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Group 6 Metal Complexes of the η^5-Pentamethyl[60]fullerene

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A molybdenum pentamethyl[60]fullerene bromo tricarbonyl complex, Mo(η^5-$C_{60}Me_5$)Br$(CO)_3$ (**3**), was successfully synthesized by the reaction of $C_{60}Me_5Br$ (**2**) with $Mo(CO)_3(EtCN)_3$. Treatment of **3** with I_2 afforded an iodo complex, Mo(η^5-$C_{60}Me_5$)I$(CO)_3$ (**4**). The reaction employing $C_{60}Me_5K$ (**5**) prepared from $C_{60}Me_5H$ (**1**) and KH, followed by treatment with $Mo(CO)_3(EtCN)_3$ and then Diazald, gave a nitrosyl complex, Mo(η^5-$C_{60}Me_5$)(NO)$(CO)_2$ (**6**). Complex **6** was converted to a molybdenum(IV) complex, Mo(η^5-$C_{60}Me_5$)Cl_2(NO)(CO) (**7**), by the reaction with PCl_5. A molybdenum(VI) complex, Mo(η^5-$C_{60}Me_5$)O_2Br (**8**), was obtained by exposure of **3** in air. Tungsten- and chromium-nitrosyl complexes, W(η^5-$C_{60}Me_5$)(NO)$(CO)_2$ (**9**) and Cr(η^5-$C_{60}Me_5$)(NO)$(CO)_2$ (**10**), were synthesized similarly to **6**. Complex **10** gave a dithiocarbonate complex, Cr(η^5-$C_{60}Me_5$)(η^2-S_2COEt)(NO) (**11**) through the reaction among **10**, ethanol, and carbon disulfide. Compounds **1**, **3**, **4**, **6**, **8**, and **11** were characterized by X-ray crystallography.

Introduction

Transition metal complexes of the penta(organo)[60]fullerenes,[1] M(η^5-$C_{60}R_5$)L_n (M = metal atoms, R = alkyl, aryl groups, L = ligands),[2−7] have recently become intriguing functional organometallic compounds. Liquid crystalline functions,[3h] ultrafast photoinduced charge separation properties,[8] asymmetric organic transformations,[4d,e] and photocurrent generation of self-assembled monolayers[9] are representative examples. The η^5-$C_{60}R_5$ complexes of the group 7−10 metals Re,[2] Fe,[3] Ru,[4] Ir,[5] Rh,[6] Ni,[7] Pd,[7] and Pt[7] have been prepared, but none of the early transition metal η^5-$C_{60}R_5$ complexes have been synthesized. One reason for the lack of such examples is the synthetic problem caused by the electron-withdrawing nature of the fullerene moiety, which intrinsically does not prefer to be bonded to an electron-deficient metal atom of the early transition metals.

For some time, we have tried to obtain the η^5-$C_{60}R_5$ complexes of the group 6 metal complexes, since the group 6 metals are known to give a variety of oxidation states from zero to six[10] and hence are of considerable interest. They are more oxophilic than the late transition metals and produce organometallic complexes containing metal−oxygen, metal−nitrogen, and other metal−heteroatom bonds.[10] Such properties have formed the background of the rich chemistry of the group 6 metals related to artificial nitrogen fixation,[11] metalloenzymes,[12−14]

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(1) (a) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850–12851. (b) Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 7912–7913. (c) Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. *J. Organomet. Chem.* **2000**, *599*, 32–36. (d) Sawamura, M.; Toganoh, M.; Kuninobu, Y.; Kato, S.; Nakamura, E. *Chem. Lett.* **2000**, 270–271. (e) Nakamura, E.; Sawamura, M. *Pure Appl. Chem.* **2001**, *73*, 355. (f) Hamasaki, R.; Matsuo, Y.; Nakamura, E. *Chem. Lett.* **2004**, *33*, 328–329. (g) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *Org. Lett.* **2006**, *8*, 1463–1466. (h) Matsuo, Y.; Iwashita, A.; Nakamura, E. *Chem. Lett.* **2006**, *35*, 858–859. (i) Matsuo, Y.; Muramatsu, A.; Tahara, K.; Koide, M.; Nakamura, E. *Org. Synth.* **2006**, *83*, 80–87.

(2) Toganoh, M.; Matsuo, Y.; Nakamura, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3530–3532.

(3) (a) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354–9355. (b) Toganoh, M.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13974–13975. (c) Nakamura, E. *Pure Appl. Chem.* **2003**, *75*, 427–434. (d) Nakamura, E. *J. Organomet. Chem.* **2004**, *689*, 4630–4635. (e) Herber, R. H.; Nowik, I.; Matsuo, Y.; Toganoh, M.; Kuninobu, Y.; Nakamura, E. *Inorg. Chem.* **2005**, *44*, 5629–5635. (f) Matsuo, Y.; Isobe, H.; Tanaka, T.; Murata, Y.; Murata, M.; Komatsu, K.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 17148–17149. (g) Matsuo, Y.; Tahara, K.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 7154–7155. (h) Matsuo, Y.; Muramatsu, A.; Kamikawa, Y.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 9586–9587.

(4) (a) Matsuo, Y.; Nakamura, E. *Organometallics* **2003**, *22*, 2554–2563. (b) Matsuo, Y.; Kuninobu, Y.; Ito, S.; Nakamura, E. *Chem. Lett.* **2004**, *33*, 68–69. (c) Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 8457–8466. (d) Matsuo, Y.; Mitani, Y.; Zhong, Y.-W.; Nakamura, E. *Organometallics* **2006**, *25*, 2826–2832. (e) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *Chem. Asian J.* **2007**, *2*, 358–366.

(5) Matsuo, Y.; Iwashita, A.; Nakamura, E. *Organometallics* **2005**, *24*, 89–95.

(6) (a) Sawamura, M.; Kuninobu, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2000**, *122*, 12407–12408. (b) Toganoh, M.; Matsuo, Y.; Nakamura, E. *J. Organomet. Chem.* **2003**, *683*, 295–300. (c) Matsuo, Y.; Nakamura, E. *Inorg. Chim. Acta* **2006**, *359*, 1979–1982.

