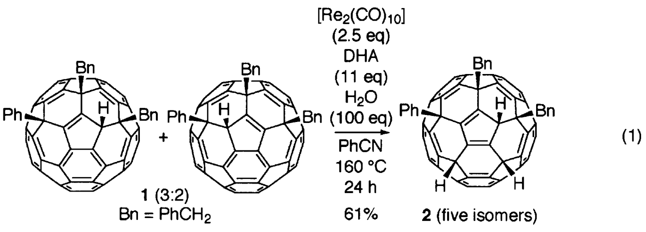
Hydrogenation of Fullerenes

Rhenium-Templated Regioselective Polyhydrogenation Reaction of [60]Fullerene**

*Motoki Toganoh, Yutaka Matsuo, and Eiichi Nakamura**

With the progress of the science of fullerenes, regioselective polyfunctionalization reactions have acquired a unique importance in the development of new research areas.[1] Owing to the isotropic structure of [60]fullerene, regiocontrol of polyfunctionalization is a fundamental problem, on which considerable effort has been expended to provide useful solutions to the synthesis of polyalkylated fullerene molecules.[2] On the other hand, in spite of a significant number of synthetic routes and suggested utilities in materials applications,[3] polyhydrogenated fullerenes can still only be produced as a mixture of many compounds owing to the lack of control of both the regioselectivity and the number of hydrogen atoms delivered to the fullerene molecule.[4] Herein we report a new class of polyhydrogenation method, a rhenium-templated transfer hydrogenation from 9,10-dihydroanthracene (DHA) to [60]fullerene or its derivatives. The reaction of a [60]fullerene adduct **1** with DHA in the presence of $[Re_2(CO)_{10}]$ and water affords cyclopentadiene **2** [Eq. (1)], which can be converted into the corresponding metal complexes, such as an iron(II) complex **3** and a rhenium(I) complex **4** (Scheme 1). The reaction with the rhenium cluster under anhydrous conditions, on the other hand, results in hydrometallation reaction that affords a variety of the η^5-Re hydrofullerene complexes (**4**, **6**, **8**, and **9**, Scheme 2). The new hydrogenation/hydrometallation can also be described as a transfer hydrogenation reaction (see below) and represents the first method for completely regiocontrolled delivery of hydrogen atoms to a fullerene molecule.[5]



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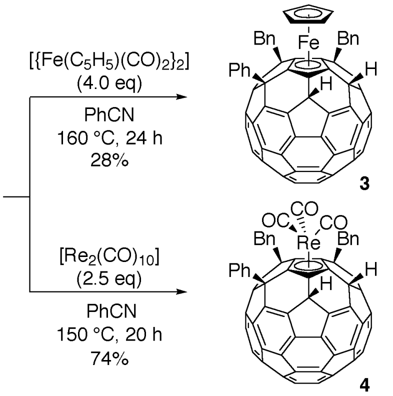
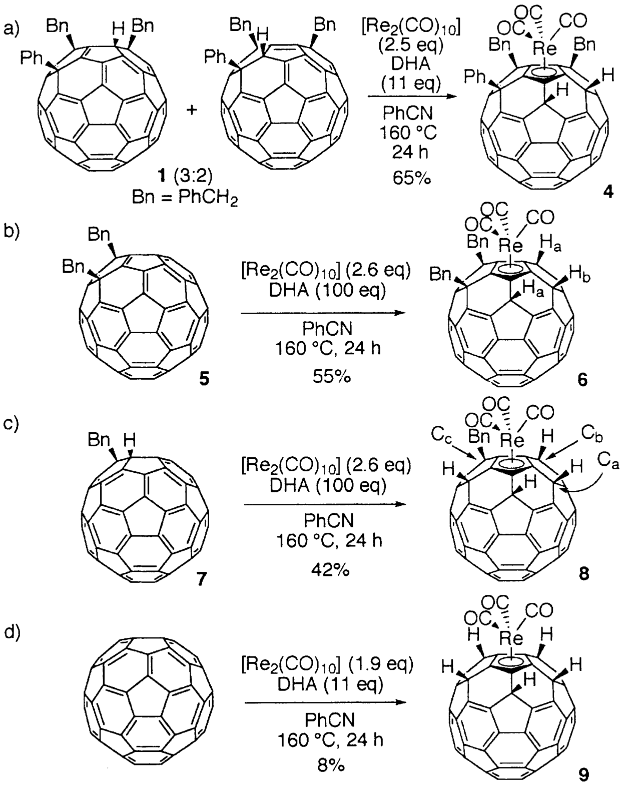


Scheme 1. Preparation of metal η^5 complexes by C–H bond activation.

The hydrogenation reaction is illustrated for the reaction of the fullerene tri-adduct $C_{60}(H)(PhCH_2)_2(Ph)$[6] (**1**) (a near 3:2 mixture of regioisomers as to the position of the hydrogen atom as shown in Equation (1)) with DHA (11 equiv) in the presence of $[Re_2(CO)_{10}]$ (2.5 equiv) and H_2O (100 equiv) in PhCN at 160 °C for 24 h [Eq. (1)]. The dihydrogenation product $C_{60}(H)_3(PhCH_2)_2(Ph)$ (**2**) was obtained in 61 % yield (obtained as a regio-mixture as to the position of the



Scheme 2. Hydrometallation reaction affording rhenium-hydrofullerene complexes.

