Synthesis and Reactivity of Bucky Ruthenocene Ru(η^5-$C_{60}Me_5$)(η^5-C_5H_5)

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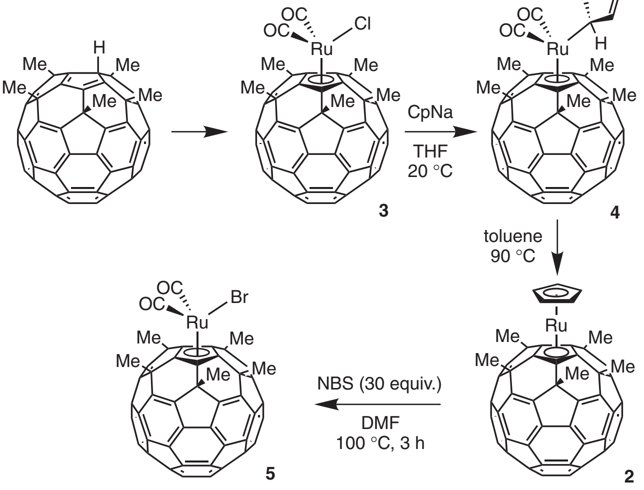
Metathetical coupling of an η^5-fullerene ruthenium complex Ru(η^5-$C_{60}Me_5$)Cl(CO)$_2$ and sodium cyclopentadienide gives a molecular hybrid of ruthenocene and fullerene, Ru(η^5-$C_{60}Me_5$)(η^5-C_5H_5) (bucky ruthenocene), the structure of which was determined by spectroscopic and crystallographic analyses. The molecule shows unique reactivity among known ferrocene and ruthenocene compounds.

Quantitative penta-addition of an organocopper reagent to [60]fullerene[1] electronically isolates one out of total 12 pentagons of the fullerene molecule to create a new cyclopentadienide (Cp) ligand embedded in the fullerene skeleton (for instance; $C_{60}Me_5$[1d] denoted hereafter as MeFCp). We recently reported the synthesis of the first "sandwich" complex in this series of compounds, Fe(η^5-$C_{60}Me_5$)(η^5-C_5H_5) (**1**),[2] where the MeFCp moiety is linked to another Cp group with an Fe(II) atom. This molecule nicknamed "bucky ferrocene" is very stable, yet may be too stable and unreactive for further chemical elaboration of the Cp ring or for the preparation of metal-containing carbon materials. We, therefore, focused on ruthenium, a neighbor of iron, because of its larger atomic radius and its electron-rich character. Herein we report the synthesis, structure, electrochemical, and reactivity studies of "bucky ruthenocene," Ru(η^5-$C_{60}Me_5$)(η^5-C_5H_5) (**2**).

The target molecule being composed of MeFCp, metal, and Cp moieties, there are a priori two synthetic schemes to obtain **2**; metal-MeFCp + Cp, and MeFCp + metal-Cp. The second approach was employed in the synthesis of bucky ferrocene,[2] since the Fe–MeFCp compounds needed in the first route are unstable. In the ruthenium chemistry, the necessary Ru–MeFCp complex is available. Thus, we first synthesized Ru(η^5-$C_{60}Me_5$)Cl(CO)$_2$ (**3**) by the reaction of [RuCl$_2$(CO)$_3$]$_2$ and $C_{60}Me_5K$ as described before.[3] This chloride complex was then allowed to react with sodium cyclopentadienide in THF. This reaction afforded an η^1-cyclopentadienyl complex, Ru(η^5-$C_{60}Me_5$)(η^1-C_5H_5)(CO)$_2$ (**4**) in 90% yield as determined by ^{1}H NMR analysis. The assignment of the η^1-structure rests on the nonequivalent signals of the Cp ring protons, which are broadened likely because of the fluxional behavior of the η^1-Cp ruthenium complex.[4] Variable temperature study and other detailed examinations were impossible, because this very unstable intermediate could not be isolated. Upon heating the reaction mixture gave the desired η^5-complex **2** and other uncharacterizable compounds. Without isolating **4**, bucky ruthenocene **2** was obtained in a single pot in 12% yield: Sodium cyclopentadienide and **3** were first mixed in THF at room temperature, the solvent was replaced by toluene and the mixture was heated at 90 °C for 5 h (Scheme 1).[5]

The bucky ruthenocene **2** was obtained as air- and moisture-stable red crystals. Spectroscopic data of **2** was similar to those of **1**; signals due to five methyl groups and cyclopentadienyl group were observed as singlet at δ 2.26 and 5.15, respectively.