(7) Kuninobu, Y.; Matsuo, Y.; Toganoh, M.; Sawamura, M.; Nakamura, E. *Organometallics* **2004**, *23*, 3259–3266.

(8) Guldi, D. M.; Rahman, G. M. A.; Marczak, R.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 9420–9427.

(9) Matsuo, Y.; Kanaizuka, K.; Matsuo, K.; Zhong, Y.-W.; Nakae, T.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 5016–5017.

(10) Imamoto, T., Ed. *Science of Synthesis, Vol. 2, Compounds of Groups 7-3*; Thieme: Stuttgart, 2002.

(11) (a) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861–863. (b) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 540–542. (c) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955–962.

(12) (a) Holm, R. H.; Berg, J. M. *Acc. Chem. Res.* **1986**, *19*, 363–370. (b) Takuma, M.; Ohki, Y.; Tatsumi, K. *Organometallics* **2005**, *24*, 1344–1347. (c) Baba, K.; Okamura, T.; Suzuki, C.; Yamamoto, H.; Yamamoto, T.; Ohama, M.; Ueyama, N. *Inorg. Chem.* **2006**, *45*, 894–901.

(13) (a) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, 1994. (b) Sigel, A.; Sigel, H., Eds. *Molybdenum and Tungsten: Their Roles in Biological Processes*; Marcel Dekker: New York, 2002.

(14) (a) Einsle, O.; Tezcan, F. A.; Andrade, S.-L. A.; Schmid, B.; Yoshida, M.; Howard, J.-B.; Rees, D. C. *Science* **2002**, *297*, 1696–1700. (b) Dos Santos, P. C.; Dean, D. R.; Hu, Y.; Ribbe, M. W. *Chem. Rev.* **2004**, *104*, 1159–1174.

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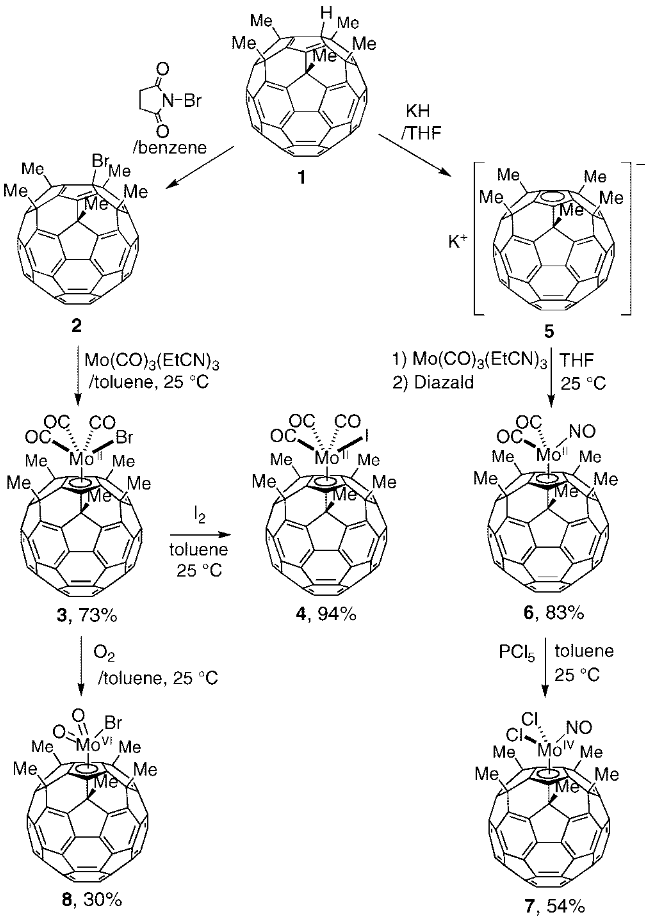
Scheme 1



and others.[15] We herein report the syntheses, structures, and derivatization of the group 6 metal η^5-pentamethyl[60]fullerene complexes. Carbonyl, chloro, bromo, iodo, nitrosyl, oxo, and dithiocarbonate complexes were synthesized (Scheme 1), and some of them were characterized by X-ray crystallography.

Results and Discussion

Structures of the Pentamethyl[60]fullerene Ligand. To start the studies on the synthesis of group 6 metal complexes, we first examined the X-ray crystal structure of the pentamethyl[60]fullerene ligand. In our previous report we often referred to the X-ray structure of pentaaryl[60]fullerenes C_{60}(biphenyl)$_5$H[16] and [K(thf)$_6$][$C_{60}Ph_5$][17] and pentaalkyl[60]fullerenes $C_{60}(CH_2SiMe_2R)_5H$ (R = Me, Ph, and biphenyl),[18] but not to the X-ray structure of $C_{60}Me_5H$ (**1**).[1d,i] A single crystal of **1** suitable for X-ray analysis was obtained on recrystallization by slow diffusion of ethanol into a solution of **1** in CS_2. The structure shown in Figure 1 indicates that the cyclopentadiene structure, embedded in the fullerene skeleton, is not hindered much by the five methyl groups. The structure of the bottom 50π-electron conjugated system in **1** was also found to be essentially the same as that in the pentaaryl complexes.

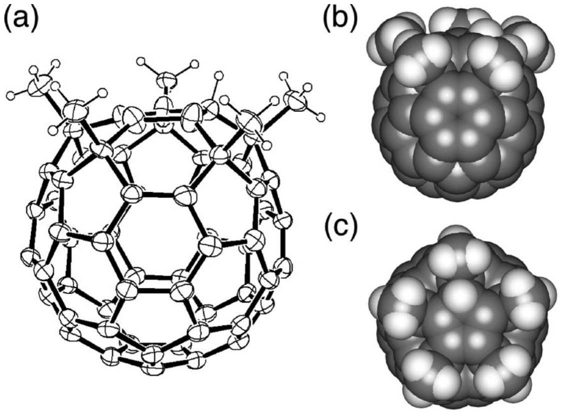


Figure 1. X-ray crystal structure of $\mathbf{1}\cdot CS_2$. Solvent molecules are omitted for clarity. The hydrogen atom is disordered on the five carbon atoms of the cyclopentadiene moiety. (a) ORTEP drawing at the 30% ellipsoid probability level. (b) Side view of the space-filling model. (c) Top view of the space-filling model.

