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Substitution Reactions of a μ_3-η^1:η^2:η^1-C_{60} Triosmium Cluster Complex and Formation of a Novel μ_3-η^1:η^1:η^2-C_{60} Bonding Mode

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Decarbonylation of $Os_3(CO)_8(CNR)(\mu_3\text{-CNR})(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (**1**; R = CH_2Ph) with Me_3NO/MeCN and subsequent thermal reactions with various 2e-donor ligands afford the respective substitution products $Os_3(CO)_7(CNR)(\mu_3\text{-CNR})(L)(C_{60})$ (L = $(\mu\text{-H})_2$ (**2**), CNR (**3**), PMe_3 (**4**), PPh_3 (**5**)) in high yields. Compounds **2**−**5** have been characterized by spectroscopic (MS, IR, and ^{1}H, ^{13}C, and ^{31}P NMR) and microanalytical data. Compounds **3** and **4** consist of three isomeric forms due to a 3-fold rotation on the outer Os center with a terminal benzyl isocyanide ligand, whereas **2** and **5** exist as a single isomer. The molecular structures of **2**−**5** have been determined by X-ray single-crystal diffraction studies. The hydride ligands of **2** have not been directly located, but ligand arrangements around the inner Os atom of the open-chain Os_3 framework suggest that the two hydride ligands bridge the two Os−Os edges, respectively. The added isocyanide ligand in **3** is coordinated to an equatorial site on the inner Os center. The PMe_3 ligand in **4** is positioned at the axial site of the inner Os atom. The μ_3-η^1:η^2:η^1-C_{60} interactions between C_{60} and metal clusters are not significantly altered by substitution of the corresponding ligands in **2**−**4**. The PPh_3 ligand in **5**, however, is bound at the less hindered equatorial site of the outer Os center and leads to an orbital reorganization of the C_6 ring of C_{60} from μ_3-η^1:η^2:η^1-C_{60} (**1**) to μ_3-η^1:η^1:η^2-C_{60} (**5**).

Introduction

The interaction between metal clusters and the carbon cluster C_{60} is one of the most interesting topics in the area of exohedral metallofullerene chemistry.[1] In particular, the metal cluster−C_{60} complexes can be viewed as molecular analogues of metal and carbon hybrid materials, namely, carbon nanotubes decorated with metal nanoparticles, which may lead to useful application in future catalytic and electronic materials.[2] Our previous work demonstrated that the existing C_{60} bonding modes on the cluster framework can be converted to new ones by modifying the coordination sphere of metal centers to which C_{60} is coordinated. The first example of reversible interconversion between μ-η^2:η^2-C_{60} and μ_3-η^2:η^2:η^2-C_{60} has been observed on an Os_5C cluster framework by addition or elimination of 2e-donor ligands such as carbon monoxide and benzyl isocyanide.[3] Further efforts have resulted in transformation of a π-type μ_3-η^2:η^2:η^2-C_{60} species to a new σ-type μ_3-η^1:η^2:η^1-C_{60} ligand on a triosmium cluster framework upon insertion of a benzyl isocyanide ligand into an Os−Os bond.[4] This strategy provides a new synthetic route to C_{60}−metal σ-complexes, which have been rather unexplored, although such complexes are potentially useful in the selective functionalization of C_{60}.[5] Our results have opened up opportunities for further manipulation of the C_{60} bonding modes and prompted us to explore the reactivity of $Os_3(CO)_8(CNR)(\mu_3\text{-CNR})(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (**1**; R = CH_2Ph) toward various 2e-donor ligands such as dihydrogen, benzyl isocyanide, and phosphines (PMe_3 and PPh_3). Herein we wish to report the first example of a σ-type μ_3-η^1:η^1:η^2-C_{60} (1,2-σ adduct) bonding mode induced by PPh_3 substitution on the metal center and various 2e-donor-substituted derivatives of **1**, as shown in Scheme 1. A preliminary account of some of this work has appeared.[6]

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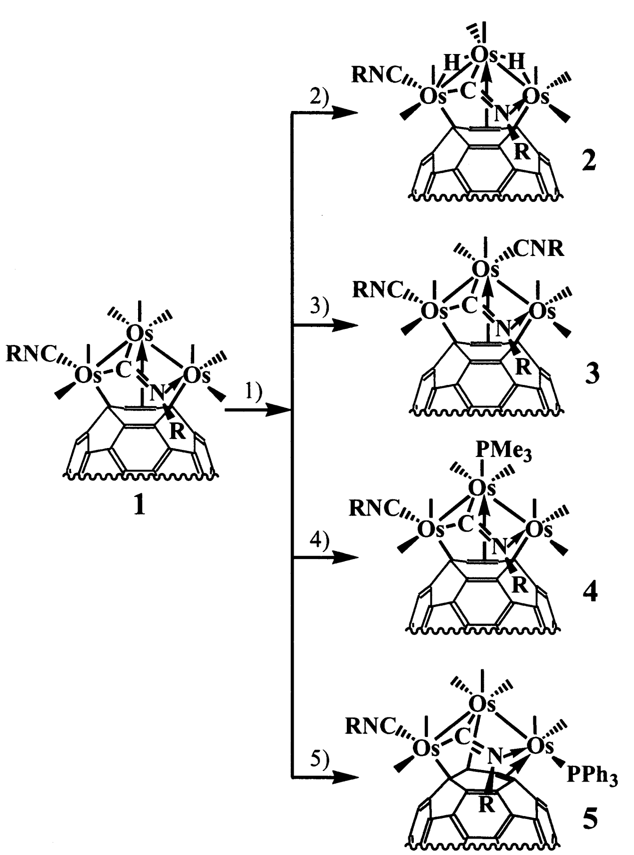
Scheme 1[a]



[a] Legend: (1) Me_3NO/MeCN, room temperature, 0.5 h; (2) 1 atm of H_2, 60 °C, 1.5 h, 65%; (3) 3 equiv of RNC, 100 °C, 1 h, 56%; (4) 5 equiv of PMe_3, 50 °C, 1 h, 49%; (5) 3 equiv of PPh_3, 70 °C, 4 h, 70%. R = CH_2Ph.

Results and Discussion

Synthesis and Characterization of 2−5. Synthetic procedures for **2**−**5** are summarized in Scheme 1. Decarbonylation of $Os_3(CO)_8(CNR)(\mu_3\text{-}CNR)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (**1**; R = CH_2Ph) with Me_3NO/MeCN and subsequent reaction with dihydrogen (1 atm) in chlorobenzene at 60 °C affords a dihydride-substituted product, $Os_3(CO)_7(CNR)(\mu_3\text{-}CNR)(\mu\text{-}H)_2(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (**2**), in 65% yield. Analogous reactions with benzyl isocyanide and phosphines (PMe_3 and PPh_3) give the benzyl isocyanide substituted product $Os_3(CO)_7(CNR)_2(\mu_3\text{-}CNR)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (**3**) and phosphine-substituted complexes $Os_3(CO)_7(CNR)(\mu_3\text{-}CNR)(PR_3)(C_{60})$ (R = Me (**4**), Ph (**5**)) in high yields, respectively. Compounds **2**−**5** are soluble in various solvents such as CS_2, dichloromethane, toluene, and chlorinated benzenes. All new compounds are formulated by the molecular ion isotope patterns (*m*/*z* (highest peak): 1724 (**2**); 1839 (**3**); 1798 (**4**); 1984 (**5**)) in the positive ion FAB mass spectra and by microanalytical data.

