Communications to the Editor

Synthesis and X-ray Structure of a Diels–Alder Adduct of C_{60}

Yves Rubin,* Saeed Khan, Darón I. Freedberg, and Chahan Yeretzian

Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024-1569

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Since the achievement of the preparative-scale isolation of buckminsterfullerene (C_{60}),[1,2] efforts to prepare derivatives of C_{60} have led to the synthesis and X-ray characterization of osmylated[3] and platinum complexes[4] and, subsequently, of several other derivatives.[5] Buckminsterfullerene undergoes Diels–Alder reactions with anthracene, furan, and cyclopentadiene.[6] However, no X-ray crystallographic characterization of these Diels–Alder adducts has been reported, and their mass spectral characterization is hampered because they undergo fast cycloreversion to their components and only C_{60} is observed.[6,7] To solve these problems, we propose a concept in which the aromatization of intermediate **3** (Scheme I), resulting from Diels–Alder cycloaddition of C_{60} and **2**, provides increased overall stability to the resulting adduct **1**.[8] Thus, for compound **1** to undergo a retro-Diels–Alder reaction providing free C_{60}, the stabilization energy provided by the aromatic system has to be overcome to give also the unstable *o*-quinodimethane intermediate **4**.[9,10]

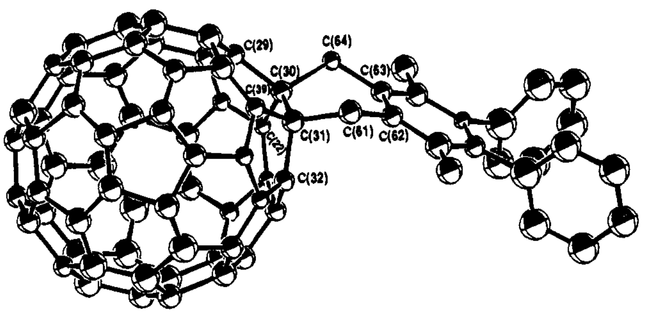
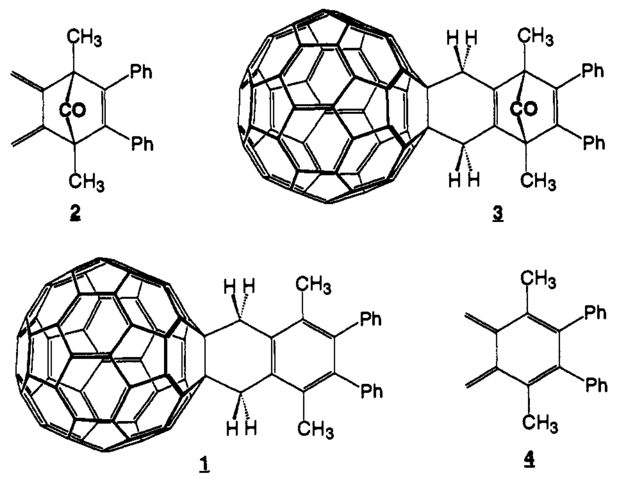


Figure 1. X-ray crystal structure of the Diels–Alder adduct **1**. A solvent molecule of 1,2-dichlorobenzene in the crystal lattice is not shown.

Scheme I



We now report that the reaction of C_{60}[11] with 1.5 equiv of compound **2**[8] affords the stable adduct **1** in 60% yield (toluene, reflux, 5 h) after silica gel chromatography with toluene/hexane, (9:1)–(6:4).[12] Monoadduct **1** is isolated as black, prismatic single crystals by diffusion–crystallization from *o*-dichlorobenzene/cyclohexane. The crystal structure of **1** is shown in Figure 1.[13] As

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(12) Representative physical data for adduct **1**: mp >360 °C; ^{1}H NMR (CS_2/CD_2Cl_2, 5:1, −42 °C) δ (ppm) 2.29 (s, 6 H, CH_3), 4.61 (d, J = 13.8 Hz, 2 H, CH_2), 4.79 (d, J = 13.8 Hz, 2 H, CH_2), 6.95–7.15 (m, 10 H, Ph); ^{13}C NMR (CS_2/acetone-d_6, 2:1, 2-day accumulation) δ (ppm) 18.0, 42.1, 66.3, 126.5, 128.1 (br), 130.8 (br), 131.3, 136.2, 140.7, 141.4, 141.7, 142.1, 142.5, 142.7, 143.0, 143.6, 145.2, 145.9 (br), 146.3, 146.7, 146.9, 148.1; UV/vis ($CHCl_3$) λ_{max} (nm) 258 (ϵ 105 900), 310 (34 900), 323 sh (32 000), 407 sh (5770), 435 (4320), 704 (570); LD-TOF MS, m/z 1004 (M^+, 2), 720 (M^+ − 4, 100). Anal. Calcd for $C_{82}H_{20}\cdot C_6H_4Cl_2$ (1152.08): C, 91.75; H, 2.10. Found: C, 91.59; H, 1.85.