Syntheses and Reactivities of the Molybdenum−Pentamethyl[60]fullerene Complexes. We first tried to synthesize the molybdenum complexes of the pentamethyl[60]fullerene, since molybdenum complexes tend to afford NMR-active diamagnetic Mo(II), -(IV), and -(VI) complexes. We chose a molybdenum(0) tricarbonyl tris(propionitrile) complex, $Mo(CO)_3(EtCN)_3$,[19] as a starting material, because the propionitrile ligand is a labile ligand that can form coordinatively unsaturated reactive intermediates. We anticipated that this low-valent Mo(0) complex reacts with a bromopentamethyl[60]fullerene, $C_{60}Me_5Br$ (**2**),[20] through oxidative addition to give the desired Mo(II) complexes. Treatment of $Mo(CO)_3(EtCN)_3$ with **2** in THF at room temperature afforded a Mo(II) bromo tricarbonyl complex, Mo(η^5-$C_{60}Me_5$)Br(CO)$_3$ (**3**), in 73% yield (Scheme 1). A hexacarbonyl complex, $Mo(CO)_6$, a commonly used Mo(0) source, was too stable to react with **2**. Complex **3** was air-sensitive in solution and gradually decomposed into a mixture containing **1** and its oxidized compounds[21] together with an oxo molybdenum pentamethyl[60]fullerene complex (vide infra). The IR spectrum of **3** exhibited three strong absorption peaks due to stretching vibrations of the carbonyl groups at 2044, 1979, and 1937 cm^{-1}. These are assigned to two symmetric and one asymmetric stretching vibration frequency, indicating that three carbonyl groups are attached to the metal center. In the ^{1}H NMR spectrum of **3**, one signal due to the five methyl groups was observed at δ 2.47, indicating free rotation of the η^5-$C_{60}Me_5$ ligand around the molybdenum−fullerene axis on the NMR time scale. The signal pattern of the ^{13}C NMR was consistent with this pseudo C_{5v} symmetry. X-ray crystallographic characterization was performed using a single crystal obtained by slow diffusion of ethanol to a toluene solution of **3** (Figure 2). The crystal structure revealed a four-legged piano stool structure, which presents a new structure among the previously reported three- and two-legged metal η^5-penta(organo)[60]fullerene complexes. The larger coordination space of the $C_{60}Me_5$ ligand than the C_{60}-Ar_5 ligand tolerates the four-ligand coordination. Three carbonyl ligands comfortably fit with two methyl groups, while the bromo ligand was located above a methyl group (Figure 2c). Steric hindrance between the bromo ligand and the methyl group

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[15] Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152–4205.

[16] Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702–705.

[17] Matsuo, Y.; Tahara, K.; Nakamura, E. *Chem. Lett.* **2005**, *34*, 1078–1079.

[18] Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 432–433.

[19] Kubas, G. J.; Van der Sluys, L. S. *Inorg. Synth.* **1990**, *28*, 29–33.

[20] Matsuo, Y.; Kuninobu, Y.; Muramatsu, A.; Sawamura, M.; Nakamura, E. Organometallics **2008**, *27*, 3403–3409.

[21] Al-Matar, H.; Abdul-Sada, A. K.; Avent, A. G.; Taylor, R. *Org. Lett.* **2001**, *3*, 1669–1671.

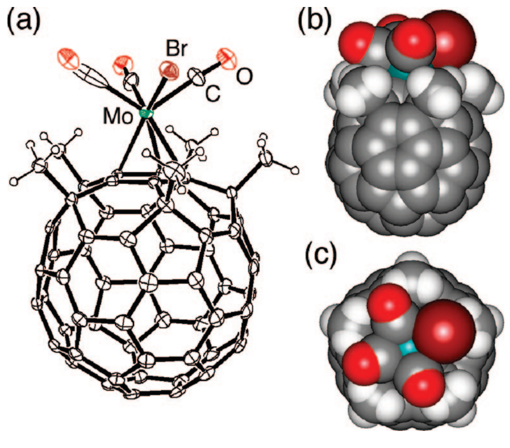

Figure 2. X-ray crystal structure of **3**·(toluene)$_2$. Solvent molecules are omitted for clarity. The bromine atom and one of three carbonyl ligands are disordered. The bond length between the molybdenum atom and the bromine atom with a site occupancy of 0.9 is 2.627(2) Å. (a) ORTEP drawing at the 30% ellipsoid probability level. (b) Side view of the space-filling model. (c) Top view of the space-filling model.

caused inequivalent Mo−C(fullerene) bond lengths ranging from 2.458(5) to 2.311(6) Å. An average bond length of five Mo−C(fullerene) bonds in **3** (2.37 Å) was slightly longer than that in an ordinary cyclopentadienyl complex Mo(η^5-C_5H_5)Br(CO)$_3$ (2.33 Å).[22]

An analogous iodo complex, Mo(η^5-$C_{60}Me_5$)I(CO)$_3$ (**4**), was obtained in 94% yield by the reaction of **3** with I_2 in toluene at room temperature (Scheme 1). In contrast to our expectation, oxidation of the metal center from II to IV did not take place at all. The use of PCl_5 and Br_2 did not yield any high-valent complex, either. The failure to react can be attributed to the electron-deficient nature of the metal center caused by the electron-withdrawing $C_{60}Me_5$ ligand. Steric hindrance between the large iodine atoms and the fullerene ligand is also considered to disturb the formation of metal trihalide complexes. We suspect that the smaller electronegativity of the iodine atom than the bromine atom (2.66 vs 2.96, Pauling) favors this halogen replacement to compensate the electron-deficiency of the fullerene group. The iodo complex **4** was also characterized by the X-ray crystallographic analysis (Supporting Information). Single crystals of **4** were obtained by the same method as **3**, using carbon disulfide and ethanol. The essence of the molecular structure of **4** was the same as that of **3**, except for the molybdenum−halogen bond (2.627(2) Å for **3**; 2.802(2) Å for **4**).

