this respect, an ice surface allows diverse chemical species to be formed and kinetically stabilized, and this may play an important role in photochemical processes on interstellar or stratospheric ice particles.

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First Example of the μ_3-η^1,η^2,η^1-C_{60} Bonding Mode: Ligand-Induced Conversion of π to σ C_{60}–Metal Complexes**

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A consistent theme in the chemistry of exohedral metallofullerenes has been the pursuit of new bonding modes of C_{60} with metal centers and their novel chemical reactivities. Continuous development in C_{60}–metal chemistry led to the synthesis of various π complexes with η^2-,[1] η^5-,[2] μ-η^2,η^2-,[3] and μ_3-η^2,η^2,η^2-C_{60}[4] bonding modes. However, the chemistry of C_{60} σ complexes has remained relatively unexplored, although such complexes are very important in selective functionalization of C_{60}. Examples of C_{60}–metal σ complexes have scarcely been reported, and none has been structurally characterized.[5] We are interested in the conversion of existing C_{60} bonding modes to new ones by modifying the coordination sphere of metal center(s) to which C_{60} is coordinated. Our efforts resulted in the first example of reversible interconversion between μ-η^2,η^2- and μ_3-η^2,η^2,η^2-C_{60} on an Os_5C cluster framework by addition of 2e-donor ligands such as carbon monoxide or benzyl isocyanide.[3d] In contrast, a μ_3-η^2,η^2,η^2-C_{60} ligand on a triosmium cluster framework exhibits a drastically different behavior upon addition of benzyl isocyanide. It transforms into a new σ-type μ_3-η^1,η^2,η^1-C_{60} ligand with concomitant Os–Os bond cleavage, providing a new synthetic route to C_{60}–metal σ complexes. Here we report the first example of a novel ligand-induced conversion of π to σ C_{60}–metal complexes, as well as the first structural characterization of C_{60}–metal σ bonding.

A mixture of $[Os_3(CO)_8(CNR)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})]$ (**1**) and an excess (30 equiv) of benzyl isocyanide in C_6H_5Cl was heated at 80 °C for 40 h. Removal of the volatile materials in vacuo, subsequent purification by a preparative TLC (SiO_2, CS_2), and recrystallization (CH_2Cl_2/*n*-C_6H_{14}) afforded two brown compounds **2a** and **2b** (Scheme 1). The two compounds were formulated as $[Os_3(CO)_8(CNR)_2(C_{60})]$ on the basis of microanalytical data and molecular ion isotope multiplets at *m*/*z* 1750 (highest peak) in the positive-ion FAB mass spectra.

An X-ray crystallographic study revealed the structure of **2a** (Figure 1a). The Os1–Os3 bond of the Os_3 triangle in **1** was ruptured on addition of an RNC ligand, which is coordinated

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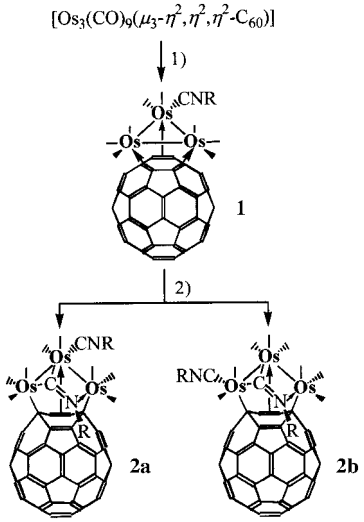

Scheme 1. 1) 1.2 equiv of $PhCH_2N{=}PPh_3$, C_6H_5Cl, RT, 12 h, 76%; 2) 30 equiv of RNC, C_6H_5Cl, 80 °C, 40 h, 27% (**2a**), 22% (**2b**). R = $CH_2C_6H_5$.