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cyclopentadienyl hydrogen atom; all yields reported herein are based on the fullerene compound). The assigned structure rests on the ^1H NMR and mass spectra, and was subsequently confirmed by the single-crystal X-ray analysis of its rhenium derivative **4** (see below).

The cyclopentadiene **2** was readily converted into the corresponding η^5-Fe and η^5-Re complexes through C–H bond activation (Scheme 1).[7] Upon heating of **2** with $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2]$ (4.0 equiv) in PhCN at 160 °C for 24 h, **2** afforded $[(\eta\text{-}C_5H_5)Fe\{C_{60}(H)_2(PhCH_2)_2(Ph)\}]$ (**3**) in 28% yield. Similarly, treatment of **2** with $[Re_2(CO)_{10}]$ (2.5 equiv) gave $[Re(CO)_3\{C_{60}(H)_2(PhCH_2)_2(Ph)\}]$ (**4**) in 74% yield. The rhenium η^5-complex **4** showed IR (2024 and 1939 cm^{-1}), mass atmospheric pressure chemical ionization (APCI) sepctra ($[M^+]$ 1252), and NMR spectra consistent with the assigned structure. The two protons attached to the fullerene skeleton appear as doublet signals at $\delta = 5.32$ and 5.51 ppm, which are coupled with each other with $^5J_{HH} = 2.8$ Hz. In the ^{13}C NMR spectrum the signals of the two carbon atoms attached to these protons (both at $\delta = 44.35$ ppm) show the same $^1J_{CH}$ value of 145 Hz, which indicates 29% s character[8] (that is $sp^{2.4}$) of these "sp^3" carbon atoms.[9]

Unambiguous structure determination of **4** was by X-ray crystallographic analysis of a single crystal (Figure 1), obtained by slow diffusion of hexane to a CS_2 solution of **4**.[10] The X-ray data clearly indicates that cyclopentadienyl rhenium moiety is surrounded by five sp^3 carbon centers (rather than sp^2 centers) as in the penta-alkylated [60]fullerene metal η^5-complexes reported previously.[7,11] The geometry around the rhenium center is similar to that of $[(\eta\text{-}C_5H_5)Re(CO)_3]$,[12] as the three phenyl rings bound to the fullerene core in **4** point away from the metal center to minimize steric interaction with the carbonyl ligands.

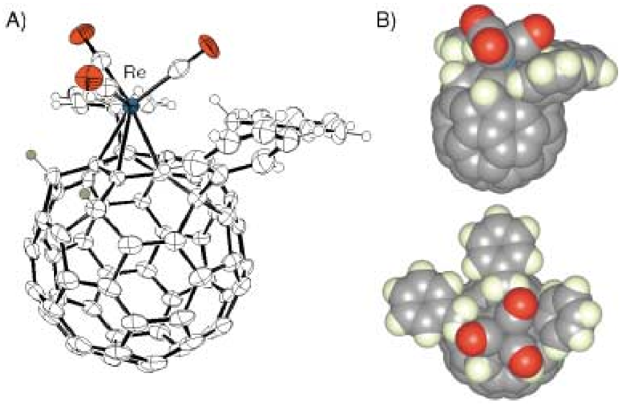

Figure 1. Molecular structure of the hydrofullerene rhenium complex **4**. A) ORTEP drawing with thermal ellipsoids at 30% probability. The CS_2 molecule found in the unit cell was omitted for clarity. B) Space-filling models.

The rhenium-templated polyhydrogenation under anhydrous conditions provides a direct entry to a variety of rhenium η^5-complexes of hydrofullerenes (Scheme 2). Treatment of **1** with DHA (11 equiv) and $[Re_2(CO)_{10}]$ (2.5 equiv) at 160 °C for 24 h in anhydrous PhCN directly afforded the rhenium complex **4** in 65% yield (Scheme 2a).[13] Similarly, the reaction of a dialkyl fullerene $C_{60}(PhCH_2)_2$ (**5**)[14] with DHA and $[Re_2(CO)_{10}]$ afforded a trihydrogenation product $[Re(CO)_3\{C_{60}(H)_3(PhCH_2)_2\}]$ (**6**) in 55% yield (Scheme 2b). The molecular weight determined from the mass spectrum (APCI, $[M^-]$ 1176) is consistent with the assigned structure. The IR (2020 and 1924 cm^{-1}) and NMR spectra are similar to those of **4**. For instance, the protons H_a and H_b are coupled to the neighboring sp^3 carbon atoms with $^1J_{CH} = 144$ Hz and 145 Hz, respectively. We therefore assigned the cyclopentadienyl rhenium structure **6** to the product. In the same manner, the reaction of a monoalkyl fullerene $C_{60}(H)(PhCH_2)$[15] (**7**) under the same conditions afforded a tetrahydrogenation product $[Re(CO)_3\{C_{60}(H)_4(PhCH_2)\}]$ (**8**) in 42% yield (Scheme 2c). The ^{13}C NMR signals indicated the presence of only three kinds of sp^3 fullerene carbon atoms ($C_a = 44.19$ ppm, $C_b = 44.56$ ppm, and $C_c = 55.77$ ppm), which indicates C_s symmetry on the NMR time scale (supported also by the ^1H NMR spectrum). Carbon atoms C_a and C_b have $^1J_{CH} = 145$ Hz. Mass (APCI, $[M^-]$ 1086) and IR spectra (2020, 1922 cm^{-1}) are also consistent with its structure.