Next we investigated the synthesis of the molybdenum η^5-pentamethyl[60]fullerene complexes by the use of a nucleophilic pentamethyl[60]fullerene anion.[1d,i] With this approach, we synthesized a nitrosyl (nitric oxide) complex,[23] because the nitrosyl ligand comprises a formal three-electron donor with small steric bulkiness and because it is recently attracting broad interest for C−H bond activation.[24]A potassium complex of the pentamethyl[60]fullerene, [K(thf)$_n$][$C_{60}Me_5$] (**5**), synthesized by deprotonation of **1** with KH in THF, was allowed to react with Mo(CO)$_3$(EtCN)$_3$ in THF at room temperature. An assumed initial intermediate,[25] an anionic molybdenum complex, [K^+][Mo(η^5-$C_{60}Me_5$)(CO)$_3^-$], was treated with Diazald (= *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) for 2 h to obtain the nitrosyl complex Mo(η^5-$C_{60}Me_5$)(NO)(CO)$_2$ (**6**) in 83% yield (Scheme 1). The reaction with the tris(acetonitrile) complex Mo(CO)$_3$(MeCN)$_3$[26] instead of the tris(propionitrile) complex gave the same product in slightly lower yield. Complex **6** was stable in air and easily purified with silica gel column chromatography. The synthesis of **6** could be conducted on a 1 g scale. In the IR spectrum of **6**, an absorption due to the nitrosyl group was observed at 1660 cm^{-1}. Two absorption peaks due to symmetric and asymmetric stretching vibrations of the carbonyl groups were observed at 2009 and 1935 cm^{-1}, indicating that two carbonyl ligands are coordinated to the molybdenum center. The ^{1}H and ^{13}C NMR data revealed η^5-coordination of the $C_{60}Me_5$ ligand, as in the case of **3**. The molecular structure of **6** was unambiguously determined by X-ray analysis using single crystals obtained by recrystallization from CS_2/ethanol. The observed linear bonding mode of the nitrosyl ligand indicates that the nitrosyl ligand functions as a three-electron ligand and that complex **6** is an 18-electron complex. This compact three-electron nitrosyl ligand must be contributing toward stabilization of this metal−fullerene complex.

With the stable molybdenum complex **6** in hand, we investigated the oxidation of **6** for the synthesis of a high-valent molybdenum complex with the intention of obtaining an answer to the question about the tolerance of the mismatch of the electron-deficient metal center and the electron-deficient η^5-fullerene ligand. Treatment of a solution of **6** in toluene with PCl_5 resulted in carbon monoxide gas evolution to produce a 16-electron molybdenum(IV) dichloro complex, Mo(η^5-$C_{60}Me_5$)(NO)Cl_2 (**7**), in 54% yield (Scheme 1). The IR spectrum displayed no absorption peak due to the carbonyl groups (ν_{CO}, ca. 1900−2000 cm^{-1}) and one characteristic absorption peak due to the nitrosyl ligand (ν_{NO}, 1688 cm^{-1}). Signals in the ^{1}H and ^{13}C NMR spectra are in good agreement with the composition of **7** with an η^5-coordination of the fullerene ligand. Compound **7** was stable as a solid, but gradually decomposed in solution in air, affording **1** and its oxidized product.[21] Coordinatively unsaturated 16-electron group 6 metal nitrosyl complexes[27] of the type M(η^5-C_5H_5)(NO)R_2 have attracted special attention because of their catalytic activity for the C−H bond activation of alkanes.[24]

An additional high-valent molybdenum complex was obtained through air oxidation of the bromo tricarbonyl complex **3** (Scheme 1). A solution of **3** in toluene was exposed to air for 7 days, affording an oxo molybdenum(VI) complex, Mo(η^5-$C_{60}Me_5$)O_2Br (**8**), in 30% yield together with **1** and its oxidized side products.[21] Compound **8** was isolated by recrystallization from toluene solution and characterized by ^{1}H and ^{13}C NMR as well as single-crystal X-ray structure analysis. The bond lengths between the molybdenum and oxygen atoms are 1.697(5) and 1.699(4) Å, indicative of a Mo=O double bond, as known for other cyclopentadienyl dioxo molybdenum complexes.[28] Complex **8** represents an electron-deficient d^0 metal complex bearing an electron-withdrawing fullerene ligand. This

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(22) Boyle, T. J.; Takusagawa, F.; Heppert, J. A. *Acta Crystallogr.* **1990**, *C46*, 892–893.

(23) (a) Hayton, T. W.; Legzdins, P.; Sharp, W. B. *Chem. Rev.* **2002**, *102*, 935–991. (b) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

(24) (a) Tran, E.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 5071–5072. (b) Pamplin, C. B.; Legzdins, P. *Acc. Chem. Res.* **2003**, *36*, 223–233. (c) Tsang, J. Y. K.; Fujita-Takayama, C.; Buschhaus, M. S. A.; Patrick, B. O.; Legzdins, P. *J. Am. Chem. Soc.* **2006**, *128*, 14762–14763.

(25) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126–131.

(26) King., R. B. *J. Organomet. Chem.* **1967**, *8*, 139–148.

(27) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41–48.

(28) Kawaguchi, H.; Yamada, K.; Lang, J.-P.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10346–10358.

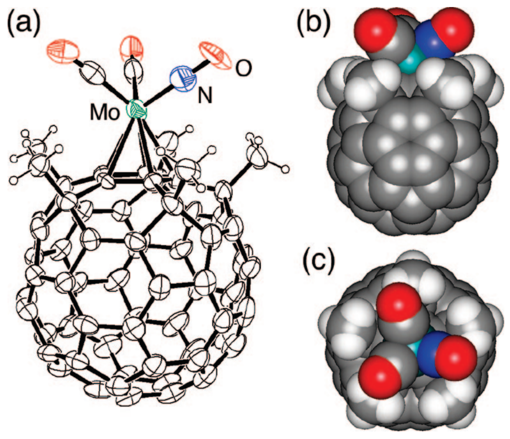


Figure 3. X-ray crystal structure of **6**·CS_2. Solvent molecules are omitted for clarity. Bond lengths: Mo−N = 1.83(2) Å, N−O = 1.23(2) Å. Bond angle: Mo−N−O = 178.0(2)°. (a) ORTEP drawing at the 30% ellipsoid probability level. (b) Side view of the space-filling model. (c) Top view of the space-filling model.