The IR spectra of **2**−**5** show terminal N≡C stretching bands at around 2185 cm^{-1} and bridging N=C bands in the range of 1625−1605 cm^{-1}. The high-energy band of **3** at 2181 cm^{-1} is stronger than those of **3**−**5**, because **3** has two terminal RNC ligands. The carbonyl stretching bands appear in the typical 2100−1950 cm^{-1} range.

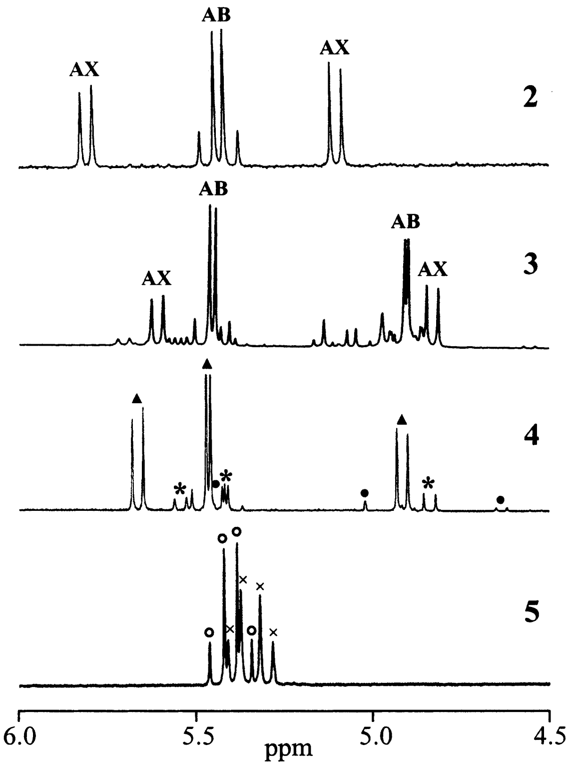


Figure 1. ^1H NMR spectra (400 MHz, $CS_2/CDCl_3$ (1:1), 298 K, benzylic region) of **2**−**5**.

The ^1H NMR spectra (benzylic region of the isocyanide ligand) of compounds **2**−**5** are shown in Figure 1. The ^1H NMR spectrum of **2** shows an AX (δ 5.81 and 5.10 with J_{HH} = 13 Hz) and an AB (δ 5.47 and 5.40 with J_{HH} = 16 Hz) pattern for the diastereotopic benzylic hydrogens of the two isocyanide ligands and an AX (δ −11.14 and −12.78 with J_{HH} = 13 Hz) pattern for the two hydride ligands. Compound **2** exists as a single isomer in solution. The ^1H NMR spectrum of **3** exhibits very complicated patterns, and its 2D $^1H-^1H$ COSY spectrum shows nine off-diagonal cross-peaks (three peaks for each isomer; see the Supporting Information). This observation indicates that compound **3** consists of three isomeric forms, which are likely to result from a 3-fold rotation of the isocyanide ligand on the outer Os center as previously proposed for **1**.[4] Resonances due to the major isomer of **3** (denoted as ▲) involve three diastereotopic benzylic signals of an AX pattern (δ 5.61 and 4.83 with J_{HH} = 13 Hz) and two AB (δ 5.48 and 5.42 with J_{HH} = 16 Hz; δ 4.93 and 4.88 with J_{HH} = 15 Hz) patterns, although they could not be specifically assigned to each of the three different isocyanide ligands. The 2D $^1H-^1H$ COSY spectrum of **4** contains three off-diagonal cross-peaks, confirming that it also consists of three isomers in a 0.81:0.15:0.04 ratio at room temperature, as shown in Figure 2. AX (δ 5.67 and 4.92 with J_{HH} = 12 Hz) and AB (δ 5.49 and 5.44 with J_{HH} = 16 Hz) patterns are assigned to the major isomer (denoted as ▲), and two sets of smaller resonances (denoted as * and ●) are due to the minor isomers (see Figure 1). Three isomers of **4** may be derived from an analogous 3-fold rotation of the isocyanide ligand on the outer Os center, as observed in **1** and **3**.[4] The ^1H NMR spectrum of **5** reveals two AB patterns (δ 5.43 and 5.36 with J_{HH} = 16 Hz (denoted as ○ in Figure 1); δ 5.41 and 5.31 with J_{HH} = 14 Hz (denoted as × in Figure 1)) for the two isocyanide ligands, implying that compound **5** exists as a single isomer in solution.

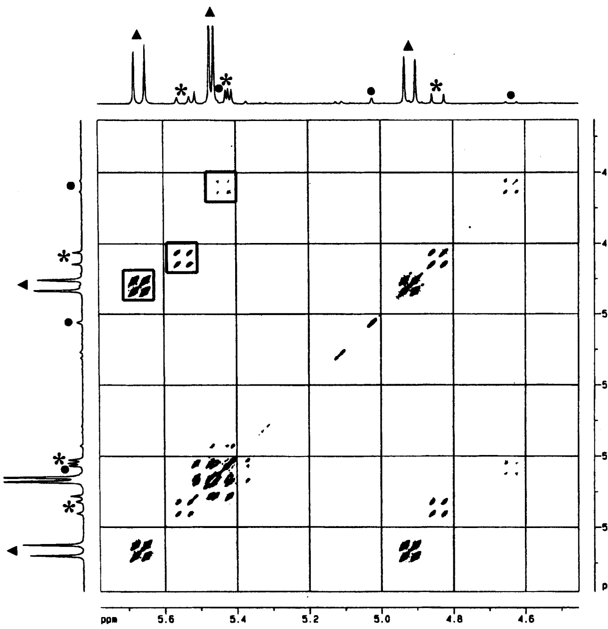


Figure 2. 2D ^{1}H−^{1}H COSY spectrum (400 MHz, CS_2/$CDCl_3$ (1:1), 298 K, benzylic region) of **4**. Three off-diagonal peaks are clarified by the rectangles. Signals from two minor isomers are denoted by * and ●, respectively.