Finally, the reaction of [60]fullerene with DHA and $[Re_2(CO)_{10}]$ afforded the hydrometallated product **9** albeit in low yield (Scheme 2d). The compound **9** had mass (APCI $[M^-]$ 996), IR (2017, 1921, and 1901 cm^{-1}) and NMR spectra consistent with the assigned structure. The ^1H NMR spectrum has only one singlet signal at $\delta = 5.23$ ppm, and the ^{13}C NMR spectrum has only nine signals (indicating C_{5v} symmetry on the NMR time scale) namely, those of an sp^3 ($\delta = 44.73$ ppm, $^1J_{CH} = 145$ Hz), an sp^2 cyclopentadienide ($\delta = 102.97$ ppm), a carbonyl carbon atom ($\delta = 190.64$ ppm), and six sp^2 carbon atoms assigned to the remaining carbon atoms of the fullerene core.

All the reactions described above proceeded cleanly and gave exclusively one regioisomer of the desired hydrogenation product, accompanied only by Diels–Alder adducts between the starting fullerene compound and anthracene (dehydrogenation product of DHA),[16] as well as recovered starting fullerene compound.[17] The solvent PhCN was uniquely effective among the variety of aromatic and other high-boiling-point solvents used. Simple polyhydrogenation products other than **2** have not been obtained to date in synthetically significant yields, this is due to the instability of such polyhydrogenated products towards oxygen and light.[5] On the other hand, the metal complexes **3**, **4**, **6**, **8**, and **9** are very stable.

The mechanism of the present reaction remains unclear. There are nonetheless pieces of experimental information that give some insight into the reaction pathway. First, consumption of [60]fullerene by reaction with DHA in the presence of $[Re_2(CO)_{10}]$ is much faster than in its absence, and, under the latter conditions, the reaction produced a mixture of various hydrogenated products, of which $C_{60}(H)_{36}$ was predominant.[4] Second, the reaction of $[Re_2(CO)_{10}]$ (2.8 equiv) with $C_{60}(H)_{36}$ (prepared by the reaction with DHA and which is thus contaminated with various other hydrogenated products) at 160 °C in PhCN did not give **9** but only produced [60]fullerene. Therefore, hydrofullerenes such as $C_{60}(H)_{36}$ are unlikely to be involved in the reaction pathway. Third, the reaction of a deuterated compound [D]**1** ($C_{60}(D)(PhCH_2)_2(Ph)$, > 99 % D) with DHA (10 equiv) and $[Re_2(CO)_{10}]$ (2.5 equiv) at 160 °C in PhCN for 24 h afforded a deuterated product [D]**4** ($[Re(CO)_3\{C_{60}(H)(D)(PhCH_2)_2(Ph)\}]$) in 17 % yield and its diprotio compound **4** in 43 % yield. It is thus likely that the cyclopentadienyl C–D bond cleavage occurred first to generate a {Re-D} intermediate (transfer deuteration), which delivers the deuterium atom back to the periphery of the cylopentadienyl moiety. Similar C–H bond activation may also be involved in the reaction of **7**. Finally, the rhenium complex **4** could not be converted into the metal-free compound **2** under the wet conditions where **2** was obtained, which suggests that **2** was not formed via **4** in Equation (1).

In summary, we have developed a new transfer hydrogenation reaction to introduce hydrogen atoms regioselectively to [60]fullerene and its derivatives. The reaction under anhydrous conditions provides a flexible method for the synthesis of the η^5-metal complexes of a variety of hydrofullerenes, while the reaction under wet conditions has proven to be effective for the synthesis of the trihydro compound **2**. In contrast to the known polyhydrogenation reactions that invariably produce mixtures of products,[5,18] the control of both the regioselectivity and the numbers of hydrogen atoms is remarkably high. The η^5-structures of the metal complexes[7,11] reported herein are the first examples of such hydrofullerenes. The similarity of the regioselectivity of the formation of **4**, **6**, **8**, and **9** to that of the regioselective polyalkylation reported previously[2b,19] suggests certain mechanistic kinship among these reactions, for example, an electron-transfer mechanism. We anticipate that the hydrofullerene metal complexes will serve as useful molecules in materials chemistry and catalysis.[1,3,20]

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