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Ligand-Induced Conversion of π to σ C_{60}−Metal Cluster Complexes: Full Characterization of the μ_3-η^1:η^2:η^1-C_{60} Bonding Mode

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The reaction of $Os_3(CO)_9(\mu_3$-η^2:η^2:η^2-$C_{60})$ (**1**) with $PhCH_2N{=}PPh_3$ in chlorobenzene affords the benzyl isocyanide substituted product $Os_3(CO)_8(CNR)(\mu_3$-η^2:η^2:η^2-$C_{60})$ (**2a**, R = CH_2Ph) in 76% yield. Photolysis of **1** in the presence of an excess of benzyl isocyanide gives the isocyanide-inserted product $Os_3(CO)_9(\mu_3$-CNR$)(\mu_3$-η^1:η^2:η^1-$C_{60})$ (**2b**) in 11% yield. Thermal reaction of **2a** with an excess of RNC in chlorobenzene at 80 °C produces two isocyanide-inserted, isomeric products, $Os_3(CO)_8(CNR)(\mu_3$-CNR$)(\mu_3$-η^1:η^2:η^1-$C_{60})$ (**3a**, 22%; **3b**, 27%). The two isomers **3a** and **3b** can be selectively prepared by photolysis of **2a** in the presence of excess isocyanide in 49% yield and by decarbonylation of **2b** with Me_3NO/MeCN and subsequent reaction with isocyanide in 56% yield, respectively. Compounds **2a**,**b** and **3a**,**b** have been characterized by microanalytical and spectroscopic methods. In particular, the sp^3 carbons of M−C(C_{60}) σ-interactions in μ_3-η^1:η^2:η^1-C_{60} complexes exhibit unique upfield resonances around 39 ppm in the ^{13}C NMR spectra, compared to the π-bonded sp^3 carbon resonances observed in the range of 95−65 ppm. The X-ray crystallographic studies for **2a**,**b** and **3a**,**b** reveal that μ_3-η^2:η^2:η^2-C_{60} ligands in **1** and **2a** transform into new σ-type μ_3-η^1:η^2:η^1-C_{60} ligands in **2b** and **3a**,**b** by insertion of the isocyanide ligand concomitant with Os−Os bond cleavage, forming a bent triosmium framework. In compounds **2b** and **3b**, a boat-shaped 1,4-cyclohexadiene-like C_6 ring in the C_{60} molecule is clearly observed and the M−C_{60} σ-bond distances (average 2.24 Å) are shorter than the π-bond lengths (average 2.41 Å). This study represents a novel ligand-induced conversion of π to σ C_{60}−metal complexes.

Introduction

A consistent theme in exohedral metallofullerene chemistry has been the pursuit of new bonding modes of C_{60} with metal centers and their novel chemical reactivities.[1] Continuous development in C_{60}−metal complexes has led to the synthesis of various π complexes with η^2-,[2] η^5-,[3] μ-η^2:η^2-,[4,5] and μ_3-η^2:η^2:η^2-C_{60}[6] bonding modes. The chemistry of C_{60}−metal σ-complexes, however, has remained relatively unexplored, although such complexes are very important in the selective functionalization of C_{60}. The first transition-metal−C_{60} σ-complexes, $(Cp_2ZrCl)_nC_{60}H_n$ (Cp = η^5-C_5H_5; $n = 1-3$), as a mixture of hydrozirconation 1,2-adducts of C_{60}, have been successfully employed, though not fully characterized, for the functionalization of C_{60} such as preparation of hydrogenated fullerenes and unusual Diels−Alder fullerene products with bromo- and hydroxycyclopentadiene.[7] Another M−C(C_{60}) σ-bond complex, $C_{60}\{Re(CO)_5\}_2$, has been prepared by photolysis of $Re_2(CO)_{10}$ with C_{60}, but it is known to decompose over a period of 1 day to regenerate starting materials.[8] Other σ-bond complexes, $C_{60}\{M(CO)_3(\eta^5$-$C_5H_4CO_2R)\}_2$

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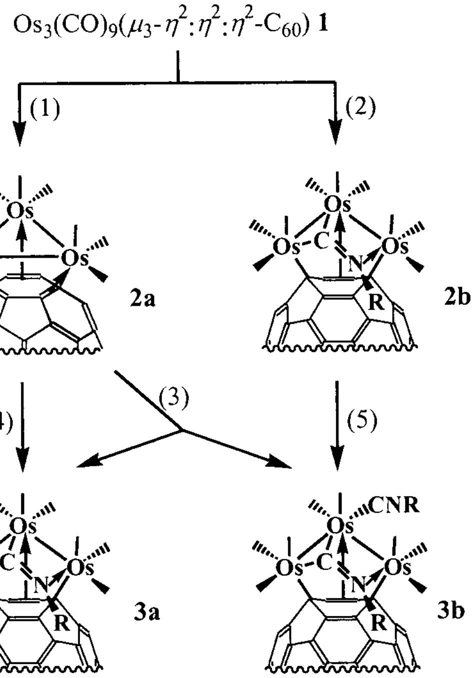
(M = Mo, R = Et; M = W, R = Me), have been recently prepared from the reactions between C_{60}^{2-} and 2 equiv of corresponding metal halides, and they also show limited thermal stability in solution.[9] The organometallic groups in the Re−, Mo−, and W−C_{60} complexes are proposed to attach to the 1,4-positions of the C_6 ring of C_{60}, but none have been structurally characterized. Cocrystallization of C_{60} and silver(I) nitrate has been observed to form $C_{60}\{Ag(NO)_3\}_5$, whose structural characterization reveals that a curved silver nitrate network encapsulates the fullerene and one of the silver ions has η^1 coordination with a single carbon atom in C_{60}.[10]

We have been interested in conversion of the existing C_{60} bonding modes to new ones by modifying the coordination sphere of metal centers to which C_{60} is coordinated. Our efforts have 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 or elimination of 2e-donor ligands such as carbon monoxide and benzyl isocyanide.[5] In an ongoing effort to establish the general trends in the reactivity of face-capping μ_3-η^2:η^2:η^2-C_{60} metal cluster complexes, we have examined the reactivity of $Os_3(CO)_9(\mu_3$-η^2:η^2:η^2-$C_{60})$ (**1**) toward a benzyl isocyanide ligand. Insertion of the isocyanide ligand into an Os−Os bond induces conversion of the π-type μ_3-η^2:η^2:η^2-C_{60} ligand to a new σ-type μ_3-η^1:η^2:η^1-C_{60} ligand, providing a new synthetic route to C_{60}−metal σ complexes. Herein we report a novel ligand-induced conversion of π (**1** and **2a**) to σ (**2b**, **3a**, and **3b**) C_{60}−metal complexes as shown in Scheme 1, as well as the first complete structural characterization of C_{60}−metal σ bonding. A preliminary account of some of this work has appeared.[11]