The ^{13}C{^{1}H} NMR spectrum (carbonyl region) of **2** reveals 7 inequivalent carbonyl resonances at δ 178.2, 178.2, 172.8, 172.4, 171.0, 170.8, and 170.7, whereas compound **3** exhibits 21 signals in the range of δ 181.5−170.9, consistent with 7 inequivalent carbonyl ligands for each isomer. The ^{13}C NMR spectrum of **4** also shows 7 carbonyl resonances at δ 184.5 (J_{PC} = 8 Hz), 181.8 (J_{PC} = 7 Hz), 181.7, 180.4 (J_{PC} = 9 Hz), 179.2 (J_{PC} = 8 Hz), 176.4, and 171.0, of which 4 signals are coupled to the phosphorus atom of the PMe_3 ligand (see the Supporting Information). The two equatorial carbonyls on the PMe_3-coordinated Os atom show $^2J_{PC}$ couplings, and carbonyl ligands on the adjacent Os centers may exhibit $^3J_{PC}$ couplings. The best candidates for the $^3J_{PC}$ coupling are the carbonyls C(1B) and C(3C) on the Os(1) and Os(3) atoms (vide infra), respectively, since significant $^3J_{PC}$ couplings have been observed for carbonyl ligands trans to a phosphine ligand in metal cluster complexes.[7] The ^{13}C NMR spectrum of **5** comprises seven signals at δ 181.6, 181.2, 180.3 (J_{PC} = 4 Hz), 175.9, 172.2, 169.6, and 166.8 (J_{PC} = 4 Hz), where the two P−C coupled resonances are ascribed to the axial and equatorial carbonyl ligands on the PPh_3-bound, outer Os atom, respectively. These assignments are based upon earlier observations that the resonances of axial carbonyls in this type of cluster appear at lower field than those of equatorial carbonyls.[8]

The ^{13}C NMR spectra of the C_{60} moieties for compounds **2**−**5** contain 56 distinct sp^2 (171−140 ppm) and 4 sp^3 (101−39 ppm) carbon signals due to their asymmetric structures. The ^{13}C{^{1}H} NMR spectra (sp^3 carbon region of C_{60}) of **2**−**5** are shown in Figure 3. Compound **2** shows two lower field resonances at δ 101.3 and 89.3 and two higher field resonances at δ 40.7 and 40.5, which are assigned to the M−C(C_{60}) π-bonded and σ-bonded carbon atoms, respectively. The ^{13}C NMR resonances of the C_{60} moiety typically appear in the unique regions of δ 40−38 for the σ-bonded atoms and δ 95−65 for the π-bonded atoms in previously reported μ_3-η^1:η^2:η^1-C_{60} triosmium complexes.[4a] Compound **3** exhibits 12 signals in the sp^3 carbon region of C_{60} for the three isomers. The six lower field resonances at δ 92.5, 90.7, 83.8, 68.3, 65.7, and 58.8 are assigned to the π-bonded carbon atoms, and the other six higher field resonances at δ 47.3, 42.9, 42.6, 41.5, 41.3, and 39.1 are assigned to the σ-bonded carbons. Compounds **4** and **5** show two lower field resonances (δ 79.5 (J_{PC} = 11 Hz), 78.0 (J_{PC} = 12 Hz) for **4**; δ 98.9, 54.0 for **5**) for the π-bonded sp^3 carbon atoms and two higher field resonances (δ 40.0, 39.4 for **4**; δ 47.8, 44.9 for **5**) for the σ-bonded sp^3 carbon atoms. Resonances due to the minor isomers of **4** are too weak to be detected. It is notable that the compound **4** exhibits two doublets at δ 79.5 and 78.0 with P−C couplings (see the inset of Figure 3) due to two π-bonded sp^3 carbon atoms of C_{60} trans to the PMe_3 ligand. The benzylic carbon resonances of the isocyanide ligand are easily distinguishable from the sp^3 carbons of C_{60} by negative signals of the DEPT experiment (θ = 135°) and are denoted as ● in Figure 3. Compounds **2** and **3** (three isomers), **4** (three isomers), and **5** reveal two, nine, two (major isomer only), and two benzylic carbon resonances in the range of δ 79−48, respectively (see Experimental Section).

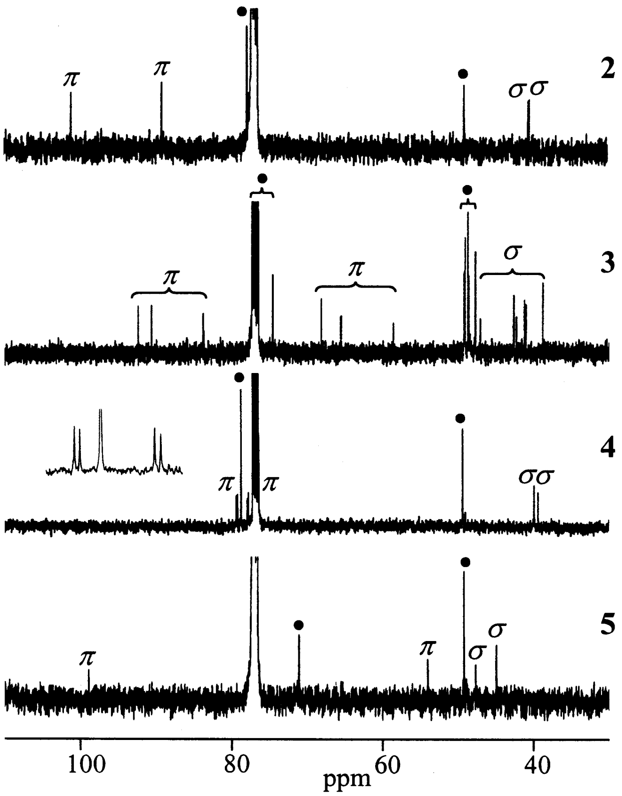


Figure 3. ^{13}C{^{1}H} NMR spectra (100 MHz, CS_2/$CDCl_3$ (1:1), 298 K, sp^3 carbon region) of **2**−**5**. The benzylic carbon resonances of the RNC ligands are denoted by ●. The inset is the expanded spectrum of **4** at δ 80−77 in CS_2/$C_6D_4Cl_2$ (1:1).

X-ray Crystal Structures of 2−5. Details of the crystallographic data for **2**−**5** are summarized in Table

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Table 1. Crystallographic Data for 2−5

	2	**3**$\cdot C_6H_4Cl_2$	**4**$\cdot CS_2$	**5**$\cdot C_6H_4Cl_2$
formula	$C_{83}H_{14}N_2O_7Os_3$	$C_{91}H_{21}N_3O_7Os_3\cdot C_6H_4Cl_2$	$C_{86}H_{23}N_2O_7Os_3P\cdot CS_2$	$C_{101}H_{29}N_2O_7Os_3P\cdot C_6H_4Cl_2$
fw	1721.56	1985.70	1873.76	2130.82
syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a, Å	20.10(1)	13.150(2)	14.685(3)	12.984(3)
b, Å	23.46(2)	26.853(5)	13.935(3)	13.429(2)
c, Å	12.359(8)	19.273(5)	29.747(5)	22.122(4)
α, deg	90	90	90	107.39(3)
β, deg	102.60(1)	109.89(2)	103.297(3)	90.99(3)
γ, deg	90	90	90	103.08(3)
V, Å^3	5685(6)	6400(2)	5924(2)	3570(1)
Z	4	4	4	2
D_{calcd}, Mg m^{-3}	2.011	2.061	2.101	1.982
temp, K	298(2)	298(2)	233(2)	298(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	6.756	6.099	6.587	5.495
$\theta_{\mathrm{min,max}}$, deg	1.35, 23.00	1.36, 22.00	1.44, 23.00	1.62, 23.00
R_F[a]	0.0502	0.0745	0.0763	0.0413
R_w[b]	0.1407	0.1743	0.1685	0.0960
GOF	1.062	1.333	1.088	1.073

