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Iron−Carbene Bonded to a Planar Tetraoxo Surface Defined by Dimethoxy-*p*-*tert*-butylcalix[4]arene Dianion

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*Summary: A reactive coordinatively unsaturated iron(II) bonded to a quasi-planar O_4 environment in [calix[4](OMe)$_2$(O)$_2$Fe] (**2**) has been obtained from the reaction of the free ligand **1** with Fe_2Mes_4 (Mes = 1,3,5-$Me_3C_6H_2$). The reaction of **2**, which adds a variety of monodentate ligands, [calix[4](OMe)$_2$(O)$_2$FeL] (L = thf, **3**; Bu^tNC, **4**), with Ph_2CN_2 led to the first high-spin iron(II) carbene bonded to an oxo matrix, [calix[4](OMe)$_2$(O)$_2$Fe=CPh$_2$] (**5**).*

An iron−carbon functionality supported exclusively by an oxygen donor set has no precedent.[1] In the case of a preorganized geometry, such a set of donor atoms would mimic quite nicely the coordination environment experienced by iron in some iron oxide based heterogeneous catalysts.[2] In order to achieve such a result, we chose as a binding matrix for iron(II) dimethoxy-*p*-*tert*-butylcalix[4]arene.[3] The two methoxy groups not only adapt the O_4 set of calix[4]arene to the iron oxidation state but also provide an additional protection against any strong dimerization.[4,5] The starting compound **2** is accessible only through the reaction with the easily available Fe_2Mes_4.[6] The use of iron-halides led to compounds containing Fe−X bonds that were very difficult to free from the alkali-metal salts. The coordinative unsaturation of **2**, along with the oxygen environments makes iron(II) particularly prone to display a great variety of coordinative and redox chemistry.

We report here not only the synthesis of the first monomeric calix[4]arene iron(II) but also the quite surprising high-spin iron(II)−carbene functionality fixed over an O_4 oxo surface.[7] Complex **2** adds a number of monodentate ligands in the only accessible axial position, thus forming complexes such as **3** and **4** (Scheme 1).[8]

The reaction with diazoalkanes gave iron−carbene derivatives[9] with variable stabilities as a function of the substituents at the carbene carbon. The diphenylcarbene derivative **5**,[10] which is an unprecedented high-spin (5.2 μ_B at 295 K) iron(II) carbene,[9] showed an unusual thermal stability and resistance to hydrolysis. It can be decomposed only by acids or oxygen. In the former case the anionic iron(II) complex **6** formed, while the reaction with O_2 produces benzophenone and the μ-oxo iron(III) dimer **7**. The formulations reported in

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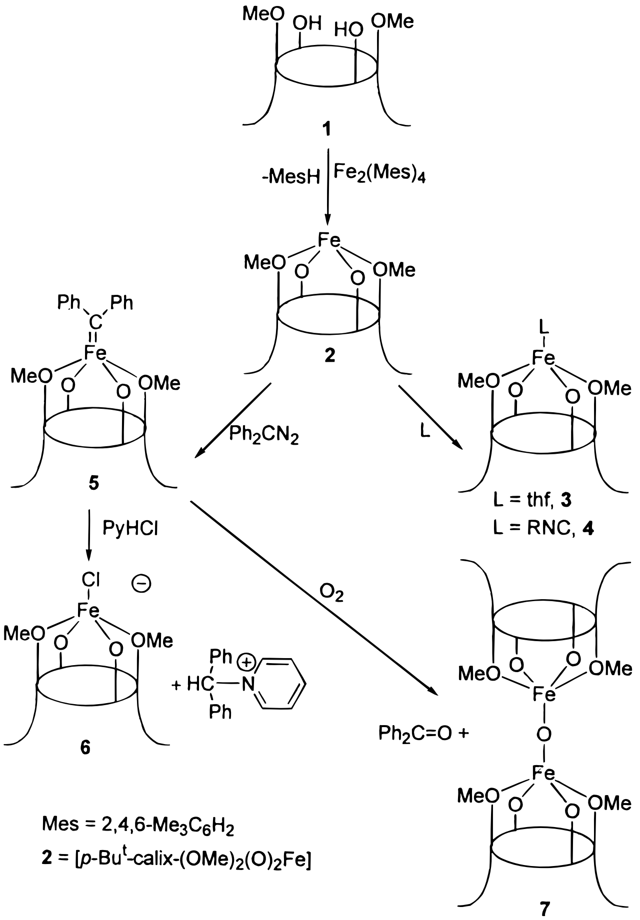
[8] Procedure for **2**−**4**: Fe_2Mes_4 (7.39 g, 12.56 mmol) was added to a cold (−30 °C) toluene suspension (150 mL) of **1** (17.0 g, 25.15 mmol), and the resultant dark red suspension was stirred overnight and warmed to room temperature. Most of the solvent was then removed by decantation, *n*-hexane (100 mL) was added, and the mixture was stirred overnight. The product was obtained as a fluffy electrostatic white solid, which was washed with *n*-hexane (40 mL), filtered, and dried *in vacuo* (14.77 g, 45.4%). Anal. Calcd for **2**·C_7H_8·C_6H_{14}, $C_{59}H_{80}FeO_4$: C, 77.99; H, 8.81. Found: C, 78.06; H, 8.81. Reaction of **2** with THF or Bu^tNC gave the corresponding adducts **3** and **4**. In the latter case a bright yellow solid was obtained from Et_2O by filtering and drying *in vacuo* (2.26 g, 84.9%). Anal. Calcd for **4**·Et_2O, $C_{55}H_{77}FeNO_5$: C, 74.42; H, 8.68; N, 1.58. Found: C, 74.82; H, 8.57; N, 1.51. IR (Nujol, ν_{max}/cm^{-1}): 2172 (s). μ_{eff}: 5.25 μ_B at 295 K. The solvation degree of the complexes was determined *via* both microanalysis and thermal decomposition, followed by a GC analysis.