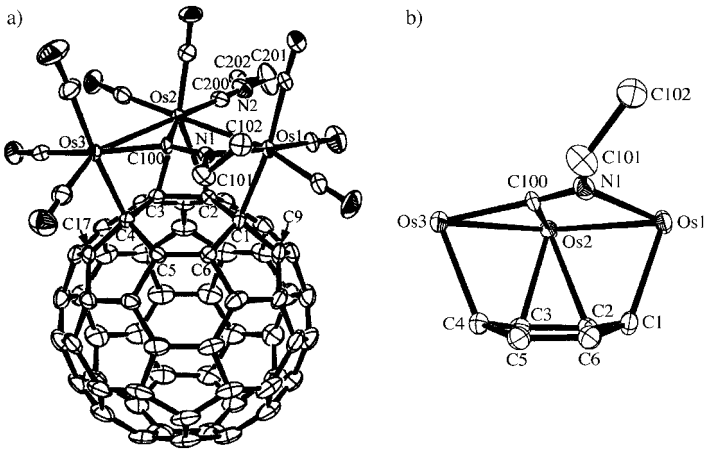

Figure 1. a) Molecular structure with atomic labeling scheme for **2a**. Only *ipso*-carbon atoms (C102 and C202) of the phenyl groups are shown for clarity. b) An expanded view of the boat-shaped μ_3-η^1,η^2,η^1-C_6 part of the C_{60} ligand. Selected bond lengths [Å]: Os1-Os2 2.925(1), Os2-Os3 2.900(1), Os1-C1 2.25(1), Os2-C2 2.46(1), Os2-C3 2.37(1), Os3-C4 2.26(1), C1-C2 1.50(1), C2-C3 1.44(1), C3-C4 1.52(1), C4-C5 1.53(1), C5-C6 1.36(1), C6-C1 1.52(1).

to the three osmium centers in a 4e-donor μ_3-η^2(C),η^1(N) bonding mode. Similar bonding of the isocyanide ligand was previously observed for an Os_6 cluster.[6] The other isocyanide ligand (2e donor) occupies an equatorial position on the Os2 atom. The formal electron counts for Os1, Os2, and Os3 are 18, 19, and 17, respectively. The formal electron deficiency at the Os3 center appears to be compensated by a stronger Os3–C100 interaction (1.99 Å) as compared to Os2–C100 (2.18 Å). The bond lengths and angles for the terminal isocyanide and carbonyl ligands are within the expected ranges.

The two outer Os, atoms Os1 and Os3, coordinate to the C1 and C4 atoms, respectively, of the C_{60} ligand in a σ fashion, while the inner Os2 atom is π-coordinated to the C2 and C3 atoms in an η^2 mode. The two σ bonds Os1–C1 (2.25 Å) and Os3–C4 (2.26 Å), are shorter than the Os2–(C2,C3) π bond (av 2.42 Å). The bond lengths C2–C3 (1.44 Å) and C5–C6 (1.36 Å) reveal double-bond character, and the other four C–C bonds (av 1.52 Å) exhibit single-bond character. The sums of the three angles around sp^3-hybridized C1 (∢C2-C1-C9 + ∢C6-C1-C9 + ∢C2-C1-C6 = 328°) and C4 (∢C3-C4-C5 + ∢C5-C4-C17 + ∢C3-C4-C17 = 327°) are considerably smaller than those of the other four carbon atoms (av 351°) with sp^2 hybridization. Thus, the two sp^3-hybridized carbon atoms C1 and C4 are pulled away from the smooth curvature of the C_{60} ligand, which is manifested in the boat shape of the C_6 ring, with C1 and C4 at the bow and stern positions, as shown in Figure 1b. The dihedral angles between the C2-C3-C5-C6 plane and the two adjacent planes C1-C2-C6 and C3-C4-C5 are 12.5 and 13.1°, respectively.