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

Table 2. Selected Interatomic Distances (Å) and Esd's for 2−5

	2	3	4	5
Os(1)−Os(2)	2.972(2)	2.920(1)	2.918(1)	2.932(1)
Os(2)−Os(3)	2.896(1)	2.900(1)	2.913(1)	2.877(1)
Os(1)···Os(3)	4.686(1)	4.614(1)	4.607(1)	4.600(2)
Os(1)−N(1)	2.14(1)	2.11(1)	2.06(2)	2.166(6)
Os(2)−C(100)	2.12(1)	2.17(2)	2.13(2)	2.154(8)
Os(3)−C(100)	2.01(1)	1.97(2)	2.00(2)	1.980(8)
C(100)−N(1)	1.26(2)	1.27(2)	1.28(2)	1.25(1)
Os(3)−C(300)	2.02(1)	2.05(2)	2.01(2)	2.05(1)
C(300)−N(3)	1.17(2)	1.14(2)	1.15(2)	1.13(1)
Os(2)−C(200)		2.03(2)		
C(200)−N(2)		1.10(2)		
Os(2)−P(2)			2.360(4)	
Os(1)−P(1)				2.395(3)
Os(1)−C(1)	2.23(1)	2.23(2)	2.25(2)	2.309(8)
Os(1)−C(2)	2.94(1)	2.80(2)	2.91(2)	2.591(8)
Os(2)−C(2)	2.39(1)	2.48(2)	2.40(2)	2.689(8)
Os(2)−C(3)	2.35(1)	2.31(2)	2.36(1)	2.237(7)
Os(3)−C(4)	2.25(1)	2.23(2)	2.23(2)	2.248(7)
C(1)−C(2)	1.50(2)	1.48(3)	1.49(2)	1.43(1)
C(2)−C(3)	1.43(2)	1.47(3)	1.43(2)	1.47(1)
C(3)−C(4)	1.50(2)	1.51(3)	1.53(2)	1.57(1)
C(4)−C(5)	1.51(2)	1.51(3)	1.50(3)	1.49(1)
C(5)−C(6)	1.37(2)	1.38(3)	1.38(2)	1.39(1)
C(6)−C(1)	1.51(2)	1.50(3)	1.49(2)	1.50(1)

Table 3. Selected Interatomic Angles (deg) and Esd's for 2−5

	2	3	4	5
Os(2)−Os(1)−Os(3)	36.44(4)	37.40(3)	37.78(3)	37.21(3)
Os(1)−Os(2)−Os(3)	105.99(4)	104.90(3)	104.36(3)	104.73(3)
Os(2)−Os(1)−N(1)	68.5(2)	70.9(4)	71.3(4)	70.4(2)
Os(1)−Os(2)−C(100)	63.5(4)	63.7(6)	62.4(6)	63.3(2)
Os(3)−Os(2)−C(100)	43.9(4)	42.8(6)	43.3(6)	43.5(2)
Os(2)−Os(3)−C(100)	46.9(3)	48.5(5)	47.0(6)	48.5(2)
Os(2)−C(100)−N(1)	121(1)	118(1)	120(2)	121.4(6)
Os(3)−C(100)−N(1)	149(1)	152(1)	149(2)	148.9(7)
Os(1)−N(1)−C(100)	107(1)	107(1)	105(1)	103.8(5)
Os(2)−Os(3)−C(300)	109.9(3)	112.0(6)	106.4(5)	109.1(3)
Os(1)−Os(2)−C(200)		91.0(6)		
Os(1)−Os(2)−C(2B)	123.7(4)		84.2(5)	89.3(3)
Os(2)−Os(1)−C(1C)	104.3(3)	97.7(6)	95.8(6)	95.2(3)
Os(3)−Os(2)−C(2B)	128.2(4)		167.4(5)	161.6(3)
Os(3)−Os(2)−C(2C)		71.2(6)	73.5(4)	70.7(3)
Os(1)−Os(2)−P(2)			95.7(1)	
Os(3)−Os(2)−P(2)			98.0(1)	
Os(2)−Os(1)−C(1A)	98.3(4)	96.2(8)	99.6(5)	85.6(3)
Os(2)−Os(3)−C(3A)	99.9(4)	96.3(7)	102.7(5)	97.6(3)
Os(2)−Os(1)−P(1)				173.85(5)
C(2)−C(1)−C(6)	110.8(9)	112(1)	112(1)	113.8(7)
C(1)−C(2)−C(3)	123.2(9)	123(2)	123(2)	124.8(7)
C(2)−C(3)−C(4)	122.5(9)	121(2)	122(2)	118.9(7)
C(3)−C(4)−C(5)	110.8(9)	112(2)	111(2)	112.0(6)
C(4)−C(5)−C(6)	124(1)	124(2)	124(2)	124.7(7)
C(1)−C(6)−C(5)	124(1)	123(2)	124(2)	122.9(8)
C(2)−C(1)−C(9)	112.2(9)	111(2)	114(2)	115.9(7)
C(6)−C(1)−C(9)	101.0(9)	102(1)	102(1)	103.0(7)
C(1)−C(2)−C(12)	119(1)	123(2)	119(2)	119.9(7)
C(3)−C(2)−C(12)	109(1)	107(2)	109(2)	107.4(7)
C(2)−C(3)−C(14)	107.4(9)	106(2)	107(1)	105.8(6)
C(4)−C(3)−C(14)	120.7(9)	120(2)	119(1)	115.6(7)
C(3)−C(4)−C(17)	112.1(9)	112(2)	111(1)	113.8(6)
C(5)−C(4)−C(17)	101.6(9)	100(1)	103(1)	101.5(6)

1. Selected interatomic distances and angles are listed in Tables 2 and 3.

The molecular structure and the atomic labeling scheme of **2** are shown in Figure 4. The triosmium framework of **2** adopts an open-chain geometry with a bent angle (∠Os(1)−Os(2)−Os(3)) of 105.99(4)°. The Os(1), Os(2), and Os(3) atoms are bonded to three, two, and two terminal carbonyl ligands, respectively. A terminal isocyanide ligand is equatorially bonded to the Os(3) center. A bridging isocyanide ligand is coordinated to the three osmium centers in a 4e-donor μ_3-η^2 bonding mode, which has been previously observed in Os_3 and Os_6 clusters.[4a] The C(100) atom is connected to the Os(2) and Os(3) atoms, and the N(1) atom is bound to the Os(1) atom. The positions of the two hydride ligands could not be directly located from X-ray data. The two hydride ligands are proposed to bridge the Os(1)−Os(2) and Os(2)−Os(3) edges on the basis of the enlargement of M−M−ligand angles coplanar with and adjacent to the M−H−M linkages (∠Os(1)−Os(2)−C(2B) = 123.7(4)°, ∠Os(2)−Os(1)−C(1C) = 104.3(3)°, and ∠Os(3)−Os(2)−C(2B) = 128.2(4)°). See the ∠Os(3)−Os(2)−C(2C) angles (average 71.8 Å) of **3**−**5** for comparison with the ∠Os(3)−Os(2)−C(2B) angle of **2** in Table 3. The presence of the bridging hydride ligand is further confirmed by the significant elongation of the Os(1)−Os(2) bond (2.972(2) Å), which is associated with a single, unsupported μ-hydride ligand.[10] Note that the average Os(1)−Os(2) bond length in **3**−**5** is 2.923(1) Å.

