solution at 0 °C affords four novel ring-opened polyene complexes $[Mn(CO)_3Fe(CO)_3\{C_8H_7(OEt)Ar\}]$ (Ar = Ph 2, *o*-MeC_6H_4 3, *m*-MeC_6H_4 4, *p*-MeC_6H_4 5), of which the structure of 2 has been established by a single-crystal X-ray diffraction study.

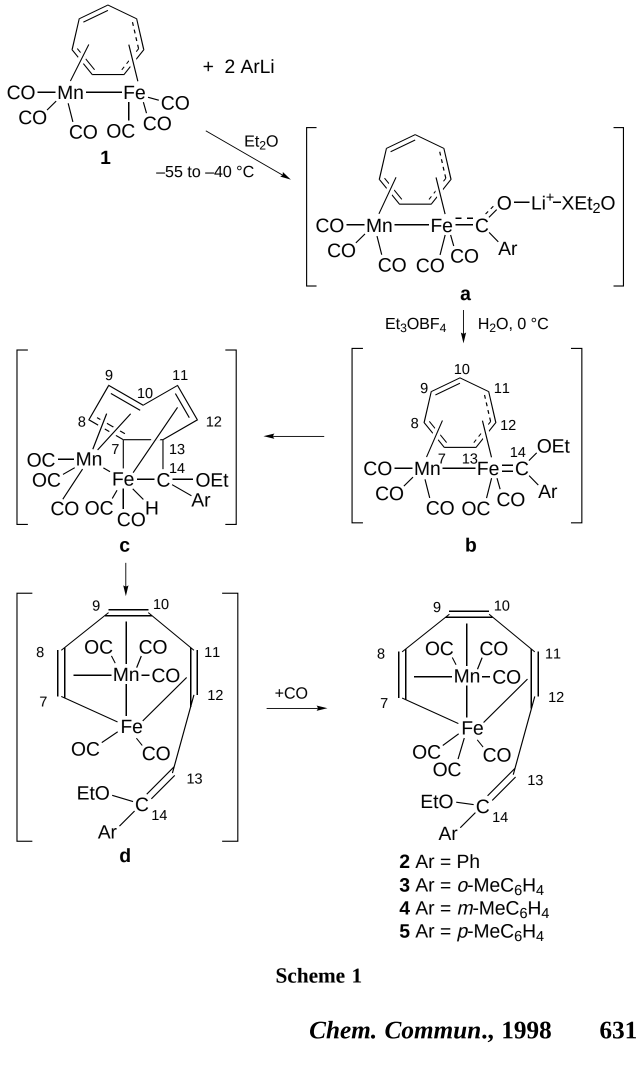
In recent years, alkene-coordinated transition metal carbene and carbyne complexes and/or their isomerized products, as part of a broader investigation of transition metal carbene and carbyne complexes, have been examined extensively in our laboratory. We found that the isomerizations of the alkene ligands and resulting products depend not only on the alkene ligands but also on the central metals.[1–5] For instance, (cycloheptatriene)-tricarbonyliron $[Fe(C_7H_8)(CO)_3]$, reacted with aryllithium and subsequent alkylation with Et_3OBF_4 gave no product containing ethyl group but the novel compound $[(Cl_3C\text{-cyclo-}C_7H_8)(CO)_2Fe(COC_6H_4Me\text{-}o)]$, in which the Cl_3C group was derived from a metathetical reaction of solvent CH_2Cl_2 molecules aided by iron at Et_3OBF_4, or ring-opened diallyl-like compound $[(CO)_2Fe\{C(OEt)(C_6H_4Me\text{-}o)C_7H_8\}]$ depending on the alkylation conditions.[3] While the cycloheptatrienediiron hexacarbonyl $[Fe_2(C_7H_8)(CO)_6]$, where the two iron atoms are directly bonded to each other, reacted with aryllithium reagents under analogous conditions to yield the novel isomerized bridging carbyne complexes $[Fe_2(CO)_4\{\mu\text{-}\eta^4:\eta^3\text{-}C_7H_7C(OEt)\text{-}Ar(\mu\text{-}C(OEt)\}]$.[4] In order to further investigate the effect of different binuclear central metals on the isomerizations of the alkene ligands and the reaction products, we chose μ-(1–3-η : 4–7-η-cycloheptatrienyl)tricarbonylirontricarbonylmanganese, $[Mn(CO)_3Fe(CO)_3(C_7H_7)]$ **1**,[6] where the cycloheptatrienyl ligand is η^4 and η^3 respectively bonded to the $Mn(CO)_3$ and $Fe(CO)_3$ units, and the Mn and Fe atoms are directly bonded to each other, as the starting material for the reaction with aryllithium reagents. These reactions led to nucleophilic addition to and cleavage of the cycloheptatrienyl ring to afford novel ring-opened polyene complexes. We report herein these novel reactions and the structures of the resulting products.

