

Reversible Interconversion between $\mu, \eta^2: \eta^2$ - and $\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀ on a Carbido Pentaosmium Cluster Framework

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Decarbonylation of Os₅(CO)₁₄(PPh₃) by 2 equiv of Me₃NO/CH₃CN at room temperature followed by reaction with C₆₀ in refluxing chlorobenzene produces Os₅C(CO)₁₁(PPh₃)($\mu_3, \eta^2: \eta^2$ -C₆₀) (**1**) in 44% yield. Thermal treatment of **1** at 80 °C under 1 atm of carbon monoxide affords Os₅C(CO)₁₂(PPh₃)($\mu, \eta^2: \eta^2$ -C₆₀) (**2**) in good yield (72%). Upon thermolysis of **2** at 132 °C, **2** is cleanly reconverted to **1** (73%) by loss of a carbonyl ligand. Reaction of **1** with benzyl isocyanide at room temperature gives the addition product Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**3**) in 85% yield. Thermolysis of **3** at 100 °C forms the isomeric Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)($\mu, \eta^2: \eta^2$ -C₆₀) (**4**) in 64% yield. Treatment of **4** with 1 equiv of Me₃NO/CH₃CN at room temperature followed by heating at 132 °C in chlorobenzene gives Os₅C(CO)₁₀(CNCH₂C₆H₅)(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**5**) in 71% yield. Compound **5** can be alternatively prepared from the reaction of **1** with excess Ph₃P=NCH₂Ph at room temperature in 59% yield. Heating a chlorobenzene solution of **5** at 55 °C under 3 atm of carbon monoxide produces **4** as the only major product (16%). Treatment of Ru₅C(CO)₁₁(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**1'**) with benzyl isocyanide at room temperature forms Ru₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**3'**) in 90% yield. Reaction of **1'** with benzyl isocyanide at a slightly elevated temperature of 40 °C affords Ru₅C(CO)₁₀(CNCH₂C₆H₅)(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**5'**) in an almost quantitative yield of 96%. Compounds **1–5**, **3'**, and **5'**, isolated as crystalline solids, have been characterized by microanalytical and spectroscopic methods. Molecular structures of **1–4** and **5'** have been elucidated by X-ray crystallographic studies.

Introduction

Exohedral metallofullerenes have attracted much current attention concerning the effects of metal coordination on the chemical and physical properties of C₆₀.¹ Most approaches to forming metal complexes have been based on metal–C₆₀ π -complex chemistry, which has resulted in η^2 -, $\mu, \eta^2: \eta^2$ -, and $\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀ ligands in monometallic (for most metals),² bimetallic (Re₂, Ru₂, Ir₂),³ and metal cluster complexes (Re₃(μ -H)₃, Ru₃, Os₃, Ru₅C, Ru₆C, PtRu₅C),⁴ respectively. Metal clusters can potentially accommodate all the known C₆₀ bonding modes, but the interaction of C₆₀ with cluster frame-

works has been, thus far, dominated by the face-capping cyclohexatriene-like bonding mode: $\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀. The $\mu, \eta^2: \eta^2$ -C₆₀ bonding mode has never been observed on a cluster framework, although it has been postulated as an intermediate for the transformation of Os₃(CO)₁₁(η^2 -C₆₀) to Os₃(CO)₉($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) by loss of carbonyl ligands.^{4d}

We have been interested in the conversion of the existing C₆₀ bonding modes to new ones as well as in the interconversion among them by modifying the coordination sphere of metal centers in metal–C₆₀ cluster complexes. Our efforts have resulted in the novel transformation of a π -type $\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀ species to a new σ -type $\mu_3, \eta^1: \eta^2: \eta^1$ -C₆₀ ligand on a triosmium cluster framework upon insertion of a benzyl isocyanide ligand into an Os–Os bond.⁵ By employing similar approaches to an Os₅C cluster system, we have observed the elusive $\mu, \eta^2: \eta^2$ -C₆₀ bonding mode on an Os₅C cluster framework

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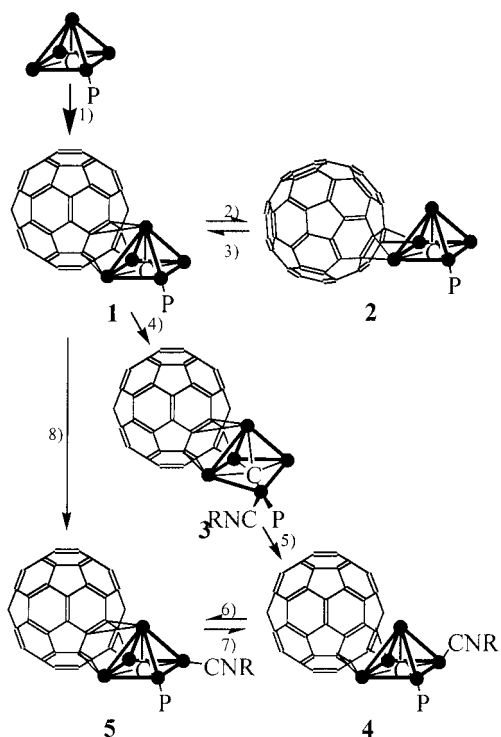
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Scheme 1^a

^a R = CH₂C₆H₅, P = PPh₃. Legend: (1) (a) 2Me₃NO, CH₃CN/CH₂Cl₂ (1:2), room temperature, 2 h, (b) C₆₀, ClC₆H₅, 132 °C, 16 h, 44%; (2) CO (1 atm), ClC₆H₅, 80 °C, 30 h, 72%; (3) ClC₆H₅, 132 °C, 6 h, 73%; (4) RNC, ClC₆H₅, room temperature, 15 h, 85%; (5) ClC₆H₅, 100 °C, 12 h, 64%; (6) (a) Me₃NO, CH₃CN/ClC₆H₅ (3:5), room temperature, 2 h, (b) ClC₆H₅, 132 °C, 1 h, 71%; (7) CO (3 atm), ClC₆H₅, 55 °C, 36 h, 16%; (8) excess Ph₃P=NCH₂Ph, ClC₆H₅, room temperature, 12 h, 59%.