Scheme 1.

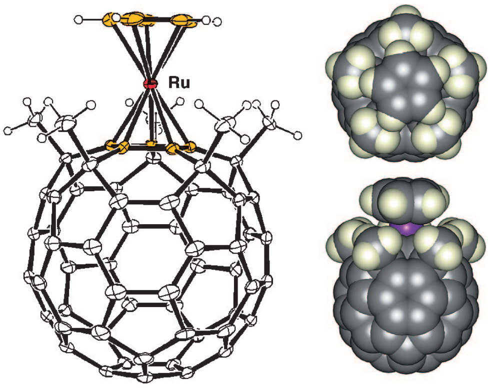


Figure 1. Molecular structure of **2**. Solvent molecules in the crystal packing are omitted for clarity. Selected bond distances (Å); Ru–C(MeFCp, averaged) = 2.20(1), Ru–C(Cp, averaged) = 2.19(1), Ru–centroid(MeFCp) = 1.837, Ru–centroid(Cp) = 1.826.

The ^{13}C NMR spectrum displayed only ten signals due to the C_{5v} symmetric structure.

The structure of **2** was unambiguously determined by X-ray analysis (Figure 1).[6] The crystal structure showed a striking difference from that of its iron analog in that the two Cp rings in **1** are eclipsed and those in **2** staggered. In the bucky ferrocene, each hydrogen atom of the top Cp ring is fitted between two adjacent methyl groups to minimize steric congestion,[2] because the carbon–Fe bond lengths are too short to comfortably accommodate the five methyl groups in the "sandwich" structure. In the crystal of the bucky ruthenocene, the longer Ru–C bond length stretches the "sandwich" structure, and hence each hydrogen atom of the Cp ligand has no contact with the methyl groups of the MeFCp ligand. The distance between the two pentagons flanking the metal is longer in **2** (3.66 Å) than in **1** (3.35 Å).

Another significant difference between the bucky ruthenocene and the bucky ferrocene is the location of the metal atom relative to the two pentagons bonded to it. Thus, the distance between the metal and each Cp carbon atoms in **2** (Ru–C(Cp), 2.19(1) Å) is essentially the same as that between the metal and each MeFCp carbon atoms (Ru–C(MeFCp), 2.20(1) Å). Note that the latter in **1** (2.09(1) Å) is substantially longer than the former (2.03(1) Å) probably owing to weaker Fe(II)–MeFCp bonding caused by the fact that the 2p carbon orbitals of the hold-back MeFCp ring point away from the iron atom.[2] The equal Ru–carbon lengths in **2**, in turn, indicate that the Ru atom of larger atomic radius and more polarizable d orbitals tolerates the 2p orbital orientation that is unfavorable for the Fe atom.

In contrast to the bucky ferrocene **1** that shows rather ill-defined electrochemical behavior,[2] **2** undergoes reversible two-step one-electron reductions in THF (-1.43 and -2.01 V, vs Fc/Fc$^+$, Figure 2a). Reduction potentials of **2** are comparable to those of the parent $C_{60}Me_5H$ ($E_{1/2} = -1.45$ and -2.07 V),[3] indicating that the electrons go into the fullerene moiety. Upon oxidation, **2** shows irreversible one-step two-electron oxidation in benzonitrile ($E_p = 0.81$ V) like the parent ruthenocene ($RuCp_2$) that is known to be oxidized in an irreversible one-step two-electron manner ($E_p = 0.30$ V).[7] Reversible oxidation of **2** was achieved by the use of $Bu_4NB[C_6H_3\text{-}(CF_3)_2\text{-}3,5]_4$ in dichloromethane: Reversible one-electron oxidation occurs at 0.85 V (Figure 2b), similar to the oxidation of $RuCp_2$ (0.56 V) by using the same electrolyte.[8] The higher oxidation potential of **2** indicates the electron-withdrawing character of the MeFCp ligand.

