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Synthesis and characterization of $(CH_3C(CH_2PPh_2)_3)RhH(\eta^2\text{-}C_{60})$

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Abstract

The title complex, (triphos)$RhH(\eta^2\text{-}C_{60})$ (**2**) (triphos = $CH_3C(CH_2PPh_2)_3$), was prepared by the reaction (80°C, toluene) of C_{60} with a trihydride rhodium complex (triphos)RhH_3 (**1**) in high yield (86%) as green crystals and characterized by spectroscopic (mass, ^{1}H-, ^{31}P-, and ^{13}C-NMR) and analytical data. The molecular structure of **2** was determined by a single crystal X-ray diffraction study. The rhodium atom is octahedrally coordinated by three *fac*-phosphorus atoms, a hydrogen atom and an η^2-C_{60} ligand. The cyclic voltammetric study of **2** reveals two reversible redox waves which are shifted to more negative potentials by ca. 290 mV compared to free C_{60}, reflecting both metal-to-C_{60} π-back-donation effect and the electron-donating nature of the triphos ligand. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metallofullerene; Rhodium; Crystal structure; Cyclic voltammetry

1. Introduction

There has been considerable current interest on metallofullerenes [1] concerning the effect of metal coordination on the properties of C_{60} since the first synthesis of the organometallic derivative of C_{60}, $Pt(PPh_3)_2(\eta^2\text{-}C_{60})$ [2]. Numerous reports of other metal-coordinated C_{60} complexes have included those of Ta, Mo, W, Fe, Ru, Co, Rh, Ir, Ni, and Pd, in which all the mononuclear metals are bound in an η^2-fashion at the 6–6 ring junction [1,3–5]. Subsequent development in metal–C_{60} π-complex chemistry has led to the synthesis of μ-η^2,η^2-C_{60} complexes for Re, Ru and Ir metals [6] and μ_3-η^2,η^2,η^2-C_{60} complexes for Ru and Os metals [7].

Rhodium hydride complexes have been reported to be efficient catalyst precursors for hydrogenation and hydroformylation reactions of olefins [8]. Rhodium olefin complexes, (triphos)$RhH(\eta^2$-alkene) (triphos = $CH_3C(CH_2PPh_2)_3$), have been prepared from the reaction between (triphos)RhH_3 (**1**) and various alkenes, and systematically studied to examine the influence of the alkene substituents on the reactivity of the olefin complexes [9]. The C_{60} ligand in transition metal–C_{60} complexes is known to act as an electronegative alkene. Herein we report the synthesis of (triphos)$RhH(\eta^2\text{-}C_{60})$ from the reaction of **1** with C_{60}, together with its spectroscopic, electrochemical, and structural characterization.

2. Experimental

2.1. General comments

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was dried by distillation over sodium. C_{60} (99.5%) was purchased from Southern Chemical Group. The trihydride complex, (triphos)RhH_3 (**1**), was prepared according to the literature procedure [10].

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The IR spectrum was obtained on a Bomem MB-100 FT-IR spectrophotometer. ^{1}H-NMR (300 MHz), ^{13}C-NMR (75 MHz), and ^{31}P-NMR (122 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Phosphorus chemical shifts are relative to external 85% H_3PO_4. The positive-ion FAB mass spectrum (FAB$^+$) was obtained by the staff of the Korea Basic Science Institute. Elemental analysis was provided by the staff of the Korea Advanced Institute of Science and Technology.

*2.2. Preparation of (triphos)RhH(η^2-C_{60}) (**2**)*

A mixture of (triphos)RhH_3 (50.7 mg, 0.0694 mmol) and C_{60} (50.0 mg, 0.0694 mmol) in toluene was heated at 80°C for 40 min with stirring to give a deep green solution. The solvent was evaporated and the residue was extracted with chloroform to remove unreacted C_{60}. Evaporation of the solvent and recrystallization in chloroform afforded compound **2** (86.5 mg, 0.0597 mmol, 86%) as green crystals. ^{1}H-NMR ($CDCl_3$, 298 K) δ 8.1–6.7 (m, phenyl, 30H), 2.7–2.5 (m, CH_2, 6H), 1.65 (m, CH_3, 3H), -9.53 (dd, Rh–H, 1H, $J_{PH} = 174$, $J_{RhH} = 6.8$ Hz). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K) δ 171.5(2C), 166.6(2C), 149.2(2C), 149.0(2C), 147.2(1C), 146.4(1C), 146.1(2C), 145.9(2C), 145.4(2C), 145.2(2C), 145.1(2C), 145.1(4C), 145.0(2C), 144.9(2C), 144.9(2C), 144.8(1C), 144.7(1C), 143.7(2C), 143.4(4C), 143.4(2C), 143.1(2C), 142.9(2C), 142.8(2C), 142.8(2C), 142.7(2C), 142.3(2C), 142.2(2C), 142.1(2C), 141.2(2C) (29 C_{60} signals, 58C), 136.1–127.8 (phenyl), 38.1, 32.8 (m, CH_2), 30.1 (s, CH_3), 27.3 (s, C–CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K) δ 20.9 (dd, 2P, $J_{RhP} = 135$, $J_{PP} = 28$ Hz), 7.7 (br). IR (Nujol mull) ν(Rh–H) 2052 cm^{-1}. FAB$^+$ MS m/z 1448 [M$^+$]. Anal. Calc. for $C_{101}H_{40}P_3Rh$: C, 83.7; H, 2.78. Found: C, 84.1; H, 2.77.