and furthermore demonstrated that the two C₆₀ bonding modes $\mu, \eta^2: \eta^2$ and $\mu_3, \eta^2: \eta^2: \eta^2$ are reversibly interconvertible. In addition, we have explored the reactivity of Ru₅C–C₆₀ cluster complexes in order to examine the parallelism between the homologous Ru₅C and Os₅C cluster systems. Herein we present the full details of the synthesis and characterization of the new Ru₅C and Os₅C compounds with $\mu, \eta^2: \eta^2$ - or $\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀ ligands, as summarized in Scheme 1. A preliminary description of the results shown in this paper has appeared (Scheme 1).⁶

Results and Discussion

Synthesis and Characterization. Decarbonylation of Os₅C(CO)₁₄(PPh₃) with 2 equiv of Me₃NO/CH₃CN at room temperature for 2 h followed by reaction with C₆₀ in refluxing chlorobenzene for 16 h affords the face-capping C₆₀ compound Os₅C(CO)₁₁(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**1**) in 44% yield (see Scheme 1). Comparison of solution IR (ν_{CO}) spectra of **1** and the known ruthenium analogue Ru₅C(CO)₁₁(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**1'**) reveals that both compounds are isostructural.^{4b,c} Heating a chlorobenzene solution of **1** under 1 atm of carbon monoxide at 80 °C for 30 h results in an addition of a carbonyl ligand to **1** to produce the $\mu, \eta^2: \eta^2$ -C₆₀ complex Os₅C(CO)₁₂(PPh₃)($\mu, \eta^2: \eta^2$ -C₆₀) (**2**) in good yield (72%). Upon thermolysis of **2** at 132 °C for 6 h, **2** is cleanly reconverted

to **1** (73%) by loss of a carbonyl ligand, which demonstrates the first reversible interconversion between $\mu, \eta^2: \eta^2$ -C₆₀ and $\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀ ligands.

To understand detailed pathways of the reversible interconversion of the two C₆₀ bonding modes in **1** and **2** and the apparent accompanying C₆₀ rotation on the cluster framework (vide infra), the interaction of **1** with a benzyl isocyanide ligand has been investigated. This would provide an insight into the fate of the incoming carbonyl ligand in the transformation of **1** to **2**. Reaction of **1** with benzyl isocyanide at room temperature for 15 h gives the addition product Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**3**) with a ruptured Os–Os bond (vide infra) in 85% yield. Two doublets (AB pattern, $J = 16.4$ Hz) at δ 4.78 and 4.49 are observed due to the two diastereotopic methylene hydrogens of the benzyl isocyanide ligand in the ¹H NMR spectrum of **3**. Thermolysis of this kinetic product **3** in chlorobenzene at 100 °C for 12 h affords the isomeric thermodynamic product Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)($\mu, \eta^2: \eta^2$ -C₆₀) (**4**) in 64% yield. Complex **4** shows two singlets at δ 5.54 and 5.47 for the two diastereotopic hydrogens of the isocyanide moiety in the ¹H NMR spectrum. Decarbonylation of **4** with 1 equiv of Me₃NO/CH₃CN at room temperature for 2 h followed by heating in chlorobenzene at 132 °C for 1 h forms Os₅C(CO)₁₀(CNCH₂C₆H₅)(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**5**) in 71% yield. Compound **5** can be alternatively prepared from the reaction of **1** with excess Ph₃P=NCH₂Ph⁷ at room temperature in 59% yield. Triphenylphosphinoalkylimine reagents are known to react with metal carbonyl complexes to yield metal isocyanide substituted compounds.⁸ Heating a chlorobenzene solution of **5** at 55 °C under 3 atm of carbon monoxide for 36 h produces the $\mu, \eta^2: \eta^2$ -C₆₀ complex **4** as the only isolable product (16%) with extensive decomposition, which is another demonstration of the reversible interconversion between $\mu, \eta^2: \eta^2$ -C₆₀ and $\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀ by addition and loss of a carbonyl ligand. Compounds **1**–**5** have been formulated on the basis of the molecular ion peaks in negative- or positive-ion FAB mass spectra and elemental analysis data.

To find the parallelism between the homologous Ru₅C and Os₅C cluster systems, the reactivity of Ru₅C(CO)₁₁(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**1'**) has been examined. Treatment of **1'** with benzyl isocyanide in chlorobenzene at room temperature for 4 h affords Ru₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2$ -C₆₀) (**3'**) in 90% yield, which is formulated by the presence of a strong molecular ion peak in the positive-ion FAB mass spectrum. Compound **3'** exhibits IR patterns similar to those of **3**, implying the same structural features for both compounds. Two doublets at δ 4.11 and 3.85 (AB pattern, $J = 16.3$ Hz) along with a set of minor signals at δ 4.10 and 3.83 with a similar pattern ($J = 16.4$ Hz) were observed for the two diastereotopic methylene hydrogens of the benzyl isocyanide ligand in the ¹H NMR spectrum of **3'**, indicating the presence of two isomers in solution in a 3:2 ratio at room temperature. The geminal coupling constants of methylene hydrogens in **3'** are comparable to that (16.4 Hz) observed for compound **3**. The two isomers of **3'** might have resulted from the switching of

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Table 1. Crystallographic Data for Os₅C(CO)₁₁(PPh₃)(μ₃,η²:η²:η²-C₆₀) (1), Os₅C(CO)₁₂(PPh₃)(μ,η²:η²-C₆₀) (2), Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)(μ₃,η²:η²:η²-C₆₀) (3), Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)(μ,η²:η²-C₆₀) (4), and Ru₅C(CO)₁₀(CNCH₂C₆H₅)(PPh₃)(μ₃,η²:η²:η²-C₆₀) (5')