The cyclohexatriene-like C_6 ring of C_{60} in **1** has undergone orbital reorganization to form a 1,4-cyclohexadiene-like ring in **2a**. It can be envisaged that the 4e-donor RNC ligand formally provides two electrons to the antibonding orbital of the Os1–Os3 bond in **1** and thus results in its scission. The remaining two electrons of the RNC ligand interrupt two π interactions in **1** to give two M–C σ bonds (Os1–C1 and Os3–C4) and an uncoordinated C=C bond (C5=C6) in **2a**. The 1,4-addition isomers of σ C_{60}–metal complexes have been reported previously in a few cases such as $[C_{60}\{Re(CO)_5\}_2]$[5a] and $[C_{60}\{Mo(CO)_3(\eta^5\text{-}C_5H_4CO_2Et)\}_2]$.[5c]

The structure of **2b** is shown in Figure 2. Compound **2b** differs from **2a** only in that the terminal isocyanide ligand is coordinated to the outer Os3 atom. Other structural data of

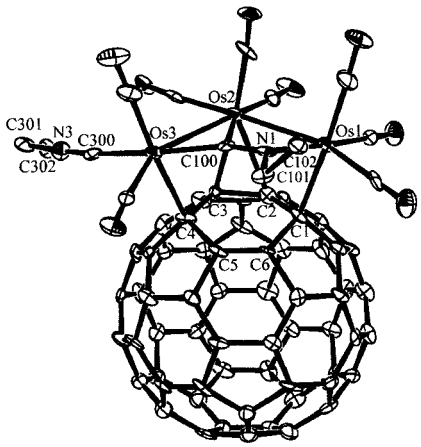

Figure 2. Molecular structure with atomic labeling scheme for **2b**. Only *ipso*-carbon atoms (C102 and C302) of the phenyl groups are shown for clarity. Selected bond lengths [Å]: Os1-Os2 2.918(1), Os2-Os3 2.913(1), Os1-C1 2.23(2), Os2-C2 2.48(2), Os2-C3 2.30(2), Os3-C4 2.25(2), C1-C2 1.43(3), C2-C3 1.47(3), C3-C4 1.53(2), C4-C5 1.50(3), C5-C6 1.33(3), C6-C1 1.53(3).

2b are essentially identical to those of **2a**. In the conversion of **1** to **2a** and **2b**, it is noteworthy that an M–C_{60} π interaction can be transformed into a σ interaction with orbital reorganization in the C_6 ring of the C_{60} ligand by electronic modification of the metal coordination sphere.

When a mixture of **1** and excess RNC in C_6H_5Cl was irradiated by a medium-pressure Hg lamp for 12 h at room temperature, **2b** formed exclusively as the major product

(49%). Compound **2a** was shown to be stable towards transformation into **2b** under similar irradiation conditions, and this implies the photochemical route selectively forms **2b** from **1**. Compounds **2a** and **2b** were not interconvertible upon prolonged heating at 80 °C, that is, no intermetal movement of the isocyanide ligand occurs in these clusters.

In conclusion, we have demonstrated the first transformation of the bonding mode of C_{60} from μ_3-η^2,η^2,η^2 (π) to μ_3-η^1,η^2,η^1 (σ) on an Os_3 framework induced by an external ligand (**1** → **2a** + **2b**). We have shown that the selective formation of isomer **2b** can be accomplished by UV irradiation. Efforts are currently underway to understand the thermal and photochemical conversion pathways of the π and σ C_{60}–metal interactions. Reactivity studies and selective functionalization of the C_{60} ligand of **2a** and **2b** are also in progress.

Experimental Section

Details on the synthesis as well as full spectroscopic characterization of **1**, **2a**, and **2b** are given in the Supporting Information. For the X-ray structure analyses, data were collected on a CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) by using ω scans. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151706 (**1**), CCDC-151707 (**2a**), and CCDC-151708 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

2a: Analysis calcd for $C_{85}H_{14}N_2O_8S_2Os_3$ (**2a**·CS_2): C 55.92, H 0.77, N 1.53, S 3.51; found: C 55.50, H 0.68, N 1.29, S 3.57; IR (C_6H_{12}): $\tilde{\nu} = 2079$ (s), 2068 (s), 2019 (s), 1986 cm^{-1} (s) (CO); $\tilde{\nu} = 2189$ (w), 1634 cm^{-1} (vw) (CN); ^1H NMR (400 MHz, CS_2/$CDCl_3$, 298 K): $\delta = 7.49$–6.98 (m, 10H; Ph), 5.50 (d, 1H, $J_{H,H} = 13$ Hz; CH_2), 4.95 (br s, 2H; CH_2), 4.87 (d, 1H, $J_{H,H} = 13$ Hz; CH_2); ^{13}C NMR (carbonyl region, 100 MHz, $C_6H_4Cl_2$/$C_6D_5CD_3$, 298 K): $\delta = 179.96$, 179.00, 178.32, 176.74, 175.74, 174.55, 173.39, 168.95; MS (FAB^+): m/z: 1754 [M^+].

