Synthesis of Metal Fullerene Complexes by the Use of Fullerene Halides

Yutaka Matsuo,[†] Yoichiro Kuninobu,[#] Ayako Muramatsu,[‡] Masaya Sawamura,[§] and Eiichi Nakamura*[,†,‡]

Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received February 13, 2008

$K(C_{60}R_5)$ (**1**, R = Me, Ph) was generated by deprotonation of $C_{60}R_5H$ (**2**) and allowed to react with *N*-fluoropyridinium triflate and *N*-chloro- and *N*-bromosuccinimide in benzene at 25 °C for 10 min to obtain halogenated fullerenes $C_{60}R_5X$ (**3a**: R = Me, X = F; **3b**: R = Me, X = Cl; **3c**: R = Me, X = Br; **4a**: R = Ph, X = F; **4b**: R = Ph, X = Cl, **4c**: R = Ph, X = Br) in good yield. The pentamethyl[60]fullerene halides are useful for the synthesis of a variety of η^5-fullerene metal complexes. The reaction of the fullerene bromide **3c** with the low-valent transition metal complexes $Na[Re(CO)_4]$, $Fe(CO)_5$, $Ru_3(CO)_{12}$, and $Na[Co(CO)_4]$ gave $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**5**), $Fe(\eta^5\text{-}C_{60}Me_5)Br(CO)_2$ (**6**), $Ru(\eta^5\text{-}C_{60}Me_5)Br(CO)_2$ (**7**), and $Co(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**8**), respectively. The structures of halide **3c** and rhenium complex **5** were determined by X-ray crystallography. Electrochemical measurements on **3b** and **3c** were also performed. The iron complex **6** was converted into $Fe(\eta^5\text{-}C_{60}Me_5)Cp$ (**9**), $Fe(\eta^5\text{-}C_{60}Me_5)Me(CO)_2$ (**10**), $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCH)$ (**11**), and $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2(CCPh)$ (**12**), by ligand exchange reactions.

Introduction

The transition metal η^5-fullerene complexes of type $M(\eta^5\text{-}C_{60}R_5)L_n$ (M = metal atoms, R = organic groups, L = ligands)[1–5] belong to a new class of organometallic compounds that exhibit unique functions, such as an ability to form liquid crystalline materials,[5d] to form a photoinduced charge separation state,[6] and to effect asymmetric organic transformations.[2f,g] The synthesis of these complexes has been achieved by the reaction of a $C_{60}R_5$ anion (**1**)[1,7] with appropriate transition metal halides (Scheme 1a),[2] by metal-mediated C−H bond activation of $C_{60}R_5H$ (**2** in Scheme 1b),[3] and by hydrometalation of [60]fullerene (Scheme 1c).[4] In this article, we report a fourth approach that relies on the reaction of a fullerene halide (**3** or **4**) either with a metal anion or with a low-valent metal complex (Scheme 1d,e).

The synthesis of penta(organo)fullerene halides $C_{60}R_5X$ (X = halides) was first described by R. Taylor et al. in 1994. They synthesized $C_{60}Cl_6$[8] and allowed it to react with methyllithium to obtain $C_{60}Me_5Cl$ (**3b**)[9] in 4.5% yield among other products, or with benzene in the presence of $FeCl_3$ to obtain $C_{60}Ph_5Cl$ (**4b**) in 68% yield.[10] The synthesis of $C_{60}Me_5X$ (**3a**: X = F; **3b**: X = Cl; **3c**: X = Br) and $C_{60}Ph_5X$ (**4a**: X = F; **4b**: X =

* Corresponding author. E-mail: nakamura@chem.s.u-tokyo.ac.jp.
[†] Japan Science and Technology Agency.
[#] Present address: Graduate School of Natural Science and Technology, Okayama University.
[‡] The University of Tokyo.
[§] Present address: Department of Chemistry, School of Science, Hokkaido University.

(1) (a) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850. (b) Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 7912. (c) Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. *J. Organomet. Chem.* **2000**, *599*, 32. (d) Sawamura, M.; Toganoh, M.; Kuninobu, Y.; Kato, S.; Nakamura, E. *Chem. Lett.* **2000**, 270. (e) Nakamura, E.; Sawamura, M. *Pure Appl. Chem.* **2001**, *73*, 355. (f) Hamasaki, R.; Matsuo, Y.; Nakamura, E. *Chem. Lett.* **2004**, *33*, 328. (g) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *Org. Lett.* **2006**, *8*, 1463. (h) Matsuo, Y.; Iwashita, A.; Nakamura, E. *Chem. Lett.* **2006**, *35*, 858. (i) Matsuo, Y.; Muramatsu, A.; Tahara, K.; Koide, M.; Nakamura, E. *Org. Synth.* **2006**, *83*, 80.

(2) (a) Sawamura, M.; Kuninobu, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2000**, *122*, 12407. (b) Matsuo, Y.; Nakamura, E. *Organometallics* **2003**, *22*, 2554. (c) Matsuo, Y.; Kuninobu, Y.; Ito, S.; Nakamura, E. *Chem. Lett.* **2004**, *33*, 328. (d) Kuninobu, Y.; Matsuo, Y.; Toganoh, M.; Sawamura, M.; Nakamura, E. *Organometallics* **2004**, *23*, 3259. (e) Matsuo, Y.; Iwashita, A.; Nakamura, E. *Organometallics* **2005**, *24*, 89. (f) Matsuo, Y.; Nakamura, E. *Inorg. Chim. Acta* **2006**, *359*, 1979. (g) Matsuo, Y.; Mitani, Y.; Zhong, Y.-W.; Nakamura, E. *Organometallics* **2006**, *25*, 2826. (h) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *Chem. Asian J.* **2007**, *2*, 358.

(3) (a) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354. (b) Nakamura, E. *Pure Appl. Chem.* **2003**, *75*, 427. (c) Nakamura, E. *J. Organomet. Chem.* **2004**, *689*, 4630. (d) Herber, R. H.; Nowik, I.; Matsuo, Y.; Toganoh, M.; Kuninobu, Y.; Nakamura, E. *Inorg. Chem.* **2005**, *44*, 5629. (e) Matsuo, Y.; Isobe, H.; Tanaka, T.; Murata, Y.; Murata, M.; Komatsu, K.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 17148. (f) Matsuo, Y.; Tahara, K.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 7154.

(4) (a) Toganoh, M.; Matsuo, Y.; Nakamura, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3530. (b) Toganoh, M.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13974.

(5) (a) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702. (b) Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 432. (c) Okada, S.; Arita, R.; Matsuo, Y.; Nakamura, E.; Oshiyama, A.; Aoki, H. *Chem. Phys. Lett.* **2004**, *399*, 157. (d) Matsuo, Y.; Muramatsu, A.; Kamikawa, Y.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 9586. (e) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 3052.

(6) Guldi, D. M.; Rahman, G. M. A.; Marczak, R.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 9420.

(7) Matsuo, Y.; Tahara, K.; Nakamura, E. *Chem. Lett.* **2005**, *34*, 1078.

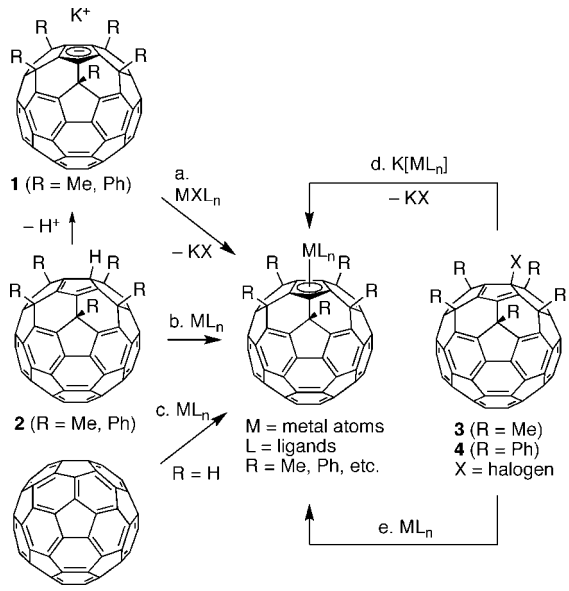
(8) Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1230.