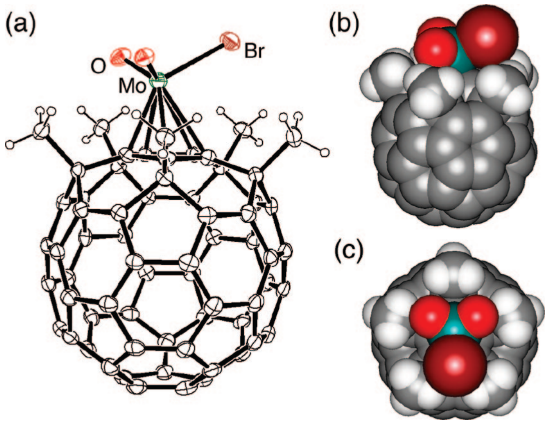
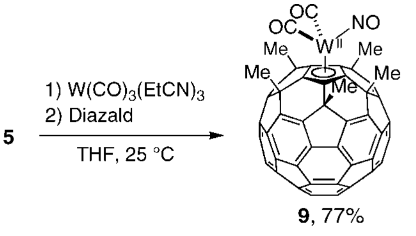


Figure 4. X-ray crystal structure of **8**. (a) ORTEP drawing at the 30% ellipsoid probability level. Bond lengths: Mo−Br = 2.4520(9) Å, Mo−O = 1.699(4) and 1.697(5) Å. (b) Side view of the space-filling model. (c) Top view of the space-filling model.

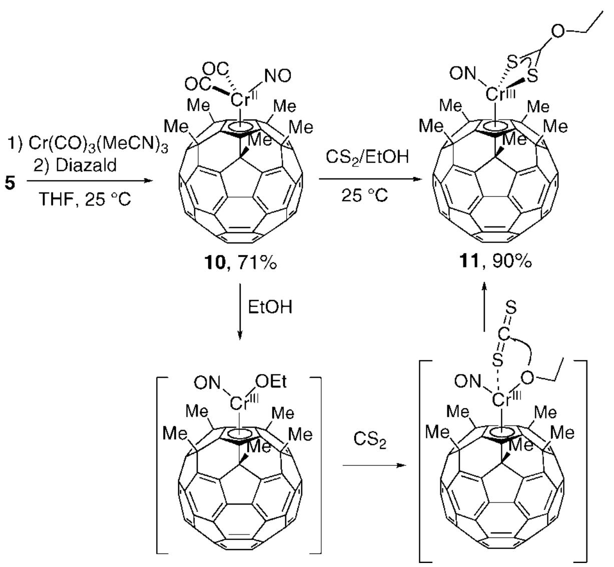
result suggests to us that the synthesis of group 4 and 5 metal complexes may be possible, but has not been achieved in our hands.

Synthesis of the Tungsten−Pentamethyl[60]fullerene−Nitrosyl Complex. We examined the synthesis of the tungsten complex using a similar starting material, $W(CO)_3(EtCN)_3$. The reaction of the potassium complex **5** with $W(CO)_3(EtCN)_3$ in THF, followed by the treatment with Diazald, afforded the corresponding tungsten nitrosyl complex $W(\eta^5\text{-}C_{60}Me_5)(NO)(CO)_2$ (**9**) as an air-stable compound in 77% yield (eq 1). This compound was characterized by IR, NMR, and high-resolution APCI-MS spectra and judged to have a quite similar structure to the molybdenum complex **6**. The reactivity of **9** seems to be similar to **6** or lower than **6**.



(1)

Scheme 2



Synthesis and Reactivity of the Chromium−Pentamethyl[60]fullerene−Nitrosyl Complex. The first-row transition metals have attracted interest because of their ubiquity on Earth and because of their high reactivity. We synthesized chromium complexes of the pentamethyl[60]fullerene with the aid of a labile tris(nitrile) complex (Scheme 2). Treatment of the potassium complex **5** with tris(acetonitrile) tricarbonyl chromium complex $Cr(CO)_3(MeCN)_3$[26] in THF caused a color change of the solution from dark red to dark green. This change suggests the formation of an anionic chromium complex,[25] $[K^+][Cr(\eta^5\text{-}C_{60}Me_5)(CO)_3^-]$. Addition of Diazald to this solution caused evolution of carbon monoxide gas and afforded a chromium(II) complex $Cr(\eta^5\text{-}C_{60}Me_5)(NO)(CO)_2$ (**10**) in 71% yield. This chromium nitrosyl complex **10** was an air-sensitive compound, in contrast to the molybdenum and tungsten congeners **6** and **9**. The product **10** in toluene solution in air degraded by 50% after 1 h, giving the oxidized compounds of **1**.[21]

Complex **10** in toluene reacted with ethanol to afford the ethoxy chromium(III) complex $Cr(\eta^5\text{-}C_{60}Me_5)(NO)(OEt)$ (Scheme 2), which was characterized with LC-MS. In order to trap this ethoxy complex, we conducted the reaction in carbon disulfide. A solution of **10** in carbon disulfide was treated with a few drops of ethanol. This reaction resulted in the insertion of carbon disulfide into the chromium−oxygen bond to afford a dithiocarbonate complex, $Cr(\eta^5\text{-}C_{60}Me_5)(\eta^2\text{-}S_2COEt)(NO)$ (**11**), in 90% yield. The chromium(III) complex **11** was stable in air and NMR-silent and was characterized by its IR spectrum and X-ray crystal structure analysis (Figure 5). Related cyclopentadienyl chromium dithiocarbonate complexes such as $Cr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}S_2CO^iPr)(CO)_2$ have been crystallographically characterized.[29] Because metal−dithiocarbonates are related to metal−carbonates, activation of carbon dioxide using a precursor of the dithiocarbonates may be an interesting subject of future studies.[30] We attempted to examine the reaction of **9** with CO_2 in the presence of alcohol, but did not obtain any favorable result because of the concomitant decomposition of **9** under these conditions.

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[29] (a) Goh, L. Y.; Weng, Z.; Leong, W. K.; Leung, P. H. *Organometallics* **2002**, *21*, 4398–4407. (b) Ng, V. W. L.; Kuan, S. L.; Weng, Z.; Leong, W. K.; Vittal, J. J.; Koh, L. L.; Tan, G. K.; Goh, L. Y. *J. Organomet. Chem.* **2005**, *690*, 2323–2332.

