Communications

Outer-Sphere Organometallic Chemistry of C_{60}: Synthesis and X-ray Structure of a Strained [η^4-(Cyclohexadieno)buckminsterfullerene]iron Tricarbonyl Complex

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Received February 15, 1996[⊗]

*Summary: Treatment of 1,2-(3,5-Cyclohexadieno)buckminsterfullerene with $Fe_3(CO)_{12}$ in refluxing benzene affords [η^4-1,2-(3,5-cyclohexadieno)buckminsterfullerene]iron tricarbonyl (**1**) in 14% yield. The crystal structure of **1** shows that significant steric compression exists between the $Fe(CO)_3$ and C_{60} moieties.*

Since the discovery of C_{60},[1] advances in its organometallic chemistry have greatly contributed to the meteoric development of this interdisciplinary area. Among other highlights, an osmate ester was the first crystallographically characterized C_{60} derivative, confirming its icosahedral geometry.[2] The importance of the organometallic chemistry of C_{60} relies on the interesting properties that can arise from the interaction of the metallic center with the π-surface of such an unusual system. Metal−ligand charge transfer may result in large second-order nonlinear optical activity for this type of compound.[3] Also, it is important to point out the potential for coupled redox processes involving both the metal and the C_{60} moieties. After Fagan's report of the first transition-metal complex having a metal directly bonded to C_{60},[4] several other compounds of this type were synthesized,[5] showing that C_{60} and other fullerenes tend to act as η^2 ligands through their [6,6] double bonds reacting with electron-rich metals. Only a very few examples of organometallic complexes in which the metal is not directly attached to C_{60} have been reported.[6] Herein, we describe the synthesis of the first structurally characterized iron-containing C_{60} compound, namely [η^4-1,2-(3,5-cyclohexadieno)buckminsterfullerene]iron tricarbonyl (**1**), which displays interesting π-compression effects.

We have previously reported the synthesis of 1,2-(3,5-cyclohexadieno)buckminsterfullerene (**2**).[7] This synthesis has been optimized with a straightforward protocol, affording **2** in two steps with C_{60} as the starting material. Reaction of C_{60} with 1-[(trimethylsilyl)oxy]-1,3-butadiene and subsequent hydrolysis affords 1,2-(3-hydroxy-4-cyclohexeno)buckminsterfullerene (**3**).[8] The elimination of water in **3** in the presence of *p*-toluenesulfonic acid and careful exclusion of oxygen (toluene, reflux) provides **2** in 60% overall yield from C_{60} (Scheme 1). The synthesis of complex **1** was carried out by reaction of **2** with triiron dodecacarbonyl in refluxing

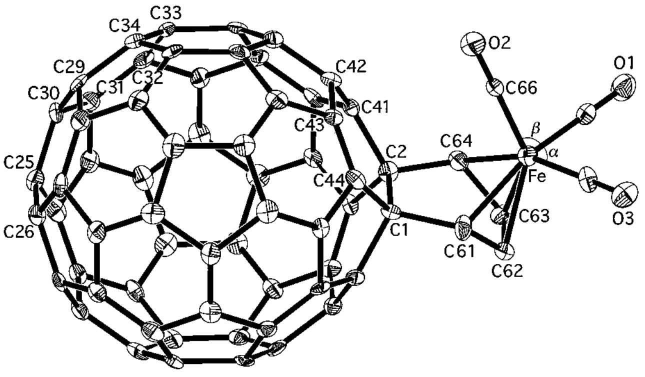

Figure 1. ORTEP representation of the X-ray crystal structure of **1**. Selected bond lengths (Å): C1−C2 = 1.586(9), Fe−C61 = 2.091(8), Fe−C62 = 2.055(7), Fe−C63 = 2.051(7), Fe−C64 = 2.102(7).

