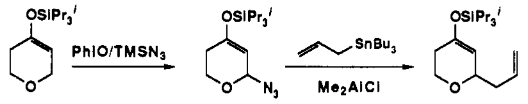
Scheme IV



16 17 18(62%)

of allyltri-*n*-butylstannane to enones is known,[6] the regiospecific trapping of the enolate with silylating agents, particularly TIPSCl or TIPSOTf, is a low-yielding reaction.[7] Consequently, the formation of **8** (80%) is noteworthy. Acetylenic anions are nontransferable ligands in organocuprate chemistry, and indirect methods have been developed to make β-acetylenic ketones.[8] Recently Kim[9] has reported the trialkylsilyl triflate promoted addition of alkynylzinc to enones. The enonium ion **2a** can be trapped with terminal acetylenes by treatment with *n*-BuLi followed by Me$_2$AlCl to give excellent yields of **9**, **10**, and **11** (98, 70, and 84%, respectively). Trimethylsilyl enol ethers trap **2a** to give the mixed TIPS enol ether-ketones **12** and **13** (3:1 diastereomers).[10] This transformation should find useful applications since it allows direct differentiation between the two ketone functionalities. Hydrozirconation of phenylacetylene followed by Me$_2$AlCl and addition of **2** gave the styrene **14** (46%).[11]

It is possible to perform a one-pot conversion of a TIPS enol ether into its β-carbon-substituted derivative. This is illustrated in Scheme IV for the conversion of the 4-pyranone TIPS enol ether **16** into **17** (not isolated) and for the direct treatment with allyltri-*n*-butylstannane/Me$_2$AlCl to give the β-allyl adduct **18** (62%).

This simple and versatile new methodology should find many applications in both the individual reactions and overall strategies of organic synthesis.

Acknowledgment. The National Institutes of Health and the National Science Foundation are thanked for their support of this research (GM 32718). Rhône Poulenc are thanked for a graduate fellowship (J.L.).

Supplementary Material Available: Listings of spectral details for compounds **4–15** and **18** (11 pages). Ordering information is given on any current masthead page.

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Unusual Electrochemical Properties of the Higher Fullerene, Chiral C_{76}

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Approximately a year ago, it was discovered that the fullerenes C_{60} and C_{70} have an exceptionally high electron affinity. Two,[1a] three,[1b,c] four,[1d] and five reversible reduction steps[1e] have been recorded for C_{60}, and the two fullerenes were found to have essentially the same redox properties.[1b] No *reversible* oxidation waves were observed in the cyclic voltammograms of both carbon spheres. An explanation for the high electron affinity in terms of pyracyclene units was proposed and shown to be a good model for predicting the chemical reactivity of C_{60}.[1b] Recently, some of us reported the isolation in pure form and structural characterization of three higher fullerenes, chiral C_{76}[2] (Figure 1) and the two isomers C_{2v}-C_{78} and D_3-C_{78}.[3] The onset of the electronic absorption by these compounds occurs at much lower energy than the optical absorption onset measured for C_{60} and C_{70}, and the result of calculations on the electronic structure of the higher fullerenes was used to predict that C_{76} would be both a better donor and a better acceptor than C_{60}.[2,4] Since milligram quantities of the title fullerene have become available in the recent past, it was imperative to determine its electrochemical properties by cyclic voltammetry (CV).

For the isolation of the higher fullerenes, C_{60} and C_{70} were first removed by two chromatographic runs on neutral alumina with hexanes/toluene (95:5) as the eluent. The higher fullerene fraction was subsequently separated in three sequential runs on a 25 × 2.5 cm Vydac 201-TP C18 reversed-phase column with acetonitrile/toluene (50:50) as the eluent, giving pure C_{76}, C_{2v}-C_{78}, and D_3-C_{78} as well as a C_{84} fraction containing two isomers.[3,5-7]