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[9] Rivera, A. V.; Sheldrick, G. M.; Hursthouse, M. B. *Acta Crystallogr., Sect. B* **1978**, *34*, 1985.

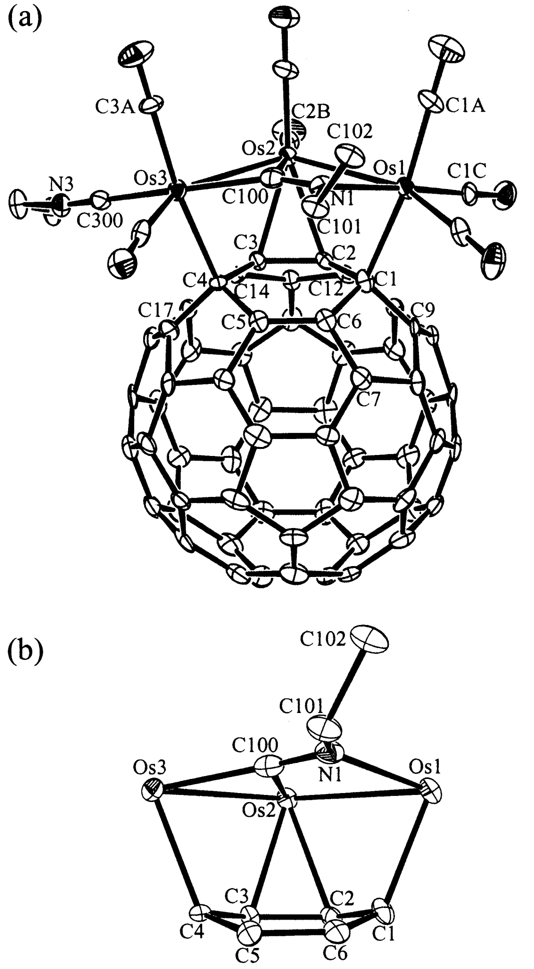

Figure 4. (a) Molecular structure with atomic labeling scheme for **2**. Only ipso carbons of the phenyl groups are shown for clarity. (b) Expanded view of the μ_3-η^1:η^2:η^1-C_6 part of the C_{60} ligand.

The formal electron counts for the Os(1), Os(2), and Os(3) centers are 18.5, 18, and 17.5, respectively. The formal electron deficiency of the Os(3) atom may be compensated by a stronger Os(3)−C(100) interaction (2.01(1) Å) as compared to Os(2)−C(100) (2.12(1) Å).

The interaction between the triosmium centers and the C_6 ring of C_{60} shows a typical μ_3-η^1:η^2:η^1 bonding mode, as previously observed in μ_3-η^1:η^2:η^1-C_{60} complexes such as **1** and $Os_3(CO)_9(\mu_3\text{-}CNCH_2Ph)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}C_{60})$.[4] The outer Os(1) and Os(3) atoms 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) (2.23(1) Å) and Os(3)−C(4) (2.25(1) Å), are shorter than the Os(2)−(C(2),C(3)) π-bonds (2.39(1) and 2.35(1) Å). The C_6 ring of the C_{60} moiety exhibits a 1,4-disubstituted cyclohexadiene-like nature. The C(2)−C(3) (1.43(2) Å) and the uncoordinated C(5)−C(6) (1.37(2) Å) bonds exhibit a double-bond character, while the other four C−C bonds (average 1.51(2) Å) show a single-bond character. The sums of the three angles around C(1) (∠C(2)−C(1)−C(6) + ∠C(2)−C(1)−C(9) + ∠C(6)−C(1)−C(9) = 324.0(9)°) and C(4) (∠C(3)−C(4)−C(5) + ∠C(3)−C(4)−C(17) + ∠C(5)−C(4)−C(17) = 324.5(9)°) are considerably smaller than those of the other four carbon atoms (average 352(1)°), indicating that the C(1) and C(4) atoms are pulled away from the smooth surface of C_{60} due to the sp^3 hybridization of M−C σ-bonds. The C_6 ring of C_{60} thus adopts a boat shape with C(1) and C(4) at the bow and stern positions, as shown in Figure 4b.

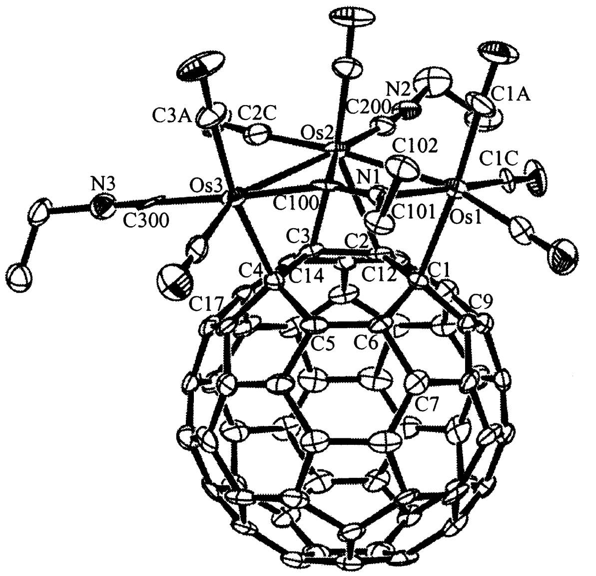

Figure 5. Molecular structure with atomic labeling scheme for **3**. Only ipso carbons of the phenyl groups are shown for clarity.

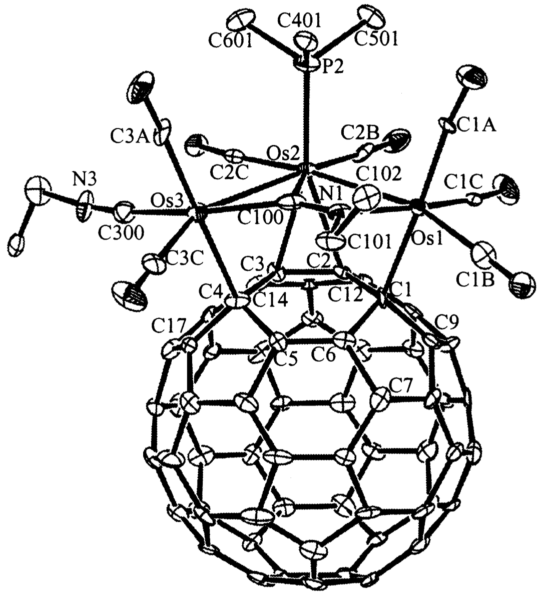

Figure 6. Molecular structure with atomic labeling scheme for **4**. Only ipso carbons of the phenyl groups are shown for clarity.