X-ray data for **2a**: Brown crystals were obtained by slow diffusion of hexane into a solution of **2a** in CS_2 at room temperature. A crystal of dimensions $0.12 \times 0.14 \times 0.42$ mm was used for data collection: $C_{84}H_{14}N_2O_8Os_3 \cdot CS_2$, $M_r = 1825.7$; monoclinic, space group $P2_1/c$, $Z = 4$, $\rho_{calcd} = 2.105$ g cm^{-3}, $a = 19.4334(2)$, $b = 10.6922(2)$, $c = 29.0892(2)$ Å, $\beta = 107.615°$, $V = 5760.9(1)$ Å^3. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give $R = 0.0448$ and $R_w = 0.0695$ (based on F^2) for 878 variables and 11 490 observed reflections with $I > 2\sigma(I)$ and $1.47 < \theta < 26.23$. Data collection at $T = 293(2)$ K.

2b: Analysis calcd for $C_{84}H_{14}N_2O_8Os_3$: C 57.66, H 0.81, N 1.60; found: C 56.76, H 0.61, N 1.22; IR (C_6H_{12}): $\tilde{\nu} = 2085$ (vs), 2052 (s), 2026 (vs), 2015 (w), 1992 (w), 1982 (w), 1968 cm^{-1} (m) (CO); $\tilde{\nu} = 2185$ (w), 1629 cm^{-1} (vw) (CN); ^1H NMR (400 MHz, CS_2/$CDCl_3$, 298 K): $\delta = 7.49$–7.19 (m, 10H; Ph), 5.66 (d, 1H, $J_{H,H} = 13$ Hz; CH_2), 5.48 (d, 1H, $J_{H,H} = 16$ Hz; CH_2), 5.41 (d, 1H, $J_{H,H} = 16$ Hz; CH_2), 4.88 (d, 1H, $J_{H,H} = 13$ Hz; CH_2); ^{13}C NMR (carbonyl region, 100 MHz, $C_6H_4Cl_2$/$C_6D_5CD_3$, 223 K): $\delta = 181.9$, 176.9, 176.1, 175.8, 175.5, 174.5, 173.2, 169.2; MS (FAB^+): m/z 1754 [M^+].

X-ray crystal data for **2b**: Brownish black crystals were obtained by slow diffusion of methanol into a solution of **2b** in toluene at room temperature. A crystal of dimensions $0.41 \times 0.29 \times 0.11$ mm was used for data collection: $C_{84}H_{14}N_2O_8Os_3$, $M_r = 1749.6$; monoclinic, space group $P2_1/c$, $Z = 4$, $\rho_{calcd} = 2.024$ g cm^{-3}, $a = 19.9376(8)$, $b = 23.0770(9)$, $c = 12.8318(5)$ Å, $\beta = 103.462(1)°$, $V = 5741.7(4)$ Å^3. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give $R = 0.0779$ and $R_w = 0.1995$ (based on F^2) for 851 variables and 8192 observed reflections with $I > 2\sigma(I)$ and $1.37 < \theta < 23.34$. Data collection at $T = 193(2)$ K.

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Expanding the Pyrimidine Diphosphosugar Repertoire: The Chemoenzymatic Synthesis of Amino- and Acetamidoglucopyranosyl Derivatives**

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An extensive body of in vivo genetic evidence indicates that the glycosyltransferases involved in secondary metabolism are extremely promiscuous with respect to their nucleotide diphosphosugar (NDP-sugar) donor.[1] Yet, in vitro experiments in this area are limited to only a few examples, partly because of the lack of the required NDP-sugar substrates for

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