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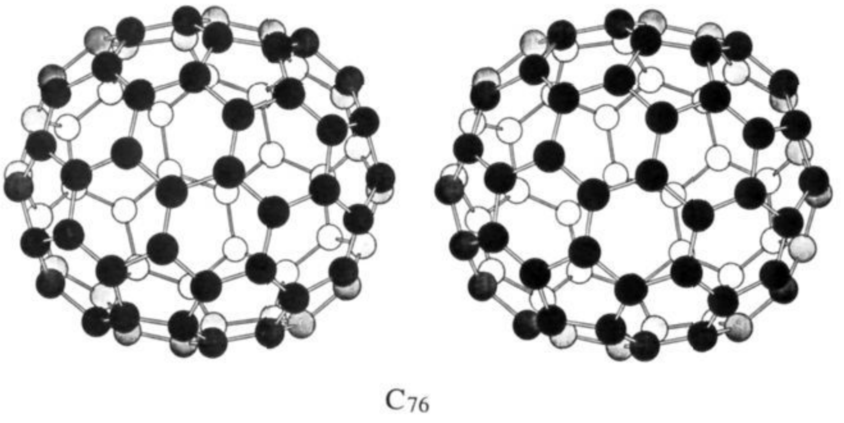

Figure 1. Stereodrawing of C_{76}.

Table I. Half-Cell Potentials[a]

compd	scan rate (mV/s)	half-cell potential (mV) THF	PhCN	CH_2Cl_2
C_{76}	100	$+354,^{b,f}$ $-64,^{g}$ $-560,^{h}$ $-1161,^{i}$ $-1605,^{j}$ -2112^{k}	$-246,^{h}$ $-674,^{i}$ -1224^{j}	$-287,^{h}$ $-620,^{i}$ -1065^{j}
C_{76}	1000	$+349,^{b,f}$ $-46,^{g}$ $-564,^{h}$ $-1155,^{i}$ $-1606,^{j}$ -2110^{k}	$-240,^{h}$ $-670,^{i}$ $-1200,^{j}$ -1535^{k}	$+1360,^{c,e}$ $+905,^{c,f}$ $+500,^{c,g}$ $-283,^{h}$ $-628,^{i}$ $-1705,^{j}$ -1495^{k}
C_{60}	100	$-228,^{h}$ $-826,^{i}$ $-1418,^{j}$ -1916^{k}	$-392,^{h}$ $-812,^{i}$ -1298^{j}	$-486,^{h}$ $-854,^{i}$ -1339^{j}
Fc[d]	100	+620	+524	+503
rest potentials of C_{76} (mV)		−299	+125	+39

[a] Half-cell potentials are defined as $E_1 = {}^1/_2(E_{p,red} + E_{p,ox})$; 0.1 M Bu_4NBF_4, electrolyte; Ag/AgCl, ref. [b] Due to adsorption (peak separation <59 mV). [c] Irreversible oxidation peak. [d] Fc = ferrocene. [e–k] Oxidation couples corresponding to the given potentials: *e*, (+3/+2); *f*, (+2/+1); *g*, (+1/0); *h*, (0/−1); *i*, (−1/−2); *j*, (−2/−3); *k*, (−3/−4).

Figure 2 shows typical cyclic voltammograms of C_{76} and, for comparison, of tetrathiafulvalene (TTF) and C_{60}, recorded in THF with a commercial BAS 100A apparatus. Table I shows the solvent and scan rate effect on the position of the voltammetric waves. All values are relative to Ag/AgCl with internal ferrocene for calibration. The following are salient features:

(1) In sharp contrast to C_{60} and C_{70}, in THF, the higher fullerene exhibits both reversible reduction *and* oxidation waves. In addition to four reduction steps, the CV of C_{76} shows one reversible oxidation step.[8] We propose that the extended linear benzo- and cyclopentadieno-annellated acene substructures present in the higher fullerene but absent in C_{60} and C_{70} are responsible for the observed oxidation at remarkably low potential.

(2) The reduction waves of C_{76} do not correspond to those of C_{60} (and C_{70}). The only feature that the higher fullerene has in common with C_{60} and C_{70} is that there is no apparent correlation of the CV waves with solvent polarity.

(3) Whereas high-level calculations using density-functional theory[4] predicted that the HOMO–LUMO gap in C_{76} should be on the order of 1.07 eV, the "electrochemical gap" found by us is only approximately 0.4 eV.

(4) In THF, the higher fullerene shows a CV wave at a potential which is less positive than the first wave of TTF and should therefore be more easily oxidized.