[30] (a) Kersting, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3987–3990. (b) Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004–2005.

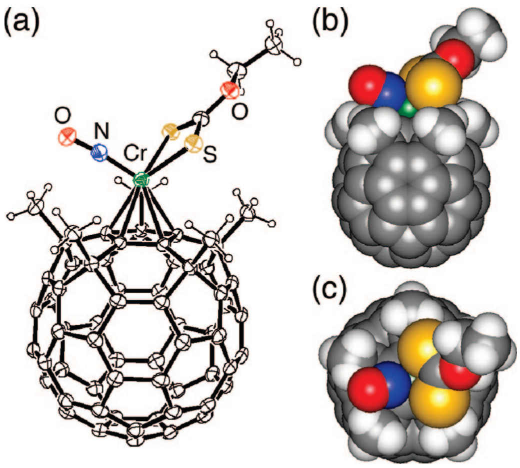

Figure 5. X-ray crystal structure of **11**·$(CS_2)_{0.5}$. Solvent molecules are omitted for clarity. Bond lengths: Cr−N = 1.688(5) Å, N−O = 1.194(6) Å. Bond angle: Cr−N−O = 173.8(5)°. (a) ORTEP drawing at the 30% ellipsoid probability level. (b) Side view of the space-filling model. (c) Top view of the space-filling model.

Summary

We reported on the synthesis of a series of group 6 metal complexes of the η^5-pentamethyl[60]fullerene ligand. These new members of the transition metal $C_{60}Me_5$ complexes were found to have a rich reactivity profile with a variety of oxidation states from II to VI. We anticipate that the present group 6 metal complexes can be built into a functionalized fullerene skeleton[3h,9,31] and can be converted to photoelectrochemically and magnetically active compounds useful in materials science. Catalysis would be another attractive application, for instance, nitrogen fixation. Given the unique electronic and steric[7] features of the pentamethyl[60]fullerene ligand, we expect that the present compounds would be useful for a variety of chemical and materials investigations.

Experimental Section

General Procedures. All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under nitrogen or argon using standard Schlenk techniques. All reactions were monitored by high-pressure liquid chromatography (HPLC) equipped with a Cosmosil Buckyprep column (Nacalai Tesque; 4.6 × 250 mm; flow rate = 2.0 mL/min; eluent, toluene/isopropanol, 7:3) and a UV detector (Shimadzu SPD-M10Avp). Preparative HPLC was performed with a Buckyprep column (Nacalai Tesque; 20 × 250 mm; flow rate = 20 mL/min; toluene/isopropanol, 7:3). Isolated yields were calculated on the basis of the starting fullerene compounds. All NMR spectra were recorded on JEOL ECA-500 (500 MHz) and ECX-400 (400 MHz) spectrometers. Spectra were reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for the ^{1}H NMR, from solvent carbon (e.g., δ 77.00 ppm for chloroform) for the ^{13}C NMR. Routine mass spectra were acquired by atmospheric pressure ionization (APCI) using a quadrupole mass analyzer on a Waters ZQ-S spectrometer, and high-resolution mass spectra (HRMS) by APCI using a time-of-flight mass analyzer on a JEOL JMS-T100LC (AccuTOF) spectrometer with a calibration standard of C_{60}. IR and UV−vis spectra were recorded on Applied Systems Inc. React-IR 1000 and JASCO V-570. HRMS data were obtained for air-stable compounds. The NMR spectra for all compounds are stored in the Supporting Information for the proof of purity.

Materials. THF and toluene were distilled from Na/K alloy. Hexane, CS_2 and acetonitrile were distilled from CaH_2. These solvents were thoroughly degassed by trap-to-trap distillation and stored under argon. A THF solution of KO^{t}Bu was purchased from Sigma-Aldrich Co. and used as received. Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) was purchased from Tokyo Kasei Co. $C_{60}Me_5H$ (**1**) was prepared according to our previous report.[11i] $C_{60}Me_5Br$ (**2**) was prepared by the reaction of **1** with *N*-bromosuccinimide in benzene. Tris(nitrile) complexes $Cr(CO)_3(MeCN)_3$, $Mo(CO)_3(EtCN)_3$, and $W(CO)_3(EtCN)_3$ were prepared according to the literature procedures.[19,26]

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro-[60]fulleren-1-yl]bromotricarbonylmolybdenum (3). A mixture of $Mo(CO)_3(EtCN)_3$ (116 mg, 0.336 mmol) and **2** (137 mg, 0.157 mmol) was dissolved in toluene (20 mL). After the brown mixture was stirred for 15 min at 25 °C, the solution was passed through a pad of silica gel and the solvent was removed under reduced pressure. The resulting solid was purified by preparative HPLC separation (Buckyprep, retention time = 8 min). An eluent containing the title compound was quickly concentrated and subjected to precipitation with hexane to prevent decomposition of the product. After drying in vacuo, the title compound was obtained as a red powder (121 mg, 73%). IR (powder, cm^{-1}): 2044 (s), 1979 (s), 1937 (s) (ν_{CO}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 15H, $C_{60}CH_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 30.89 (5C, $C_{60}\mathit{C}H_3$), 52.18 (5C, $\mathit{C}_{60}CH_3$), 121.23 (5C, C_{60}(Cp)), 143.47 (10C, C_{60}), 143.85 (10C, C_{60}), 147.05 (5C, C_{60}), 148.26 (10C, C_{60}), 148.66 (5C, C_{60}), 151.98 (10C, C_{60}), 201.01 (3C, CO).

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro-[60]fulleren-1-yl]iodotricarbonylmolybdenum (4). To a solution of **3** (9.69 mg, 0.00918 mmol) in toluene (5 mL) was added iodine (9.40 mg, 0.0367 mmol). After stirring for 11 h at 25 °C, the solution was passed through a pad of silica gel and the filtrate was concentrated to ca. 1 mL under reduced pressure. Reprecipitation was performed by an addition of methanol into the concentrated solution to obtain a red solid. The red precipitate was collected by filtration and washed with hexane. After drying in vacuo, the title compound was obtained as a red powder (9.50 mg, 94%). ^{1}H NMR (400 MHz, toluene-d_8): δ 2.17 ppm (s, 15H, $C_{60}C\mathit{H}_3$). An attempt to obtain a ^{13}C NMR spectrum failed due to instability and low solubility of this compound.