As shown in Figures 5 and 6, the overall structural features of **3** and **4** are similar to those of **2**, except that the added benzyl isocyanide and trimethyl phosphine ligands are coordinated to the Os(2) centers, respectively. The benzyl isocyanide ligand in **3** is terminally bound at an equatorial position of the Os(2) atom. The PMe_3 ligand in **4**, however, is positioned at the axial site of the Os(2) atom, which is an unusual coordination to triosmium cluster frameworks for the phosphine

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(10) (a) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *14*, 1843. (b) Churchill, M. R. *Adv. Organomet. Chem.* **1998**, *28*, 330.

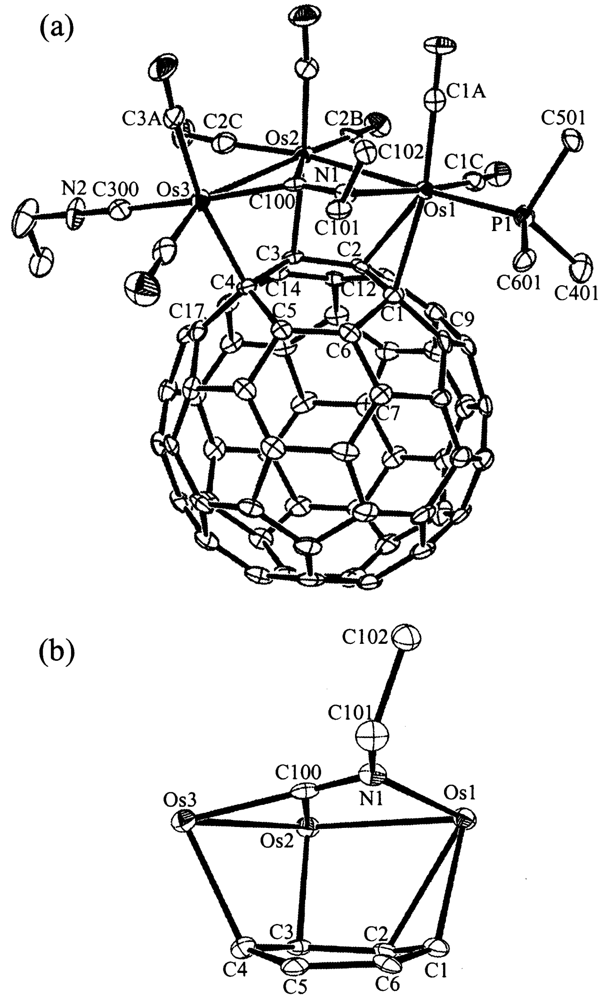

Figure 7. (a) Molecular structure with atomic labeling scheme for **5**. Only ipso carbons of the phenyl groups are shown for clarity. (b) Expanded view of the μ_3-η^1:η^1:η^2-C_6 part of the C_{60} ligand.

ligands.[11] The two axial carbonyls on the Os(1) and Os(3) atoms are pushed away from the PMe_3 ligand (∠Os(2)−Os(1)−C(1A) = 99.6(5)°, ∠Os(2)−Os(3)−C(3A) = 102.7(5)°), presumably to relieve the steric congestion among axial ligands. The μ_3-η^1:η^2:η^1 interactions in **3** and **4** between metal clusters and C_{60} are not significantly altered from that in **1** by substitution of CO with isocyanide and phosphine ligands.

The molecular structure of **5** is shown in Figure 7. The added PPh_3 ligand occupies the outer equatorial position of the Os(1) atom by replacing a carbonyl ligand. Interestingly, the C_6 ring of the C_{60} moiety has undergone orbital rearrangement from μ_3-η^1:η^2:η^1-C_{60} in **1** to μ_3-η^1:η^1:η^2-C_{60} in **5** upon coordination of PPh_3. The Os(1) center is π-coordinated to the C(1) and C(2) atoms in an η^2 mode, and the two Os(2) and Os(3) atoms are bonded to the C(3) and C(4) atoms, respectively, in a σ fashion. The σ-bonds (Os(2)−C(3) = 2.237(7) Å; Os(3)−C(4) = 2.248(7) Å) are shorter than the π-bonds (Os(1)−C(1) = 2.309(8) Å; Os(1)−C(2) = 2.591(8) Å), as commonly observed in **2**−**4**. The Os(1)−C(2) bond length (2.591(8) Å) in **5** compares with other nonbonding Os(1)···C(2) distances (2.94(1) Å in **2**, 2.80(2) Å in **3**, and 2.91(2) Å in **4**). The nonbonding Os(2)···C(2) distance in **5** (2.689(8) Å) is longer than the Os(2)−C(2) bond lengths (2.39(1) Å in **2**, 2.48(2) Å in **3**, and 2.40(2) Å in **4**). The C(1)−C(2) (1.43(1) Å) and C(5)−C(6) (1.39(1) Å) bonds reveal a double-bond character, and the other four C−C bonds (average 1.51(1) Å) show a single-bond character, clearly revealing the 1,3-cyclohexadiene-like nature of the C_6 ring of C_{60}.

All bond lengths and angles, including carbonyl and isocyanide ligands for **2**−**5**, are within the expected ranges.

Concluding Remarks

The inner osmium center of **1** is coordinated to three carbonyl ligands and a double bond of C_{60} and thus is most electron-deficient among three metal centers. Consequently, the carbonyl groups on the inner osmium atom are the site of attack by the nucleophilic Me_3NO reagent; a carbonyl group on the Os(2) center in **1** is substituted by dihydrogen, benzyl isocyanide, and trimethylphosphine for the formation of **2**−**4**. The two hydride ligands in **2** obviously bridge the two metal edges. The benzyl isocyanide ligand in **3** occupies an equatorial site of the Os(2) atom, which is arranged as far from the isocyanide ligand on the Os(3) center as possible. The PMe_3 ligand in **4**, however, is coordinated to the axial site of the Os(2) center, although tertiary phosphines and bulky isocyanide ligands are known to occupy only equatorial sites in triosmium cluster complexes.[12] This unusual axial coordination of the PMe_3 ligand in **4** may be ascribed to the donor property of the PMe_3 ligand, which stabilizes the trans electron-withdrawing interaction of C_{60} through metal-to-C_{60} π-back-donation. The equatorial preference for the bulky ligands in triangular triosmium complexes (ca. 60°) may be reduced by the large bent angle of ∠Os(1)−Os(2)−C(3) (average 105.00°) in **2**−**5**. A bulky phosphine ligand, PPh_3 (cone angle of 145° vs 118° for PMe_3),[13] is bonded at the least hindered Os(1) site (∠Os(2)−Os(1)−N(1) = 70.4(2)°) among the three osmium centers in **5** and causes an orbital reorganization of the C_6 ring of C_{60} from the μ_3-η^1:η^2:η^1 mode (1,4-σ type) in **1** to the μ_3-η^1:η^1:η^2 mode (1,2-σ type) in **5**. The metal center coordinated by the donor PPh_3 ligand, apparently, prefers π-interaction with C_{60}, as observed in **4**. Three isomeric forms in **3** and **4** may be attributed to an analogous 3-fold rotation on the Os(3) center with a benzyl isocyanide ligand, as shown in **1**. Compounds **2** and **5** exist as a single isomer, which could be the predominant isomeric form to be detected by NMR spectroscopy.