Results and Discussion

Synthesis and Characterization of 2a,b and 3a,b. Synthetic procedures for **2a**,**b** and **3a**,**b** are summarized in Scheme 1. Decarbonylation of $Os_3(CO)_9(\mu_3$-η^2:η^2:η^2-$C_{60})$ (**1**) with Me_3NO/MeCN and subsequent reaction with benzyl isocyanide in chlorobenzene at 60 °C affords the benzyl isocyanide substituted product $Os_3(CO)_8(CNR)(\mu_3$-η^2:η^2:η^2-$C_{60})$ (**2a**; R = CH_2Ph) in 50% yield. Compound **2a** can be alternatively prepared in a better yield (76%) from the reaction of **1** with $PhCH_2N{=}PPh_3$ in chlorobenzene at room temperature. (Triphenylphosphino)alkylimine reagents are known to react with metal carbonyl complexes to yield metal isocyanide substituted compounds.[12] On the other hand, irradiation of a chlorobenzene solution of **1** in the presence of an excess (30 equiv) of benzyl isocyanide by a medium-pressure Hg lamp for 3 days at room temperature gives the isocyanide-inserted product $Os_3(CO)_9(\mu_3$-CNR$)(\mu_3$-η^1:η^2:η^1-$C_{60})$ (**2b**) in a low yield (11%). Thermal reaction of **2a** with an excess (30 equiv) of benzyl isocyanide in chlorobenzene at 80 °C for 40 h affords two isocyanide-inserted, isomeric complexes, $Os_3(CO)_8(CNR)(\mu_3$-CNR$)$-$(\mu_3$-η^1:η^2:η^1-$C_{60})$ (**3a**,**b**) in 22% and 27% yield, respectively. Compounds **2a** and **3a**,**b** are soluble in various solvents such as CS_2, dichloromethane, toluene, and chlorinated benzenes, while **2b** is soluble only in CS_2. All the new compounds were formulated by the molecular ion isotope multiplets (*m*/*z* (highest peak): 1633 (**2a**); 1661 (**2b**); 1750 (**3a**,**b**)) in the positive ion FAB mass spectra and by microanalytical data.

Scheme 1[a]



[a] Legend: (1) 1.2 equiv of $RN{=}PPh_3$, room temperature, 12 h, 76%; (2) 30 equiv of RNC, *hν*, room temperature, 3 days, 11%; (3) 30 equiv of RNC, 80 °C, 40 h, 22% (**3a**), 27% (**3b**); (4) 30 equiv of RNC, *hν*, room temperature, 12 h, 49%. (5) (i) Me_3NO/MeCN, 0 °C, 1 h; (ii) 5 equiv of RNC, 70 °C, 1 h, 56%. R = CH_2Ph.

The IR spectra of **2a**,**b** and **3a**,**b** (see Figure 1) clearly indicates the coordination modes of the RNC ligands to the metal centers. The higher energy bands (**2a**, 2189 cm^{-1}; **3a**, 2185 cm^{-1}; **3b**, 2189 cm^{-1}) are assigned to the N≡C stretching of the terminal RNC ligand and the lower energy bands (**2b**, 1639 cm^{-1}; **3a**, 1629 cm^{-1}; **3b**, 1634 cm^{-1}) are assigned to the N=C stretching of the bridging RNC ligand. The carbonyl stretching bands appear in the typical 1950−2100 cm^{-1} range.

The ^1H NMR spectrum of **2a** exhibits a singlet at δ 5.18 for the methylene protons of the terminal RNC ligand, whereas that of **2b** shows two doublet resonances at δ 5.62 and 4.97 with J_{HH} = 13 Hz for the two diastereotopic methylene protons of the bridging RNC ligand. The ^1H NMR spectrum of **3a** shows two sets of two doublets (AB pattern, δ 5.48 and 5.41 with J_{HH} = 16 Hz, and AX pattern, δ 5.66 and 4.88 with J_{HH} = 13 Hz) for the two isocyanide ligands of the major isomer along with two sets of similar patterns due to the minor isomers. The 2D ^1H−^1H COSY spectrum confirms that compound **3a** exists as three isomeric forms in a 0.9:0.07:0.03 ratio at room temperature (see Supporting Information). The molecular structure of **3a** (vide infra) suggests that the three isomers have resulted from the 3-fold rotation of the isocyanide ligand on the Os(3)

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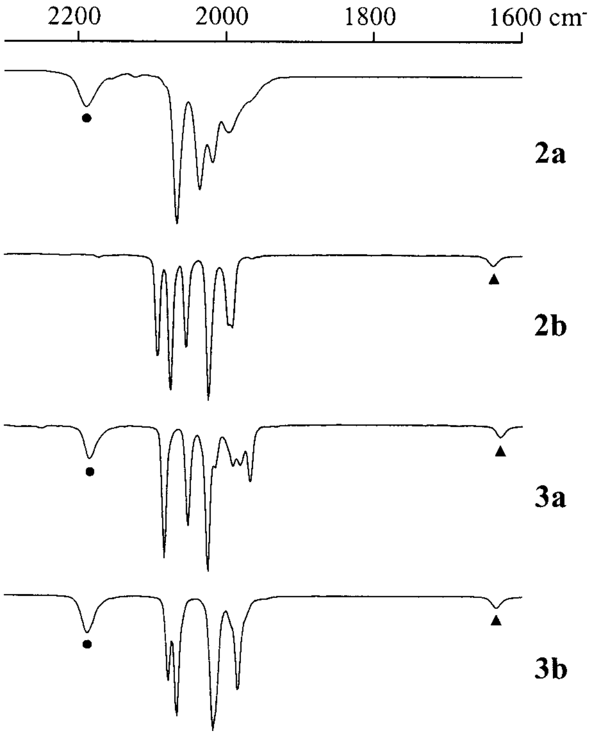

Figure 1. IR spectra (carbonyl and NC stretching region) of **2a**,**b** and **3a**,**b**. The stretching bands for isocyanides are denoted with ● (terminal) and ▲ (bridging).