	1·CS ₂ ·0.5H ₂ O	2	3	4·0.5CS ₂	5'·2CS ₂
formula	C ₉₁ H ₁₆ O _{11.5} PS ₂ Os ₅	C ₉₁ H ₁₅ O ₁₂ POs ₅	C ₉₈ H ₂₂ NO ₁₁ POs ₅	C _{98.5} H ₂₂ NO ₁₁ PSOs ₅	C ₉₉ H ₂₂ NO ₁₀ PS ₄ Ru ₅
fw	2339.1	2282.0	2371.1	2409.2	2049.7
cryst syst	triclinic	monoclinic	orthorhombic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>Fdd2</i>	<i>P</i> $\bar{1}$	<i>P2₁/c</i>
<i>a</i> (Å)	10.0093(2)	41.821(8)	48.766(10)	9.970(3)	18.875(3)
<i>b</i> (Å)	13.5022(2)	19.375(4)	55.356(11)	17.383(6)	13.779(19)
<i>c</i> (Å)	26.9630(3)	18.550(4)	10.054(2)	21.365(10)	28.923(4)
α (deg)	77.415(1)	90	90	101.62(6)	90
β (deg)	80.705(1)	116.04(3)	90	99.09(3)	104.184(2)
γ (deg)	70.586(1)	90	90	98.49	90
<i>V</i> (Å ³)	3338.5(1)	13504(5)	27140(9)	3519(2)	7292.7(17)
<i>Z</i>	2	8	16	2	4
ρ _{calcd} (g cm ⁻³)	2.326	2.245	2.321	2.274	1.867
μ (mm ⁻¹)	9.639	9.470	9.428	9.119	1.220
θ _{min,max}	0.78, 22.00	1.08, 23.00	1.11, 23.36	0.99, 22.00	1.45, 25.55
<i>R</i> _{int}	0.0844	0.1388	0.1185	0.1373	0.0433
<i>R</i> 1 ^a	0.1280	0.0606	0.0738	0.1696	0.0579
w <i>R</i> 2 ^b	0.3107	0.1535	0.1760	0.4094	0.2109

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

the coordination sites for PPh₃ and benzyl isocyanide ligands on the bridging ruthenium atom (vide infra). A chlorobenzene solution of **3'** has been warmed to prepare a ruthenium analogue of **4**, Ru₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)(μ,η²:η²-C₆₀) (**4'**). However, selective formation of a red-brown compound (**5'**) at 40 °C has been observed, which exhibits IR (ν_{CO}) spectrum patterns very similar to those of **5**. A singlet (δ 4.26) for the two methylene hydrogens of **5'** has been observed in the ¹H NMR spectrum, as in compound **5** (δ 5.45). Coupled with these observations, compound **5'** is formulated as Ru₅C(CO)₁₀(CNCH₂C₆H₅)(PPh₃)(μ₃,η²:η²:η²-C₆₀) by the presence of a strong molecular ion peak in the positive-ion mass spectrum. Formation of a ruthenium analogue of **4'** has not been detected. In contrast to the Os₅C cluster compounds, the Ru–C₂(C₆₀) interaction is apparently much stronger than the Ru–C(CO) interaction in this Ru₅C cluster system, which thus prefers carbonyl loss to scission of the Ru–C₂(C₆₀) bond. Compound **5'** can also be obtained in an almost quantitative yield of 96% from reaction of **1'** with 1 equiv of benzyl isocyanide in chlorobenzene at 40 °C. Attempts to prepare ruthenium analogues of the μ,η²:η²-C₆₀ complex (**2'** and **4'**) from reaction of **1'** or **5'** with carbon monoxide under various conditions resulted only in the decomposition of the starting materials, which also supports the robustness of the Ru₅C–C₆₀ interaction.

X-ray Crystallographic Studies. Selected crystallographic details for **1–4** and **5'** are shown in Table 1. The metal–metal bond lengths and selected bond distances for the C₆₀ ligands of **1–4** and **5'** are listed in Tables 2 and 3, respectively.

The molecular structure of **1** is isomorphous with that of the ruthenium analogue **1'**, as illustrated in Figure 1.^{4b,c} The square-pyramidal metal framework of the starting material Os₅C(CO)₁₄(PPh₃) is retained in **1**. The μ₃,η²:η²:η²-C₆₀ ligand is coordinated on the triangular Os(1,2,3) face, and PPh₃ is bonded to the axial position of the basal Os(5) atom. Each of the three osmium atoms coordinated by the C₆₀ ligand contains two terminal carbonyl ligands, while three two-electron-donor ligands are observed on each of the remaining osmium atoms. The alternations in the metal–C(C₆₀) distances or in the

Table 2. Internuclear Distances for the Cluster Frameworks in Os₅C(CO)₁₁(PPh₃)(μ₃,η²:η²:η²-C₆₀) (1), Os₅C(CO)₁₂(PPh₃)(μ,η²:η²-C₆₀) (2), Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)(μ₃,η²:η²:η²-C₆₀) (3), Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)(μ,η²:η²-C₆₀) (4), and Ru₅C(CO)₁₀(CNCH₂C₆H₅)(PPh₃)(μ₃,η²:η²:η²-C₆₀) (5')^a

	1	2	3	4	5'
M1–M2	2.863(3)	2.861(1)	2.884(2)	2.862(4)	2.826(1)
M1–M3	2.860(3)	2.862(1)	2.793(2)	2.880(4)	2.826(1)
M1–M4	2.844(3)	2.810(1)	2.857(2)	2.858(4)	2.856(1)
M1–M5	2.906(3)	2.854(2)		2.843(3)	2.856(1)
M2–M3	2.875(3)	2.901(1)	2.881(1)	2.889(3)	2.858(1)
M2–M5	2.902(3)	2.863(1)	2.959(2)	2.893(4)	2.864(1)
M3–M4	2.853(3)	2.818(1)	2.865(2)	2.843(4)	2.820(1)
M4–M5	2.906(3)	2.946(1)	2.995(2)	2.914(3)	2.873(1)
M1–C100	2.14(5)	2.16(2)	2.15(3)	2.29(6)	2.12(1)
M2–C100	1.96(5)	2.05(2)	1.93(3)	1.74(7)	2.02(1)
M3–C100	2.01(5)	2.06(2)	2.11(3)	2.06(6)	2.04(1)
M4–C100	2.14(5)	2.07(1)	2.00(3)	2.36(7)	2.00(1)
M3–C100	2.07(5)	2.01(2)	2.18(3)	2.12(6)	2.03(1)

^a M = Os for **1–4**; M = Ru for **5'**.

