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Half-Sandwich Metallocene Embedded in a Spherically Extended π-Conjugate System. Synthesis, Structure, and Electrochemistry of $Rh(\eta^5\text{-}C_{60}Me_5)(CO)_2$

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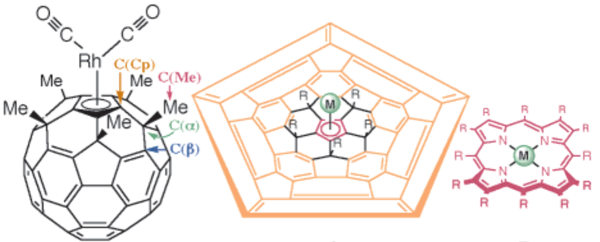
We report herein the synthesis, structure, physical, and electrochemical properties of a new transition metal−cyclopentadienide complex $Rh(\eta^5\text{-}MeFCp)(CO)_2$ (**1**), wherein a half-sandwich metallocene is embedded in the C_{60} skeleton [$C_{60}R_5^-$ (FCp^- hereafter); for R = Me: $MeFCp^-$].[1] We have previously shown for some metal salts of the FCp anions that this anion is unique for its endohedral homoconjugation between the top cyclopentadienide and the bottom C_{50}/50-π electron system.[2] We now describe the chemistry of its transition metal complex **1** that has been shown to possess an extended electronic array including the bottom C_{50} core, the cyclopentadienide, the rhodium metal, and the two CO ligands. The system is robust under the conditions of two-electron oxidation/reduction, allowing the MeFCp complex to be oxidized and reduced without loss of the transition metal atom.[3] Such stability against redox conditions is prerequisite for the use of such a transition metal complex for catalysis, and preliminary experiments indicated that the rhodium complex **1** indeed catalyzes an organic reaction. The physical and chemical properties of **1** suggest a common feature for the FCp transition metal complex (see Schlegel diagram **A**) and a porphyrin metal complex (**B**) in that both represent highly delocalized metal/extended π-conjugated systems with an important difference that the latter is electron-rich and the former electron-deficient.



$Rh(\eta^5\text{-}MeFCp)(CO)_2$ (**1**) A B

$Rh(\eta^5\text{-}MeFCp)(CO)_2$ (**1**) was readily prepared through the transmetalation of MeFCpK with $Rh_2Cl_2(CO)_4$ in HMPA at 55 °C for 19 h.[4] MeFCpK, in turn, was synthesized by *t*-BuOK-deprotonation of MeFCpH, which is available in quantitative yield by a one-step 5-fold reaction of a methylcopper reagent to C_{60}.[1c] The complex was isolated in 51% yield (based on MeFCpH) after aqueous workup followed by preparative HPLC separation [Bucky Prep. (Nacalai Tesque Co.)]. Further purification by recrystallization from CS_2/Et_2O gave wine red crystals of **1**. Unlike the FCp^- metal salts (metal = K and Tl) that we reported previously, this transition metal complex **1** is stable against both air and mildly acidic and basic aqueous medium. APCI-MS showed only one set of signals (M^+ at *m*/*z* 954) corresponding to a molecular ion signal.

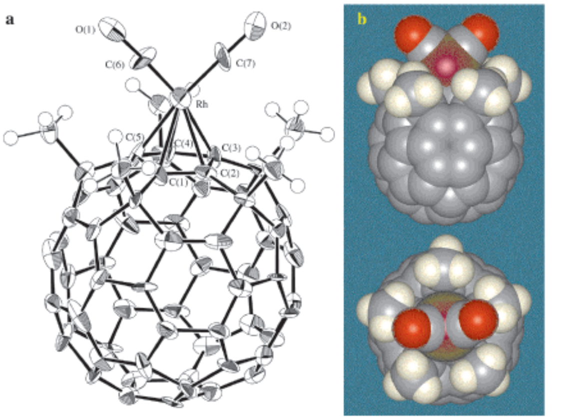


Figure 1. Molecular structure of $Rh(\eta^5\text{-}MeFCp)(CO)_2$ (**1**) determined by X-ray diffraction. Selected bond lengths (Å): Rh−C(1), 2.27(4); Rh−C(2), 2.22(3); Rh−C(3), 2.12(4); Rh−C(4), 2.19(4); Rh−C(5), 2.13(4); Rh−C(6), 1.63(5); Rh−C(7), 1.65(4); C(1)−C(2), 1.35(6); C(2)−C(3), 1.41(5); C(3)−C(4), 1.39(5); C(1)−C(5), 1.42(6); C(6)−O(1), 1.23(6); C(7)−O(2), 1.26(5). (a) ORTEP drawing with 20% probability level ellipsoids. (b) Space-filling models.