atom. The ^{1}H NMR spectrum and 2D ^{1}H−^{1}H COSY spectrum of **3b** indicates that it exists as two isomers (0.87:0.13) in solution (see Supporting Information). The minor isomer of **3b** is likely to be formed by the site exchange between an equatorial carbonyl and the isocyanide ligand on the Os(2) center (vide infra) via a restricted 3-fold rotation, which is commonly observed in phosphine-substituted triosmium carbonyl μ_3-η^2:η^2:η^2-C_{60} complexes such as $Os_3(CO)_{9-n}(PMe_3)_n(\mu_3$-$\eta^2$:$\eta^2$:$\eta^2$-$C_{60})$ (n = 1−3).[6c,d]

The ^{13}C NMR spectrum of the carbonyl region of **2a** shows two resonances at δ 179.9 and 177.6 in a 1:3 ratio at 298 K, implying a fast, localized 3-fold rotation of ligands on each osmium atom. The carbonyl ligands on the isocyanide-substituted osmium center, however, may undergo the restricted 3-fold rotation proposed by Pomeroy and co-workers,[13] without requiring the bulky isocyanide ligand to enter an axial site. The resonances at δ 179.9 and 177.6 can be obviously assigned to the two carbonyl ligands on the osmium atom coordinated with an isocyanide ligand and the six carbonyl groups on the other two osmium atoms, respectively. The ^{13}C NMR spectrum (298 K) of **2b** reveals nine carbonyl resonances at δ 178.3, 178.0, 174.0, 172.6, 172.3, 170.1, 169.9, 168.3, and 162.8 for the nine inequivalent carbonyl ligands. The ^{13}C NMR spectrum (233 K) of **3a** shows eight carbonyl resonances of the major isomer overlapped with smaller signals of the two minor isomers, whereas that (298 K) of **3b** exhibits eight well-resolved carbonyl resonances for the two isomers (major isomer, δ 180.0, 179.0, 178.3, 176.7, 175.7, 174.6, 173.4, and 169.0; minor isomer, δ 179.6, 179.5, 179.1, 176.5, 176.1, 175.2, 174.1, and 169.2).

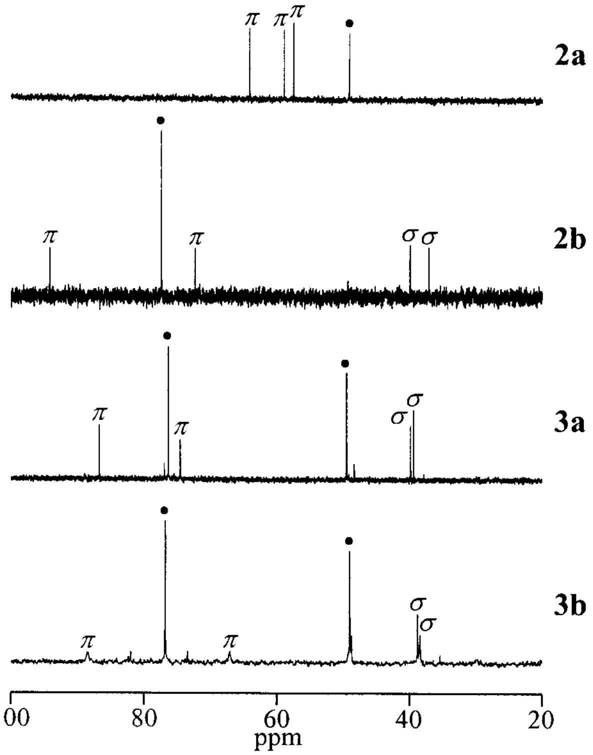

Figure 2. $^{13}C\{^1H\}$ NMR spectra (400 MHz, 297 K, sp^3 carbon region) of **2a**,**b** and **3a**,**b**. The methylene carbon resonances of the RNC ligands are denoted with ●. Smaller peaks due to minor isomers are also observed in the spectra of **3a**,**b**.

The ^{13}C NMR resonances of the C_{60} moiety typically appear in the regions of δ 175−135 for the sp^2 carbon atoms and δ 85−50 for the sp^3 carbon atoms.[1c] The C_s-symmetric nature of **2a** in solution reveals three sp^3 carbon resonances (δ 64.3, 59.1, and 57.6) and 29 sp^2 carbon resonances in the region of δ 156−143, which is consistent with the previously reported pattern of C_s-symmetric $Os_3(CO)_8(PMe_3)(\mu_3$-η^2:η^2:η^2-$C_{60})$.[6d] In contrast, all 60 carbon atoms in **2b** and **3a**,**b** are distinct because of asymmetry in the three complexes, and 56 sp^2 carbon atoms of each compound are observed in the δ 168−140 range. The chemical shifts of the sp^3 carbons in the C_{60}−metal σ complexes $C_{60}\{M(CO)_3(\eta^5$-C_5H_4-$CO_2R)\}_2$ (M = Mo, R = Et; M = W, R = Me) have been reported to be δ 60.7 and 62.0,[9] respectively, which are also within the expected range. However, sp^3 carbons involved in M−C(C_{60}) σ bonding of the μ_3-η^1:η^2:η^1-C_{60} complexes **2b** and **3b** appear in the unique chemical shift region, as shown in Figure 2. The two upfield signals of each compound around 39 ppm (δ 40.0, 37.2 for **2b**; δ 39.8, 39.4 for **3a**; δ 38.9, 38.5 for **3b**) are assigned to the two carbon atoms bonded to the metal centers in a σ fashion, and the other two downfield signals in the range of 95−65 ppm (δ 94.1, 72.3 for **2b**; δ 86.7, 74.6 for **3a**; δ 88.5, 67.1 for **3b**) are assigned to the two carbon atoms involved in π bonding. Such a notable upfield shift of the σ-bonded carbons may be ascribed to the shielding effect of the osmium metals. The sp^3 carbons in π bonds are considered to resonate at lower fields than those in σ bonds because of the partial sp^2 characters of π bonds in the Dewar−Chatt type metal−C_{60} bonding.[1f] Smaller peaks from the minor isomers of **3a**,**b** are also seen in the ^{13}C NMR spectra.