2.3. Electrochemical measurements

The cyclic voltammograms of **2** and free C_{60} were recorded on a BAS-100B electrochemical analyzer. The conventional three-electrode system of a platinum working electrode (1.6 mm diameter) and a platinum counter wire electrode (5 cm length × 0.5 mm diameter) was used. The reference electrode was an 0.05 M Ag/$AgNO_3$ electrode filled with 0.1 M [(n-Bu)$_4$N]ClO_4 in acetonitrile. All measurements were performed at ambient temperature under an nitrogen atmosphere in a dry deoxygenated 0.1 M 1,2-dichlorobenzene solution. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc$^+$) as the internal standard.

*2.4. X-ray data collection and structure determination of **2***

Crystals of **2** suitable for an X-ray diffraction study were obtained by slow evaporation from a chloroform solution. Data collection was carried out on a CAD4 diffractometer using graphite monochromated Mo–K$_\alpha$ radiation. Relevant crystallographic data are summarized in Table 1. The cell parameters were determined by least-squares method of 25 reflections with $10.28 < \theta < 13.55°$, and intensity data for 8179 independent reflections were collected with the range $-16 < h < 16$, $0 < k < 21$, $-14 < l < 14$ using $\omega/2\theta$ scan mode (ω-scan angle $= (0.8 + 0.35 \tan\theta)°$, $2\theta_{max} = 45.9°$). One orientation reflection was checked every 300 reflections and three standard reflections were monitored every 3 h, which revealed no significant decay over the course of data collection. The intensity data were corrected for Lorentz-polarization and absorption factors. All calculations were carried out using the NRCVAX PC software package [11]. The structure was solved by direct and different Fourier methods and refined by the full-matrix least-squares methods employing unit weights. All non-hydrogen atoms were refined anisotropically. The metal hydride was located from the difference electron density map and refined with an isotropic thermal parameter. Final agreement factors for 3637 reflections [$F_o > 3\sigma(F_o)$] were $R_f = 7.2$ and $R_w = 9.4\%$, with $(\Delta/\sigma)_{max} = 0.078$, $\Delta\rho_{max}/\Delta\rho_{min} = 0.820/-0.430$ e Å^{-3} in final $\Delta\rho$ map, and goodness-of-fit = 0.59 (for details of crystallographic data for compound **2** see Section 4).

Table 1
Crystal and structure determination data for **2**

Empirical formula	$C_{101}H_{40}P_3Rh$
Formula weight	1449.3
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	15.274(2)
b (Å)	19.809(2)
c (Å)	13.464(2)
α (°)	102.86(1)
β (°)	115.65(1)
γ (°)	82.313(9)
V (Å^3)	3577(1)
Z	2
D_{calc} (g cm^{-3})	1.346
Temperature (K)	288
Crystal size (mm)	0.23 × 0.17 × 0.13
λ (Mo–K$_\alpha$) (Å)	0.71069
μ (mm^{-1})	0.35
Transmission factors	0.65–1.00
No. of reflections measured	8179
No. of unique reflections	7949
No. of reflections ($F_o > 3\sigma(F_o)$)	3637
R_f [a]	0.072
R_w [b]	0.094
Goodness-of-fit [c]	0.59

[a] $R_f = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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

[c] Goodness-of-fit $= [\Sigma(|F_o| - |F_c|)^2/(\text{no. of reflections} - \text{no. of parameters})]^{1/2}$.

3. Results and discussion

3.1. Synthesis and characterization of **2**

The trihydride complex, (triphos)RhH$_3$ (**1**), has been previously reported to react with various alkenes by Bianchini et al [9]. In particular, electron-withdrawing alkenes stabilize *cis*-hydride–η^2-alkene complexes of the formula (triphos)RhH(η^2-alkene), whereas electron-rich alkenes do not form η^2-adducts but are hydrogenated to alkanes to produce dimeric (triphos)RhH(μ-H)$_2$HRh(triphos) complex. The reaction of **1** with C$_{60}$ at 80°C in toluene and subsequent recrystallization of the reaction residue in chloroform affords (triphos)RhH(η^2-C$_{60}$) (**2**) as green crystals in 86% yield. Compound **2** is soluble in common solvents such as dichloromethane, chloroform, tetrahydrofuran, and toluene to form green solutions, but is insoluble in hexane and methanol. It is stable in deareated solutions and in the solid state. However, it decomposes slowly in solution at high temperatures (>100°C).