S0276-7333(97)00751-6 CCC: $14.00

Scheme 1



Mes = 2,4,6-Me$_3$C$_6$H$_2$
2 = [*p*-Bu^t-calix-(OMe)$_2$(O)$_2$Fe]

Scheme 1 are supported by preliminary X-ray analyses on **3**,[11] **6**,[11] and **7**,[11] while details are given here only for **5**. Its structure is shown in Figure 1 with a selection of structural parameters.[12]

Its structure consists of discrete complex molecules of formula [Fe(calix(OMe)$_2$)(CPh$_2$)] and a dichloromethane solvent molecule of crystallization in the stoichiometric molar ratio of 1/3. One dichloromethane molecule is present in the calixarene cavity as a guest. As is usually observed in metal dimethoxycalixarene derivatives, the macrocycle assumes an elliptical cross-section conformation, as indicated by the dihedral angles they form with the “reference” plane through the C7, C14, C21, and C28 bridging methylene carbon atoms (dihedral angles 131.9(2), 111.7(3), 133.3(2), and 110(8)° for A−D, respectively) and by the values of the distances between opposite *para* carbon atoms (C4···C17, 8.969(11) Å, C10···C24, 7.361(15) Å). The O$_4$ core shows remarkable tetrahedral distortions ranging from −0.223(5) to 0.216(5) Å, the metal being displaced by 0.550(2) Å from the mean plane. The iron to oxygen distances Fe−O1 and Fe−O3 (1.854(6) and 1.828(5) Å, respectively) suggest some double-bond character,[4,5c] in agreement with the approximate linearity of the Fe−O−C bond angles (Fe−O1−C1, 152.2(5)°; Fe−O3−C20, 161.0(5)°). The Fe−O2 and Fe−O4 bond distances (2.225(7) and 2.256(6) Å, respectively) are much longer, like those found for Fe−O(ether) bond distances.[4,5c] The Fe−C47 bond distance (1.946(8) Å) is rather longer than the values usually quoted in the literature for terminal Fe−C(carbene) bond distances.[9a,13] This lengthening[13a] may be ascribed to the intraligand steric hindrance involving the H49

