Unusual Reaction of Tricarbonyl(*o*-quinodimethane)iron with *o*-Lithiobenzyldimethylamine: Crystal Structure of $[Fe\{Me_2NCH_2C_6H_4C(OEt)CH_2C_6H_4CH_2\}(CO)_3]$

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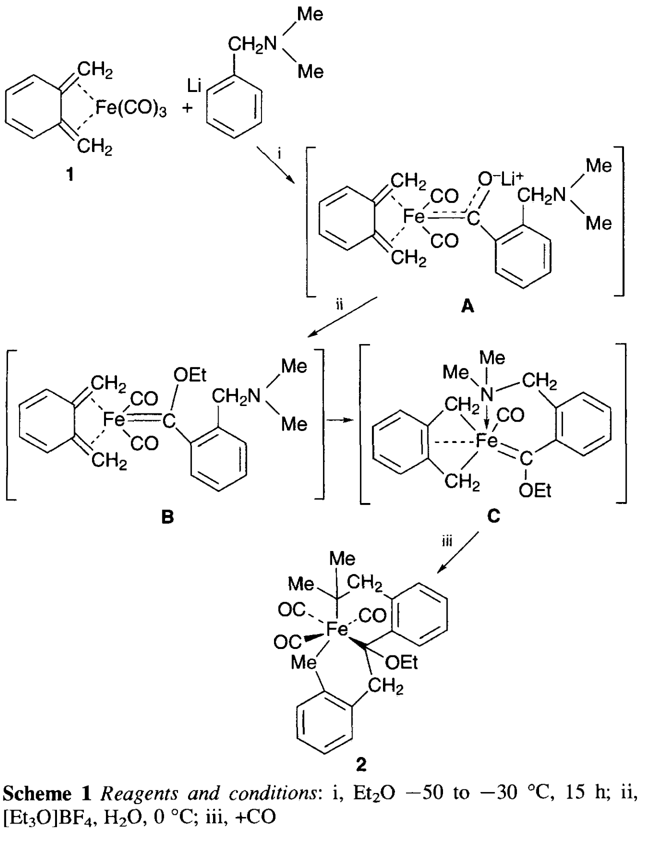
The reaction of $[Fe\{o\text{-}(CH_2)_2C_6H_4\}(CO)_3]$ **1** with $o\text{-}LiC_6H_4CH_2NMe_2$, in Et_2O at low temperature, followed by alkylation of the acylmetallate intermediate formed with $[Et_3O]BF_4$ in aqueous solution at 0 °C gives a novel chelated isomerized carbene complex $[Fe\{Me_2NCH_2C_6H_4C(OEt)CH_2C_6H_4CH_2\}(CO)_3]$ **2** whose structure is established by X-ray crystallography.

In recent years, olefin-coordinated transition-metal carbene complexes and/or their isomerized products have been examined extensively in our laboratory. We have previously observed several isomerizations of olefin ligands, and a series of isomerized carbene complexes with novel structure were isolated by the reactions of olefin-ligated metal carbonyls with nucleophiles. We found that the reaction products depend not only on the polyalkene ligands and central metals but also on the nucleophiles used.[1–8] In an extension of our research on olefin-coordinated metal carbene complexes, we have now studied the reaction of an acyclic conjugated diene-ligated carbonyliron with nucleophile in order to investigate the effect of olefin ligand and nucleophile on the isomerization of olefin ligands and the reaction products. Herein we report a novel reaction of tricarbonyl-(*o*-quinodimethane)iron **1**, in which the *o*-quinodimethane is bonded to $Fe(CO)_3$ *via* both conjugated exocyclic diene moieties, with *o*-lithiobenzyldimethylamine at low temperature followed by alkylation with $[Et_3O]BF_4$, which led to the coordination of the N atom to Fe and the formation of a new C–C bond leading to a novel chelated isomerized carbene complex.

$[Fe\{o\text{-}(CH_2)_2C_6H_4\}(CO)_3]$ **1**[9] was treated with a 10–20% molar excess of *o*-lithiobenzyldimethylamine, $o\text{-}LiC_6H_4CH_2NMe_2$,[10] at −50 to −30 °C for 15 h and the acylmetallate obtained was subsequently treated with $[Et_3O]BF_4$ in aqueous solution at 0 °C. After removal of the solvent under vacuum, the residue was chromatographed on an alumina column at low temperature and the crude product was recrystallized from light petroleum–CH_2Cl_2 solution at −80 °C to afford the brick-red crystalline complex $[Fe\{Me_2NCH_2C_6H_4C(OEt)CH_2C_6H_4CH_2\}(CO)_3]$ **2**† in 62% yield (Scheme 1).

The mechanism of the reaction (Scheme 1) is as yet unclear, but it could involve an unstable alkoxycarbene intermediate (**B**) and a metallacyclic intermediate (**C**)[1] formed by rearrangement of π-bonding of the double bond in the *o*-quinodimethane ligand of **B**. Metallacycle **C** can arise through breaking of a C–Fe σ bond and coordination of the N atom to Fe to form a new C–C bond and Fe–N bond accompanied by dissociation of the diene π bonds. Subsequently, such an intermediate **C** can abstract one molecule of CO to satisfy the 18-electron configuration and be converted into the stable chelated isomerized carbene complex **2**.