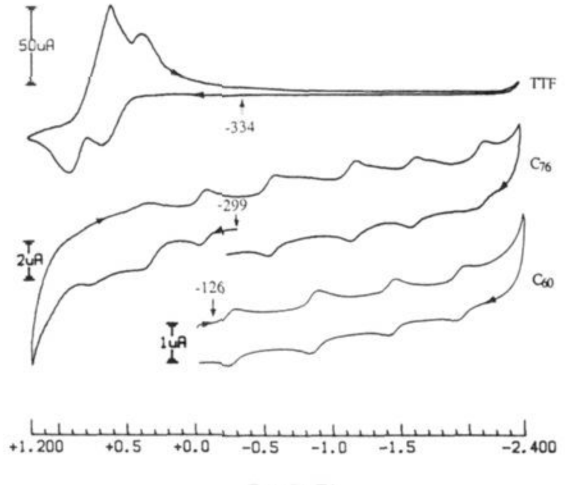

Figure 2. Cyclic voltammograms of TTF, C_{76}, and C_{60} in THF with 0.1 M Bu_4N^+ BF_4^- at ambient temperature. The arrows point to rest potentials. Working and counter electrodes were Pt, the geometric area of the working electrode was 0.0314 cm^2, the reference electrode was Ag/AgCl, and the scan rate was 1000 mV/s (Table I). The concentration of C_{76} is 0.7 mM; that of C_{60} is <0.5 mM (solubility problems prevented accurate determination).

(5) In benzonitrile (scan rate 100 mV/s), the first reduction wave of C_{76} is more positive than that of C_{60} by 146 mV. In CH_2Cl_2, compared to C_{60}, the corresponding wave is more positive by 199 mV. In these two solvents, the oxidation wave is shifted to more positive potentials than in THF and, furthermore, becomes irreversible.

Thus, the higher fullerene C_{76} is expected to exhibit organic electron donor properties, and acceptor-doped materials should be stable. This exciting possibility is currently being actively pursued.

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(8) It is possible that another, more difficult oxidation at higher positive potential will be observable under other conditions, which will have to be developed in the future.

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A Metalloporphyrin–Carborane Sandwich Compound: Synthesis and X-ray Crystal Structure of (OEP)Zr(η^5-1,2-$C_2B_9H_{11}$)

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Metallocarboranes containing a wide variety of metal centers, cluster geometries, and coligands have been studied in recent years.[1-10] The recent synthesis of metalloporphyrin-η^5-cyclopentadienyl compounds of scandium[11] suggested to us that η^5-7,8-dicarbolide-containing species related to these compounds should be at least as stable. Compounds containing both a porphyrin and a carborane have been studied previously,[12] in particular for their potential use in biochemical applications such as boron neutron capture therapy.[13] We sought to extend this chemistry to what we believed would be a synthetically much simpler and more versatile approach, wherein the carborane and porphyrin ligands were bound to the same metal in a novel sandwich structure. We now describe the first example of a such a compound, the π-sandwich species (OEP)Zr(η^5-7,8-$C_2B_9H_{11}$) (OEP = dianion of octaethylporphyrin). It is interesting to note that bis-porphyrin sandwiches Zr(por)$_2$[14,15] and the zirconacarborane $[Zr(1,6\text{-}C_2B_{10}H_{12})]^{2-}$[16] have been reported previously.

The simple metathesis reaction between (OEP)ZrCl$_2$[17] and the 7,8-dicarbolide anion[18] $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ in refluxing THF proceeds as shown in eq 1.

$$(OEP)ZrCl_2 + Na_2C_2B_9H_{11} \rightarrow (OEP)Zr(\eta^5\text{-}C_2B_9H_{11}) + 2NaCl \quad (1)$$

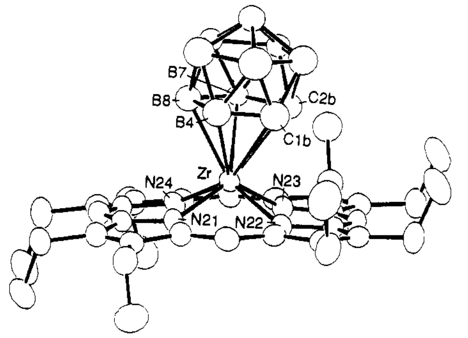

Figure 1. ORTEP view of the molecular structure of (OEP)Zr(η^5-$C_2B_9H_{11}$). Selected distances (Å) and angles (deg): Zr–N(av), 2.214 (4); Zr–C1B, 2.586 (9); Zr–C2B, 2.549 (7); Zr–B4, 2.539 (10); Zr–B7, 2.482 (8); Zr–B8, 2.488 (9); N21–Zr–N23, 132.1 (2); N22–Zr–N24, 131.5 (2); N22–Zr–C1B, 75.5 (2); N24–Zr–C1B, 153.0 (2).