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro-[60]fulleren-1-yl]dicalbonylnitrosylmolybdenum (6). To compound **1** (1.00 g, 1.26 mmol) and an excess amount of KH was added THF (200 mL) at 25 °C. After vigorous stirring for 2 h at this temperature, a dark red supernatant containing $C_{60}Me_5K$ (**5**) was transferred to a solution of $Mo(CO)_3(EtCN)_3$ (652 mg, 1.89 mmol) in THF (20 mL). After stirring for 2 h at 25 °C, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (404 mg, 1.89 mmol) was added to the solution of the reaction. Gas evolution was observed, and the resulting solution was stirred for 2 h. The solvent was removed under reduced pressure to obtain a dark brown residue. The solution of this residue in toluene (100 mL) was passed through a pad of silica gel, and the filtrate was concentrated to ca. 5 mL under reduced pressure. Hexane (ca. 100 mL) was added to the concentrated solution to obtain a red solid. This red precipitate was collected by filtration and washed with hexane. After drying in vacuo, the title compound was obtained. Yield: 83%. IR (powder, cm^{-1}): 2962 (m), 2919 (m), 2856 (m) (ν_{C-H}), 2009 (s), 1935 (s) (ν_{CO}), 1660(s) (ν_{NO}). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.34 (s, 15H, $C_{60}C\mathit{H}_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 31.85 (5C, $C_{60}\mathit{C}H_3$), 51.50 (5C, $\mathit{C}_{60}CH_3$), 119.39 (5C, C_{60}(Cp)), 143.74 (10C, C_{60}),

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[31] (a) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807–815. (b) Matsuo, Y.; Fujita, T.; Nakamura, E. *Chem. Asian J.* **2007**, *2*, 948–955. (c) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 3052–3053. (d) Isobe, H.; Cho, K.; Solin, N.; Werz, D. B.; Seeberger, P. H.; Nakamura, E. *Org. Lett.* **2007**, *9*, 4611–4614.

Table 1. Crystal Data and Structure Analysis Results for 1, 3, 4, 6, 8, and 11

	1·CS_2	**3**·(toluene)$_2$	**4**·$(CS_2)_{1.5}$	**6**·CS_2	**8**	**11**·$(CS_2)_{0.5}$
formula	$C_{66}H_{15}S_2$	$C_{82}H_{31}BrMoO_3$	$C_{69.50}H_{15}IMoO_3S_3$	$C_{68}H_{15}MoNO_3S_2$	$C_{65}H_{15}BrMoO_2$	$C_{68.50}H_{20}CrNO_2S_3$
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Pccn* (No. 56)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
R, R_w ($I > 2\sigma(I)$)	0.107, 0.273	0.069, 0.158	0.093, 0.240	0.157, 0.418	0.069, 0.184	0.084, 0.225
R_1, wR_2 (all data)	0.195, 0.366	0.115, 0.183	0.128, 0.280	0.177, 0.440	0.095, 0.208	0.105, 0.255
GOF on F^2	1.04	1.03	1.03	1.77	1.06	1.03
a, Å	9.996(3)	11.697(2)	16.872(2)	27.280(4)	37.595(3)	10.006(3)
b, Å	19.995(7)	19.067(2)	12.726(2)	14.993(1)	9.9180(8)	11.455(3)
c, Å	18.673(7)	22.379(3)	20.054(1)	19.193(3)	21.144(2)	19.938(5)
α, deg	90	90	90	90	90	80.38(1)
β, deg	101.00(2)	96.709(6)	90.298(6)	90	112.160(5)	75.29(1)
γ, deg	90	90	90	90	90	66.89(1)
V, Å^3	3664(2)	4956(1)	4305.8(7)	7850(2)	7301(1)	2027(1)
Z	4	4	4	8	8	2
T, K	153(2)	153(2)	153(2)	153(2)	120(2)	153(2)
cryst size, mm	0.40, 0.25, 0.15	0.38, 0.18, 0.05	0.50, 0.30, 0.10	0.30, 0.15, 0.10	0.30, 0.10, 0.05	0.30, 0.20, 0.10
D_{calcd}, g/cm^{-3}	1.58	1.66	1.877	1.78	1.83	1.70
$2\theta_{min}$, $2\theta_{max}$, deg	4.16, 51.32	4.24, 51.18	4.82, 51.26	4.50, 51.48	4.68, 51.62	4.32, 51.48
no. reflns measd (unique)	4250	8839	7110	6548	6718	6994
no. reflns measd ($I > 2\sigma(I)$)	1878	5727	4762	4733	4879	5219
no. params	613	834	708	677	623	683
Δ, e Å^{-3}	0.62, −0.56	0.85, −1.06	2.07, −1.29	0.32, −0.93	0.80, −1.26	0.591, −0.923

144.25 (10C, C_{60}), 146.80 (5C, C_{60}), 148.00 (10C, C_{60}), 148.63 (5C, C_{60}), 152.78 (10C, C_{60}), 225.99 (2C, CO). HRMS (APCI−): *m*/*z* calcd for $C_{67}H_{15}MoNO_3$ [M^-], 973.0157; found, 973.0120.

[(1,2,3,4,5-*η*)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro-[60]fulleren-1-yl]dichloronitrosylmolybdenum (7). To a solution of **6** (35.4 mg, 0.0362 mmol) in toluene (20 mL) was added PCl_5 (22.6 mg, 0.109 mmol). After gas evolution was observed, the solution was stirred for 10 min. The reaction mixture was quickly passed through a pad of silica gel, and the filtrate was concentrated to ca. 1 mL under reduced pressure. Hexane (ca. 20 mL) was added to the concentrated solution to obtain a red solid, and the red precipitate was collected by filtration. The resulting red solid was washed with hexane and dried in vacuo to obtain the title compound (19.4 mg, 54%). IR (powder, cm^{-1}): 2964 (m), 2923 (m), 2861 (m) (ν_{C-H}), 1688 (s) (ν_{NO}). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.47 (s, 15H, $C_{60}CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 27.83 (5C, $C_{60}CH_3$), 53.50 (5C, $C_{60}CH_3$), 134.52 (5C, C_{60}(Cp)), 143.47 (10C, C_{60}), 143.96 (10C, C_{60}), 146.89 (5C, C_{60}), 148.23 (10C, C_{60}), 148.71 (5C, C_{60}), 152.04 (10C, C_{60}).