(9) Al-Matar, H.; Abdul-Sada, A. K.; Avent, A. G.; Fowler, P. W.; Hitchcock, P. B.; Rogers, K. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **2002**, 53.

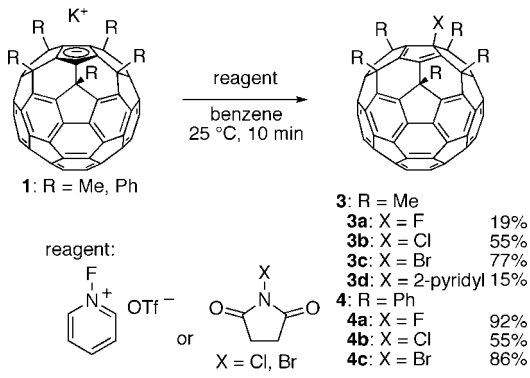
(10) (a) Avent, A. G.; Birkett, P. R.; Crane, J. D.; Darwish, A. D.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1463. (b) Birkett, P. R.; Taylor, R.; Wachter, N. K.; Carano, M.; Paolucci, F.; Roffia, S.; Zerbetto, F. *J. Am. Chem. Soc.* **2000**, *122*, 4209. (c) Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Hahn, I.; Kroto, H. W.; Langley, G. J.; O'Loughlin, J.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1211.

10.1021/om8001262 CCC: $40.75
Publication on Web 06/21/2008

Scheme 1



Scheme 2



Cl; **4c**: X = Br) is much more straightforward and high yielding. Herein the fullerene bromide **3c** was found to be useful for the synthesis of the corresponding transition metal−penta(organo)-fullerene complexes Re(η^5-$C_{60}Me_5$)$(CO)_3$ (**5**), Fe(η^5-$C_{60}Me_5$)-$Br(CO)_2$ (**6**), Ru(η^5-$C_{60}Me_5$)$Br(CO)_2$ (**7**), and Co(η^5-$C_{60}Me_5$)-$(CO)_2$ (**8**), which will find uses in materials applications.[11,12]

Results and Discussion

Synthesis and Characterization of Penta(organo)[60]-fullerene Halides. Penta(organo)fullerene halides $C_{60}R_5X$ **3a**−**c** and **4a**−**c** were synthesized by reaction of the corresponding potassium complex $[K(thf)_n][C_{60}R_5]$ (R = Me, Ph, **1**)[1,7] with *N*-fluoropyridinium triflate and *N*-chloro- and *N*-bromosuccinimide in benzene at room temperature in up to 92% yield (Scheme 2). We could synthesize the halides also by the reaction of the protio compound **2** with these halogenating reagents in benzene at 50 °C, but the yield remained low (about 20%). The synthesis of fluoride **3a** accompanied the formation of a pyridine adduct, $C_{60}Me_5$(2-pyridyl) (**3d**, 15% yield). The halides thus obtained are air- and moisture-stable reddish-orange solids.

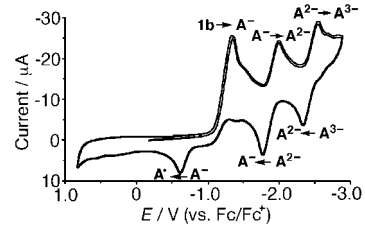
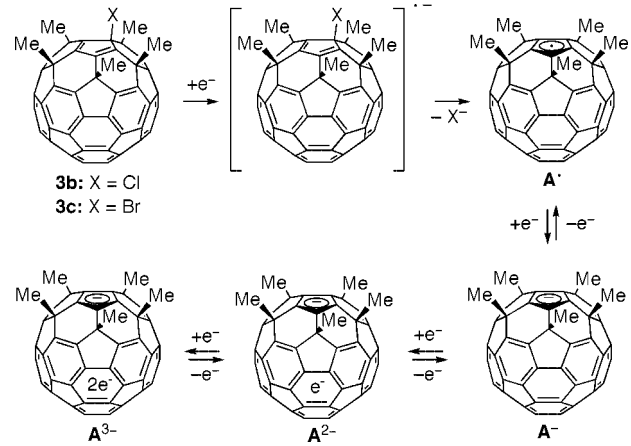


Figure 1. Cyclic voltammogram of **3b** at a scan rate of 100 mV/s at 25 °C in a 1.0 mM THF solution containing $[Bu_4N][ClO_4]$ (100 mM) as supporting electrolyte.

Scheme 3



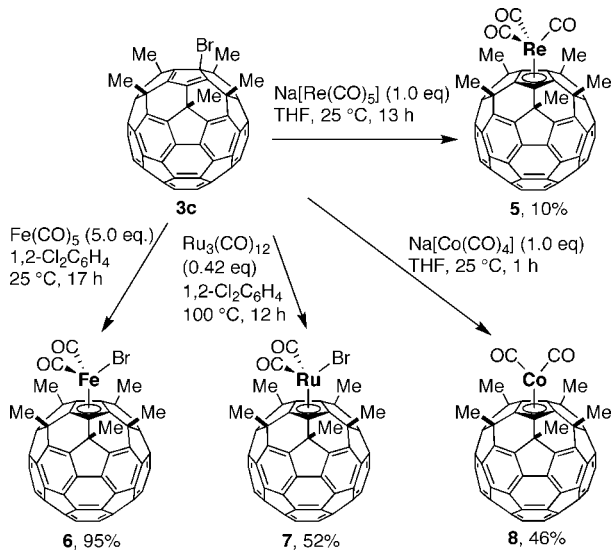
APCI-MS spectra of the products exhibited the parent ion signals for all halides. In the ^1H and ^{13}C NMR spectra of the pentamethylated fullerene halides **3a**, **3b**, and **3c**, three signals due to the methyl groups were observed in the ratio 2:2:1, in agreement with the expected C_s symmetry of **1a**−**c**. The ^1H and ^{13}C NMR spectra of the pentaphenylated fullerene halides **4a**, **4b**, and **4c** also showed C_s symmetry, suggesting fast rotation of the phenyl group on the NMR time scale.

Electrochemical Studies of Penta(organo)[60]fullerene Halides. The redox properties of pentamethylated fullerene halides **3b** and **3c** were examined. The electrochemistry of $C_{60}Ph_5Cl$ (**4b**) was previously reported by Birkett et al.[10b] Figure 1 shows the cyclic voltammogram of **3b** in THF. The halide **3b** showed no oxidation wave within the THF window, but showed irreversible reduction waves on the reduction side. In the course of the reduction, $C_{60}Me_5^-$ and its oxidized species $C_{60}Me_5^{\bullet}$ were observed. The result indicated that the C−Cl bond of **3b** was cleaved by the reduction process. The first step of the reduction at $E_{pc} = -1.35$ V vs Fc/Fc^+ is ascribed to the two-electron reduction, where the first electron is used for the formation of the radical $C_{60}Me_5^{\bullet}$ (**A**) and a chloride anion (Cl^-) and, in the second reduction, $C_{60}Me_5^{\bullet}$ is reduced to form the anion $C_{60}Me_5^-$ ($\mathbf{A}^-$) (Scheme 3). The anion subsequently undergoes a quasi-reversible two-electron reduction process to give a dianion $C_{60}Me_5^{2-}$ ($\mathbf{A}^{2-}$) and a trianion $C_{60}Me_5^{3-}$ ($\mathbf{A}^{3-}$) at $E_{1/2} = -1.88$ and -2.44 V vs Fc/Fc^+, respectively. These reduction potentials show good agreement with the values reported previously for the dianion and trianion formation by electrochemical reduction of $C_{60}Ph_5^-$ ($E_{1/2} = -1.84$ and -2.52 V vs Fc/Fc^+) and $C_{60}(biphenyl)_5^-$ ($E_{1/2} = -1.69$ and -2.26 V

(11) (a) Nakamura, E.; Tahara, K.; Matsuo, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2003**, *125*, 2834. (b) Matsuo, Y.; Tahara, K.; Sawamura, M.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 8725.