Molecular structure of $Rh(\eta^5\text{-}MeFCp)(CO)_2$ (**1**) was determined by X-ray diffraction. An ORTEP diagram, space-filling models, and selected bond lengths are shown in Figure 1.[5] The rhodium atom is bonded to the Cp carbon atoms [C(Cp)] in an η^5-fashion with an averaged interatomic distance of 2.19 Å. One of the five Cp carbon atoms is slightly above the Cp plain, bent toward the rhodium atom, and bonded to the rhodium atom with a Rh−C distance of 2.12 Å. The averaged value of Rh−C(Cp) distances is 3% and 5% shorter than the corresponding values of $Rh(\eta^5\text{-}C_5Me_5)(CO)_2$ (2.26 Å)[6] and $Rh(\eta^5\text{-}C_5Ph_5)(CO)_2$ (2.29 Å),[7] respectively.[8] Another striking feature is the high degree of pyramidalization of the Cp carbons toward the Rh metal (the C(Cp)−C(α) bonds are pushed by an average of 22.6° down from the Cp plane). This bending, in turn, pushes the five methyl groups far from each other, keeping a wide space for the metal and the ligands (Figure 1b). This space looks wide enough to allow the metal to undergo ligand exchange and chemical reactions (vide infra). With the short Rh−C(Cp) distance as well as the ^{13}C NMR data below, we conclude that the rhodium atom is covalently bonded to the MeFCp ligand.

Covalent bonding between the rhodium metal and the FCp ligand is further supported by the solution ^{13}C NMR spectrum of

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[1] (a) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc*. **1996**, *118*, 12850. (b) Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. *J. Organomet. Chem*. **2000**, *59*, 32. (c) Sawamura, M.; Toganoh, M.; Kuninobu, Y.; Kato, S.; Nakamura, E. *Chem. Lett*. **2000**, 270. (d) Sawamura, M.; Toganoh, M.; Suzuki, K.; Hirai, A.; Iikura, H.; Nakamura, E. *Org. Lett*. **2000**, *2*, 1919. (e) Sawamura, M.; Iikura, H.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc*. **1998**, *120*, 8285.

[2] Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem*. **1997**, *62*, 7912.

[3] In sharp contrast, transition metal complexes with η^2-fullerene ligand [$ML_n(\eta^2\text{-}C_{60})$] tend to lose their metal fragment upon both reduction at the fullerene ligand and oxidation at the metal center. See: (a) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc*. **1992**, *114*, 7807. For reviews on organometallic complexes of fullerenes, see: (b) Stephens, A. H. H.; Green, M. L. H. Adv. *Inorg. Chem*. **1997**, *44*, 11. (c) Balch, A. L.; Olmstead, M. M. *Chem. Rev*. **1998**, *98*, 2123. See also: (d) Xia, A.; Selegue, J. P.; Carrillo, A.; Brock, A. P. *J. Am. Chem. Soc*. **2000**, *122*, 3973.

[4] We have so far been unsuccessful in the preparation of the corresponding rhodium complex with the PhFCp ligand.

[5] Diffraction study was carried out by an imaging plate method with a MacScience DIP-2030 diffractometer. Absorption correction was performed using intensity measurements: monoclinic, $P2_1/n$; $a = 9.958(1)$ Å, $b = 23.185(4)$ Å, $c = 15.977(3)$ Å, $\beta = 93.603(9)°$, $V = 3681.42(2)$ Å^3; $Z = 3$; $T = 210$ K; 5410 reflections measured, 1443 observed ($I > 3.00s(I)$); $\theta_{max} = 23.58°$; 631 parameters; $R = 0.066$; $Rw = 0.073$; $S = 5.42$. $(\Delta/\sigma)_{max} = 0.41$.