The product precipitated from the reaction solution over the course of several hours; recrystallization from dichloromethane/diethyl ether afforded the material as an analytically pure dichloromethane solvate in 74% yield. It is insoluble in hydrocarbons, but crystallizes as large dark red needles from a variety of polar solvents such as dichloromethane, acetonitrile, and pyridine. The complex is air-stable as a solid or in solution and may be heated to over 480 °C without melting or noticeable decomposition. It has been fully characterized by MS, NMR spectroscopy, and X-ray crystallography.[19]

In the EI MS, the highest mass peak corresponds to the parent ion at *m/e* 755 followed by loss of the carborane fragment to give the base peak at *m/e* 622 [(OEP)Zr$^+$]. A very strong B–H stretch at 2514 cm^{-1} in the infrared spectrum is in the usual range for typical carborane complexes containing the (η^5-$C_2B_9H_{11}$) ligand.[1] Multinuclear NMR spectroscopy provided valuable evidence for the solution structure of the compound. As expected, the methylene protons of the OEP ligand are diastereotopic and give rise to two complex multiplets centered at δ 4.1 ppm in the ^1H NMR spectrum. For the carborane ligand, the two CH groups appear as a singlet at −2.84 ppm. This is an unusually high-field resonance for this signal, which is typically found around 2–4 ppm. However, we note that upfield shifts of a similar magnitude are found for the η^5-cyclopentadienyl ligands in the related (OEP)Sc(η^5-C_5R_5) derivatives[11] and are attributable to shielding by the aromatic OEP ligand. A broad upfield signal centered at −3.4 ppm is assigned to the three BH protons of the $C_2B_3H_5$ ring, whereas the remaining BH signals appear as a very broad resonance at δ 0.5 ppm. There are no extraordinary shifts in either the ^{13}C or ^{11}B NMR spectra. Thus, the $^{13}C\{^1H\}$ spectrum of the sandwich complex shows a broad, weak singlet at δ 49.0 ppm due to the carborane carbons along with the usual OEP signals. The usual five-peak pattern commonly observed for η^5-7,8-$C_2B_9H_{11}$ derivatives was seen in the $^{11}B\{^1H\}$ NMR spectrum.[7] Conclusive evidence for the pentahapto sandwich structure was obtained by X-ray crystallography (Figure 1).[20]

Crystals suitable for X-ray diffraction were grown from dichloromethane/pyridine. The zirconium occupies the 12th vertex

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(19) Selected characterization data for (OEP)Zr(η^5-$C_2B_9H_{11}$): UV/vis λ (log ϵ) (10^{-5} M, CH_2Cl_2) 400 (4.4), 526 (3.2), 564 (3.6); mp >480 °C; IR (Nujol mull) 2514 vs (ν_{B-H}); ^1H NMR (400 MHz, $CDCl_3$) 10.65 (s, 4 H), 4.29 (m, 8 H), 4.15 (m, 8 H), 1.89 (t, 24 H), 0.4 (v br), −2.84 (s, 2 H), −3.4 (v br); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 147.8, 144.3, 102.6, 49.0, 20.2, 18.3; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, referenced to external $BF_3 \cdot Et_2O$ at 0 ppm) −0.276, −5.475, −11.61, −14.36, −22.99. Anal. Calcd for $C_{38.25}H_{55.5}B_9Cl_{0.5}N_4Zr$: C, 59.1; H, 7.19; N, 7.20. Found: C, 58.8; H, 7.52; N, 7.63.

(20) Crystal data for $ZrB_9N_4C_{38}H_{55}$: space group $P\bar{1}$ with $a = 10.966$ (2), $b = 12.707$ (2), $c = 14.832$ (2) Å; $\alpha = 83.501$ (4), $\beta = 85.314$ (5), $\gamma = 78.316$ (4)°; $V = 2007$ Å^3, $d_{calcd} = 1.26$ g cm^{-3}, and $Z = 2$. Data were collected at 25 °C with Mo Kα ($\lambda = 0.7107$ Å) and $2\theta = 45°$. A total of 5784 unique data were collected. The structure was solved by Patterson methods and refined by least-squares and Fourier techniques using 438 variables against 3915 data, for which $F^2 > 3\sigma(F^2)$, to give $R = 5.2\%$, $R_w = 6.2\%$, and GOF = 1.67. The crystal structure was determined at UCLA.

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