(12) (a) Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E.; Zhou, S.-Q.; Chu, B. *Chem. Lett.* **2000**, 1098. (b) Zhou, S.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944. (c) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807. (d) Isobe, H.; Homma, T.; Nakamura, E. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 14895.

Scheme 4



vs Fc/Fc^+).[13] In the anodic process, oxidation of the anion $\mathbf{A}^-$ to the radical $\mathbf{A}^\bullet$ was observed at 0.61 V vs Fc/Fc^+. A comparable observation was also reported for $C_{60}Ph_5Cl$.[10b] The bromide **3c** showed an electrochemical behavior similar to **3b** except for the first reduction, i.e., the C−X bond cleavage process, whose reduction potential was −1.14 V vs Fc/Fc^+. Note that the first reduction potentials of **3b** and **3c** were positively shifted compared with that of $C_{60}Me_5H$ ($E_{1/2} = -1.48$ V vs Fc/Fc^+),[1d] which must reflect the electron-withdrawing property of the halogen atoms. Such a low potential in the first reduction is the reason that the organometallic syntheses reported below were successful.

Synthesis of Rhenium and Cobalt Complexes via Transmetalation with 3c. We next investigated the synthesis of organometallic complexes via the (formal) nucleophilic substitution route by the use of the pentamethyl[60]fullerene halides **3** (Scheme 4). First, we examined route d shown in Scheme 1, which involves the reaction of the penta(organo)fullerene bromide **3c** with alkali metal salts of the transition metal complexes. Treatment of **3c** with the anionic rhenium complex $Na[Re(CO)_5]$ gave the desired rhenium tricarbonyl complex $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**5**) in only 10% yield (Scheme 4) through a nucleophilic substitution pathway. The major products were $C_{60}Me_5H$ (and its oxidation products due to air oxidation of intermediates and/or the product during and after the reaction). The result is consistent with the assumption that the reaction involves fast electron transfer from the low-valent rhenate $Na[Re(CO)_5]$ to **3c**, which generates the radical $C_{60}Me_5^\bullet$ or the anion $C_{60}Me_5^-$, which, however, do not react further with the rhenate. In the reaction of the pentaphenyl[60]fullerene halides **4** under various conditions, such a nonproductive pathway was dominant and gave none of the desired products.

Characterization of **5** was achieved with APCI-MS, NMR, and IR measurements, as well as X-ray crystallography. The ^1H and ^{13}C NMR spectra showed C_{5v} symmetry for the $C_{60}Me_5$ ligand. The carbonyl ligand on the rhenium metal was characterized by the ^{13}C NMR spectrum and IR spectrum. The stretching vibrations of the three carbonyl groups, ν(CO), were observed at 2022 and 1932 cm^{-1}. These wavenumbers are similar to those found for the cyclopentadienyl rhenium tricarbonyl complex $ReCp(CO)_3$ (2019, 1897 cm^{-1})[14] and our previously reported rhenium tri(organo)dihydrofullerene complex $Re(\eta^5\text{-}C_{60}Bn_2PhH_2)(CO)_3$ (2024, 1939 cm^{-1}).[4]

The cobalt−penta(methyl)[60]fullerene dicarbonyl complex $Co(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**8**) was synthesized by the reaction of **1c** with $Na[Co(CO)_4]$ in THF at 25 °C in 46% yield. Characterization of **8** was performed with NMR and MS analyses. In the ^1H and ^{13}C NMR spectra, compound **8** exhibited a C_{5v} symmetric spectral pattern with chemical shift values similar to those of the corresponding rhodium complex $Rh(\eta^5\text{-}C_{60}Me_5)(CO)_2$.[2a] In the FAB-MS spectrum, the molecular ion signal ($m/z = 910$) of cobalt complex **8** was observed. In the IR spectrum, symmetric and asymmetric stretching vibrations due to the two carbonyl groups were observed at 2019 and 1965 cm^{-1}, respectively. The cobalt complex **8** was very sensitive to light in air, and we could not perform any further investigations of **8**. The ordinary cyclopentadienyl complex $CoCp(CO)_2$ in solution is also light sensitive and readily forms a dimer, $Co_2Cp_2(CO)_3$.[15] We suspect that a similar decomposition process may be occurring because of the strong light absorption property of the fullerene ligand in **8**.

Syntheses of Iron and Ruthenium Complexes via Oxidative Addition to 3c. Next, we examined the oxidative addition route (Scheme 1e) by the use of low-valent transition metal complexes. Treatment of **3c** with $Fe(CO)_5$ in 1,2-dichlorobenzene at 25 °C afforded the iron bromo dicarbonyl complex $Fe(\eta^5\text{-}C_{60}Me_5)Br(CO)_2$ (**6**) in 95% yield (Scheme 4). The iron carbonyl complex **6** in solution was sensitive to air and light and decomposed to give $C_{60}Me_5H$ and its oxidation products. Complex **6** was identified by its spectral properties, which were similar to those of the ruthenium halo dicarbonyl complexes $Ru(\eta^5\text{-}C_{60}Me_5)Cl(CO)_2$[2b] and $Ru(\eta^5\text{-}C_{60}Me_5)Br(CO)_2$ (**7**).[2c] The IR spectrum exhibited symmetric and asymmetric stretching vibrations of the carbonyl groups at 2037 and 1996 cm^{-1}, which are comparable to those of $FeCpBr(CO)_2$ (2048 and 2002 cm^{-1}).[16]

Ruthenium complex **7** was also obtained with the oxidative addition method. As compared with the previously reported route,[2b,c] the new route has the advantage of having a readily available starting rhenium complex, because commonly available $Ru_3(CO)_{12}$ can be used in this reaction instead of the more expensive $[RuCl_2(CO)_3]_2$ that was used in the previous synthesis. Heating **3c** with $Ru_3(CO)_{12}$ in 1,2-dichlorobenzene at 100 °C afforded the bromo dicarbonyl complex **7**[2c] in moderate yield. The same procedure was applied to **3b** to obtain $Ru(\eta^5\text{-}C_{60}Me_5)Cl(CO)_2$ in 38% yield. These complexes can be derivatized to various ruthenium−pentamethyl[60]fullerene complexes[2b] and used in asymmetric transformation reactions.[2f,g] A similar reaction of C_5Ph_5Br with $[Ru_3(CO)_{12}]$ has been reported by Connelly and Manners.[17]

X-ray Crystallographic Study of the Rhenium−Penta(methyl)[60]fullerene Complex. Red single crystals of **5** suitable for X-ray diffraction were obtained by recrystallization from CS_2/ethanol (Figure 2). The $C_{60}Me_5$ ligand coordinates to the rhenium atom in an η^5-fashion with an average Re−C(C_{60})

(13) (a) Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 8457. (b) Aprahamian, I.; Eisenberg, D.; Hoffman, R. E.; Sternfeld, T.; Matsuo, Y.; Jackson, E. A.; Nakamura, E.; Scott, L. T.; Sheradsky, T.; Rabinovitz, M. *J. Am. Chem. Soc.* **2005**, *127*, 9581.

(14) (a) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578. (b) Tellers, D. M.; Skoog, S. J.; Bergman, R. G.; Gunnoe, T. B.; Harman, W. D. *Organometallics* **2000**, *19*, 2428.

(15) (a) Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4998. (b) Campbell, J. M.; Martel, A. A.; Chen, S.-P.; Waller, I. M. *J. Am. Chem. Soc.* **1997**, *119*, 4678.

(16) Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1976**, *110*, 331.

