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Preparation and Characterization of Rhodium C_{60} Complexes $[Rh(acac)(L)_2(C_{60})]$ (L = py, 4-Mepy, 3,5-Me_2py)

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A series of novel C_{60} rhodium complexes $[Rh(acac)(L)_2(\eta^2\text{-}C_{60})]$ (L = pyridine, 4-methylpyridine, 3,5-dimethylpyridine) were prepared by the reaction of $[Rh(acac)(C_2H_4)_2]$ with C_{60} followed by treatment with pyridine or its derivatives. The molecular structure of $[Rh(acac)(3,5\text{-}Me_2py)_2(\eta^2\text{-}C_{60})]\cdot C_6H_6$ was determined by the X-ray crystallographic analysis.

The chemistry of C_{60} has been attracting widespread and enthusiastic interest. Much effort has been paid to the preparation of organometallic derivatives of C_{60}, and several types of complexes such as $[M(PR_3)_2(C_{60})]$ (M = Ni, Pd, Pt; R = Ph, Et),[1)] $[C_{60}\{M(PEt_3)_2\}_6]$ (M = Ni, Pd, Pt),[1b,2)] $[IrCl(CO)(PPh_2R)_2(C_{60})]$ (R = Ph, $CH_2C_6H_4OCH_2Ph$),[3)] $[C_{60}\{Ir_2Cl_2(C_8H_{12})_2\}_2]$,[4)] $[(\eta^5\text{-}C_9H_7)\text{-}Ir(CO)(C_{60})]$,[5)] $[C_{60}(OsO_4)(4\text{-}Bu^tC_5H_4N)_2]$,[6)] and polymeric $[Pd(C_{60})]_n$[7)] have been described. More recently, a rhodium C_{60} complex $[RhH(CO)(PPh_3)_2(C_{60})]$ (**1a**) was synthesized and characterized by the X-ray crystallographic study.[8)] We have been interested in the chemical transformation of C_{60} on organometallic complexes, and have now independently prepared two series of rhodium complexes of C_{60}, $[RhH(CO)\{P(p\text{-}C_6H_4R)_3\}_2(C_{60})]$[9)] (**1a**, R = H; **1b**, R = Me; **1c**, R = F) and $[Rh(acac)(L)_2(C_{60})]$ (**2a**, L = 3,5-dimethylpyridine (3,5-Me_2py); **2b**, L = pyridine (py); **2c**, L = 4-methylpyridine (4-Mepy); acac = 2,4-pentanedionate). Here we wish to report briefly the synthesis and characterization of the latter series of complexes.

When a benzene solution of $[Rh(acac)(C_2H_4)_2]$[10)] (25.8 mg, 0.10 mmol) and C_{60} (72 mg, 0.10 mmol) was stirred at room temperature under N_2, brown precipitate gradually deposited during 24 h, which was collected, washed with benzene, and dried (**3**, 49.8 mg, 52%[11)]). Although low solubility of **3** in common organic solvents prevented further purification and characterization, it was tentatively formulated as $[Rh(acac)(C_2H_4)(C_{60})]_n$ and/or $[Rh(acac)(C_{60})]_n$ based on the IR spectrum (KBr, 1570, 1551, 1516 cm^{-1}) and the reactivity described below. Treatment of **3** (50.0 mg) with 3,5-dimethylpyridine (0.5 ml) at room temperature gave a dark green solution within a few minutes. The reaction mixture was diluted with benzene (5 ml), stirred for 30 min, and filtered. Slow diffusion of hexane into the filtrate yielded $[Rh(acac)(3,5\text{-}Me_2py)_2(C_{60})]\cdot C_6H_6$ (**2a**$\cdot C_6H_6$) as black crystals (43.6 mg, 68%). Similar reactions of **3** with pyridine and 4-methylpyridine gave **2b** (69%) and **2c**$\cdot C_6H_6$ (66%), respectively, as black crystals.

Although the NMR spectra of complexes **2** were not able to be measured due to their low solubilities in

$[Rh(acac)(C_2H_4)_2]$ + C_{60} ⟶ $[Rh(acac)(C_2H_4)(C_{60})]_n$ or $[Rh(acac)(C_{60})]_n$

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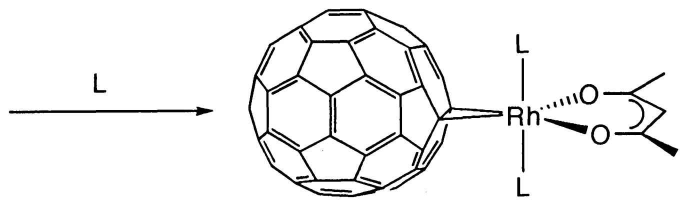

2a: L = 3,5-Me_2py
2b: L = py
2c: L = 4-Mepy

usual NMR solvents, their IR and visible absorption spectra as well as the elemental analysis data are in accordance with the formula (Table 1). It should be pointed out that visible absorption spectra with λ_{max} 430–450, 580–600, and 620–660 nm (green color) have often been observed for η^2-C_{60} complexes,[1,5,8,9)] and these intense absorptions, assignable to the charge-transfer bands, may be used as an indicator for the formation of η^2-C_{60} complexes.