Table 3. Selected Internuclear Distances for the C₆₀ Ligand in Os₅C(CO)₁₁(PPh₃)(μ₃,η²:η²:η²-C₆₀) (1), Os₅C(CO)₁₂(PPh₃)(μ,η²:η²-C₆₀) (2), Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)(μ₃,η²:η²:η²-C₆₀) (3), Os₅C(CO)₁₁(CNCH₂C₆H₅)(PPh₃)(μ,η²:η²-C₆₀) (4), and Ru₅C(CO)₁₀(CNCH₂C₆H₅)(PPh₃)(μ₃,η²:η²:η²-C₆₀) (5')^a

	1	2	3	4	5'
M–C1	2.28(5)	2.27(2)	2.27(2)	2.27(8)	2.28(1)
M–C2	2.30(5)	2.19(1)	2.19(3)	2.16(6)	2.26(1)
M–C3	2.26(5)	2.18(2)	2.26(3)	2.33(8)	2.23(1)
M–C4	2.24(5)	2.23(2)	2.30(3)	2.17(4)	2.21(1)
M–C5	2.29(5)		2.17(2)		2.22(1)
M–C6	2.18(4)		2.24(2)		2.22(1)
C1–C2	1.46(7)	1.41(2)	1.51(4)	1.40(9)	1.43(1)
C2–C3	1.50(7)	1.53(2)	1.41(4)	1.45(4)	1.45(1)
C3–C4	1.48(7)	1.39(2)	1.46(4)	1.45(9)	1.45(1)
C4–C5	1.49(7)	1.45(2)	1.52(4)	1.55(3)	1.47(1)
C5–C6	1.54(7)	1.41(2)	1.40(4)	1.29(9)	1.41(1)
C6–C1	1.39(6)	1.49(2)	1.45(4)	1.54(10)	1.48(1)

^a M = Os for **1–4**; M = Ru for **5'**.

C–C distances within the C₆ ring (C₆₀) are not observed in **1**, unlike the case for the isostructural **1'**.^{4b,c}

The structure of **2** (Figure 2) shows that a carbonyl ligand is added to the Os(1) atom, and the Os(1)–C₂–(C₆₀) π-interaction is removed as compared to that of **1**.

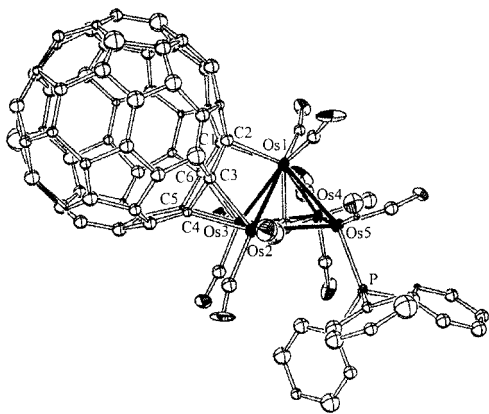


Figure 1. Molecular structure of $\text{Os}_5\text{C}(\text{CO})_{11}(\text{PPh}_3)(\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60})$ (**1**) (30% thermal ellipsoids).

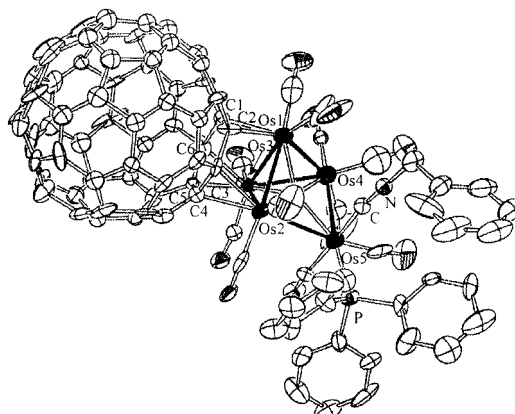


Figure 3. Molecular structure of $\text{Os}_5\text{C}(\text{CO})_{12}(\text{PPh}_3)(\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60})$ (**3**) (30% thermal ellipsoids).

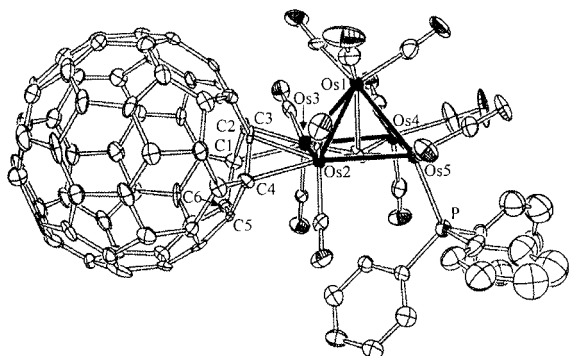


Figure 2. Molecular structure of $\text{Os}_5\text{C}(\text{CO})_{12}(\text{PPh}_3)(\mu, \eta^2: \eta^2\text{-C}_{60})$ (**2**) (30% thermal ellipsoids).

Two adjacent double bonds, C(1,2) and C(3,4), in a C₆ ring of the C₆₀ ligand bridge the two basal Os(2) and Os(3) atoms in a $\mu, \eta^2: \eta^2$ mode. A similar $\mu, \eta^2: \eta^2\text{-C}_{60}$ bonding mode with two metal centers has been previously observed only for dinuclear metal compounds.³ Interestingly, the third uncoordinated double bond C(5,6) in the C₆ ring is disposed away from the Os(1,2,3) triangle of the Os₅C square-pyramidal framework; the C₆₀ ligand has apparently rotated 180° upon the center of the basal Os(2)–Os(3) bond during the conversion **1** → **2** as compared to the C₆₀ disposition in **1**. The inner carbon atoms C(2,3) of the butadiene-like moiety exhibit a stronger interaction with osmium atoms (Os(3)–C(2) = 2.19(1) Å and Os(2)–C(3) = 2.18(2) Å) than do the outer carbon atoms C(1,4) (Os(3)–C(1) = 2.27(2) Å and Os(2)–C(4) = 2.23(2) Å).