(17) Connelly, N. G.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1989**, 283.

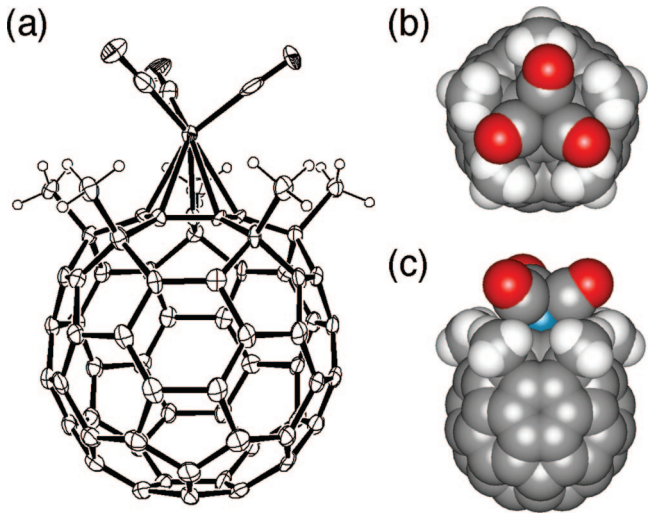
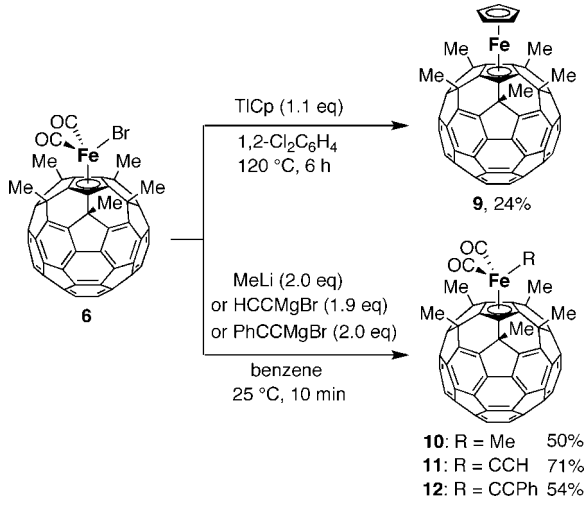


Figure 2. Molecular structure of the rhenium tricarbonyl complex $Re(\eta^5\text{-}C_{60}Me_5)(CO)_3$ (**5**) with 30% probability level ellipsoids. A CS_2 molecule in the unit cell is omitted for clarity. (a) ORTEP drawing. (b) CPK model, top view. (c) CPK model, side view.

Scheme 5



bond length of 2.327(11) Å. The average bond lengths of Re−C(CO) (1.911(18) Å) and C(CO)−O(CO) (1.159(19) Å) are almost the same as those of $Re(\eta^5\text{-}C_{60}Bn_2PhH_2)(CO)_3$ (1.909(12) and 1.165(15) Å).[4]

Derivatization of Iron Bromo Dicarbonyl Complex. Complex **6**, having the bromo ligand, is useful as a starting material for the synthesis of other iron−pentamethyl[60]fullerene complexes. A transmetalation reaction of the bromo ligand afforded the buckyferrocene $Fe(\eta^5\text{-}C_{60}Me_5)Cp$ (**9**),[3] the methyl complex $Fe(\eta^5\text{-}C_{60}Me_5)(CO)_2Me$ (**10**; ν(CO) = 2004, 1953 cm^{-1}; δ_{Me} (^1H) = −20.8 ppm), alkynyl complexes $Fe(\eta^5\text{-}C_{60}Me_5)(CCH)(CO)_2$ (**11**; ν(CO) = 2035, 1991 cm^{-1}) and $Fe(\eta^5\text{-}C_{60}Me_5)(CCPh)(CO)_2$ (**12**; ν(CO) = 2035, 1990 cm^{-1}) (Scheme 5), which were characterized by comparison of spectral data for ordinary cyclopentadienyl complexes, $FeCp(CO)_2Me$[18] (ν(CO) = 2010, 1955 cm^{-1}; δ_{Me} (^1H) = −23.5 ppm), $FeCp(CO)_2(CCH)$[19] (ν(CO) = 2050, 1998 cm^{-1}), and $FeCp(CO)_2(CCPh)$[20] (ν(CO) = 2045, 2000 cm^{-1}) as well as the corresponding ruthenium−penta(methyl)[60]fullerene complexes $Ru(\eta^5\text{-}C_{60}Me_5)Me(CO)_2Me$, $Ru(\eta^5\text{-}C_{60}Me_5)(CCH)(CO)_2$, and $Ru(\eta^5\text{-}C_{60}Me_5)(CCPh)(CO)_2$.[2b]

Conclusion

We have developed a new and convenient synthetic entry to the pentamethyl- and pentaphenyl[60]fullerene halides and new routes to the rhenium, iron, ruthenium, and cobalt complexes of pentamethyl[60]fullerene. The substitution reactions between fullerene halides with anionic metal complexes are complementary to the previously reported substitution approaches using fullerene anions and metal halides. The described oxidative addition approach represents a powerful method for the synthesis of useful metal−halo complexes, which does not produce any alkali metal halide side-products. These new synthetic methods will significantly broaden the repertoire of the metal−penta(organo)-[60]fullerene complexes and will contribute to the development of materials science and catalysis applications of metal fullerene complexes.

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. THF was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation. Benzene was distilled from calcium hydride. $C_{60}Me_5H$ and $C_{60}Ph_5H$ were prepared according to the literature.[1] A THF solution of *t*-BuOK was purchased from Sigma-Aldrich Co. and used as received. *N*-Fluoropyridinium triflate, *N*-chlorosuccinimide, and *N*-bromosuccinimide were purchased from Tokyo Kasei Co. and were recrystallized from benzene. MeLi was purchased from Kanto Chemical Co., Inc. HCCMgBr was purchased from Sigma-Aldrich Co. PhCCMgBr was prepared from the reaction of phenylacetylene and ethylmagnesium bromide.

HPLC analyses were performed on a Shimadzu LC-10A system equipped with a SPD-M10A diode array detector and a Cosmosil-Buckyprep column (4.6 × 250 mm, Nacalai Tesque Inc.). Preparative HPLC separations were performed by the use of a Buckyprep column (20 mm × 250 mm) using toluene/2-propanol (7:3 or 1:1) as eluent. All ^1H (400 MHz) and $^{13}C\{^1H\}$ (100 MHz) spectra were recorded on a JEOL ECX400 spectrometer. Spectra were reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for the ^1H NMR. Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 or THF-d_8 at δ 25.20 and 67.40 ppm. Other spectra were recorded on the following instruments: IR, JASCO IR-420 and ReactIR 1000; UV/vis spectra, Hitachi U3500 and Shimadzu SPD-6A; mass spectra, Shimadzu LCMS-QP8000 and JEOL JMS-T100LC APCI/ESI-TOF mass spectrometers. High-resolution MS data for the iron complexes were not obtained because of instability, in particular, light sensitivity of these compounds.

Preparation of $C_{60}Me_5F$ (3a). To a suspension of $C_{60}Me_5H$ (202 mg, 0.251 mmol) in THF (10 mL) was added a solution of *t*-BuOK (1.0 M, 0.28 mL, 0.028 mmol) in THF. After stirring for 1.5 h, *N*-fluoropyridinium triflate (93.1 mg, 0.377 mmol) was added. The mixture was stirred for 0.5 h. After dilution with toluene, the mixture was washed with water. The organic phase was concentrated in vacuo. Preparative HPLC separation (toluene/2-propanol = 7:3, flow rate = 18 mL/min, retention time = 7.5−9.0 min) afforded **3a** (37.9 mg, 19% yield) and a side-product, $C_{60}Me_5$(2-pyridyl) (**3d**) (32.2 mg, 15%), as air-stable reddish-orange solids.