Table 1. Spectral and analytical data for complexes **2**

Complexes	IR[a)] /cm^{-1}	VIS[b)]; λ_{max} /nm (logε /$M^{-1}cm^{-1}$)	E. A.; Found (Calcd) /% C	H	N
2a·C_6H_6	1578, 1514	432 (4.07), 593 (3.65), 621(sh)	84.17	2.98	2.67
			(84.02)	(2.57)	(2.31)
2b	1576, 1512	429 (4.08), 582 (3.65), 620(sh)	83.14	2.03	2.20
			(83.34)	(1.59)	(2.59)
2c·C_6H_6	1576, 1512	430 (4.04), 593 (3.61), 623(sh)	83.39	2.59	2.56
			(83.98)	(2.29)	(2.36)

a) KBr method. b) **2a**, in C_6H_6/3,5-Me_2py (4:1); **2b**, in C_6H_6/py (4:1); **2c**, in C_6H_6/4-Mepy (4:1).

The molecular structure of **2a** was unambiguously determined by the X-ray diffraction study.[12)] The ORTEP drawing is shown in Fig. 1. The molecule has a crystallographic mirror plane that bisects the C_{60} ligand and passes through the Rh1, N1, N2, C35, C39, and C42 atoms. The Rh1 atom takes the trigonal bipyramidal geometry, where the 3,5-Me_2py ligands occupy the axial positions and the acac and C_{60} ligands lie on the equatorial plane. The Rh1, O1, O1*, C1, and C1* atoms are essentially coplanar, in contrast to **1a** in which the dihedral angles between the P_2Rh and C_2Rh planes were found to be 22.3° and 21.9° (for two crystallographycally independent molecules).[8a)] The 3,5-Me_2py ligands are perpendicular to the Rh1–C_{60}

vector, minimizing the steric congestion with C_{60}.

The C_{60} moiety is coordinated to the rhodium in an η^2 fashion through a 6:6 ring junction. The Rh1–C1 distance (2.08(1) Å) is shorter than those in **1a** (2.151(8)–2.168(7) Å).[8a)] Sterically less demanding acac and 3,5-Me_2py ligands probably enable the stronger interaction between the Rh atom and C_{60} than in **1a**. The C1–C1* distance (1.50(3) Å) is similar to those found in other η^2–C_{60} complexes,[1,2,3a,8a)] and is longer than the average C–C bond distance at the free 6:6 ring junctions in **2a** (1.40 Å). The angle between the C1–C1* bond and the C1–C2–C5 plane (44°) is larger than that between the C32–C32* bond and the C32–C29–C31 plane (29°). This clearly indicates the C1–C1* bond is pulled away from the C_{60} core toward the rhodium. Similar deformation of C_{60} molecule caused by the coordination has been observed in other C_{60} complexes.[1,3a,8a)]

Preliminary experiments have revealed that the contact of **2a** in C_6H_6/3,5-Me_2py (4:1) with CO causes instantaneous reaction to give a mixture containing C_{60} and [Rh(acac)$(CO)_2$]. Further reactions of complexes **1**, **2**, and **3** as well as synthesis of different types of C_{60} complexes are under investigation.