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

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S0276-7333(96)00118-5 CCC: $12.00

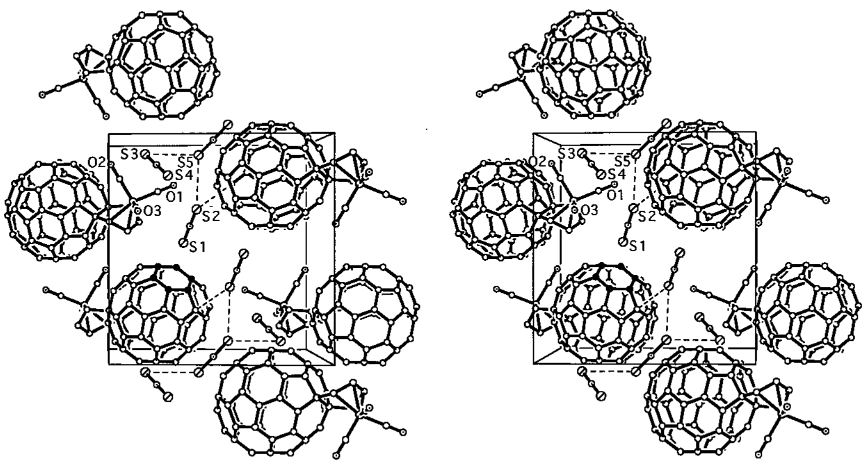
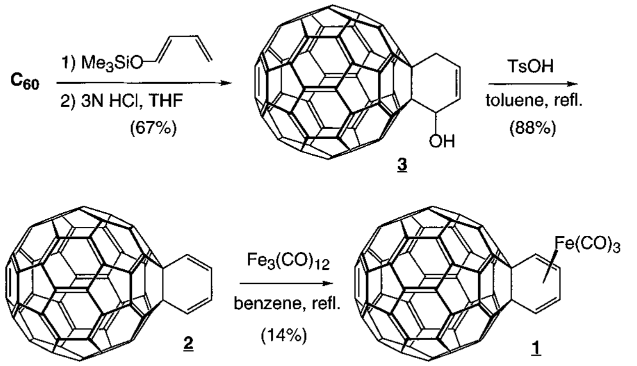


Figure 2. Stereoview of the unit cell for **1** showing close contacts between CS_2 molecules and atoms from the C_{60} surfaces and carbonyl ligands. Selected distances (Å): S5−S3 = 3.582, S5−S2 = 3.611, S2−C25 = 3.394, S1−C29 = 3.759, S1−C30 = 3.604, S1−C31 = 3.461, S1−C32 = 3.467, S1−C33 = 3.650, S1−C34 = 3.795, S3−O2 = 3.389, S4−O3 = 3.692.

Scheme 1



benzene under argon over 3 h. Chromatographic purification of the resulting material on silica gel gives the title compound **1** as a brown solid in 14% yield. This low yield presumably reflects the great instability of diene **2**.[7,9]

Compound **1** is stable for only a short time in solution and for longer periods in the solid state. The ^1H NMR of **1** in $CS_2/CDCl_3$ shows the upfield shift of the second-order AA′BB′ system (δ 4.74, δ 6.13) compared to **2** (AA′BB′ centered at δ 6.60). Due to the poor solubility of **1** in all solvents investigated, its ^{13}C NMR spectrum is not completely resolved in the C_{60} region (25 signals), but the chemical shifts of the two olefinic carbons bonded to iron at 70.96 and 87.35 ppm (CS_2/C_6D_6, 5:1) show the expected upfield shift compared to **2**. The stretching frequencies for the carbonyl groups in the FT-IR spectrum of **1** appear as three strong bands at 2057, 1992, and 1985 cm^{-1}, values that do not greatly differ from those of other (η^4-diene)$Fe(CO)_3$ complexes.[10]