(18) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
(19) Kim, P. J.; Masai, H.; Sonogashira, K.; Hagihara, N. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 181.
(20) (a) Bruce, M. I.; Harbourne, D. A.; Waugh, F.; Stone, F. G. A. *J. Chem. Soc. (A)* **1968**, 356. (b) Green, M. L. H.; Mole, T. *J. Organomet. Chem.* **1968**, *12*, 404.

3a. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 6H, Me), 2.34 (s, 6H, Me), 2.36 (s, 3H, Me). ^{1}H NMR (400 MHz, $CDCl_3/CS_2$): δ 2.21 (s, 6H, Me), 2.29 (s, 3H, Me), 2.32 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CS_2$): δ 24.97 (d, $J_{F-C} = 1.7$ Hz, 2C, Me), 26.37 (d, $J_{F-C} = 1.7$ Hz, 2C, Me), 26.57 (d, $^3J_{F-C} = 19.0$ Hz, 1C, Me), 50.27 (d, $^3J_{F-C} = 1.7$ Hz, 2C, sp^3-C_{60}), 51.61 (2C, sp^3-C_{60}), 53.49 (d, $^2J_{F-C} = 27.3$ Hz, 1C, sp^3-C_{60}), 82.18 (d, $^1J_{F-C} = 338$ Hz, 1C, $C(sp^3$-$C_{60})$-F), 142.47 (2C), 142.72 (2C), 143.43 (2C), 143.63 (2C), 143.66 (2C), 143.74 (2C), 144.04 (2C), 144.19 (2C), 144.51 (2C), 145.24 (2C), 146.35 (1C), 146.37 (2C), 146.43 (2C), 146.44 (2C), 147.12 (2C), 147.44 (2C), 147.50 (2C), 147.55 (1C), 147.88 (2C), 147.96 (2C), 147.99 (2C), 148.16 (2C), 148.18 (2C), 148.35 (1C), 151.15 (2C), 151.17 (2C), 152.78 (2C), 156.12 (2C). ^{19}F NMR (376.4 MHz, $CDCl_3/CS_2$): δ 47.05 (q, $^4J_{F-H} = 9.0$ Hz, 1F). IR (KBr) ν/cm^{-1}, 2962 (m), 2920 (m), 2859 (w), 1513 (s), 1445 (s), 1417 (w), 1373 (w), 1288 (w), 1266 (w), 1239 (w), 1201 (w), 1179 (w), 1127 (w), 1104 (w), 1063 (w), 1028 (w), 1010 (w), 998 (w), 982 (m), 955 (w), 685 (m), 660 (w), 656 (w), 576 (w), 569 (w), 555 (m), 545 (m), 528 (m), 521 (m), 509 (w), 499 (m), 461 (w). UV−vis (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2): λ_{max}/nm (ϵ), 258 (76 600), 271 (74 900), 355 (21 600, shoulder), 393 (12 500), 470 (3830, shoulder). APCI-MS (+): m/z 814 (M^+), (−) m/z 795 ($[M - F]^-$). HR-APCI-MS (+): m/z found 814.1100; calcd for **3a** 814.1158.

3d. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H, Me), 2.21 (s, 6H, Me), 2.52 (s, 6H, Me), 7.37 (dd, $^3J_{C-H} = 7.6$ Hz, $^3J_{C-H} = 4.4$ Hz, 1H, pyridyl), 7.82 (td, $^3J_{C-H} = 7.6$ Hz, $^4J_{C-H} = 2.0$ Hz, 1H, pyridyl), 7.91 (d, $^3J_{C-H} = 7.6$ Hz, 1H, pyridyl), 8.81 (dt, $^3J_{C-H} = 4.4$ Hz, $^4J_{C-H} = 2.0$ Hz, 1H, pyridyl). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 26.57 (2C, Me), 27.23 (2C, Me), 32.36 (1C, Me), 50.68 (2C, sp^3-C_{60}), 53.56 (2C, sp^3-C_{60}), 54.71 (1C, sp^3-C_{60}), 71.71 (1C, sp^3-C_{60}), 119.73 (1C, pyridyl), 121.88 (1C, pyridyl), 136.67 (1C, pyridyl), 142.70 (2C), 143.22 (2C), 143.78 (2C), 143.87 (2C), 143.92 (1C), 143.99 (2C), 144.09 (2C), 144.49 (2C), 144.90 (2C), 145.19 (2C), 145.53 (2C), 146.24 (2C), 146.62 (2C), 146.80 (2C), 146.90 (2C), 147.29 (1C, pyridyl), 147.61 (1C), 147.78 (2C), 147.82 (2C), 147.95 (2C), 148.21 (2C), 148.26 (2C), 148.28 (2C), 148 51 (2C), 149.24 (2C), 152.12 (2C), 153.57 (2C), 155.70 (1C, pyridyl), 156.98 (2C), 158.69 (2C). IR (KBr): ν/cm^{-1} 2960 (m), 2919 (m), 2859 (w), 1581 (m), 1515 (m), 1458 (m), 1447 (m), 1428 (m), 1417 (w), 1370 (w), 1287 (w), 1266 (w), 1239 (w), 1200 (w), 1127 (w), 1093 (w), 1051 (w), 997 (w), 924 (w), 879 (w), 795 (w), 782 (w), 747 (w), 729 (w), 694 (w), 686 (m), 655 (w), 577 (w), 569 (w), 561 (w), 552 (m), 541 (m), 527 (m), 519 (m). UV−vis (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2): λ_{max}/nm, (ϵ) 260 (72 000), 270 (71 500), 347 (21 500), 355 (20 700, shoulder), 393 (12 200), 470 (3860, shoulder). APCI-MS (+): m/z 874 ($[M + H]^+$), (−) m/z 873 ($[M]^-$). HR-APCI-MS (+): m/z found 873.1509; calcd for **3d** 873.1518.

Preparation of $C_{60}Me_5Cl$ (3b). To a suspension of $C_{60}Me_5H$ (501 mg, 0.628 mmol) in benzene (20 mL) was added a solution of *t*-BuOK (1.0 M, 0.75 mL, 0.075 mmol) in THF. After stirring for 5.5 h, *N*-chlorosuccinimide (109 mg, 0.816 mmol) was added. The mixture was stirred for 10 min. After the mixture was diluted with toluene, the mixture was washed with water. The organic phase was concentrated in vacuo. After preparative HPLC separation (toluene/2-propanol = 7:3, flow rate = 18 mL/min, retentions time = 7.0−8.0 min), **3b** (285 mg, 55% yield) was obtained as air-stable reddish-orange solids. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 6H, Me), 2.35 (s, 6H, Me), 2.55 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.55 (2C, Me), 26.53 (2C, Me), 33.58 (1C, Me), 50.65 (2C, sp^3-C_{60}), 52.49 (2C, sp^3-C_{60}), 54.25 (1C, sp^3-C_{60}), 77.64 (1C, $C(sp^3$-$C_{60})$-Cl), 142.79 (2C), 142.99 (2C), 143.20 (2C), 143.58 (2C), 143.87 (2C), 144.15 (2C), 144.24 (2C), 144.37 (2C), 144.41 (2C), 145.12 (2C), 145.13 (2C), 146.74 (2C), 146.80 (2C), 147.70 (2C), 147.86 (2C), 147.94 (2C), 148.13 (2C), 148.27 (2C), 148.28 (2C), 148.30 (2C), 148.31 (2C), 148.52 (2C), 152.40 (2C), 153.41 (2C), 154.63 (2C), 156.92 (2C). IR (KBr): ν/cm^{-1}, 2963 (m), 2920 (m), 2859 (m), 1444 (s), 1417 (w), 1373 (w), 1287 (w), 1265 (w), 1238 (w), 1201 (w), 1129 (w), 815 (m), 797 (m), 686 (m), 656 (w), 576 (w), 553 (m), 543 (m), 526 (m). UV−vis (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2): λ_{max}/nm (ϵ), 258 (110 000), 272 (105 000), 338 (33 900), 354 (30 600), 394 (17 400), 475 (5020, shoulder). APCI-MS (+): m/z 830. HR-APCI-MS (+): m/z found 830.0864; calcd for **3b** 830.0862.