[6] Lichtenberger, D. L.; Blevins, C. H., II; Ortega, R. B. *Organometallics* **1984**, *3*, 1614.

[7] Behrens, U.; Edelmann, F. *Z. Naturforsch., Teil B* **1986**, *41*, 1426.

[8] The Rh−C(Cp) distances of **1** are comparable with Rh−C(C_{60}) of $RhH(CO)(\eta^2\text{-}C_{60})(PPh_3)_2$ (averaged value, 2.16 Å). See: Balch, A. L.; Lee, J. W.; Noll, B. C.; Olmstead, M. M. *Inorg. Chem*. **1993**, *32*, 3577.

10.1021/ja005564h CCC: $19.00

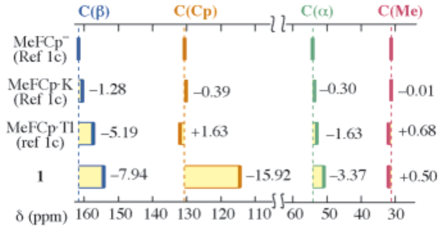

Figure 2. The ^{13}C NMR spectrum change of MeFCp upon metal coordination.

1 (THF-d_8, 25 °C). The spectrum showed 10 signals, two singlet peaks in the sp^3 region, one doublet (δ 114.08, $J_{\mathrm{Rh-C}} = 3.7$ Hz) for the Cp carbons [C(Cp)], six singlet peaks in the sp^2 region (δ 144.75−154.06), and one doublet (δ 192.03, $J_{\mathrm{Rh-C}} = 84.2$ Hz) for the carbonyl carbons. The ^{103}Rh−^{13}C coupling at C(Cp) is spectral proof of the covalent Rh−Cp bonding. The spectrum showed only one singlet at δ 2.41 due to the equivalent methyl groups. All ^{1}H and ^{13}C NMR features indicated time-averaged local C_{5v} symmetry of the MeFCp moiety in solution.

Strong electronic interaction between the rhodium metal and the bottom C_{50}-polyene moiety was found through comparison of the ^{13}C NMR chemical shift values of C(Cp), C(Me), C(α), and C(β) atoms in the MeFCp anion and some metal complexes (Figure 2). Much larger shifting of the C(Cp) and C(β) signals in **1** than in the FCp anion and K and Tl salts shows that the Rh−Cp interaction in **1** is much stronger than in others. Especially noteworthy is the large upfield shift of the C(β) signal (−7.94 ppm) in **1** as compared with the very small change for C(α) and C(Me). This difference is consistent with through-space $\pi-\pi$ interaction (i.e., endohedral homoconjugation)[2] rather than with the inductive effects of the rhodium metal through C−C σ bonds (which will affect the chemical shift change at both C(Me) and C(β)).

Cyclic voltammetry measurements (0.1 M TBAP in THF, 25 °C, V vs Fc/Fc$^+$, 0.1 V/s) revealed that the rhodium complex **1** is robust under redox conditions, allowing the FCp complex to be oxidized and reduced without dissociation from the metal atom. The cathodic potential scan (−0.58 to −2.47 V, Figure 3a) showed two reversible one-electron redox couples at $E_{1/2} = -1.35$ and −1.94 V with peak-to-peak separations (ΔE_{p}) of 81 and 80 mV, respectively.[9] The reduction potential of −1.35 and −1.94 V falls comfortably in the range expected for reduction of the fullerene core. In contrast, an ordinary rhodium Cp complex, Rh(η^5-Cp)(CO)$_2$, cannot be reduced up to $E_{\mathrm{p}} = -2.70$ V, where the metal center is irreversibly reduced and lost from the complex. These results indicate that one can introduce two electrons to **1** without destruction of the Rh−FCp covalent bonding.[3]