(13) Compound **1** ($C_{82}H_{20}\cdot C_6H_4Cl_2$; M_r = 1152.08) crystallized in the monoclinic space group $P2_1/n$ with cell dimensions of a = 16.293 (3) Å, b = 18.008 (4) Å, and c = 16.954 (4) Å, β = 105.56 (2)°, V = 4791.9 Å^3, and an occupation of Z = 4 in the unit cell. Data were collected at 20 °C on a Rigaku AFC5R diffractometer using graphite-monochromated Cu Kα radiation, to a maximum 2θ = 120°, giving 6420 unique reflections; the structure was solved by direct methods (SHELX86), yielding R = 0.098, R_w = 0.105 for 1315 independent reflections with $I > 3\sigma(I)$.

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with other adducts,[3-5] cycloaddition of 2 to C_{60} occurs across a 6,6 ring junction of the framework. The average bond lengths for the 5,6- and 6,6-junctions in the C_{60} framework, other than those related to atoms connected to C(30) and C(31), are 1.43 (4) and 1.39 (4) Å, respectively, in good agreement with the observed values for the osmylated and platinum complexes.[3b,4b] The four sp^2–sp^3 bond lengths C(22)–C(30), C(29)–C(30), C(31)–C(32), and C(31)–C(39) average 1.52 (4) Å, and the C(30)–C(31) bond length is 1.62 (4) Å. These values reproduce almost exactly those of the osmate adduct.[3b] It seems likely that the length of the C(30)–C(31) bond is greatly increased because the overall bending deformation of the sp^3 angles at C(30) and C(31) is accommodated at the cost of increased bond stretching. Figure 1 shows that the cyclohexene unit defined by C(30)–C(31)–C(61)–C(62)–C(63)–C(64) is clearly in a stable boat conformation. The ground-state conformation of cyclohexenes is generally a C_2-symmetrical half-chair.[14a] The angle between the two mean planes defined by C(61)–C(31)–C(30)–C(64) and C(61)–C(62)–C(63)–C(64) is 135.0 (3)°, and the corresponding dihedral angles are planar within ±5°.

The UV/vis spectrum of 1[12] has absorption features virtually identical with those of the related dioxirane adduct.[5g] The LD-TOF mass spectrum of 1 shows that our working hypothesis is valid:[12] the parent ion P (m/z = 1004), although weak relative to that of C_{60} (m/z = 720), is clearly observed in contrast to other Diels–Alder adducts.[6,7,10] In the ^{13}C NMR spectrum of 1,[12] the fullerene region of the spectrum (140–150 ppm) has three peaks corresponding to two carbon atoms and 11 corresponding to four carbon atoms (a broad signal at 145.9 ppm integrates to 12 carbons). The C(30) and C(31) carbon atoms appear at 66.3 ppm and the CH_3 and CH_2 groups at 18.0 and 42.1 ppm, respectively. Five signals are observed for the three tertiary and four quaternary aromatic carbon atoms of the diene component in the binary solvent systems used (CS_2/$CDBr_3$ and CS_2/acetone-d_6). However, the relative intensities of these peaks (for carbons with similar environments) imply overlap of some of the absorptions. Interestingly, the 500-MHz ^{1}H NMR spectrum of 1 at 26 °C displays a broad doublet centered at 4.73 ppm for the two methylene protons. The doublet coalesces at 35 °C, reflecting conformational exchange between the two boat forms of the molecule (the methyl groups appear as a sharp singlet at 2.29 ppm). Variable temperature experiments reveal that the ring inversion is in the slow exchange region below −20 °C, giving an AB quartet with a chemical shift difference of 94.8 Hz (J = 13.8 Hz).[15] Our experiments yield an activation energy $\Delta G^{*} = 14.6 \pm 0.1$ kcal/mol for the boat-to-boat barrier of inversion in 1. If the transition state for this inversion is planar, the barrier is substantially higher than the calculated (MM3)[16] potential energy difference between the boat and planar conformations of cyclohexene (7.5 kcal/mol).[14] The high barrier of inversion in 1 can be attributed to severe torsional and angular constraints imparted by the rigidity of the C_{60} backbone.[17] Experimental and theoretical studies with model compounds are under way to further assess the origin of this effect.

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Supplementary Material Available: Experimental details of the crystal structure determination for 1, fully labeled view of the structure, and tables of atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths (15 pages); listing of observed and calculated structure factors for 1 (8 pages). Ordering information is given on any current masthead page.

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Generation and Characterization of Isomeric Iron–Silylene and Iron–Silene Cationic Complexes in the Gas Phase

R. Bakhtiar, C. M. Holznagel, and D. B. Jacobson*

Department of Chemistry
North Dakota State University
Fargo, North Dakota 58105-5516

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Transition metal–silylene complexes ($L_nM{=}SiR_2$) are postulated intermediates in a number of transition metal-mediated transformations, including Rochow's direct process,[1] catalytic redistribution of silanes,[2] various silylene-transfer reactions,[3] and dehydrogenative coupling reactions of silanes with transition metals.[4,5] Although transition metal–carbene, –germylene, –stannylene, and –plumbylene complexes are well-known, the corresponding transition metal–silylene species have been synthetically elusive with silylene complexes being only recently generated and characterized.[6-8] The related transition metal–silene complexes ($L_nM(R_2Si{=}CR_2)$) have been proposed as intermediates in metal-mediated rearrangements of organosilicon ligands,[9,10] including β-hydrogen transfer of a bound silyl group.[9a,11] Stable transition metal–silene complexes have recently been synthesized and characterized.[12,13] The difficulty in synthesizing

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* Author to whom correspondence should be addressed.

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