Preparation of $C_{60}Me_5Br$ (3c). Bromide **3c** was synthesized as for **3b**, using the following reagents: $C_{60}Me_5H$ (1.00 g, 1.26 mmol), *t*-BuOK (1.0 M, 1.50 mL, 1.50 mmol) in THF, *N*-bromosuccinimide (289 mg, 1.62 mmol), benzene (40 mL). Yield: 848 mg (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 6H, Me), 2.43 (s, 6H, Me), 2.67 (s, 3H, Me). ^{1}H NMR (400 MHz, $CDCl_3/CS_2$): δ 2.29 (s, 6H, Me), 2.41 (s, 6H, Me), 2.65 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.68 (2C, Me), 26.37 (2C, Me), 37.73 (1C, Me), 50.60 (2C, sp^3-C_{60}), 52.73 (2C, sp^3-C_{60}), 54.10 (1C, sp^3-C_{60}), 69.54 (1C, $C(sp^3$-$C_{60})$-Br), 141.91 (2C), 142.76 (2C), 143.05 (2C), 143.52 (2C), 143.82 (2C), 143.87 (2C), 144.19 (5C), 144.35 (2C), 144.42 (2C), 145.16 (4C), 146.71 (2C), 146.76 (2C), 147.64 (2C), 147.87 (2C), 147.95 (1C), 148.06 (2C), 148.28 (6C), 148.51 (2C), 148.58 (2C), 152.00 (2C), 153.34 (2C), 155.18 (2C), 157.15 (2C). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CS_2$): δ 24.52 (2C, Me), 26.22 (2C, Me), 37.52 (1C, Me), 50.26 (2C, sp^3-C_{60}), 52.39 (2C, sp^3-C_{60}), 53.83 (1C, sp^3-C_{60}), 69.43 (1C, $C(sp^3$-$C_{60})$-Br), 141.57 (2C), 142.63 (2C), 142.75 (2C), 143.20 (2C), 143.68 (2C), 143.73 (2C), 143.89 (2C), 144.04 (2C), 144.12 (2C), 144.20 (2C), 144.35 (1C), 144.77 (2C), 144.86 (2C), 146.44 (2C), 146.48 (2C), 147.39 (2C), 147.62 (2C), 147.72 (1C), 147.83 (2C), 148.05 (6C), 148.19 (2C), 148.25 (2C), 151.64 (2C), 152.96 (2C), 154.84 (2C), 156.78 (2C). IR (KBr): ν/cm^{-1}, 2963 (m), 2920 (m), 2859 (m), 1443 (s), 1417 (w), 1372 (w), 1287 (w), 1264 (w), 1238 (w), 1200 (w), 1129 (w), 806 (w), 782 (m), 756 (w), 685 (m), 656 (w), 576 (w), 552 (m), 541 (m), 526 (m). UV−vis (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2): λ_{max}/nm (ϵ), 259 (104 000), 271 (100 000), 340 (32 500), 354 (29 600), 393 (17 300), 475 (4880, shoulder). FAB-MS (+): m/z 874 (M^+). APCI-MS (+): m/z 874 (M^+). HR-APCI-MS (+): m/z found 874.0371; calcd for **3c** 874.0357.

Preparation of $C_{60}Ph_5F$ (4a). Fluoride **4a** was synthesized with a similar procedure for the synthesis of **3a**, using the following reagents: $C_{60}Ph_5H$ (100 mg, 90.3 μmol), *t*-BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, *N*-fluoropyridinium triflate (26.8 mg, 108 μmol), THF (5.0 mL). Yield: 93.1 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3/CS_2 = 1:3$): δ 7.01−7.19 (m, 11H, Ph), 7.31−7.38 (m, 6H, Ph), 7.49−7.51 (m, 4H, Ph), 7.84−7.87 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CS_2 = 1:3$): δ 58.21 (2C, sp^3-C_{60}), 60.28 (2C, sp^3-C_{60}), 61.93 (1C, sp^3-C_{60}), 67.75 (1C, $C(sp^3$-$C_{60})$-F), 127.16 (1C, Ph), 127.59 (2C, Ph), 127.73 (2C, Ph), 127.84 (4C, Ph), 127.90 (2C, Ph), 127.96 (2C, Ph), 127.99 (4C, Ph), 128.65 (4C, Ph), 128.90 (4C, Ph), 130.10 (2C, Ph), 137.73 (2C, Ph), 137.92 (1C, Ph), 142.72 (2C), 143.10 (2C), 144.01 (1C), 144.10 (2C), 144.11 (2C), 144.16 (2C), 144.40 (2C), 144.58 (2C), 144.64 (2C), 145.07 (2C), 145.15 (2C), 145.58 (2C), 147.09 (2C), 147.11 (2C), 147.22 (2C), 147.36 (2C), 147.39 (2C), 147.58 (2C), 147.82 (2C), 147.98 (1C), 148.06 (2C), 148.46 (2C), 148.49 (2C), 148.53 (2C), 148.57 (2C), 148.61 (2C), 151.45 (2C), 155.62 (2C). IR (KBr): ν/cm^{-1}, 1598 (w), 1492 (m), 1463 (w), 1447 (m), 1419 (w), 1261 (m), 1237 (w), 1158 (w), 1069 (w), 1031 (m), 1012 (m), 964 (w), 943 (w), 910 (w), 889 (w), 735 (m), 692 (s), 668 (m), 656 (m). UV−vis (in toluene/2-propanol = 7:3): λ_{max}/nm, 287, 340, 354 (shoulder), 394, 470. APCI-MS (±): m/z 1124 ($M^{\pm}$).

Preparation of $C_{60}Ph_5Cl$ (4b). Chloride **4b** was synthesized with a similar procedure for the synthesis of **3b**, using the following reagents: $C_{60}Ph_5H$ (201 mg, 0.181 mmol), *t*-BuOK (1.0 M, 0.22 mmol, 0.22 mL) in THF, *N*-chlorosuccinimide (31.4 mg, 0.235 mmol), benzene (8.0 mL). Yield: 114 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10−7.40 (m, 17H, Ph), 7.64−7.69 (m, 4H, Ph), 7.93−7.98 (m, 4H, Ph). ^{1}H NMR (400 MHz, $CDCl_3/CS_2 = 1:1$):