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Table 1. Crystallographic Data for 2a,b and 3a,b

	2a·$0.25CS_2$	**2b**·$0.5CS_2$	**3a**	**3b**·CS_2
formula	$C_{76}H_7NO_8Os_3\cdot 0.25CS_2$	$C_{77}H_7NO_9Os_3\cdot 0.5CS_2$	$C_{84}H_{14}N_2O_8Os_3$	$C_{84}H_{14}N_2O_8Os_3\cdot CS_2$
fw	1651.46	1698.50	1749.57	1825.70
syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	23.5677(2)	12.967(2)	19.9376(8)	19.4334(2)
b, Å	12.6912(2)	19.590(4)	23.0770(9)	10.6922(2)
c, Å	31.0373(1)	20.488(4)	12.8318(5)	29.0892(2)
α, deg	90	100.559(3)	90	90
β, deg	95.289(1)	100.797(3)	103.462(1)	107.615(1)
γ, deg	90	99.800(3)	90	90
V, Å	9243.8(2)	4912(2)	5741.7(4)	5760.9(1)
Z	8	2	4	4
D_{calcd}, Mg m^{-3}	2.373	2.297	2.024	2.105
temp, K	298(2)	233(2)	193(2)	293(2)
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
μ, mm^{-1}	8.328	7.862	6.693	6.745
$\theta_{\mathrm{min,max}}$, deg	1.32, 26.51	1.32, 25.00	1.37, 23.34	1.47, 26.23
$R_F{}^a$	0.0693	0.0819	0.0779	0.0448
$R_w{}^b$	0.1649	0.2065	0.1995	0.1052
GOF	1.057	1.068	1.158	1.009

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) with Esd's for 2a

Bond Distances			
Os(1)−Os(2)	2.8736(7), 2.8794(9)	Os(2)−Os(3)	2.8932(8), 2.9022(9)
Os(1)−Os(3)	2.9219(8), 2.9016(9)	Os(1)−C(100)	1.98(2), 1.98(2)
Os(1)−C(1)	2.22(1), 2.25(1)	Os(1)−C(2)	2.27(1), 2.29(1)
Os(2)−C(3)	2.25(1), 2.25(1)	Os(2)−C(4)	2.31(1), 2.31(1)
Os(3)−C(5)	2.22(1), 2.24(1)	Os(3)−C(6)	2.29(1), 2.32(1)
C(1)−C(2)	1.42(2), 1.42(2)	C(2)−C(3)	1.48(2), 1.49(2)
C(3)−C(4)	1.42(2), 1.43(2)	C(4)−C(5)	1.47(2), 1.47(2)
C(5)−C(6)	1.46(2), 1.46(2)	C(6)−C(1)	1.45(2), 1.44(2)
Bond Angles			
Os(2)−Os(1)−Os(3)	59.89(2), 60.27(2)	Os(1)−Os(2)−Os(3)	60.88(2), 60.24(2)
Os(2)−Os(1)−C(100)	148.5(4), 152.3(5)	Os(3)−Os(1)−C(100)	88.8(4), 92.4(5)
C(2)−C(1)−C(6)	119(1), 118(1)	C(1)−C(2)−C(3)	122(1), 123(1)
C(2)−C(3)−C(4)	118(1), 117(1)	C(3)−C(4)−C(5)	122(1), 121(1)
C(4)−C(5)−C(6)	118(1), 120(1)	C(5)−C(6)−C(1)	122(1), 121(1)

Selective Formation of 3a,b. In the conversion of **1** to **2b**, insertion of an isocyanide ligand into an Os−Os bond seems to be a major reaction pathway under the photolytic conditions. This observation prompted us to investigate the photolysis reaction of **2a** with isocyanide. Compound **2a** in the presence of an excess (30 equiv) of benzyl isocyanide in chlorobenzene is irradiated by an Hg lamp at room temperature for 12 h. Surprisingly, compound **3a** is produced exclusively in 49% yield. This unusual selectivity can be rationalized in terms of relative stability of radical species, which are formed by the UV light induced homolysis of Os−Os bonds. The two Os−Os bonds involving an osmium atom with a terminal isocyanide ligand may be the preferred site for the homolysis. Scission of the other Os−Os bond would lead to the formation of **3b**. Stabilization of the metal radical species by isocyanide ligands has been previously discussed.[14] The role of isocyanide ligand in the radical formation is also supported both by the low yield (11%) obtained in the conversion of **1** to **2b** and by the observation that the similar photolytic reaction of a phosphine-substituted complex, $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$, with isocyanide resulted in only extensive decomposition. Compound **3a** is shown to be stable toward transformation into **3b** under similar irradiation conditions, and this implies the photochemical route selectively forms **3a** from **2a**. In addition, compounds **3a**,**b** are not interconvertible upon prolonged heating at 80 °C; that is, no intermetallic movement of the terminal isocyanide ligand occurs in these cluster complexes.

The other isomer **3b** can also be prepared selectively by decarbonylation of **2b** with Me_3NO/MeCN and subsequent reaction with benzyl isocyanide at 70 °C in 56% yield. In this route, the carbonyl ligands on the Os(2) center seem to be the most electrophilic and thus are attacked by Me_3NO among the carbonyl sites of **2b**, presumably because the Os(2) center becomes electron deficient by metal-to-C_{60} π back-donation. The reaction of **2b** with $PhCH_2N{=}PPh_3$ reagent has been attempted, but it affords several unidentified complexes, including a trace amount of **3b**.

X-ray Crystal Structures of 2a,b and 3a,b. Details of crystallographic data for **2a**,**b** and **3a**,**b** are summarized in Table 1. Selected interatomic distances and angles are listed in Table 2 for **2a** and in Tables 3 and 4 for **2b** and **3b**, respectively.

The crystal structure of **2a** consists of two equivalent molecules of **2a** in different orientations in an asymmetric unit, and one of them is shown in Figure 3. The overall structural features of **2a** are similar to those of $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$,[6d] except that a benzyl isocyanide ligand is terminally bound to the Os(1) center in an equatorial position. The C_6 ring of C_{60} coordinates to the triosmium cluster framework in a typical face-

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(14) Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 285.

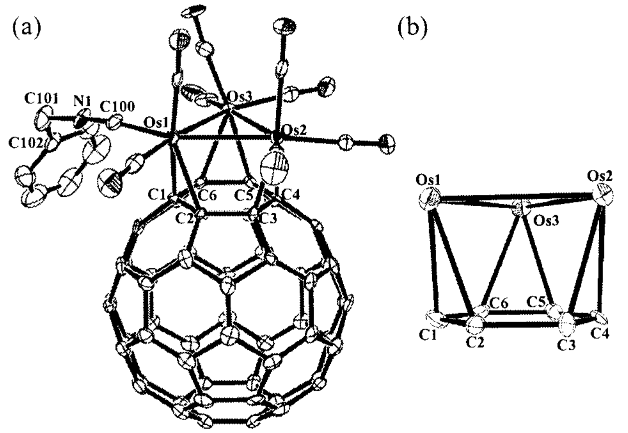

Figure 3. (a) Molecular structure with atomic labeling scheme for **2a**. (b) Expanded view of the μ_3-η^2:η^2:η^2-C_6 part of the C_{60} ligand.

