# Unusual Functionalization of $C_{60}$ *via* Hydrozirconation: Reactivity of the $C_{60}$–$Zr^{IV}$ Complex *vs.* Alkyl–$Zr^{IV}$ Complexes

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The reaction of the $C_{60}$ hydrozirconation adduct **1** with *N*-bromosuccinimide and *m*-chloroperbenzoic acid leads to the formation of Diels–Alder products with bromo- and hydroxy-cyclopentadiene, respectively.

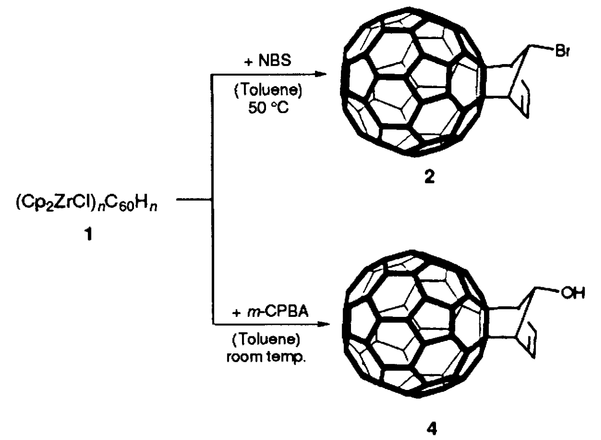
The reaction of alkenes or alkynes with Schwartz's reagent. $Cp_2Zr(H)Cl$ with Cp = $\eta^5$-$C_5H_5$, is called hydrozirconation.[1] Alkenes produce synthetically useful intermediates $Cp_2Zr(R)Cl$ with R = alkyl. The cleavage of the Zr–C bond with electrophilic reagents leads to various products R–X (with *e.g.* X = Cl, Br, I, OH, H).[1,2] The early work of Fagen *et al.* and Balch *et al.* proved that the addition of organometallic species to fullerenes takes place exclusively to 6,6 fusions. Futhermore, these reactions could be stopped after one transition metal complex has been added to the fullerene cage.[3,4] Therefore hydrozirconation should be a feasible route to a selective *mono*functionalization of fullerenes.

Recently, we could characterize the hydrozirconation adduct of $C_{60}$, $(Cp_2ZrCl)_nC_{60}H_n$ **1** with $n$ = 1, 2, 3 [eqn. (1)].

$$Cp_2Zr(H)Cl + C_{60} \xrightarrow[\text{24 h, room temp.}]{\text{(Toluene)}} \underset{\mathbf{1}}{(Cp_2ZrCl)_nC_{60}H_n} \qquad (1)$$

Hydrolysis of **1** yields a mixture of $C_{60}H_{2n}$ and unreacted $C_{60}$.[5] In view of the reactivity of alkyl–$Zr^{IV}$ complexes one would expect the corresponding $C_{60}$–$Zr^{IV}$ complex **1** to be cleaved with electrophilic reagents.[1,2] But all efforts to synthesize 1-halo- and 1-hydroxy-1,2-dihydro[60]fullerenes out of **1** using electrophilic halogenation or oxidation reagents failed. When adding iodine or *N*-chlorosuccinimide to a solution of **1** a nearly quantitative decomposition to $C_{60}$ could be observed using HPLC analysis. A totally different behaviour occurred if *N*-bromosuccinimide (NBS) or *m*-chloroperbenzoic acid (*m*-CPBA) is used for cleaving the C–Zr bond in **1**. In both instances we could isolate pure products by column chromatography.