δ 7.04−7.30 (m, 17H, Ph), 7.59−7.61 (m, 4H, Ph), 7.89−7.90 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 58.25 (2C, sp^3-C_{60}), 60.89 (2C, sp^3-C_{60}), 63.47 (1C, sp^3-C_{60}), 127.19 (1C, Ph), 127.72 (4C, Ph), 127.82 (2C, Ph), 128.45 (4C, Ph), 128.49 (4C, Ph), 128.68 (4C, Ph), 128.69 (4C, Ph), 130.03 (2C, Ph), 137.10 (2C, Ph), 138.60 (2C, Ph), 143.47 (1C, Ph), 142.78, 143.28, 143.53, 143.62, 143.74, 143.89, 144.07, 144.18, 144.29, 144.43, 145.21, 145.25, 146.66, 147.18, 147.30, 147.75, 148.06, 148.18, 148.40, 148.56, 148.62, 148.69, 150.22, 151.09, 153.61, 156.63 (signals due to sp^2 carbon atoms of C_{60}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$/CS_2 = 1:1): δ 57.95 (2C, sp^3-C_{60}), 60.63 (2C, sp^3-C_{60}), 63.21 (1C, sp^3-C_{60}), 76.13 (1C, *C*(sp^3-C_{60})-Cl), 127.00 (1C, Ph), 127.57(4C, Ph), 127.62 (2C, Ph), 128.25 (4C, Ph), 128.33 (4C, Ph), 128.49 (4C, Ph), 128.55 (4C, Ph), 129.83 (2C, Ph), 136.75 (2C, Ph), 138.26 (2C, Ph), 142.65 (2C), 143.03 (1C, Ph), 143.03 (2C), 143.23 (2C), 143.37 (2C), 143.44 (2C), 143.66 (2C), 143.94 (2C), 144.04 (2C), 144.11 (2C), 144.30 (2C), 144.94 (2C), 145.01 (2C), 146.37 (2C), 146.94 (2C+1C), 147.07 (2C), 147.54 (2C), 147.83 (1C), 147.97 (2C), 148.16 (2C), 148.35 (6C), 148.46 (2C), 149.96 (2C), 150.77 (2C), 153.29 (2C), 156.33 (2C). IR (KBr): ν/cm^{-1}, 3058 (w), 3028 (w), 2924 (w), 1599 (m), 1493 (s), 1462 (w), 1446 (m), 1418 (w), 1288 (w), 1263 (w), 1236 (w), 1204 (w), 1185 (w), 1157 (w), 1109 (w), 1070 (w), 1032 (m), 1003 (w), 911 (w), 837 (w), 788 (w), 735 (m), 694 (s), 666 (w), 584 (m), 565 (m), 543 (s), 479 (w). UV−vis (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2): λ_{max}/nm (ϵ), 260 (106 000), 273 (96 300, shoulder), 339 (32 300), 356 (28 300, shoulder), 390 (14 600), 475 (4850, shoulder). APCI-MS (+): *m*/*z* 1140 (M^+). HR-APCI-MS (+): *m*/*z* found 1140.1745; calcd for **4b** 1140.1645.

Preparation of $C_{60}Ph_5Br$ (4c). Bromide **4c** was synthesized with a similar procedure for the synthesis of **3b**, using the following reagents: $C_{60}Ph_5H$ (100 mg, 90.3 μmol), *t*-BuOK (1.0 M, 99.3 μL, 99.3 μmol) in THF, *N*-bromosuccinimide (19.2 mg, 108 μmol), benzene (5.0 mL). Yield: 91.8 mg (86%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.10−7.42 (m, 17H, Ph), 7.66−7.73 (m, 4H, Ph), 7.94−8.03 (m, 4H, Ph). ^1H NMR (500 MHz, $CDCl_3$/CS_2 = 1:3): δ 7.03−7.27 (m, 17H, Ph), 7.57−7.58 (m, 4H, Ph), 7.88 (s, 4H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$/CS_2 = 1:3): δ 57.69 (2C, sp^3-C_{60}), 60.60 (2C, sp^3-C_{60}), 67.62 (1C, sp^3-C_{60}), 69.45 (1C, sp^3-C_{60}), 127.51 (1C, Ph), 127.60 (2C, Ph), 128.35 (4C, Ph), 128.67 (12C, Ph), 128.29 (2C, Ph), 129.49 (2C, Ph), 136.83 (1C, Ph), 138.48 (2C, Ph), 141.90 (2C), 142.64 (2C), 142.99(2C), 143.21 (2C), 143.33 (2C), 143.64 (2C), 144.06 (4C), 144.33 (2C), 145.04 (2C), 145.78 (1C), 146.75 (2C), 146.95 (6C), 147.08 (2C), 147.54 (2C), 147.89 (1C), 148.04 (2C), 148.10 (2C), 148.18 (2C), 148.45 (6C), 149.94 (2C), 150.68 (2C), 153.93 (2C), 156.60 (2C). IR (KBr): ν/cm^{-1}, 3058 (w), 3028 (w), 2960 (m), 2924 (w), 1599 (m), 1493 (s), 1462 (m), 1446 (m), 1418 (w), 1288 (w), 1260 (s), 1236 (w), 1204 (w), 1185 (w), 1156 (w), 1094 (brs), 1030 (brs), 910 (w), 863 (w), 804 (s), 735 (m), 695 (s), 666 (w), 584 (m), 565 (w), 554 (w), 541 (m), 478 (w). UV−vis (1.0×10^{-5} mol·L^{-1} in CH_2Cl_2): λ_{max}/nm (ϵ), 260 (122 000), 350 (35 500), 395 (18 300), 475 (6230, shoulder). APCI-MS (+): *m*/*z* 1184.

Synthesis of Re(η^5-$C_{60}Me_5$)(CO)$_3$ (5). To a solution of $C_{60}Me_5Br$ (**3c**) (10.0 mg, 11.4 μmol) in THF (4.0 mL) was added a solution of Na[Re(CO)$_5$] (3.98 mg, 11.4 μmol) in THF (46.6 μL). After the mixture was stirred for 13 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (0.50 mL). The mixture was diluted with toluene and washed with water. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. Preparative HPLC separations (toluene/2-propanol = 7:3, flow rate = 14 mL/min, retention time = 11.5−12.5 min) afforded **5** (1.2 mg, 10%) as dark reddish-orange microcrystals. **5**: ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 15H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 32.11 (5C, Me), 50.96 (5C, sp^3-C_{60}), 110.80 (5C, C(Cp)), 143.65 (10C), 143.87 (10C), 146.72 (5C), 147.86 (10C), 148.47 (5C), 152.39 (10C), 193.40 (3C, CO). IR (KBr): ν/cm^{-1}, 2022, 1932. UV−vis (in toluene/2-propanol = 7:3) λ_{max}/nm, 285, 355, 395, 468. APCI-MS ($\pm$) *m*/*z* = 1064 ($M^{\pm}$). HR-APCI-MS (+): *m*/*z* found 1064.0602; calcd for **5** 1064.0551.

Synthesis of Fe(η^5-$C_{60}Me_5$)Br(CO)$_2$ (6). To a suspension of $C_{60}Me_5Br$ (**3c**) (660 mg, 0.754 mmol) in 1,2-dichlorobenzene (11 mL) was added Fe(CO)$_5$ (500 mL, 3.80 mmol). After stirring for 17 h at 25 °C, a dark orange precipitate was formed. Degassed hexane (40 mL) was added to the reaction mixture, and then the precipitate was filtered and washed with hexane. After the solid was dried under reduced pressure, compound **6** (707 mg, 95%) was obtained as a reddish-orange powder. ^1H NMR (400 MHz, C_6D_6): δ 2.23 (s, 15H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 28.70 (5C, Me), 51.11 (5C, sp^3-C_{60}), 105.89 (5C, C(Cp)), 143.62 (10C), 144.10 (10C), 147.38 (5C), 148.59 (10C), 148.86 (5C), 152.33 (10C), 214.06 (2C, CO). IR (KBr): ν/cm^{-1}, 2037, 1996. UV−vis (in toluene/2-propanol = 7:3): λ_{max}/nm, 288, 336 (shoulder), 356 (shoulder), 394, 466 (shoulder).