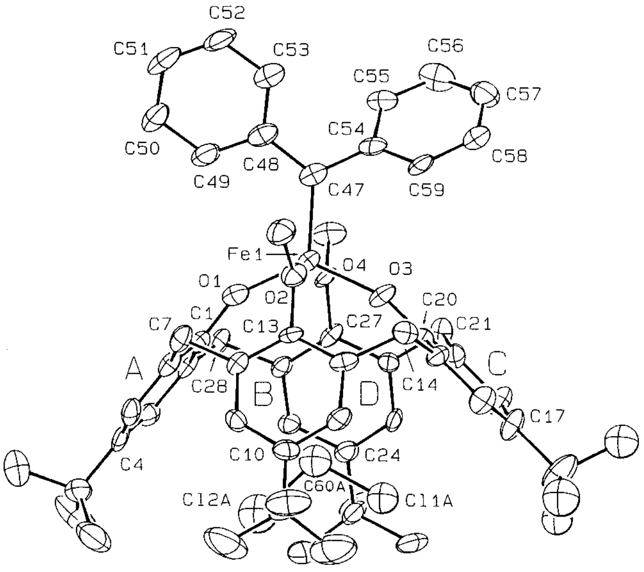


Figure 1. ORTEP drawing of complex **5** (50% probability ellipsoids). Selected bond distances (Å) are as follows: Fe1−O1, 1.854(6); Fe1−O2, 2.225(7); Fe1−O3, 1.828(5); Fe1−O4, 2.256(6); Fe1−C47, 1.946(8); C47−C48, 1.452(10); C47−C54, 1.480(10). Selected bond angles (deg): O2−Fe1−O4, 162.4(2); O1−Fe1−O3, 130.7(2); O1−Fe1−C47, 117.7(3); O3−Fe1−C47, 111.6(3); Fe1−O1−C1, 152.2(5); Fe1−O2−C13, 116.9(6); Fe1−O3−C20, 161.0(5); Fe1−O4−C27, 118.5(5); Fe1−C47−C54, 119.1(6); Fe1−C47−C48, 124.7(6); C48−C47−C54, 116.3(7).

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(10) Procedure for **5**: **2**·C$_7$H$_8$·C$_6$H$_{14}$ (3.83 g, 4.21 mmol) was added to a cold (−30 °C) solution of Ph$_2$CN$_2$ (0.94 g, 4.83 mmol) in *n*-pentane (100 mL) and the resultant deep green suspension was stirred overnight at room temperature. The deep green crystalline solid was washed with *n*-hexane (40 mL), filtered, and dried *in vacuo* (3.35 g, 82.2%). Anal. Calcd for **5**·C$_5$H$_{12}$, C$_{64}$H$_{80}$FeO$_4$: C, 79.35; H, 8.27. Found: C, 79.19; H, 8.39. Crystals suitable for X-ray analysis were obtained by recrystallizing **5** from CH$_2$Cl$_2$/pentane and contain a CH$_2$Cl$_2$ molecule of crystallization.

(11) Crystallographic data are available in the Supporting Information.

(12) Crystal data for **5**: C$_{59}$H$_{68}$FeO$_4$·3CH$_2$Cl$_2$, M_r = 1151.8, triclinic, space group $P\bar{1}$, a = 13.115(2) Å, b = 21.265(3) Å, c = 12.573(2) Å, α = 100.57(2)°, β = 117.53(2)°, γ = 76.64(2)°, V = 3013.3(10) Å^3, Z = 2, ρ_{calcd} = 1.270 g/cm^3, $F(000)$ = 1212, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 5.60 cm^{-1}, crystal dimensions 0.22 × 0.52 × 0.68 mm. The structure was solved by the heavy-atom method and anisotropically refined for all the non-H atoms except for the disordered atoms. For 3599 unique observed reflections ($I > 2\sigma(I)$) collected at T = 138 K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 50°$) and corrected for absorption the final conventional R is 0.075 (wR2 = 0.236 for the 6941 reflections having $I > 0$ used in the refinement). All calculations were carried out on a Quansan personal computer equipped with an Intel Pentium processor. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. See the Supporting Information for more details.

and H59 α-hydrogen atoms of the carbene phenyl rings and O1 and O3 (O1···H49, 2.39 Å; O1···C49, 3.226(9) Å; O3···H59, 3.10 Å; O1···C59, 3.096(10) Å). The planarity of the Fe,C47,C48,C54 system is consistent with the sp^2 carbene carbon.[14]

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Supporting Information Available: Tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **3** and **5**−**7** and Schakal drawings for **3**, **6**, and **7** (30 pages). Ordering information is given on any current masthead page.

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(14) The guest dichloromethane molecule was found to be statistically distributed over two positions (A and B), preventing the direct localization of the hydrogen atoms. The two nearly coplanar positions (dihedral angle 3.0(17)°) are oriented nearly parallel to the B and D rings (dihedral angles 21.3(12) [18.4(12)] and 21.5(12) [24.3(12)]°, respectively; values in brackets refer to molecule B) and perpendicular to the A and C rings (dihedral angles 87.9(8) [89.7(12)] and 88.0(10) [86.4(12)]°, respectively).