Table 3. Selected Interatomic Distances (Å) and Esd's for 2b and 3a,b

	2b	3a	3b
Os(1)−Os(2)	2.910(1), 2.898(1)	2.918(1)	2.9252(4)
Os(2)−Os(3)	2.874(1), 2.902(1)	2.913(1)	2.9000(4)
Os(1)···Os(3)	4.565(1), 4.591(1)	4.617(1)	4.6327(4)
Os(1)−N(1)	2.08(2), 2.11(2)	2.11(2)	2.125(7)
Os(2)−C(100)	2.22(2), 2.13(3)	2.21(2)	2.181(8)
Os(3)−C(100)	1.98(2), 1.91(2)	1.98(2)	1.992(7)
C(100)−N(1)	1.24(2), 1.23(1)	1.26(2)	1.273(9)
Os(2)−C(200)			2.014(9)
C(200)−N(2)			1.15(1)
Os(3)−C(300)		2.04(3)	
C(300)−N(3)		1.17(3)	
Os(1)−C(1)	2.24(2), 2.23(2)	2.23(2)	2.25(1)
Os(2)−C(2)	2.50(2), 2.42(2)	2.48(2)	2.46(1)
Os(2)−C(3)	2.35(2), 2.39(2)	2.30(2)	2.37(1)
Os(3)−C(4)	2.19(2), 2.23(2)	2.25(2)	2.26(1)
C(1)−C(2)	1.44(3), 1.49(2)	1.43(3)	1.50(1)
C(2)−C(3)	1.44(2), 1.43(2)	1.47(3)	1.45(1)
C(3)−C(4)	1.49(2), 1.53(3)	1.53(2)	1.52(1)
C(4)−C(5)	1.54(3), 1.50(2)	1.50(3)	1.53(1)
C(5)−C(6)	1.37(3), 1.35(2)	1.33(3)	1.36(1)
C(6)−C(1)	1.52(2), 1.53(2)	1.53(3)	1.52(1)

Table 4. Selected Interatomic Angles (deg) and Esd's for 2b and 3a,b

	2b	3a	3b
Os(2)−Os(1)−Os(3)	37.61(3), 37.70(3)	37.60(3)	37.13(1)
Os(1)−Os(2)−Os(3)	104.23(3), 104.66(3)	104.73(3)	105.37(1)
Os(2)−Os(1)−N(1)	71.9(5), 68.1(6)	70.9(5)	71.0(2)
Os(1)−Os(2)−C(100)	62.6(5), 65.3(6)	63.2(5)	63.5(2)
Os(3)−Os(2)−C(100)	43.3(5), 41.0(6)	42.7(5)	43.4(2)
Os(2)−Os(3)−C(100)	50.5(7), 47.1(8)	49.2(6)	48.7(2)
Os(2)−C(100)−N(1)	118(2), 115(2)	117(2)	118.5(6)
Os(3)−C(100)−N(1)	153(2), 151(2)	155(2)	152.5(6)
Os(2)−C(200)−N(2)			178.5(8)
Os(3)−C(300)−N(3)		174(2)	
Os(1)−N(1)−C(100)	108(1), 110(2)	107(1)	105.9(6)
C(2)−C(1)−C(6)	112(1), 111(1)	108(2)	111.9(6)
C(1)−C(2)−C(3)	125(1), 124(2)	129(2)	123.6(7)
C(2)−C(3)−C(4)	123(2), 121(2)	117(2)	120.9(7)
C(3)−C(4)−C(5)	109(1), 112(1)	113(2)	112.3(6)
C(4)−C(5)−C(6)	126(2), 124(2)	125(2)	123.9(7)
C(1)−C(6)−C(5)	122(2), 124(1)	126(2)	123.6(7)
C(2)−C(1)−C(9)	114(2), 113(1)	115(2)	114.1(7)
C(6)−C(1)−C(9)	103(2), 102(1)	104(2)	102.2(7)
C(3)−C(4)−C(17)	115(2), 111(1)	113(2)	112.8(7)
C(5)−C(4)−C(17)	96(1), 102(1)	104(2)	101.4(6)

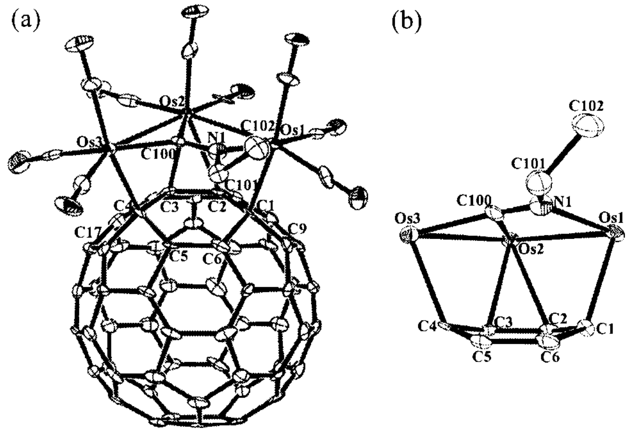

Figure 4. (a) Molecular structure with atomic labeling scheme for **2b**. Only the *ipso* carbon of the phenyl group is shown for clarity. (b) Expanded view of the boat-shaped μ_3-η^1:η^2:η^1-C_6 part of the C_{60} ligand.

capping μ_3-η^2:η^2:η^2-C_{60} bonding mode, and it is essentially parallel to the Os_3 plane. The average Os−Os distances of **2a** are 2.896(1) and 2.894(1) Å for both molecules, similar to that for $Os_3(CO)_{12}$ (2.877(3) Å).[15] The Os−C(C_{60}) bonds alternate in length, but the carbon−carbon bonds of the C_6 ring do not, as observed in structurally related $Os_3(CO)_8(PPh_3)$(μ_3-η^2:η^2:η^2-C_{60}).[6d]