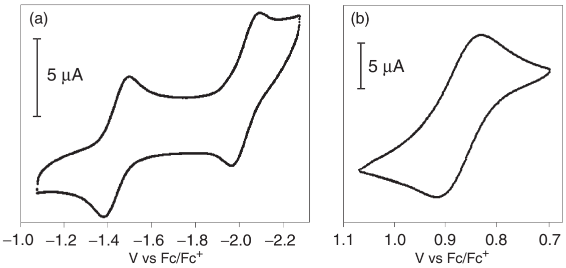


Figure 2. Cyclic voltammogram of **2** at the scan rate 100 mV/s at 25 °C (vs Fc/Fc$^+$). (a) Reduction in a 0.25 mM THF solution containing Bu_4NClO_4 as supporting electrolyte. (b) Oxidation in a 0.80 mM CH_2Cl_2 solution containing $Bu_4NB[C_6H_3\text{-}(CF_3)_2\text{-}3,5]_4$ as supporting electrolyte.

The bucky ruthenocene **2** undergoes a remarkable chemical transformation that has so far not been found for either **1**, $FeCp_2$ or $RuCp_2$.[9] Thus, treatment of **2** with 30 equiv. of *N*-bromosuccinimide (NBS) in DMF[10] at 100 °C afforded in 75% yield a MeFCp–bromodicarbonyl complex $Ru(\eta^5\text{-}C_{60}Me_5)Br(CO)_2$ (**5**), which was characterized by spectroscopic and X-ray crystallographic analyses.[11] None of the expected bromination of the Cp ring was observed, and the selective loss of the Cp group is especially interesting. To investigate the mechanism of this reaction, we carried out several experiments. Bucky ruthenocene **2** is inert to carbon monoxide (1 atm) in DMF at 180 °C, but was converted smoothly at 100 °C to **5** by the reaction with NBS or Br_2 under carbon monoxide (1.0 atm) in benzonitrile. Given the high oxidation potential of **2** and the ability of NBS to generate molecular bromine, we can consider a reasonable mechanism: The initial attack of Br^+ to the Cp ring results in the loss of the Cp ring, and the bromide anion becomes attached to the resulting cationic Ru–MeFCp intermediate. As to the origin of carbon monoxide, one interesting possibility is metal-mediated activation of DMF, but a less interesting possibility involving thermal decomposition of DMF may also be likely.

In summary, the present study on “bucky ruthenocene” showed that the bonding between the Ru atom and the MeFCp ligand as well as between the metal atom and the Cp group is considerably different from that of known ferrocene and ruthenocene compounds. We expect that, being quite reactive, bucky ruthenocene and its derivatives possess potentials that are unavailable for the rather stable bucky ferrocene compound.

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References and Notes

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5 To a solution of **3** (30 mg, 0.031 mmol) in THF (5.0 mL) was added a solution of sodium cyclopentadienide (0.032 mmol) in THF (0.032 mL) at 20 °C. After stirring for 20 min, the solvent was removed to obtain an orange solid. The crude product (mainly **4**) was extracted with toluene (5.0 mL), and heated at 90 °C for 5 h. Insoluble products were separated with a pad of silica gel, and purification with HPLC afforded orange crystals of **2** (3.5 mg, 12% overall yield). **2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 15H, Me(C_{60})), 5.15 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 31.06 (Me), 50.20 ($C_{Me}(C_{60})$), 71.35 ($C_{Cp}(C_{60})$), 97.78 (Cp), 143.12 (C_{60}), 144.28 (C_{60}), 146.97 (C_{60}), 147.92 (C_{60}), 148.18 (C_{60}), 154.62 (C_{60}). IR (powder): ν (C–H)/cm^{-1} 2960 (m), 2915 (m), 2851 (m). HRMS (APCI+) Calcd for $^{12}C_{70}{}^1H_{21}{}^{102}Ru$ (M + H): 963.0687, Found 963.0687. **4**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 15H, Me), 2.99 (m, 1H, Cp), 6.62 (br s, 4H, Cp).

6 Crystal data for **2**·$(CS_2)_2$: monoclinic space group $P\bar{1}$ (No. 2), $a = 11.793(8)$ Å, $b = 18.655(12)$ Å, $c = 37.823(12)$ Å, $\alpha = 78.97(3)°$, $\beta = 86.65(3)°$, $\gamma = 78.72(3)°$, $V = 8008.8(8)$ Å^3, $T = 153(2)$ K, $R_1 = 0.0981$ (all data), $wR_2 = 0.1709$ (all data), GOF (F^2) = 0.995. CCDC 217561.

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9 Not unexpectedly, **2** readily undergoes Friedel-Crafts reaction under standard conditions, which will be reported in a full paper.

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