In a typical procedure a solution of $Cp_2Zr(H)Cl$ (2 equiv.) in toluene is added dropwise within 30 min to $C_{60}$ dissolved in toluene. After stirring for 24 h at room temp. the dark-red reaction mixture containing **1** is treated with 10 equiv. of NBS and heated to 50 °C overnight. Using alumina (activity I) as stationary phase and hexane–toluene (80:20, v/v) as mobile phase a pure product **2** is obtained with a yield of 35%. By switching from hexane–toluene to toluene a second product **3** could be isolated. Fig. 1 shows the HPLC chromatograms of the crude reaction mixture (I) and of the isolated product **2** (II).† In the same way the solution of **1** is treated with 10 equiv. of *m*-CPBA and stirred overnight at room temp. By use of column chromatography (alumina, activity III) with hexane–toluene (80:20, v/v) as eluent traces of unreacted $C_{60}$ and unidentified side products (probably oxides) could be removed. Switching to toluene as eluent a pure product **4** is obtained with a yield of 20%.



Scheme 1 Reaction of the hydrozirconation adduct **1** with NBS and *m*-CPBA

HRMS analysis (FAB-, matrix: 3-nitrobenzyl alcohol) of the isolated products **2**, **3** and **4** revealed the elemental composition $C_{65}H_5Br$ (calculated: 863.9575, observed: 863.9581), $C_{70}H_{10}Br_2$ (calculated: 1007.9149, observed: 1007.9085) and $C_{65}H_6O$ (calculated: 802.0419, observed: 802.0403), respectively.

Taking the results of the MS analysis into account we concluded that in the case of products **2** and **4** a monoaddition and for product **3** a bisaddition of the $C_5H_5X$ (X = Br, OH) fragment has taken place. The UV–VIS spectra of **2** and **4** in *n*-hexane are virtually identical and reproduce the spectra of other 1,2-dihydro[60]fullerenes, including $C_{60}H_2$.[5,6] As for other monoaddition products a splitting of the 527 $cm^{-1}$ IR band of the fullerene leading to a characteristic pattern between 576 and 527 $cm^{-1}$ is observed.[7] This is due to the decrease of symmetry form $I_h$ for $C_{60}$ to $C_s$ for **2** and **4**.

The experimental results could be explained best with a Diels–Alder reaction between bromo- or hydroxy-cyclopentadiene and $C_{60}$ as the dienophile (Scheme 1). Therefore, the intermediate $C_{60}$–$Zr^{IV}$ complex **1** must be cleaved by the electrophilic reagent to reform free $C_{60}$. As NBS and *m*-CPBA are used in a great excess it is possible that the substituted cyclopentadiene is formed out of the cyclopentadienyl–$Zr^{IV}$ residue. To prove this we synthesized products **2**

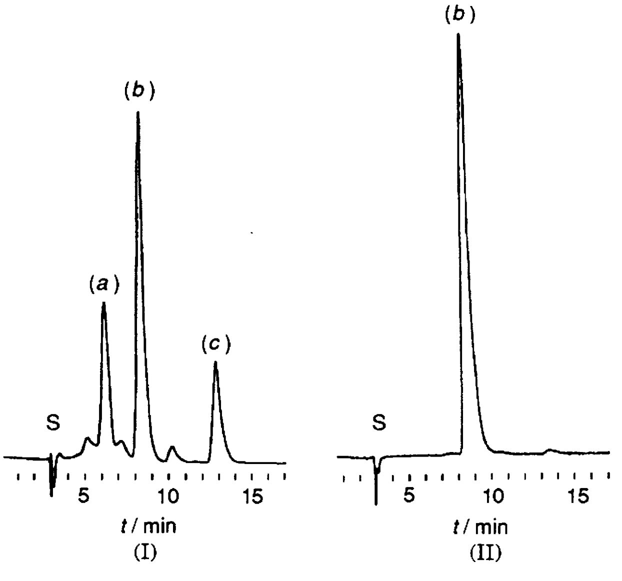


**Fig. 1** HPLC chromatograms of the crude reaction mixture (I) and of the isolated products (II) for the reaction of **1** with NBS. S: solvent, *t* retention time; peak (*a*): **3**, peak (*b*): **2** and peak (*c*): $C_{60}$.

and **4** in *one* step by mixing Schwartz's reagent, $C_{60}$ and the electrophilic reagent in the same ratio as described above.