The molecular structure of the kinetic isomer **3** is shown in Figure 3. The $\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60}$ bonding mode has been unaffected, but one of the Os_{apical}–Os_{basal} bonds in the square-pyramidal Os₅C framework of **1** has been cleaved upon addition of the two-electron-donor benzyl isocyanide ligand to the Os(5) atom. The four Os(1,2,3,4) atoms form a “butterfly” framework, and the two “wing-tip” Os(2,4) atoms are bridged by the Os(5) atom, which is coordinated with a phosphine, an isocyanide, and two carbonyl ligands. The coordination sphere of the carbido atom can be regarded as a distorted trigonal bipyramid with equatorial Os(2,3,4) and axial Os(1,2) atoms. The two Os–Os bond distances involving the bridging Os(5) atom (Os(2)–Os(5) = 2.959(2) Å and Os(4)–Os(5) = 2.995(2) Å) are slightly longer than the other five Os–Os bond distances (average 2.856(2) Å) of the butterfly framework, with the hinge Os(1)–Os(3) distance (2.793-

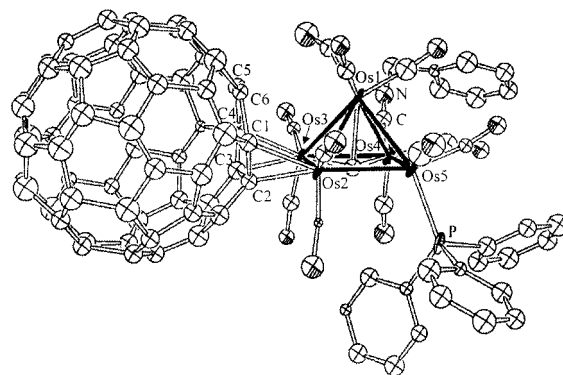


Figure 4. Molecular structure of $\text{Os}_5\text{C}(\text{CO})_{11}(\text{CNCH}_2\text{C}_6\text{H}_5)(\text{PPh}_3)(\mu, \eta^2: \eta^2\text{-C}_{60})$ (**4**) (30% thermal ellipsoids).

(2) Å) being the shortest. A structural feature similar to that of **3** has been previously observed in several M₅C clusters such as Os₅C(CO)₁₃H(OP(OMe)₂)(P(OMe)₃),⁹ [Os₅C(CO)₁₅I][−],¹⁰ and Ru₅C(CO)₁₅(NCMe).¹¹ It has been proposed that the site of the attack by the incoming ligand is a basal metal atom in the reaction of Ru₅C(CO)₁₅ and MeCN.¹¹ Similarly, it can be envisaged that the Os(1)–Os(5) bond in **1** is broken by the attack of the benzyl isocyanide ligand on the most basic Os(5) center with a donor phosphine ligand to form **3**. This structure does not show bond alternations either in the metal–C(C₆₀) distances or in the C–C distances within the C₆ ring (C₆₀).

The thermodynamic isomer **4** (Figure 4) adopts a square-pyramidal geometry for the metal framework. The $\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60}$ ligand in **3** is converted to a $\mu, \eta^2: \eta^2\text{-C}_{60}$ ligand; the two adjacent double bonds (C(1,2) and C(3,4)) in a C₆ ring of the C₆₀ ligand bridge the two basal Os(2) and Os(3) atoms, respectively. Formation of an Os–Os bond between two nonbonding osmium atoms, Os(1) and Os(5), results in the removal of one Os–C₂(C₆₀) π -bonding interaction in **3**. The benzyl isocyanide ligand occupies an equatorial position (cis to the C₆₀ ligand) on the basal Os(4) atom. In contrast to **2**, the uncoordinated double bond C(5)–C(6) is oriented

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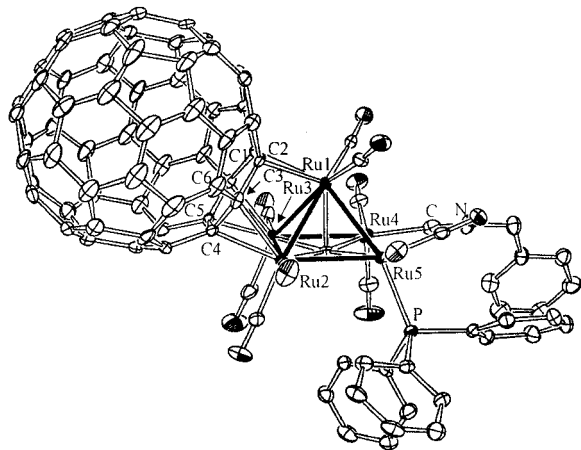


Figure 5. Molecular structure of $\text{Ru}_5\text{C}(\text{CO})_{10}(\text{CNCH}_2\text{C}_6\text{H}_5)(\text{PPh}_3)(\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60})$ (**5'**) (30% thermal ellipsoids).

toward the Os(1,2,3) triangle. Detailed speculation concerning the mechanism of formation of **4** from **3** is unwarranted, but the likely pathway would involve reformation of the Os(1)–Os(5) bond, consecutive migrations of the benzyl isocyanide ligand from Os(5) to Os(4) and a carbonyl ligand from Os(4) to Os(1), and subsequent rupture of the Os(1)–C₂(C₆₀) interaction. A detailed discussion of the bond lengths for **4** is precluded due to the poor quality of the solved crystal structure.

The molecular structure of **5'** (Figure 5), which is isomorphous with **5**, reveals that a $\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60}$ ligand is coordinated on the Ru(1,2,3) triangle and the benzyl isocyanide ligand occupies an equatorial position (trans to the C₆₀ ligand) on the basal Ru(4) atom. The overall structural features of **5'** are very similar to those of the structurally related **1** and **1'**. The structure of **5'** suggests that, for the conversion of **4** to **5**, loss of a carbonyl ligand from the apical osmium atom is compensated by the formation of the Os(1)–C₂(C₆₀) π -bond and the isocyanide ligand swings to the other equatorial site trans to the C₆₀ ligand on the same Os(4) atom. Unlike the $\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60}$ Os₅C compounds **1** and **4**, the alternations in the bond lengths in Ru–C(C₆₀) (average 2.23 (short) and 2.24 Å (long)) and in C–C of the C₆ ring (C₆₀) (average 1.43 (short) and 1.47 Å (long)) are clearly seen in this Ru₅C compound **5'**.