Crystals of compound **1** suitable for X-ray diffraction were grown by slow evaporation at 0 °C from CS_2,[11] the only solvent in which this complex is significantly soluble. The molecular structure of **1** is shown in Figure 1. It is interesting to notice the close proximity of the apical C66-O2 carbonyl moiety to the C_{60} surface. The contact distances for O2−C43, O2−C42, C66−C44, and C66−C41 are 3.24, 3.23, 3.49, and 3.49 Å, respectively, values that fall well within the van der Waals distances between these atoms. The steric compression between the $Fe(CO)_3$ and C_{60} moieties is mostly expressed in the dramatic increase of the dihedral angle between the planes defined by C61−C62−C63−C64 and C61−C1−C2−C64, which is 43.8°. This value is well above the range of 36.3°−39.9°, with an average of 38.3°, seen in other (η^4-1,3-cyclohexadiene)$Fe(CO)_3$ complexes.[12] More significantly, there is an unexpected dihedral angle deviation of 3.4° between the planes defined by C61−C1−C2−C64 and C1−C2−C25−C26. This is a strong indication for a significant steric repulsion existing between the (η^4-1,3-cyclohexadiene)$Fe(CO)_3$ and C_{60} moieties. Interestingly, this repulsion is not expressed in the location of the iron atom in relation to the diene framework or in the angles α and β (93.6(3) and

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(9) The characterization of complex **1** proved to be very difficult (see Supporting Information). For example, a very weak parent ion was observed only once after repeated mass spectroscopic attempts by FAB (UCLA and UC Riverside). Also, due to the difficulty in synthesizing complex **1**, in part due to the extreme light-/air-sensitive nature of **2**, there was insufficient material available for submission of **1** for elemental analysis.

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(11) Crystal data for **1**: $C_{67}H_4FeO_3 \cdot 2.5CS_2$, M_r = 1102.92, monoclinic, space group $P2_1/c$, a = 14.01(1) Å, b = 14.41(1) Å, c = 19.68(1) Å, β = 95.97(2)°, V = 3951(5) Å^3, Z = 4, ρ_{calcd} = 1.85 g cm^{-3}, $F(000)$ = 2204, μ = 6.98 cm^{-1}. The intensities were measured at 156 K using a Picker (Crystal Logic) diffractometer (λ (Mo Kα) = 0.710 73 Å, graphite crystal monochromator, $\theta-2\theta$ scan, $2 \le 2\theta \le 60°$) on a crystal with dimensions 0.05 × 0.22 × 0.27 mm. An absorption correction based on Ψ scans was applied. Three standard reflections were measured every 97 reflections. Of the 11 171 independent reflections collected, 4200 with $I > 3\sigma(I)$ were used for the refinement. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares using the UCLA crystallographic package to R_F = 0.060, R_w = 0.066, and GOF = 1.621 for 719 parameters (weighting scheme $w^{-1} = \sigma^2(F_o^2)$) and highest difference peak 1.08 Å^{-3} close to Fe). One solvent CS_2 sulfur (S5) was distorted and refined with equal occupancy at two positions.

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98.9(3)°, respectively), which fall within normal values.[12] A view of the crystal lattice shows that there are two and a half CS_2 molecules per complex **1** in the unit cell (Figure 2). The CS_2 molecules form a van der Waals bonded network as shown by the close contacts reported in Figure 2. Also shown are close contacts between S2 and carbon C25 of a C_{60} sphere (3.394 Å), as well as between S1 and the six-membered ring formed by C29−C30−C31−C32−C33−C34 (shaded carbons, 3.461−3.795 Å range). The CS_2 molecule defined by S3−C69−S4 is sitting in close proximity to the carbonyl oxygen atoms O2 and O3 (3.389 and 3.692 Å, respectively).

The electrochemistry of **1** is currently under investigation, as is its chemical reactivity. In particular, the substitution of the apical carbonyl group by electron-donating ligands,[13] such as *para*-substituted aryl isocyanides, will allow us to gain additional insight into the $\pi-\pi$ interactions existing in **1** and the potential of these derivatives as novel NLO materials.

Acknowledgment. This work was supported by an Arnold and Mabel Beckman Young Investigator Award and NSF Young Investigator award (No. CHE-9457693) to Y.R. A.L.V. acknowledges the Ministerio de Educacion y Ciencia of Spain for a postdoctoral fellowship.

Supporting Information Available: Text giving details of the experimental procedure and characterization of **1**, figures giving ^1H and ^{13}C NMR spectra for **1**, and details of the X-ray structure of complex **1**, including a fully labeled view of the structure and tables of atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths (17 pages). Ordering information is given on any current masthead page.

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