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 (Next Chimica), benzyl isocyanide (98%, Aldrich), trimethylphosphine (97%, Aldrich), and triphenylphosphine (99%, Aldrich) were used without further purification. Anhydrous trimethylamine N-oxide (mp 225−230 °C) was

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(11) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 157.

(12) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

(13) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

obtained from $Me_3NO\cdot 2H_2O$ (98%, Aldrich) by sublimation (three times) at 90−100 °C under vacuum. $Os_3(CO)_8(CNR)(\mu_3\text{-}CNR)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (**1**) was prepared according to the literature methods.[4] 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. ^1H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 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 $Os_3(CO)_7(CNR)(\mu_3\text{-}CNR)(\mu\text{-}H)_2(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (2). An acetonitrile solution (1 mL) of anhydrous Me_3NO (1.1 equiv, 2.4 mg, 0.032 mmol) was added dropwise to a chlorobenzene solution (50 mL) of **1** (50.0 mg, 0.0286 mmol) at room temperature. The mixture was stirred for 30 min. After evaporation of the solvent, the residue was redissolved in chlorobenzene (50 mL). The resulting solution was heated under 1 atm of H_2 pressure at 60 °C for 90 min. Evaporation of the solvent and purification by preparative TLC (CS_2/CH_2Cl_2, 10:1) gave **2** (32.0 mg, 0.0186 mmol, 65%, $R_f = 0.7$) as a brownish black solid: IR (C_6H_{12}) ν(CO) 2098 (s), 2044 (vs), 2025(vs), 2014(m), 1992 (m), 1973 (m) and ν(NC) 2188 (m), 1615 (w, br) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.51−7.32 (m, 10H, *Ph*), 5.81 (d, 1H, $J_{HH} = 13$ Hz, CH_2), 5.47 (d, 1H, $J_{HH} = 16$ Hz, CH_2), 5.40 (d, 1H, $J_{HH} = 16$ Hz, CH_2), 5.10 (d, 1H, $J_{HH} = 13$ Hz, CH_2), −11.14 (d, 1H, $J_{HH} = 13$ Hz, μ-*H*), −12.78 (d, 1H, $J_{HH} = 13$ Hz, μ-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$ (1:1), 298 K) δ 178.2 (1*C*O), 178.2 (1*C*O), 172.8 (1*C*O), 172.4 (1*C*O), 171.0 (1*C*O), 170.8 (1*C*O), 170.7 (1*C*O), 169.9−140.5 (56C, C_{60} sp^2 carbon), 135.3−127.0 (2C, N*C* and 12C, *Ph*), 101.3 (1C, C_{60} sp^3 π-bonded carbon), 89.3 (1C, C_{60} sp^3 π-bonded carbon), 78.0 (1C, CH_2), 49.1 (1C, CH_2), 40.7 (1C, C_{60} sp^3 σ-bonded carbon), 40.5 (1C, C_{60} sp^3 σ-bonded carbon); MS (FAB^+) *m/z* 1728 (M^+). Anal. Calcd for $C_{83}H_{16}N_2O_7Os_3$: C, 57.83; H, 0.94; N, 1.63. Found: C, 57.47; H, 1.07; N, 1.56.

Preparation of $Os_3(CO)_7(CNR)_2(\mu_3\text{-}CNR)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (3). An acetonitrile solution (1 mL) of anhydrous Me_3NO (1.1 equiv, 2.8 mg, 0.037 mmol) was added dropwise to a chlorobenzene solution (50 mL) of **1** (60.0 mg, 0.0343 mmol) at room temperature. The mixture was stirred for 30 min. After evaporation of the solvent, the residue was redissolved in chlorobenzene (30 mL) followed by addition of benzyl isocyanide (3 equiv, 12.1 mg, 0.103 mmol). The resulting solution was heated at 100 °C for 1 h. Evaporation of the solvent and purification by preparative TLC (CS_2/CH_2Cl_2, 10:1) gave **3** (35.3 mg, 0.0192 mmol, 56%, $R_f = 0.3$) as a black solid: IR (C_6H_{12}) ν(CO) 2069 (s), 2025 (vs), 2008 (m), 1978 (m), 1963 (m) and ν(NC) 2181 (m), 1625 (w, br) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 298 K, major isomer) δ 7.51−7.01 (m, 10H, *Ph*), 5.61 (d, 1H, $J_{HH} = 13$ Hz, CH_2), 5.48 (d, 1H, $J_{HH} = 16$ Hz, CH_2), 5.42 (d, 1H, $J_{HH} = 16$ Hz, CH_2), 4.93 (d, 1H, $J_{HH} = 15$ Hz, CH_2), 4.88 (d, 1H, $J_{HH} = 15$ Hz, CH_2), 4.83 (d, 1H, $J_{HH} = 13$ Hz, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$ (1:1), 298 K, three isomers) δ 181.5−170.9 (3 × 7C, *C*O), 169.5−139.5 (3 × 56C, C_{60} sp^2 carbon), 136.6−126.5 (3 × 3C, N*C* and 3 × 18C, *Ph*), 92.5, 90.7, 83.8 (3 × 1C, C_{60} sp^3 π-bonded carbon), 77.1, 76.5, 74.6 (3 × 1C, CH_2), 68.3, 65.7, 58.8 (3 × 1C, C_{60} sp^3 π-bonded carbon), 49.4, 49.3, 48.9, 48.8, 48.6, 47.9 (3 × 2C, CH_2), 47.3, 42.9, 42.6, 41.5, 41.3, 39.1 (3 × 2C, C_{60} sp^3 σ-bonded carbon); MS (FAB^+) *m/z* 1843 (M^+). Anal. Calcd for $C_{92}H_{23}Cl_2N_3O_7Os_3$ ($\mathbf{3}\cdot CH_2Cl_2$): C, 57.44; H, 1.21; N, 2.18. Found: C, 57.05; H, 1.07; N, 2.25.