The crystal structure of **2b** (see Figure 4) also contains two equivalent molecules in an asymmetric unit. The Os(1)−Os(3) bond of the Os_3 triangle in **1** has been ruptured upon addition of a benzyl isocyanide ligand, and the resulting Os_3 framework shows a bent geometry with an inner angle (∠Os(1)−Os(2)−Os(3)) of 104.23(3)° [104.66(3)°]. The bridging RNC ligand coordinates to the three osmium centers in a 4e-donor μ_3-η^2 bonding mode, which has been previously observed for an Os_6 cluster.[16] The formal electron counts for Os(1), Os(2), and Os(3) are 18, 19, and 17, respectively. The formal electron deficiency at the Os(3) center appears to be compensated by a stronger Os(3)−C(100) interaction (1.98(2) Å [1.91(2) Å]) as compared to the Os(2)−C(100) interaction (2.22(2) Å [2.13(3) Å]). Introduction of the 4e-donor RNC ligand has induced a transformation in the C_{60}−cluster interaction from μ_3-η^2:η^2:η^2 (**1**) to μ_3-η^1:η^2:η^1 (**2b**); the two outer osmium atoms, Os(1) and Os(3), coordinate to the C(1) and C(4) atoms of the C_{60} ligand in a σ-fashion, while the inner Os(2) atom is π-coordinated to the C(2) and C(3) atoms in an η^2 mode. The two σ-bonds, Os(1)−C(1) (2.24(2) Å [2.23(2) Å]) and Os(3)−C(4) (2.19(2) Å [2.23(2) Å]), are shorter than the Os(2)−(C(2),C(3)) π-bonds (average 2.42(2) Å [2.41(2) Å]). The C_6 ring, accordingly, has undergone orbital reorganization to have a 1,4-cyclohexadiene-like C_{60} ring; the C(2)−C(3) (1.44(2) Å [1.43(2) Å]) and C(5)−C(6) (1.37(3) Å [1.35(2) Å]) bonds exhibit double-bond character, while the other four C−C bonds (average 1.50(2) Å [1.51(2) Å]) show single-bond character. Interestingly, the C(2)−C(3) double bond is located in the 5−6 ring junction of C_{60}, which is the first example of a metal center coordination on a 5−6 ring junction in an η^2 bonding mode. The sums of the three angles around sp^3-hybridized C(1) (∠C(2)−C(1)−C(9) + ∠C(6)−C(1)−C(9) + ∠C(2)−C(1)−C(6) = 329(2)° [326(1)°]) and C(4) (∠C(3)−C(4)−C(5) + ∠C(5)−C(4)−C(17) + ∠C(3)−C(4)−C(17) = 320(1)° [325(1)°]) are considerably smaller than

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(16) Rivera, A. V.; Sheldrick, G. M.; Hursthouse, M. B. *Acta Crystallogr., Sect. B* **1978**, *34*, 1985.

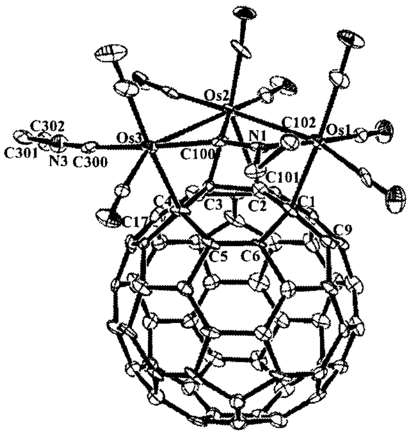

Figure 5. Molecular structure with atomic labeling scheme for **3a**. Only *ipso* carbons of the phenyl groups are shown for clarity.

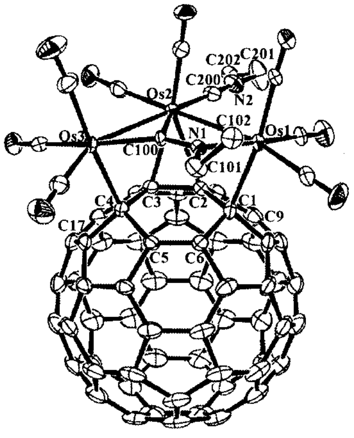

Figure 6. Molecular structure with atomic labeling scheme for **3b**. Only *ipso* carbons of the phenyl groups are shown for clarity.

those of the other four carbon atoms (average 352(1)° [352(1)°]) with sp^2 hybridization. Thus, the two sp^3-hybridized carbon atoms C(1) and C(4) 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 C(1) and C(4) at the bow and stern positions, as shown in Figure 4b. The dihedral angles between the C(2)−C(3)−C(5)−C(6) plane and the two adjacent planes C(1)−C(2)−C(6) and C(3)−C(4)−C(5) are 11(1)° [13(2)°] and 12(2)° [14(1)°], respectively.

The crystal structures of **3a**,**b** shown in Figures 5 and 6, respectively, are very similar to that of **2b**, except that a terminal benzyl isocyanide has replaced a carbonyl ligand on the Os(3) center (**3a**) or on the Os(2) center (**3b**). The bond lengths and angles for the terminal carbonyl and isocyanide ligands of **2b** and **3b** are within the expected ranges.

The cyclohexatriene-like C$_6$ rings of C$_{60}$ in μ_3-η^2:η^2:η^2-C$_{60}$ compounds (**1** and **2a**) have undergone orbital reorganization to form 1,4-cyclohexadiene-like rings in μ_3-η^1:η^2:η^1-C$_{60}$ complexes (**2b** and **3a**,**b**). For the transformation from **1** to **2b**, it can be envisaged that the added 4e-donor RNC ligand formally supplies 2e to the antibonding orbital of the Os(1)−Os(3) bond in **1**, which results in its scission. The remaining 2e of the RNC ligand leads to the conversion of two π interactions in **1** into two M−C σ bonds (Os(1)−C(1) and Os(3)−C(4)) and an uncoordinated C=C double bond (C(5)−C(6)) in **2b**. The conversion of **2a** to **3a**,**b** can be understood in a similar manner.

Concluding Remarks

We have fully characterized the unique features of the metal−C$_{60}$ σ-bonds in μ_3-η^1:η^2:η^1-C$_{60}$ compounds (**2b** and **3a**,**b**). The sp^3 carbons of M−C(C$_{60}$) σ-bonds exhibit characteristic upfield resonances (∼39 ppm) in the ^{13}C NMR spectra, and the distances of M−C(C$_{60}$) σ-bonds (average 2.24 Å) are notably shorter than the π bond lengths (average 2.41 Å). This study demonstrates 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) induced by modification of the coordination sphere of metal centers with external ligands (**1** → **2b** and **2a** → **3a**,**b**), providing a new synthetic route to C$_{60}$−metal σ complexes. The two isomers **3a,b** can be selectively prepared by the photochemical and chemical treatments of **1** in the presence of an excess of benzyl isocyanide, respectively. Efforts are currently underway to explore new reactivity and selective functionalization of the C$_{60}$ cage in these C$_{60}$−metal σ-complexes.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Solvents were dried over the appropriate drying agents and distilled immediately before use. C$_{60}$ (99.5%, SES research), OsO$_4$ (Strem), and benzyl isocyanide (98%, Aldrich) were used without further purification. Anhydrous trimethylamine *N*-oxide (mp 225−230 °C) was obtained from Me$_3$NO·2H$_2$O (98%, Aldrich) by sublimation (three times) at 90−100 °C under vacuum. PhCH$_2$N=PPh$_3$[17] and Os$_3$(CO)$_9$(μ_3-η^2:η^2:η^2-C$_{60}$) (**1**)[6e] were prepared according to the literature methods. Preparative thin-layer chromatography (TLC) plates were prepared with silica gel GF$_{254}$ (type 60, E. Merck).