The $^1H$ NMR spectra ($CS_2$–$C_6D_6$ 4:1, 300 MHz) of products **2** and **4** are consistent with the proposed [4 + 2] cycloaddition: δ 6.82 (2H, m, CH=), 5.82 (1H, m, CHBr), 4.44 (2H, m, CH) for **2** and 6.65 (2H, m, CH=), 4.26 [1H, m, C*H*(OH)], 4.00 (2H, m, CH), 2.14 (1H, s, OH) for **4**. The bridge hydrogen atom in both products is shifted downfield with respect to the Diels–Alder adduct of cyclopentadiene with $C_{60}$ due to the electron withdrawal of the bromine and the hydroxy group, respectively.[8]

Product **4** showed four reversible reduction waves whereas **2** exhibited only three reversible electroreductions by CV.[‡] The different behaviour of **2** could probably be explained with a loss of bromine: if the potential is swept beyond the third reduction the appearance of a new reoxidation wave in addition to the third one is observed. The half-wave potentials for the reduction of **2** are substantially more negative than that for the corresponding $C_{60}$ reduction and the potentials for **4** are more negative than the ones for **2** (Table 1). The reduction potentials depend on the electronegativities of the attached atoms: with decreasing electronegativity the half-wave potentials become more negative.[9] Therefore, **2** has to be more electronegative than **4**. As shown for other 1,2-dihydro[60]fullerenes there is a linear relationship between the first three reduction potentials and the LUMO/LUMO + 1 energy levels obtained by AM1 molecular orbital calculations.[9]

The Diels–Alder reaction could lead to two isomers: *exo* and *endo* with respect to the double bond in the norbornene portion of the molecule. We calculated the dipole moments for both isomers of **2** and **4** using the semiempirical AM1 method (Table 2). As one can see there are significant differences in the dipole moments, which should strongly affect the retention times. Thus, the HPLC chromatograms (*e.g.* Fig. 1) showed that the isolated products are pure compounds. Furthermore, the two isomers would at least have different $^1H$ NMR chemical shifts for the bridge hydrogen. However, the $^1H$ NMR spectra showed only one resonance for the bridge hydrogen of **2** and **4**, respectively. To estimate the energetic difference of the *exo* and *endo* isomer we used the total energy provided by the AM1 method (Table 2). The *endo* isomer is favoured for **2** as well as for **4**. Hence, we concluded that the isolated products are probably the *endo* isomers.

**Table 1** Half-wave potentials for the reduction of **2**, **4** and $C_{60}$. All potentials in mV *vs.* SCE. The ferrocene–ferrocenium system was measured at +494 mV

| Compound | $E_1$ | $E_2$ | $E_3$ | $E_4$ |
|---|---|---|---|---|
| $C_{60}$ | −496 | −908 | −1399 | −1896 |
| **2** | −585 | −985 | −1519 | −1860[a] |
| **4** | −671 | −1031 | −1548 | −1985 |

[a] Irreversible.

**Table 2** Relative energies (in kJ $mol^{-1}$) and dipole moments (in Debye) of the *exo* and *endo* isomers of **2** and **4** as calculated with the AM1 method

| | *exo* | | *endo* | |
|---|---|---|---|---|
| Compound | Rel. energy | Dipole moment | Rel. energy | Dipole moment |
| **2** | 11.9 | 3.5 | 0.0 | 1.8 |
| **4** | 26.8 | 5.5 | 0.0 | 2.7 |

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## Footnotes

[†] HPLC conditions: Macherey-Nagel Nucleosil $5C_{18}$ column (250 × 4 mm); particle size 5 μm; eluent toluene–MeCN 45:55; flow rate 1.0 ml $min^{-1}$; pressure: 80 bar, detection at 340 nm and with several diode array scans.

[‡] CV conditions: 0.1 mol $dm^{-3}$ tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in toluene–MeCN (80:20, v/v) at ambient temperature; scan rate: 100 mV $s^{-1}$; working electrode: glassy carbon disk electrode (METROHM); reference electrode: SCE.

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