Scheme 1 *Reagents and conditions*: i, Et_2O −50 to −30 °C, 15 h; ii, $[Et_3O]BF_4$, H_2O, 0 °C; iii, +CO

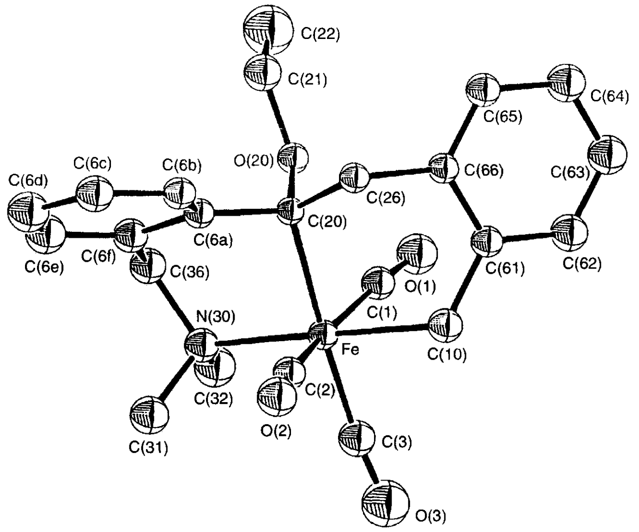


Fig. 1 Molecular structure (bond lengths in Å, angles in °) and labelling diagram for $[Fe\{Me_2NCH_2C_6H_4C(OEt)CH_2C_6H_4CH_2\}(CO)_3]$ **2**: Fe–N(30) 2.158(3), Fe–C(20) 2.120(3), Fe–C(1) 1.823(4), Fe–C(2) 1.792(4), Fe–C(3) 1.784(4), Fe–C(10) 2.124(3), C(20)–O(20) 1.449(3), C(20)–C(6a) 1.512(4), C(6a)–C(6f) 1.401(4), C(6f)–C(36) 1.495(5), C(36)–N(30) 1.496(4), C(10)–C(61) 1.479(5), C(61)–C(66) 1.395(4), C(66)–C(26) 1.496(4), C(26)–C(20) 1.531(4) Å, Fe–C(20)–O(20) 104.9(2), Fe–C(20)–C(6a) 108.8(2), Fe–C(20)–C(26) 112.4(2), Fe–N(30)–C(36), 114.4(2), Fe–C(10)–C(61) 113.5(2), C(10)–Fe–C(20) 90.5(1), C(10)–Fe–N(30) 177.7(1), C(20)–C(6a)–C(6f) 119.6(3), C(6a)–C(6f)–C(36) 120.6(3), C(6f)–C(36)–N(30) 112.2(3), C(10)–C(61)–C(66) 119.6(3), C(61)–C(66)–C(26) 118.1(3), C(66)–C(26)–C(20) 113.0(3)

Complex **2** is air- and heat-sensitive in solution but is air-stable as a solid. Its structure was established by elemental analysis, spectroscopic determinations, and single-crystal X-ray diffraction.

The X-ray structure of **2** (Fig. 1)‡ shows that the two π bonds of the *o*-quinodimethane ligand in the diene moiety have been opened, such that the carbon atom C(26) forms a new σ bond with the 'carbene' carbon C(20) [C(26)–C(20) 1.531(4) Å]. Along with the formation of the new σ bond, the N atom of the *o*-benzyldimethylamine substituent is coordinated to the Fe atom to form a six-membered ring and provides two electrons to the Fe atom. To satisfy the 18-electron configuration, one CO molecule, generated possibly by decomposition of unstable intermediate **B** or **C**, is coordinated to Fe. The stability of complex **2** is attributed to the coordination of the N atom of the *o*-quinodimethylamine substituent leading to a macrocyclic system comprised of the four six-membered rings in the molecule. This is confirmed by the fact that when other aryllithium reagents such as PhLi, *o*- or *p*-MeC_6H_4Li, *p*-$MeOC_6H_4Li$ or *p*-$CF_3C_6H_4Li$ were used in the reaction with **1** under the same conditions, no analogous products were obtained.

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Footnotes

† Satisfactory elemental analysis was obtained for complex **2**, mp 96–98 °C (decomp.); IR (ν_{CO}/cm^{-1}): 2006m, 1990vs, 1963vs (hexane); ^{1}H NMR (δ, CD_3COCD_3): 7.56, 7.22, 7.05 [m, 8H, $C_6H_4(CH_2)_2$ and $C_6H_4NMe_2$], 4.40 [d, 1 H, $C_6H_4(CH_2)_2$], 3.70 [d, 1 H, $C_6H_4(CH_2)_2$], 3.50 (q, 2 H, OCH_2CH_3), 2.82 (s, 6 H, NMe_2), 2.28 (s, 2 H, $C_6H_4CH_2N$), 1.70 [d, 1 H, $C_6H_4(CH_2)_2$], 1.28 [d, 1 H, $C_6H_4(CH_2)_2$], 0.85 (t, 3 H, OCH_2CH_3); *m/z* 435 (M^+), 407 ($M^+ - CO$), 379 ($M^+ - 2CO$), 351 ($M^+ - 3CO$).

‡ *Crystal data* for **2**: $C_{23}H_{25}FeNO_4$, $M = 435.31$, monoclinic, space group $P2_1/n$, $a = 11.005(5)$, $b = 15.594(5)$, $c = 12.332(5)$ Å, $\beta = 93.75(5)°$, $V = 2122(2)$ Å^3, $Z = 4$, $D_c = 1.369$ g cm^{-3}. Of 3683 unique reflections, 2454 with $I > 3\sigma(I)$ were observed, collected within the range $0 < 2\theta < 50°$ (Mo-Kα radiation: 0.7107 Å), and used in structure solution by Patterson-Fourier methods and refinement (full-matrix least squares) of the structure to yield the final discrepancy indices $R = 0.031$ and $R_w = 0.032$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

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