Next, we examined the behavior of **1** toward oxidation. To this end, we performed CV measurements for a wider potential scan rage (1.03 to −2.47 V). In the anodic potential scan with **1**, a two-electron oxidation peak was observed at $E_{\mathrm{p}} = 0.58$ V (Figure 3b). This must be due to metal-centered Rh(I)-to-Rh(III) oxidation. Upon reversal of the scan at 1.03 V, we observed the restoration of the two one-electron redox couples at $E_{1/2} = -1.35$ and −1.94 V after two reduction events ($E_{\mathrm{p}} = 0.47$ and −0.24 V), which indicate the regeneration of the original Rh(I) complex **1**.[10] No sign of the existence of dissociated MeFCp ligand species was detected.[3]

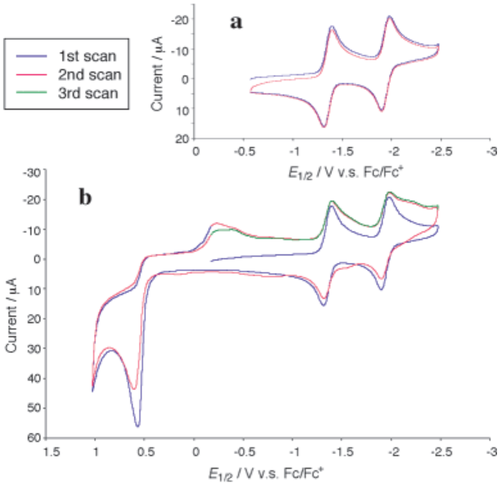

Figure 3. Cyclic voltammograms of **1**: 1.0 mM **1**, 0.1 M Bu$_4$NClO$_4$ in THF at 25 °C with a glassy carbon working electrode and a Ag/Ag$^+$ reference electrode. Scan rate = 100 mV/s. (a) Multiple scan between −0.58 and −2.47 V. (b) Multiple scan between 1.03 and −2.47 V.

The stability of **1** against the redox conditions suggested its use for catalysis. Thus, the rhodium complex **1** catalyzed hydrosilylation of acetophenone with diphenylsilane at 25 °C under 60 W visible light irradiation {[ketone] = 0.5 M in THF, [ketone]/[**1**] = 1000; 100 h; turnover number, 500 with **1**, 150 with Rh(η^5-Cp)(CO)$_2$}. The irradiation was mandatory to initiation of the reaction.

In summary, we have reported a new class of transition metal complex, wherein the metal center is covalently bonded to an extended π-conjugate system. The Rh−MeFCp complex is very robust, and the nature of the ligand can be electrochemically tuned without losing the metal−ligand covalent bonding. On the other hand, visible light irradiation of the complex initiates a catalytic reaction, which otherwise does not take place. Given the accessibility of various RFCp ligands that allows the tuning of the steric and chemical nature of the cavity surrounding the metal center as well as the above-mentioned electrochemical and photochemical properties, we expect the transition metal−FCp complexes would stimulate imagination of chemists for possible use in catalysis and in materials science.

Acknowledgment. We thank Prof. H. Nishihara, M. Murata, and M. Yamada, The University of Tokyo, for help on the CV measurements.

Supporting Information Available: Experimental procedure and spectral data for **1**, and summary of the X-ray crystal structure determination of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] The third reduction of **1** [$E_{\mathrm{p}} = -2.61$ V, $E_{1/2}(\mathbf{1}^{2-}/\mathbf{1}^{3-}) = -2.57$ V] caused partial dissociation of the Rh(CO)$_2$ fragment as indicated by the observation of oxidation waves for [MeFCp$^-$]$^{2-}$, [MeFCp$^-$]$^{-\bullet}$, and MeFCp$^-$.

[10] As seen for the back scan between 1.03 and −0.5 V shown in Figure 3b, the regeneration of Rh(I) species after the two-electron oxidation is not a simple reduction event, suggesting the intervention of dimerization of $\mathbf{1}^{2+}$ or coordination of solvent/electrolite to the electronically unsaturated rhodium center. The origin of broadening of the redox waves at $E_{1/2} = -1.35$ and −1.94 V and the small hump around −2.25 V in the 2nd and the 3rd scans is unclear at this time. The CV measurement with Rh(η^5-Cp)(CO)$_2$ under the identical conditions showed an oxidation peak at $E_{\mathrm{p}} = 0.85$ V. Reduction events in the reversed scan were more complicated than those with **1**.