$[Mn(CO)_3Fe(CO)_3(C_7H_7)]$ **1**, was treated with 2 molar equiv. of aryllithium reagents, ArLi (Ar = Ph, *o*-, *m*-, *p*-MeC_6H_4), in diethyl ether at −55 to −40 °C for 3–4 h. The acylmetalate intermediates were subsequently alkylated with Et_3OBF_4 in aqueous solution at 0 °C. After removal of the solvent under high vacuum at low temperature, the solid residue was chromatographed on an alumina column at −20 to −25 °C, and the crude product was recrystallized from light petroleum–CH_2Cl_2 solution at −80 °C to afford orange–red crystalline complexes $[Mn(CO)_3Fe(CO)_3\{C_8H_7(OEt)Ar\}]$ **2**–**5**† (Scheme 1) in 47–52% yields.

The mechanism of the reaction (Scheme 1) is as yet unclear, but it could involve unstable alkoxycarbene intermediates **b** and metalcyclobutane intermediates **c**.[7] The latter then gives intermediates **d** upon opening of the ring, as in the reactions of the tetrafluorobenzobicyclo[2.2.2]octatriene tricarbonyliron with aryllithium nucleophiles.[7] Subsequently, such an intermediate **d** can abstract one molecule of CO to satisfy an 18-electron configurational iron and be converted into the stable ring-opened polyene complexes **2**–**5**.

Complexes **2**–**5** are very sensitive to air and to heat in solution but are stable for short periods on exposure to air as solids. Their structures were established by elemental analyses, spectroscopic determination and single-crystal X-ray diffraction.

The X-ray structure of **2** (Fig. 1)‡ shows that the cycloheptatrienyl ring of **1** has been opened by cleavage of the original C(7)–C(13) σ bond, and in **2** the C(13) atom is now linked to the carbon C(14) forming a double bond C(13)–C(14) and the C(7) atom is linked to the iron atom constructing a MnFeC(7) three-membered ring. Along with the formation of the new π bond,



Scheme 1

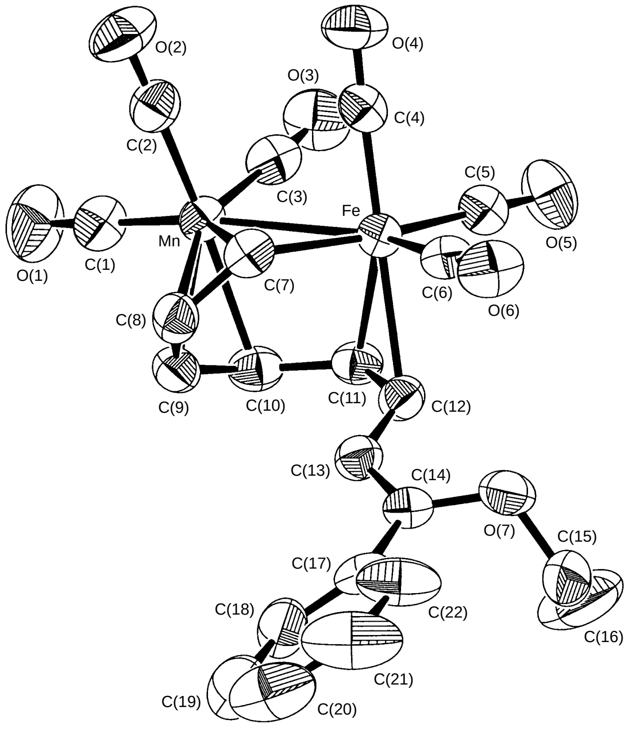


Fig. 1 Molecular structure (bond lengths in Å, angles in °) and labelling diagram for [Mn(CO)$_3$Fe(CO)$_3${C$_8$H$_7$(OEt)Ph}] **2**: Fe···Mn 2.7216(7), Fe–C(7) 1.967(4), Mn–C(7) 2.130(3), Fe–C(11) 2.211(3), Fe–C(12) 2.260(4), Mn–C(7) 2.130(3), Mn–C(8) 2.160(4), Mn–C(9) 2.144(4), Mn–C(10) 2.234(4), C(7)–C(8) 1.392(5), C(8)–C(9) 1.417(5), C(9)–C(10) 1.392(5), C(10)–C(11) 1.440(5), C(11)–C(12) 1.393(5), C(12)–C(13) 1.441(5), C(13)–C(14) 1.329(5); Fe–Mn–C(7) 45.84(10), Mn–Fe–C(7) 51.0(1), Fe–C(7)–Mn 83.2(1), Fe–C(7)–C(8) 130.3(3), C(7)–C(8)–C(9) 121.8(4), C(8)–C(9)–C(10) 122.7(4), C(9)–C(10)–C(11) 127.4(4), C(10)–C(11)–C(12) 127.3(4), C(11)–C(12)–C(13) 127.3(4), C(12)–C(13)–C(14) 124.9(4).

the alkene ligand became now a conjugated chain octatetraene with the OEt and Ph groups on the terminal carbon atom C(14), and the atomic chains C(7)C(8)C(9)C(10) and C(11)C(12) are coordinated to the orbitals of the Mn and Fe atoms in η^4- and η^2-bonding, respectively, to satisfy the 18-electron rule.