As shown above, two different orientations of the $\mu, \eta^2: \eta^2\text{-C}_{60}$ ligand have been observed in **2** and **4**, which are related by a 180° rotation with respect to the center of the two C₆₀-coordinated metal atoms. Two plausible mechanisms can be proposed to explain this apparent C₆₀ rotation. One obvious possibility would be a 180° rotation of the C₆₀ ligand, via the pathways $\mu, \eta^2: \eta^2\text{-C}_{60} \rightarrow \eta^4\text{-C}_{60} \rightarrow \mu, \eta^2: \eta^2\text{-C}_{60}$, as shown in Scheme 2a. Even though the $\eta^4\text{-C}_{60}$ bonding mode has yet to be discovered, the η^4 -cyclohexadiene moiety on a metal center has been well-documented for Os₃ cluster compounds.¹² The other mechanism, hinted at by the isocyanide ligand addition reaction of **1**, would be a metal framework rearrangement, which involves a series of Os–Os bond scission and formation to invert the square-pyramidal

Os₅C cluster framework. In this “octahedral site exchange” mechanism (see Scheme 2b), a carbonyl addition induces an Os–Os bond scission to give a bridged “butterfly” intermediate analogous to **3**, where the bridging osmium center moves into an empty vertex of an imaginary octahedron to form a half-inverted square-pyramidal geometry. Repeating similar processes may produce the inverted product. A similar cluster framework rearrangement was observed in a related cluster compound, $\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$.¹³ The reason for the two different orientations of the $\mu, \eta^2: \eta^2\text{-C}_{60}$ ligand in **2** and **4** is not clear at the moment, but it seems to be of electronic origin since the steric environments around the C₆₀ ligand appear to be essentially identical in both **2** and **4**.

Conclusion

We have shown the first examples of the $\mu, \eta^2: \eta^2\text{-C}_{60}$ bonding mode on an Os₅C cluster framework (**2** and **4**) and demonstrated reversible interconversion of the $\mu, \eta^2: \eta^2\text{-C}_{60}$ and $\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60}$ ligands (**1** \rightleftharpoons **2** and **4** \rightleftharpoons **5**) by carbonyl addition and elimination reactions. The two different dispositions of the $\mu, \eta^2: \eta^2\text{-C}_{60}$ ligand in **2** and **4** have been proposed to occur by either C₆₀ rotation or metal framework rearrangement. The conversion from $\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60}$ to $\mu, \eta^2: \eta^2\text{-C}_{60}$ has not been observed for the Ru₅C cluster, implying the relative stability of the Ru–C₂(C₆₀) π -interaction as compared to Ru–C(CO) bonding.

Experimental Section

All reactions were carried out under a nitrogen atmosphere with use of standard Schlenk techniques.¹⁴ Solvents were dried over the appropriate drying agents and distilled immediately before use. C₆₀ (99.5%, Southern Chemical Group, LLC) and OsO₄ (Strem Chemical Co.) were used without further purification. Anhydrous trimethylamine oxide (mp 225–230 °C) was obtained from Me₃NO·2H₂O (98%, Aldrich Chemical Ltd.) by sublimation (three times) at 90–100 °C under vacuum. Os₅C(CO)₁₅,¹⁵ Os₅C(CO)₁₄(PPh₃),¹⁶ Ru₅C(CO)₁₅,¹¹ and Ph₃P=NCH₂C₆H₅⁷ were prepared by the literature methods. Preparative thin-layer chromatography (TLC) plates were prepared with silica gel GF₂₅₄ (Type 60, E. Merck).

Infrared spectra were obtained on a Bruker EQUINOX-55 FT-IR spectrophotometer. ¹H (300 MHz) and ³¹P (122 MHz) NMR spectra were recorded on a Bruker AM-300 spectrometer. ¹H (400 MHz) NMR spectra were recorded on a Bruker Avance-400 spectrometer. Negative- or positive-ion FAB mass spectra (FAB[−] or FAB⁺) were obtained by the staff of the Korea Basic Science Center. All *m/z* values are referenced to ¹⁹²Os and ¹⁰²Ru. Elemental analyses were provided by the staff of the Energy & Environment Research Center at KAIST.

Preparation of Os₅C(CO)₁₁(PPh₃)($\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60}$) (1**).** A dichloromethane/acetonitrile (60/10 mL) solution of Os₅C(CO)₁₄(PPh₃) (200 mg, 0.124 mmol) was prepared in a 250 mL Schlenk flask. To this solution was added an acetonitrile solution (2 mL) of Me₃NO (19.5 mg, 0.260 mmol) dropwise at room temperature over a period of 30 min, and the solution

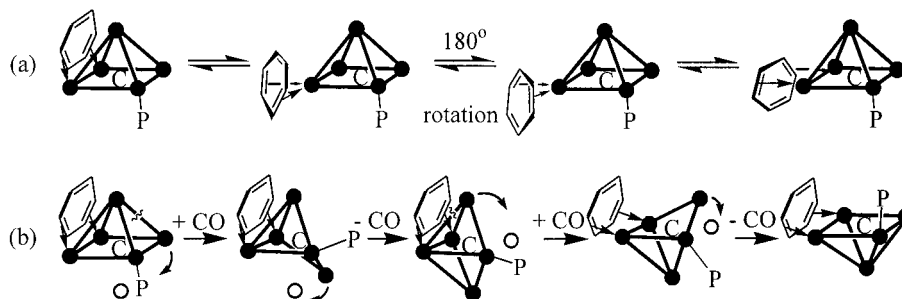
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Scheme 2. (a) “ C_{60} Rotation” Mechanism and (b) “Octahedral Site Exchange” Mechanism

^a The open circle denotes an empty vertex of the imaginary octahedral cluster framework. Only the cyclohexatriene-like C_6 portion of C_{60} is shown for clarity.

was stirred for an additional 2 h. The solvent was removed under vacuum. The yellow-orange residue dissolved in chlorobenzene (15 mL) was added dropwise to a refluxing chlorobenzene (100 mL) solution of C_{60} (134 mg, 0.185 mmol) in a 250 mL three-necked flask over a period of 30 min, and the resulting reaction mixture was heated to reflux for 16 h. Solvent removal under vacuum and purification by preparative TLC (CS_2) produced **1** ($R_f = 0.5$, 123 mg, 0.0547 mmol, 44%) as a red-brown solid: IR (CS_2) ν_{CO} 2073 (s), 2032 (s), 2021 (s), 2011 (s) cm^{-1} ; 1H NMR (300 MHz, CS_2 /external CD_2Cl_2 , 25 $^\circ C$) δ 7.83–7.73 (m, 15H); ^{31}P NMR (122 MHz, $Cl_2C_6H_4/CDCl_3$ (1/1), 25 $^\circ C$): δ 6.09; MS (FAB[−]) m/z 2261.8 [M[−]]. Anal. Calcd for $C_{90}H_{15}O_{11}PO_5$: C, 47.96; H, 0.67. Found: C, 48.13; H, 0.78.