Infrared spectra were obtained on a Bruker EQUINOX-55 FT-IR spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. Positive ion FAB mass spectra (FAB$^+$) were obtained by the staff of the Korea Basic Science Center, and all *m*/*z* values were referenced to ^{192}Os. Elemental analyses were provided by the staff of the Energy and Environment Research Center at KAIST.

Preparation of Os$_3$(CO)$_8$(CNR)(μ_3-η^2:η^2:η^2-C$_{60}$) (2a). Method A. A mixture of **1** (50.0 mg, 0.0324 mmol) and PhCH$_2$N=PPh$_3$ (1.2 equiv, 14.3 mg, 0.0389 mmol) in chlorobenzene (50 mL) was stirred for 12 h at room temperature. Evaporation of the solvent and purification by preparative TLC (CS$_2$) afforded compound **2a** (40.0 mg, 0.0246 mmol, 76%, R_f = 0.6) as a brown solid.

Method B. An acetonitrile solution (1 mL) of anhydrous Me$_3$NO (1.1 equiv, 1.1 mg, 0.015 mmol) was added to a chlorobenzene solution (20 mL) of **1** (20.0 mg, 0.0130 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the residue was redissolved in chlorobenzene (20 mL) followed by addition of benzyl isocyanide (3 equiv, 4.6 mg, 0.039 mmol). The resulting solution was heated at 60 °C for 1 h. Evaporation of the solvent and purification by preparative TLC (CS$_2$) gave **2a** (10.6 mg, 0.0065 mmol, 50%): IR (CH$_2$Cl$_2$) ν(CO) 2067 (vs), 2036 (s), 2019 (m), 1997 (w) and ν(NC) 2189 (w) cm^{-1}; ^{1}H NMR (400 MHz, CS$_2$/CDCl$_3$ (1:1), 298 K) δ 7.35−7.27 (m, 5H, *Ph*), 5.18 (s, 2H, C*H*$_2$); ^{13}C{^{1}H} NMR (100 MHz, CS$_2$/CDCl$_3$ (1:1), 298 K) δ 179.9

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(2*C*O), 177.6 (6*C*O), 156.4−142.6 (54C, C_{60} sp^2 carbon), 131.9 (1C, N*C*), 129.4−127.1 (6C, *Ph*), 64.3 (2C, C_{60} sp^3 carbon), 59.1 (2C, C_{60} sp^3 carbon), 57.6 (2C, C_{60} sp^3 carbon), 49.2 (1C, *C*H_2); MS (FAB$^+$) *m*/*z* 1637 (M$^+$). Anal. Calcd for $C_{76.25}H_7NO_8Os_3S_{0.5}$ (**1**·0.25CS_2): C, 55.45; H, 0.43; N, 0.85; S, 0.97. Found: C, 54.96; H, 0.55; N, 1.06; S, 1.13.

Preparation of $Os_3(CO)_9(\mu_3\text{-}CNR)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (2b). A chlorobenzene solution (20 mL) of **1** (50.0 mg, 0.0324 mmol) and benzyl isocyanide (30 equiv, 113.9 mg, 0.972 mmol) in a 100 mL Pyrex Schlenk tube was irradiated by a medium-pressure Hg lamp at room temperature for 3 days. Evaporation of the solvent and purification by preparative TLC (CS_2) afforded compound **2b** (6.0 mg, 0.0036 mmol, 11%, $R_f = 0.6$) as a brown solid: IR (C_6H_{12}) ν(CO) 2093 (s), 2076 (vs), 2055 (s), 2025 (vs), 1997 (m), 1992 (m), 1965 (w) and ν(NC) 1639 (br) cm^{-1}; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$ (1:1), 298 K) δ 7.52−7.41 (m, 5H, *Ph*), 5.62 (d, 1H, $J_{HH} = 13$ Hz, C*H*$_2$), 4.97 (d, 1H, $J_{HH} = 13$ Hz, C*H*$_2$); ^{13}C{^{1}H} NMR (100 MHz, CS_2/$CDCl_3$ (1:1), 298 K) δ 178.3, 178.0, 174.0, 172.6, 172.3, 170.1, 169.9, 168.3, 162.8 (9C, *C*O), 151.3−140.9 (56C, C_{60} sp^2 carbon), 134.9 (1C, N*C*), 133.7−127.2 (6C, *Ph*), 94.1 (1C, C_{60} sp^3 carbon), 77.4 (1C, *C*H_2), 72.3 (1C, C_{60} sp^3 carbon), 40.0 (1C, C_{60} sp^3 carbon), 37.2 (1C, C_{60} sp^3 carbon); MS (FAB$^+$) *m*/*z* 1665 (M$^+$). Anal. Calcd for $C_{77.5}H_7NO_9Os_3S$ (**2b**·0.5CS_2): C, 54.80; H, 0.42; N, 0.83; S, 1.89. Found: C, 54.40; H, 0.48; N, 0.84; S, 2.12.