Synthesis of Ru(η^5-$C_{60}Me_5$)Br(CO)$_2$ (7). A solution of **3c** (87.9 mg, 100 μmol) in 1,2-dichlorobenzene (9 mL) was degassed under reduced pressure over 30 min at 0 °C. Then $Ru_3(CO)_{12}$ (26.8 mg, 41.9 μmol) was added to the solution, which was stirred at 100 °C for 12 h. The solution was concentrated to dryness under reduced pressure. The residue was dissolved in toluene, and insoluble products were removed by filtration through a pad of silica gel. The crude material was purified with silica gel column chromatography (eluent: CS_2 then toluene), and the solution was concentrated under reduced pressure to give **7** (53.8 mg, 52% yield) as reddish-orange microcrystals. The product was identical with an authentic sample by HPLC and ^1H NMR.[2c]

Synthesis of Ru(η^5-$C_{60}Me_5$)Cl(CO)$_2$. A solution of **3b** (32.8 mg, 39.5 μmol) in 1,2-dichlorobenzene (3 mL) was degassed under reduced pressure over 30 min at 0 °C. Then $Ru_3(CO)_{12}$ (9.7 mg, 15.2 μmol) was added to the solution, which was stirred at 100 °C for 13 h. The solution was concentrated to dryness under reduced pressure. The residue was dissolved in toluene, and insoluble products were removed by filtration through a pad of silica gel. The crude material was purified with silica gel column chromatography (eluent: CS_2 then toluene), and the solution was concentrated under reduced pressure to give the title compound (15 mg, 38% yield) as reddish-orange microcrystals. The product was identical with an authentic sample by HPLC and ^1H NMR.[2b]

Synthesis of Co(η^5-$C_{60}Me_5$)(CO)$_2$ (8). To a solution of $C_{60}Me_5Br$ (**3c**) (20.1 mg, 23.0 μmol) in THF (5.0 mL) was added a solution of Na[Co(CO)$_4$] (4.45 mg, 22.9 μmol) in THF (0.97 mL). After the mixture was stirred for 1 h, the mixture was diluted with toluene and passed through a pad of silica gel. The solution was concentrated under reduced pressure (ca. 2 mL), and methanol was added to obtain precipitates. The title compound was obtained as orange solids (46% yield). ^1H NMR (400 MHz, THF-d_8): δ 2.43 (s, 15H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6/CS_2): δ 30.0 (5C, Me), 50.1 (5C, sp^3-C_{60}), 108.0 (5C, C(Cp)), 144.1 (5C), 144.5 (10C), 147.1 (10C), 148.3 (10C), 148.8 (10C), 153.2 (5C). One signal due to the carbonyl ligand was not observed because of low solubility of this compound. IR (KBr): ν/cm^{-1}, 2019, 1965. FAB-MS (+): *m*/*z* 910 (M^+).

Synthesis of Fe(η^5-$C_{60}Me_5$)Me(CO)$_2$ (10). To a solution of **6** (47.6 mg, 48.1 μmol) in benzene (8.4 mL) was added a 1.14 M solution of MeLi in ether (84.5 μL, 96.2 μmol) at 25 °C. After stirring for 10 min, the reaction mixture was passed through a pad of silica gel. The solution was concentrated under reduced pressure (ca. 5 mL), and methanol was added to obtain precipitates. The title compound was obtained as orange solids (22.3 mg, 50%). MeMgBr in THF could be also used in this synthesis. ^1H NMR (400 MHz, C_6D_6): δ 0.99 (s, 3H, Fe-*Me*), 2.10 (s, 15H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ −20.83 (1C, Fe-*Me*), 28.18 (5C, Me), 50.95 (5C, sp^3-C_{60}), 106.59 (5C, C(Cp)), 144.04 (10C),

144.22 (10C), 147.39 (5C), 148.55 (10C), 148.93 (5C), 153.11 (10C), 218.13 (2C, CO). IR (KBr): ν/cm^{-1}, 2004, 1953.

Synthesis of Fe(η^5-$C_{60}Me_5$)(CCH)(CO)$_2$ (11). To a solution of **6** (108 mg, 110 μmol) in benzene (19.2 mL) was added a 0.95 M solution of HCCMgBr in THF (217 μL, 206 μmol) at 25 °C. After stirring for 10 min, the reaction mixture was passed through a pad of silica gel. The solution was concentrated under reduced pressure (ca. 10 mL), and methanol was added to obtain precipitates. The title compound was obtained as orange solids (74.3 mg, 71%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.72 (s, 1H, CCH), 2.34 (s, 15H, Me). ^{1}H NMR (400 MHz, THF-d_8/CS_2 = 1:1): δ 1.80 (s, 1H, CCH), 2.57 (s, 15H, Me). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8/CS_2 = 1:1): δ 29.26 (5C, Me), 51.45 (5C, sp^3-C_{60}), 107.36 (5C, C(Cp)), 108.24 (1C, CCH), 144.35 (10C), 144.40 (10C), 147.58 (5C), 148.76 (10C), 149.07 (5C), 153.36 (10C), 213.52 (2C, CO). One of two signals due to the alkynyl group was not observed because of low solubility of this compound. IR (KBr): ν/cm^{-1}, 2038, 1992.

Synthesis of Fe(η^5-$C_{60}Me_5$)(CCPh)(CO)$_2$ (12). To a solution of **6** (102 mg, 103 μmol) in benzene (18.0 mL) was added a 0.95 M solution of PhCCMgBr in THF (217 μL, 206 μmol) at 25 °C. After stirring for 10 min, the reaction mixture was passed through a pad of silica gel. The solution was concentrated under reduced pressure (ca. 10 mL), and methanol was added to obtain precipitates. The title compound was obtained as orange solids (55.8 mg, 54%). ^{1}H NMR (400 MHz, C_6D_6): δ 2.25 (s, 15H, Me), 7.34−7.67 (m, 5H, Ph). ^{1}H NMR (400 MHz, THF-d_8/CS_2 = 1:1): δ 2.60 (s, 15H, Me), 7.10 (m, 1H, Ph), 7.21 (m, 2H, Ph), 7.33 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 28.73 (5C, Me), 50.74 (5C, sp^3-C_{60}), 107.24 (5C, C(Cp)), 126.15, 128.58, 131.64, 143.62 (10C), 144.10 (10C), 147.38 (5C), 148.59 (10C), 148.94 (5C), 152.33 (10C), 213.62 (2C, CO). Two signals due to the alkynyl group were not observed because of low solubility of this compound. IR (KBr): ν/cm^{-1}, 2035, 1991.

Electrochemical Studies. Electrochemical measurements were performed using a BAS CV-50W voltammetric analyzer. A glassy carbon electrode, a platinum coil, and an Ag/Ag$^+$ electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s. All half-wave potentials $E_{1/2} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. The potential was corrected against Fc/Fc$^+$.

X-ray Crystallographic Analysis. Single crystals **5** suitable for X-ray diffraction studies were grown and subjected to data collection. The data set was collected on a MacScience DIP2030 imaging plate diffractometer using Mo Kα (graphite-monochromated, λ = 0.71069 Å) radiation. Crystal data and data statistics are summarized in Table 1. The structure of **5** was solved by the direct method (SHELXS-97).[21] The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method, using SHELXL-97.[22] Hydrogen atoms were placed at calculated positions and refined with riding mode on their corresponding carbon atoms. In the subsequent refinement, the function $\sum w(F_o^2 - F_c^2)^2$ was minimized, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$.

Table 1. Crystal Data and Structure Analysis Results for Complex 5

	5·CS_2
formula	$C_{69}H_{15}O_3Re_1S_2$
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
R, R_w ($I > 2s(I)$)	0.0863, 0.0900
R_1, wR_2 (all data)	0.2523, 0.2565
GOF on F^2	1.067
a, Å	32.909(1)
b, Å	14.7480(7)
c, Å	19.4810(6)
α, deg	90
β, deg	122.842(2)
γ, deg	90
V, Å^3	7943.8(5)
Z	8
T, K	153(2)
cryst size, mm	0.70, 0.20, 0.10
D_{calcd}, g/cm^{-3}	1.91
$2\theta_{min}$, $2\theta_{max}$, deg	4.46, 51.12
no. reflns measd ($I > 2\sigma(I)$)	6790
no. params	677

Acknowledgment. This study was partially supported by the 21st Century COE Program for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Crystallographic data of **5** (CIF file) and NMR spectra of new compounds (PDF file). This material is available free of charge via the Internet at http://pubs.acs.org.

OM8001262

(21) Sheldrick, G. M. *SHELXS-97*, Program for the Solution of Crystal Structures; University of Göttingen: Germany, 1997.

(22) Sheldrick, G. M. *SHELXL-97*, Programs for Crystal Structure Analysis (Release 97-2); Institut für Anorganische Chemie der Universität Göttingen: Germany, 1998.