Preparation of $Os_3(CO)_7(CNR)(\mu_3\text{-}CNR)(PMe_3)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_{60})$ (4). An acetonitrile solution (1 mL) of anhydrous Me_3NO (1.1 equiv, 1.4 mg, 0.019 mmol) was added dropwise to a chlorobenzene solution (20 mL) of **1** (1 equiv, 30.0 mg, 0.0171 mmol) at room temperature. The reaction mixture was stirred for 30 min. After evaporation of the solvent, the residue was dissolved in chlorobenzene (20 mL) followed by addition of PMe_3 (5 equiv, 0.009 mL, 0.09 mmol). The resulting solution was heated at 50 °C for 1 h. Evaporation of the solvent and purification by TLC (CS_2/CH_2Cl_2, 10:1) produced compound **4** (15.0 mg, 0.0834 mmol, 49%, $R_f = 0.4$) as a black crystalline solid: IR (C_6H_{12}) ν(CO) 2066 (s), 2024 (m), 2003 (vs), 1983 (m), 1968 (s), 1955 (s), 1945 (m) and ν(NC) 2182 (m), 1613 (w) cm^{-1}; ^1H NMR (400 MHz, $CS_2/CDCl_3$, 298 K, major isomer) δ 7.60−7.30 (m, 10H, *Ph*), 5.67 (d, 1H, $J_{HH} = 12$ Hz, CH_2), 5.49 (d, 1H, $J_{HH} = 16$ Hz, CH_2), 5.44 (d, 1H, $J_{HH} = 16$ Hz, CH_2), 4.92 (d, 1H, $J_{HH} = 12$ Hz, CH_2), 1.60 (d, 9H, $J_{PH} = 9$ Hz, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$ (1:1), 298 K, major isomer) δ 184.5 (d, 1C, $J_{PC} = 8$ Hz, *C*O), 181.8 (s, 1C, *C*O), 181.7 (d, 1C, $J_{PC} = 7$ Hz, *C*O), 180.4 (d, 1C, $J_{PC} = 9$ Hz, *C*O), 179.2 (d, 1C, $J_{PC} = 8$ Hz, *C*O), 176.4 (s, 1C, *C*O), 171.0 (s, 1C, *C*O), 170.6−141.1 (56C, C_{60} sp^2 carbon), 135.7−127.5 (2C, N*C* and 12C, *Ph*), 79.5 (d, 1C, $J_{PC} = 11$ Hz, C_{60} sp^3 π-bonded carbon), 78.9 (s, 1C, CH_2), 78.0 (d, 1C, $J_{PC} = 12$ Hz, C_{60} sp^3 π-bonded carbon), 49.6 (s, 1C, CH_2), 40.0 (s, 1C, C_{60} sp^3 σ-bonded carbon), 39.4 (s, 1C, C_{60} sp^3 σ-bonded carbon), 18.5 (d, 3C, $J_{PC} = 38$ Hz, $P(CH_3)_3$); $^{31}P\{^1H\}$ NMR (162 MHz, $CS_2/CDCl_3$ (1:1), 298 K, major isomer): δ −55.0 (s); MS (FAB^+) *m/z* 1802 [M^+]. Anal. Calcd for $C_{86}H_{23}N_2O_7Os_3P$: C, 57.46; H, 1.29; N, 1.56. Found: C, 57.11; H, 1.64; N, 1.56.

Preparation of $Os_3(CO)_7(CNR)(\mu_3\text{-}CNR)(PPh_3)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_{60})$ (5). An acetonitrile solution (1 mL) of anhydrous Me_3NO (1.1 equiv, 2.8 mg, 0.037 mmol) was added dropwise to a chlorobenzene solution (50 mL) of **1** (60.0 mg, 0.0343 mmol). The reaction mixture was stirred at room temperature for 30 min. After removal of the solvent in vacuo, the residue was dissolved in chlorobenzene (30 mL) followed by addition of PPh_3 (3 equiv, 27.0 mg, 0.103 mmol). The resulting solution was heated at 70 °C for 4 h. Evaporation of the solvent and purification by preparative TLC (CS_2/CH_2Cl_2, 10:1) afforded compound **5** (47.4 mg, 0.0239 mmol, 70%, $R_f = 0.5$) as a black solid: IR (C_6H_{12}) ν(CO) 2059 (s), 2021 (vs), 1963 (m) and ν(NC) 2182 (m), 1606 (w) cm^{-1}; ^1H NMR (400 MHz, $CS_2/CDCl_3$, 298 K) δ 7.50−6.95 (m, 25H, *Ph*), 5.43 (d, 1H, $J_{HH} = 16$ Hz, CH_2), 5.41 (d, 1H, $J_{HH} = 14$ Hz, CH_2), 5.36 (d, 1H, $J_{HH} = 16$ Hz, CH_2), 5.31 (d, 1H, $J_{HH} = 14$ Hz, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$ (1:1), 298 K) δ 181.6 (s, 1C, *C*O), 181.2 (s, 1C, *C*O), 180.3 (d, 1C, $J_{PC} = 4$ Hz, *C*O), 175.9 (s, 1C, *C*O), 172.2 (s, 1C, *C*O), 169.6 (s, 1C, *C*O), 166.8 (d, 1C, $J_{PC} = 4$ Hz, *C*O), 157.9−140.7 (56C, C_{60} sp^2 carbon), 137.6−126.9 (2C, N*C* and 12C, *Ph*), 98.9 (1C, C_{60} sp^3 π-bonded carbon), 71.1 (d, 1C, $J_{PC} = 5$ Hz, CH_2), 54.0 (1C, C_{60} sp^3 π-bonded carbon), 49.2 (1C, CH_2), 47.8 (1C, C_{60} sp^3 σ-bonded carbon), 44.9 (1C, C_{60} sp^3 σ-bonded carbon); $^{31}P\{^1H\}$ NMR (162 MHz, $CS_2/CDCl_3$, 298 K) δ −9.7 (s); MS (FAB^+) *m/z* 1988 [M^+]. Anal. Calcd for $C_{107}H_{33}Cl_2N_2O_7Os_3P$ ($\mathbf{5}\cdot C_6H_4Cl_2$): C, 60.31; H, 1.56; N, 1.31. Found: C, 59.97; H, 1.75; N, 1.29.

Crystal Structure Determination. Crystals of **2**−**5** suitable for X-ray diffraction studies were obtained by an interlayer diffusion technique (hexane into a CS_2 solution of **2**; methanol into a $CS_2/C_6H_4Cl_2$ solution of **3**; methanol into a $CS_2/C_6H_4Cl_2$ solution of **4**; methanol into a $C_6H_4Cl_2$ solution of **5**). Each crystal with appropriate dimensions (0.66 × 0.42 × 0.08 mm^3 for **2**; 0.82 × 0.23 × 0.14 mm^3 for **3**; 0.94 × 0.18 × 0.04 mm^3 for **4**; 0.47 × 0.12 × 0.14 mm^3 for **5**) was mounted on a Simens SMART diffractometer/CCD area detector. A 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 34 151 (at 298 K), 7848 (at 298 K), 24 805 (at 233 K), and 21 964 (at 298 K) data were collected for **2**−**5**, 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 full-matrix least-squares methods based on F^2 (SHELX 97).[14] All non-hydrogen atoms were refined with anisotropic thermal coefficients. Details of relevant crystallographic data are summarized in Table 1.

The structures of **3** and **5** contained an 1,2-$C_6H_4Cl_2$ solvate molecule, and that of **4** involved a CS_2 solvate molecule in each asymmetric unit.

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Supporting Information Available: Figures giving the 2D $^1H-^1H$ COSY spectrum of **3** and ^{13}C NMR spectra of **4** and **5** and figures and tables giving full crystallographic and structural data for **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0205703

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