Notes and References

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† Satisfactory elemental analyses were obtained for the compounds described. **2**: mp 94–96 °C (decomp.) IR [ν(CO)/cm^{-1}]: 2040s, 1998vs, 1989vs, 1950w, 1943s (br) (cyclohexane). ^{1}H NMR (CD$_3$COCD$_3$): δ 7.82 (d, 1 H), 6.27 (t, 1 H), 5.57 (dd, 1 H), 4.95 (t, 1 H), 4.62 (d, 1 H), 4.18 (t, 1 H), 3.78 (m, 1 H), 7.43–7.36 (m, 5 H), 1.29 (t, 3 H), 3.78 (m, 2 H). *m/z* 476 ($M^+ - CO$), 448 ($M^+ - 2CO$), 420 ($M^+ - 3CO$), 392 ($M^+ - 4CO$), 364 ($M^+ - 5CO$), 336 ($M^+ - 6CO$), 280 ($M^+ - 6CO - Fe$), 225 ($M^+ - 6CO - Fe - Mn$). **3**: mp 89–91 °C (decomp.). IR [ν(CO)/cm^{-1}]: 2048s, 2000vs, 1991vs, 1955w, 1945s (br) (cyclohexane). ^{1}H NMR (CD$_3$COCD$_3$): δ 7.83 (d, 1 H), 6.29 (t, 1 H), 5.57 (dd, 1 H), 4.95 (t, 1 H), 4.60 (d, 1 H), 4.20 (t, 1 H), 3.81 (m, 1 H), 7.27–7.09 (m, 4 H), 2.32 (s, 3 H), 1.29 (t, 3 H), 3.81 (m, 2 H). *m/z* 490 ($M^+ - CO$), 462 ($M^+ - 2CO$), 434 ($M^+ - 3CO$), 406 ($M^+ - 4CO$), 378 ($M^+ - 5CO$), 350 ($M^+ - 6CO$), 294 ($M^+ - 6CO - Fe$), 239 ($M^+ - 6CO - Fe - Mn$). **4**: mp 30–32 °C (decomp.). IR [ν(CO)/cm^{-1}]: 2060s, 2010vs, 1995vs, 1960w, 1950s (br) (cyclohexane). ^{1}H NMR (CD$_3$COCD$_3$): δ 7.84 (d, 1 H), 6.30 (t, 1 H), 5.59 (dd, 1 H), 4.96 (t, 1 H), 4.62 (d, 1 H), 4.22 (t, 1 H), 3.80 (m, 1 H), 7.25–7.16 (m, 4 H), 2.33 (s, 3 H), 1.31 (t, 3 H), 3.80 (m, 2 H). *m/z* 490 ($M^+ - CO$), 462 ($M^+ - 2CO$), 434 ($M^+ - 3CO$), 406 ($M^+ - 4CO$), 478 ($M^+ - 5CO$), 350 ($M^+ - 6CO$), 294 ($M^+ - 6CO - Fe$), 239 ($M^+ - 6CO - Fe - Mn$). **5**: mp 42–44 °C (decomp.). IR [ν(CO)/cm^{-1}]: 2050s, 2001vs, 1993vs, 1958w, 1948s (br) (cyclohexane); ^{1}H NMR (CD$_3$COCD$_3$): δ 7.85 (d, 1 H), 6.30 (t, 1 H), 5.59 (dd, 1 H), 4.97 (t, 1 H), 4.60 (d, 1 H), 4.22 (t, 1 H), 3.79 (m, 1 H), 7.37–7.21 (m, 4 H), 2.33 (s, 3 H), 1.31 (t, 3 H), 3.79 (m, 2 H). *m/z* 434 ($M^+ - 3CO$), 406 ($M^+ - 4CO$), 378 ($M^+ - 5CO$), 350 ($M^+ - 6CO$), 294 ($M^+ - 6CO - Fe$), 239 ($M^+ - 6CO - Fe - Mn$).

‡ *Crystal data* for **2**: C$_{22}$H$_{17}$FeMnO$_7$, monoclinic, space group $P2_1/n$, a = 6.823(1), b = 26.698(6), c = 11.767(2) Å, β = 91.86(2)°, U = 2142.4(8) Å^3, Z = 4, D_c = 1.563 g cm^{-3}, μ = 13.06 cm^{-1} (Mo-Kα). A total of 3826 unique reflections were collected within 5–50° in the conventional ω–2θ scan mode, of which 2553 observed reflections [$I > 3.00\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares method) to give final R = 0.031 and R_w = 0.032. CCDC 182/741.

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