Preparation of $Os_3(CO)_8(CNR)(\mu_3\text{-}CNR)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (3a,b). A chlorobenzene solution (20 mL) of **2a** (20.0 mg, 0.0122 mmol) and benzyl isocyanide (30 equiv, 43.1 mg, 0.368 mmol) was heated at 80 °C for 40 h. Evaporation of the solvent and separation by preparative TLC (CS_2) afforded compounds **3a** (4.7 mg, 0.0027 mmol, 22%, $R_f = 0.5$) and **3b** (5.8 mg, 0.0033 mmol, 27%, $R_f = 0.4$) as brown crystalline solids. Compound **3a**: IR (C_6H_{12}) ν(CO) 2085 (vs), 2052 (s), 2026 (vs), 2015 (w), 1992 (w), 1982 (w), 1968 (m) and ν(NC) 2185 (w), 1629 (vw) cm^{-1}; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$ (1:1), 298 K) δ 7.49−7.19 (m, 10H, *Ph*), 5.66 (d, 1H, $J_{HH} = 13$ Hz, C*H*$_2$), 5.48 (d, 1H, $J_{HH} = 16$ Hz, C*H*$_2$), 5.41 (d, 1H, $J_{HH} = 16$ Hz, C*H*$_2$), 4.88 (d, 1H, $J_{HH} = 13$ Hz, C*H*$_2$); ^{13}C NMR (carbonyl region, 100 MHz, $C_6H_4Cl_2$/C_7D_8 (1:1), 223 K) δ 181.9, 176.9, 176.1, 175.8, 175.5, 174.5, 173.2, 169.2; ^{13}C{^{1}H} NMR (100 MHz, CS_2/$C_6D_4Cl_2$ (1:1), 298 K) δ 180.6−168.7 (8C, *C*O), 163.6−141.1 (56C, C_{60} sp^2 carbon), 135.0−126.6 (14C, *Ph* and N*C*), 86.7 (1C, C_{60} sp^3 carbon), 76.4 (1C, *C*H_2), 74.6 (1C, C_{60} sp^3 carbon), 49.4 (1C, *C*H_2), 39.8 (1C, C_{60} sp^3 carbon), 39.4 (1C, C_{60} sp^3 carbon); MS (FAB$^+$) *m*/*z* 1754 (M$^+$). Anal. Calcd for $C_{84}H_{14}N_2O_8Os_3$: C, 57.66; H, 0.81; N, 1.60. Found: C, 57.34; H, 0.65; N, 1.43. Compound **3b**: IR (C_6H_{12}) ν(CO) 2079 (s), 2068 (s), 2019 (s), 1986 (s) and ν(NC) 2189 (w), 1634 (vw) cm^{-1}; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$ (1:1), 298 K) δ 7.49−6.98 (m, 10H, *Ph*), 5.50 (d, 1H, $J_{HH} = 13$ Hz, C*H*$_2$), 4.95 (br, 2H, C*H*$_2$), 4.87 (d, 1H, $J_{HH} = 13$ Hz, C*H*$_2$); ^{13}C NMR (carbonyl region, 100 MHz, $C_6H_4Cl_2$/C_7D_8 (1:1), 298 K) δ 180.0, 179.0, 178.3, 176.7, 175.7, 174.6, 173.4, 169.0; ^{13}C{^{1}H} NMR (100 MHz, CS_2/$C_6D_4Cl_2$ (1:1), relaxation time 17 s, 298 K) δ 179.5−170.2 (8C, *C*O), 168.4−140.1 (56C, C_{60} sp^2 carbon), 134.9−126.7 (14C, *Ph* and N*C*), 88.5 (br, 1C, C_{60} sp^3 carbon), 76.8 (1C, *C*H_2), 67.1 (br, 1C, C_{60} sp^3 carbon), 49.1 (1C, *C*H_2), 38.9 (1C, C_{60} sp^3 carbon), 38.5 (1C, C_{60} sp^3 carbon); MS (FAB$^+$) *m*/*z* 1754 (M$^+$). Anal. Calcd for $C_{85}H_{14}N_2O_8S_2Os_3$ (**3b**·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.

Selective Preparation of 3a from 2a. A chlorobenzene solution (20 mL) of **2a** (1 equiv, 50.0 mg, 0.0306 mmol) with benzyl isocyanide (30 equiv, 107.7 mg, 0.918 mmol) in a 100 mL Pyrex Schlenk tube was irradiated by a medium-pressure Hg lamp at room temperature for 12 h. Evaporation of the solvent and purification by preparative TLC (CS_2) afforded **3a** (26.4 mg, 0.0151 mmol, 49%) as the only major product.

Selective Preparation of 3b from 2b. An acetonitrile solution (1 mL) of anhydrous Me_3NO (1.1 equiv, 0.29 mg, 0.0039 mmol) was added to a chlorobenzene solution (20 mL) of **2b** (1 equiv, 6.4 mg, 0.0039 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the residue was redissolved in chlorobenzene (10 mL) followed by addition of benzyl isocyanide (5 equiv, 2.3 mg, 0.020 mmol). The resulting solution was heated at 70 °C for 1 h. Solvent evaporation and purification by preparative TLC (CS_2) gave **3b** (3.8 mg, 0.0022 mmol, 56%) as the only major product.

Crystal Structure Determination. Crystals of **2a**,**b** and **3a**,**b** suitable for X-ray diffraction studies were obtained by an interlayer diffusion technique (methanol into a CS_2/CH_2Cl_2 solution of **2a**; methanol into a CS_2/$C_6H_4Cl_2$ solution of **2b**; methanol into a toluene solution of **3a**; hexane into a CS_2 solution of **3b**). Diffraction data were collected on a Simens SMART diffractometer/CCD area detector. The preliminary orientation matrix and cell constants were determined from three series of ω scans at different starting angles. Each series consisted of 15 frames collected at intervals of 0.3° ω scan with an exposure time of 10 s per frame. A total of 50 531 (at 298 K), 17 228 (at 233 K), 23 793 (at 193 K), and 30 521 (at 293 K) data were collected for **2a**,**b** and **3a**,**b**, respectively. Total reflections were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Each structure was solved by direct and different Fourier methods and was refined by the full-matrix least-squares methods based on F^2 (SHELX 97).[18] All non-hydrogen atoms were refined with anisotropic thermal coefficients. Details of relevent crystallographic data are summarized in Table 1.

The crystal structure of **2a** contained two equivalent molecules with different orientations and a half molecule of CS_2 in an asymmetric unit. In one of the two molecules, the triangular osmium portion was disordered in two orientations, and their occupancy factors were converged to 0.94 and 0.06. The structure of **2b** also included two equivalent molecules and two half-molecules of CS_2 in an asymmetric unit. The C101 and C400 atoms were refined isotropically, while the other non-hydrogen atoms were refined with anisotropic parameters. The structure of **3b** contained a molecule of **3b** and a CS_2 solvate molecule in an asymmetric unit.

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Supporting Information Available: Figures giving ^{1}H NMR spectra of **2a**,**b** and **3a**,**b**, 2D ^{1}H−^{1}H COSY and ^{13}C NMR spectra of **3a**,**b** and tables giving full structural data for **2a**,**b** and **3a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Sheldrick, G. M. SHELX97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.