Conversion of 1 to $Os_5C(CO)_{12}(PPh_3)(\mu_3, \eta^2, \eta^2-C_{60})$ (2). A chlorobenzene (20 mL) solution of **1** (10.0 mg, 0.00442 mmol) was prepared in a 300 mL pressure bottle. The solution was degassed with three freeze–thaw cycles, and the pressure bottle was charged with 1 atm of CO. The reaction mixture was heated to 80 $^\circ C$ for 30 h. Evaporation of the solvent and purification by preparative TLC (CS_2) afforded compound **2** ($R_f = 0.45$, 7.3 mg, 0.0032 mmol, 72%) as a green solid: IR (CS_2) ν_{CO} 2072 (s), 2040 (m), 2028 (m, sh), 2022 (s), 2007 (m), 1996 (w) cm^{-1} ; 1H NMR (300 MHz, CS_2 /external CD_2Cl_2 , 25 $^\circ C$) δ 7.79–7.59 (m, 15H); ^{31}P NMR (122 MHz, CS_2 /external CD_2Cl_2 , 25 $^\circ C$) δ −3.87; MS (FAB[−]) m/z 2289.8 [M[−]]. Anal. Calcd for $C_{91}H_{15}O_{12}PO_5$: C, 47.87; H, 0.66. Found: C, 47.41; H, 0.79.

Thermolysis of 2. A chlorobenzene (20 mL) solution of **2** (10.0 mg, 0.004 37 mmol) was prepared in a 50 mL three-necked flask equipped with a reflux condenser. The solution was heated to reflux for 6 h, and the solvent was removed under vacuum. Purification of the residue by preparative TLC afforded **1** (7.2 mg, 0.0032 mmol, 73%).

Preparation of the Kinetic Isomer $Os_5C(CO)_{11}(CNCH_2C_6H_5)(PPh_3)(\mu_3, \eta^2, \eta^2, \eta^2-C_{60})$ (3). A chlorobenzene (10 mL) solution of **1** (10.0 mg, 0.004 37 mmol) was prepared in a 50 mL Schlenk flask. To this solution was added a chlorobenzene (0.26 mL) solution of benzyl isocyanide (5.2 mg, 0.044 mmol), and the resulting solution was stirred at room temperature for 15 h. Solvent removal under vacuum and separation by preparative TLC (CS_2) gave **3** ($R_f = 0.1$, 8.8 mg, 0.0037 mmol, 85%) as a dark red-brown solid: IR (CH_2Cl_2) ν_{CO} 2064 (s), 2046 (m), 1997 (s), 1990 (s), 1955 (w), 1933 (w) cm^{-1} ; 1H NMR (300 MHz, CD_2Cl_2 , 25 $^\circ C$) δ 7.63–6.98 (m, 20H), 4.78 (d, $J = 16.4$ Hz, 1H), 4.49 (d, $J = 16.4$ Hz, 1H); ^{31}P NMR (122 MHz, $Cl_2C_6H_4/CDCl_3$ (1/1), 25 $^\circ C$) δ −8.42; MS (FAB⁺) m/z 2378.9 [M⁺]. Anal. Calcd for $C_{98}H_{22}NO_{11}PO_5$: C, 49.64; H, 0.94; N, 0.59. Found: C, 50.49; H, 0.83; N, 0.55.

Preparation of the Thermodynamic Isomer $Os_5C(CO)_{11}(CNCH_2C_6H_5)(PPh_3)(\mu_3, \eta^2, \eta^2-C_{60})$ (4). A chlorobenzene (20 mL) solution of **3** (10.0 mg, 0.00420 mmol) was prepared in a three-necked flask equipped with a reflux condenser. The dark red-brown solution was heated to 100 $^\circ C$ for 12 h to give a brownish green solution. Solvent removal and purification by preparative TLC (CS_2) produced **4** ($R_f = 0.15$, 6.4 mg, 0.0027

mmol, 64%) as a brownish green solid: IR (CH_2Cl_2) ν_{CO} 2046 (m), 2024 (vs), 2010 (s), 1991 (w, br) cm^{-1} ; 1H NMR (300 MHz, CS_2 /external CD_2Cl_2 , 25 $^\circ C$) δ 7.68–7.60 (m, 20H), 5.54 (s, 1H), 5.47 (s, 1H); ^{31}P NMR (122 MHz, CS_2 /external CD_2Cl_2 , 25 $^\circ C$) δ −2.87; MS (FAB⁺) m/z 2378.9 [M⁺]. Anal. Calcd for $C_{98}H_{22}NO_{11}PO_5$: C, 49.64; H, 0.94; N, 0.59. Found: C, 49.21; H, 0.88; N, 0.58.

Preparation of $Os_5C(CO)_{10}(CNCH_2C_6H_5)(PPh_3)(\mu_3, \eta^2, \eta^2-C_{60})$ (5). **Method A.** A chlorobenzene/acetonitrile (10/3 mL) solution of **4** (30.0 mg, 0.0126 mmol) was prepared in a three-necked flask equipped with a reflux condenser. To the solution was added an acetonitrile (3 mL) solution of Me_3NO (1.1 mg, 0.015 mmol) dropwise at room temperature, and the resulting solution was stirred for 2 h. After solvent removal in vacuo, the dark residue was redissolved in 10 mL of chlorobenzene, and the resulting reaction mixture was heated to reflux for 1 h. Solvent removal under reduced pressure and purification by preparative TLC (CS_2) produced **5** ($R_f = 0.2$, 21.0 mg, 0.008 93 mmol, 71%) as a red-brown solid.