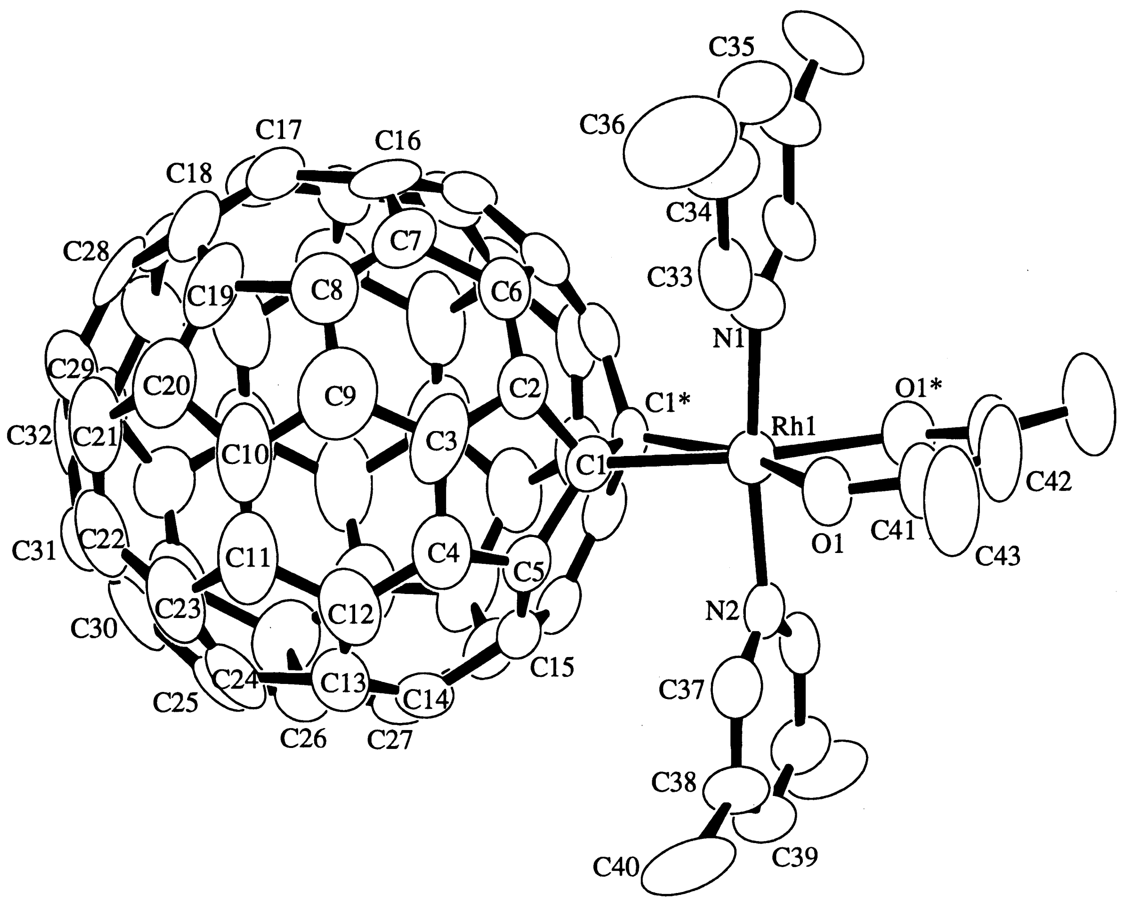

Fig. 1. ORTEP drawing of **2a**.
Selected bond distances (Å) and angles (°): Rh1–C1, 2.08(1); Rh1–O1, 2.155(9); Rh1–N1, 2.05(2); Rh1–N2, 2.00(2); C1–C1*, 1.50(3); C1–Rh1–C1*, 42.2(6); C1–Rh1–O1, 115.8(4); C1–Rh1–O1*, 158.0(4); C1–Rh1–N1, 93.4(6); C1–Rh1–N2, 92.5(5); O1–Rh1–O1*, 86.2(5); O1–Rh1–N1, 87.2(4); O1–Rh1–N2, 88.1(4); N1–Rh1–N2, 173.7(6); Rh1–C1–C1*, 68.9(3).

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9) Complexes **1a–1c** were synthesized by the reaction of C_{60} and $[RhH(CO)\{P(p\text{-}C_6H_4R)_3\}_3]$ in benzene at room temperature and purified by the silica gel column chromatography (C_6H_6–hexane) and recrystallization (C_6H_6–hexane).
Selected spectral and analytical data for **1b**: IR (KBr) 2054 (RhH), 1981 (CO) cm^{-1}; ^1H NMR (C_6D_6) δ −8.88 (t, J=9.4 Hz, 1 H, Rh*H*); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 37.7 (d, $J(^{103}Rh-^{31}P)$=140 Hz); VIS (C_6H_6) λ_{max} 442, 596, 655 nm. Anal. Found: C, 85.24; H, 3.03%. Calcd for $C_{109}H_{49}OP_2Rh$ (**1b**$\cdot C_6H_6$): C, 85.04; H, 3.21%.
1c: IR (KBr) 2058 (RhH), 1973 (CO) cm^{-1}; ^1H NMR (C_6D_6) δ −9.53 (t, J=10.6 Hz, 1 H, Rh*H*); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 36.9 (d, $J(^{103}Rh-^{31}P)$=143 Hz); VIS (C_6H_6) λ_{max} 437, 588, 644(sh) nm. Anal. Found: C, 78.85; H, 2.07%. Calcd for $C_{103}H_{31}OF_6P_2Rh$ (**1c**$\cdot C_6H_6$): C, 79,14; H, 2.00%.

10) $[Rh(acac)(C_2H_4)_2]$ has been known to undergo facile exchange of C_2H_4 ligands with olefins. For example, R. Cramer, *J. Am. Chem. Soc.*, **89**, 4621 (1967).

11) Calculated based on the formulation $[Rh(acac)(C_2H_4)(C_{60})]$.

12) Crystallographic data for **2a**$\cdot C_6H_6$: $C_{85}H_{31}N_2O_2Rh$, *FW*=1215.10, orthorhombic, *Pnma*, a=17.746(8), b=16.436(10), c=18.126(5) Å, V=5287(6) Å^3, Z=4, D_{calcd}=1.526 gcm^{-3}, D_{obsd}=1.518 gcm^{-3}, $\mu(MoK_\alpha)$=3.84 cm^{-1}, R=0.072, R_w=0.057 for 2254 unique reflections with $I>3\sigma(I)$.

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