[(1,2,3,4,5-*η*)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro-[60]fulleren-1-yl]bromodioxomolybdenum (8). A solution of **3** (10 mg) in toluene was stored in air for 7 days. This solution was subjected to recrystallization with slow diffusion of ethanol into the toluene solution. The title compound was obtained as red crystals. Yield: 30%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.59 (s, 15H, $C_{60}CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 1.59 (5C, $C_{60}CH_3$), 53.19 (5C, $C_{60}CH_3$), 117.76 (5C, C_{60}(Cp)), 143.92 (10C, C_{60}), 143.98 (10C, C_{60}), 146.67 (5C, C_{60}), 148.06 (10C, C_{60}), 148.71 (5C, C_{60}), 152.24 (10C, C_{60}).

[(1,2,3,4,5-*η*)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro-[60]fulleren-1-yl]dicalbonylnitrosyltungsten (9). A solution of **5** in THF (20 mL), which was prepared using **1** (100 mg, 0.126 mmol) through a similar procedure to that described in the synthesis of **6**, was transferred to a solution of $W(CO)_3(EtCN)_3$ (81.9 mg, 0.189 mmol) in THF (5 mL) and then stirred for 2 h at 25 °C. Diazald (40.4 mg, 0.189 mmol) was added to the reaction mixture, which was stirred for 2 h at 25 °C. The title compound was obtained by similar workup procedures to those described in the synthesis of **6**. Yield: 77%. IR (powder, cm^{-1}): 2962 (m), 2919 (m), 2860 (m) (ν_{C-H}), 2001 (s), 1922 (s) (ν_{CO}), 1663 (s) (ν_{NO}). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 15H, $C_{60}CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 31.63 (5C, $C_{60}CH_3$), 51.74 (5C, $C_{60}CH_3$), 118.04 (5C, C_{60}(Cp)), 143.79 (10C, C_{60}), 144.14 (10C, C_{60}), 146.77 (5C, C_{60}), 147.96 (10C, C_{60}), 148.65 (5C, C_{60}), 152.65 (10C, C_{60}), 216.94 (2C, CO). HRMS (APCI−): *m*/*z* calcd for $C_{67}H_{15}WNO_3$ [M^-], 1063.0534; found, 1063.0537.

[(1,2,3,4,5-*η*)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro-[60]fulleren-1-yl]dicalbonylnitrosylchromium (10). A solution of **5** in THF (20 mL), which was prepared using **1** (100 mg, 0.126 mmol) through a similar procedure to that described in the synthesis of **6**, was transferred to a solution of $Cr(CO)_3(MeCN)_3$ (49.0 mg, 0.189 mmol) in THF (5 mL) and then stirred for 20 min at 25 °C. Diazald (40.4 mg, 0.189 mmol) was added to the reaction mixture, which was stirred for 15 min at 25 °C. The title compound was obtained by similar workup procedures to those described in the synthesis of **6**. Yield: 71%. IR (powder, cm^{-1}): 2964 (m), 2921 (m), 2860 (m) (ν_{C-H}), 2009 (s), 1941 (s) (ν_{CO}), 1694(s) (ν_{NO}). ^{1}H NMR (500 MHz, toluene-d_8): δ 2.05 (s, 15H, $C_{60}CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, toluene-d_8): δ 29.90 (5C, $C_{60}CH_3$), 51.31 (5C, $C_{60}CH_3$), 114.42 (5C, C_{60}(Cp),) 144.05 (10C, C_{60}), 144.34 (10C, C_{60}), 147.17 (5C, C_{60}), 148.39 (10C, C_{60}), 148.92 (5C, C_{60}), 153.15 (10C, C_{60}), 237.20 (2C, CO). HRMS (APCI−): *m*/*z* calcd for $C_{67}H_{15}CrNO_3$ [M^-], 933.0457; found, 933.0503.

[(1,2,3,4,5-*η*)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro-[60]fulleren-1-yl]-*O*-ethyldithiocarbonatenitrosylchromium (11). Compound **10** (12.0 mg, 0.0128 mmol) was dissolved in a mixed solvent of CS_2 (5.0 mL) and ethanol (4.0 mL). The solution was stirred for 24 h at 25 °C. The solvent was removed under reduced pressure and dissolved in CS_2 (2 mL) again. The addition of hexane (ca. 20 mL) precipitated the brown solid, which was collected by filtration and washed with hexane. The filtrate was taken to dryness under reduced pressure to obtain the title compound (11.3 mg, 90%) as a brown powder. IR (powder, cm^{-1}): 2956 (m), 2919 (m), 2852 (m) (ν_{C-H}), 1675(s) (ν_{NO}). HRMS (APCI−): *m*/*z* calcd for $C_{68}H_{20}CrNO_2S_2$ [M^-], 998.0341; found, 998.0389. No NMR signals were obtained because of the paramagnetic character of the Cr(III) complex.

X-ray Crystallographic Analysis. The data sets were collected on a MacScience DIP2030 imaging plate diffractometer using Mo Kα (graphite monochromated, λ = 0.71069 Å) radiation (Table 1). The structures of **1**, **3**, **4**, **6**, **8**, and **11** were solved by the direct method (SIR97).[32] The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method using SHELXL-

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(32) Altomare, A.; Burla, M. C.; Camalli, M; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

97.[33] Hydrogen atoms were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. The positional disorder was observed in the hydrogen atom of **1**, the bromine/carbonyl ligand of **3**, and the iodine/carbonyl ligand of **4**. Bond distances of **1**, **3**, and **4** have less certainty than those of **6**, **8**, and **11**.

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Supporting Information Available: Crystallographic data of **1**, **3**, **4**, **6**, **8**, and **11** (CIF files) and NMR spectra for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM800308N

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