Method B. To a chlorobenzene solution (60 mL) of **1** (200 mg, 0.0888 mmol) was added excess $Ph_3P=NCH_2Ph$ (180 mg, 0.533 mmol) at room temperature, and the resulting solution was stirred for 12 h. Solvent removal under vacuum and purification by preparative TLC (CS_2) gave **5** (123 mg, 0.0523 mmol, 59%): IR (CH_2Cl_2) ν_{CO} 2067 (w), 2039 (m), 2020 (s, sh), 2010 (vs) cm^{-1} ; 1H NMR (300 MHz, CS_2 /external CD_2Cl_2 , 25 $^\circ C$) δ 7.80–7.58 (m, 20H), 5.45 (s, 2H); ^{31}P NMR (122 MHz, ClC_6H_5 /external CD_2Cl_2 , 25 $^\circ C$) δ 5.32; MS (FAB⁺) m/z 2350.9 [M⁺]. Anal. Calcd for $C_{97}H_{22}NO_{10}PO_5$: C, 49.72; H, 0.95; N, 0.60. Found: C, 50.16; H, 1.21; N, 0.63.

Conversion of 5 to 4. A chlorobenzene (10 mL) solution of **5** (10.0 mg, 0.00425 mmol) was prepared in a 300 mL pressure bottle. The solution was degassed with three freeze–thaw cycles, and the pressure bottle was charged with 3 atm of CO. The reaction mixture was heated to 55 $^\circ C$ for 36 h. Solvent removal under vacuum and purification by preparative TLC (CS_2) gave **4** (1.6 mg, 0.00067 mmol, 16%) as the only major product along with severe decomposition.

Preparation of $Ru_5C(CO)_{11}(CNCH_2C_6H_5)(PPh_3)(\mu_3, \eta^2, \eta^2-C_{60})$ (3'). To a chlorobenzene solution (30 mL) of $Ru_5C(CO)_{11}(PPh_3)(\mu_3, \eta^2, \eta^2, \eta^2-C_{60})$ (**1'**; 20.0 mg, 0.0111 mmol) was added a chlorobenzene solution (1 mL) of benzyl isocyanide (1.3 mg, 0.011 mmol) at room temperature, and the resulting reaction mixture was stirred for 4 h. Solvent removal under vacuum and purification by preparative TLC (CS_2) gave **3'** ($R_f = 0.1$, 18.8 mg, 0.009 75 mmol, 90%) as a red-brown solid: IR (CH_2Cl_2) ν_{CO} 2061 (s), 2042 (m), 1997 (s, br) cm^{-1} ; 1H NMR (400 MHz, $C_6D_4Cl_2$, 25 $^\circ C$) δ 8.00–7.58 (m, 20H), 4.11 (d, $J = 16.3$ Hz, $-CHH-$, major), 4.10 (d, $J = 16.4$ Hz, $-CHH-$, minor), 3.85 (d, $J = 16.3$ Hz, $-CHH-$, major), 3.83 (d, $J = 16.4$ Hz, $-CHH-$, minor), major/minor = 3/2; ^{31}P NMR (122 MHz, ClC_6H_5 /external CD_2Cl_2 , 25 $^\circ C$) δ 28.8 (s, minor), 28.6 (s, major); MS (FAB⁺) m/z 1928.6 [M⁺]. Anal. Calcd for $C_{98}H_{22}NO_{11}PRu_5$: C, 61.13; H, 1.15; N, 0.73. Found: C, 61.45; H, 1.14; N, 0.73.

Preparation of $\text{Ru}_5\text{C}(\text{CO})_{10}(\text{CNCH}_2\text{C}_6\text{H}_5)(\text{PPh}_3)(\mu_3, \eta^2: \eta^2: \eta^2\text{-C}_{60})$ (5'**).** To a chlorobenzene (30 mL) solution of **1'** (20.0 mg, 0.0107 mmol) was added a chlorobenzene solution (1 mL) of benzyl isocyanide (1.3 mg, 0.011 mmol) at room temperature. The resulting mixture was heated at 40 °C for 3 h. Solvent removal under vacuum and purification by preparative TLC (CS_2) afforded **5'** ($R_f = 0.2$, 20.2 mg, 0.0106 mmol, 96%) as a red-brown solid: IR (CH_2Cl_2) ν_{CO} 2061 (w), 2040 (m), 2020 (s, sh), 2012 (vs) cm^{-1} ; ^1H NMR (400 MHz, $\text{C}_6\text{D}_4\text{Cl}_2$, 25 °C) δ 8.00–7.58 (m, 20H), 4.26 (s, 2H); ^{31}P NMR (122 MHz, ClC_6H_5 /external CD_2Cl_2 , 25 °C) δ 46.7; MS (FAB⁺) m/z 1900.6 [M^+]. Anal. Calcd for $\text{C}_{97}\text{H}_{22}\text{NO}_{10}\text{PRu}_5$: C, 61.40; H, 1.17; N, 0.74. Found: C, 61.70; H, 1.14; N, 0.76.

X-ray Crystallographic Study. Crystals of **1** were grown by solvent evaporation from a carbon disulfide solution at room temperature. Crystals of **2–4** and **5'** were obtained by slow solvent interdiffusion at room temperature: for **2** of cyclohexane into carbon disulfide, for **3** of methanol into carbon disulfide/dichloromethane, for **4** of heptane into carbon disulfide, and for **5'** of methanol into carbon disulfide/toluene. Data collections were made on a Siemens SMART diffractometer/CCD area detector. All data processing was performed with the integrated program package SHELX97,¹⁷ and the function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/[\sigma^2(F_o^2) + (0.1123P)^2]$,

where $P = (F_o^2 + 2F_c^2)/3$. The structures were solved by direct methods,¹⁸ and hydrogen atoms were not included in the final structure factor calculations. Successful convergences of full-matrix least-squares refinement based on F^2 were indicated by the maximum shift/error for the final cycle. The final difference Fourier maps had no significant factors.

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Supporting Information Available: Tables of positional parameters, anisotropic thermal parameters, bond distances, and bond angles for the X-ray crystallographic studies of **1–4** and **5'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM010695S

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