Formulation of **2** is supported by elemental analysis and by the molecular ion [M$^+$] multiplet in the FAB$^+$ mass spectrum. The M$^+$ multiplet in the mass spectrum of **2** matches perfectly the calculated pattern: the highest peaks in the M$^+$ multiplet (*m*/*z*, found, calc.) are 1449, 1449. The IR spectrum of **2** shows a Rh–H stretching band at 2052 cm^{-1}, which compares with that at 2082 cm^{-1} in Rh(CO)H(PPh$_3$)$_2$(η^2-C$_{60}$) [3a].

The ^{1}H-NMR spectrum of **2** exhibits characteristic resonances due to the triphos ligand and the hydride ligand. The hydride resonance appears as a doublet of doublets because of couplings to the rhodium atom ($J_{\mathrm{RhH}} = 6.8$ Hz) and the *trans*-phosphorus atom ($J_{\mathrm{PH}} = 174$ Hz), which is similar to those found in analogous olefin complexes [9]. The ^{31}P{^{1}H} spectrum reveals two resonances at 20.9 and 7.7 ppm in a 2:1 ratio, assignable to the two *cis*- and one *trans*-phosphorus atoms to the hydride ligand, respectively. The low field resonance with an intensity of two, shows couplings to rhodium and *trans*-phosphorus atoms and thus appears as a doublet of doublets ($J_{\mathrm{RhP}} = 135$ and $J_{\mathrm{PP}} = 28$ Hz). The high field resonance is broad due to couplings to rhodium and two *cis*-phosphorus atoms. The C_s symmetric nature of **2** in solution shows the required number of ^{13}C-NMR resonances due to the C$_{60}$ ligand, 31 sp^2 carbon resonances (4 × 1C, 23 × 2C and 2 × 4C (accidental coincidence of four resonances)) in the region of δ 172–140, but one sp^3 carbon resonance due to the two sp^3 carbons bonded to the metal center was too weak to be detected. The chemical shifts of the C$_{60}$ sp^2 and sp^3 carbon atoms for metallofullerenes are typically in the regions δ 175–135 and 85–50, respectively. The sp^2 carbon atoms adjacent to the sp^3 ones (referred to as C2 atoms) generally resonate at uniquely low fields above ca. 155 ppm. The two resonances at δ 171.5 (2C) and 166.6 (2C) of **2** can be assigned to the C2 atoms of the C$_{60}$ ligand. The C_s symmetric complex, Rh(NO)(PPh$_3$)$_2$(η^2-C$_{60}$), has been previously reported to show 31 sp^2 and one sp^3 resonance including the two low field C2 resonances around 160 ppm by Green et al [1b].

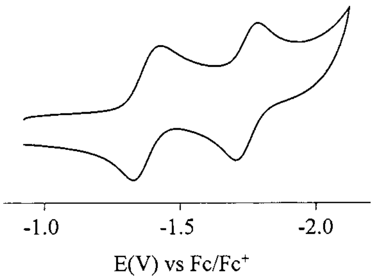

Fig. 1. Cyclic voltammogram of **2** in dry deoxygenated 1,2-dichlorobenzene (0.1 M [(*n*-Bu)$_4$N]ClO$_4$). Scan rate = 100 mV s^{-1}.

Monitoring the reaction of **1** with C$_{60}$ by ^{1}H-NMR reveals that new signals in the regions from 6.2 to 5.6 and -8.8 to -10.4 ppm grow in and disappear as the reaction proceeds. The low field resonances around 6 ppm may be attributed to fullerene hydrogen atoms and compare well with those found for the formation of (PCy$_3$)$_2$PtH(η^1-C$_{60}$H) and [{(η^5-C$_5$H$_5$)$_2$ZrCl}$_n$(η^1-C$_{60}$H$_n$)] intermediates [12]. The likely steps for the formation of **2** could involve insertion of a C$_{60}$ molecule into a Rh–H bond to form (triphos)RhH$_2$(η^1-C$_{60}$H), dihydrogen elimination owing to the acidic character of the hydrogen atom in hydrofullerene (C$_{60}$H), and η^2-coordination of the C$_{60}$ ligand.

The electrochemical properties of **2** have been examined by cyclic voltammetry in 1,2-dichlorobenzene (DCB) solution with tetrabutylammonium perchlorate as the supporting electrolyte. The cyclic voltammogram (CV) of **2** (see Fig. 1) shows two reversible redox couples at $E_{1/2} = -1.37$ and -1.75 V in the DCB potential window via C$_{60}$-localized reductions [13]. The half-wave potentials of the first and second redox waves are shifted to more negative potentials than those of free C$_{60}$ ($E_{1/2}^{0/-1} = -1.08$ and $E_{1/2}^{-1/-2} = -1.46$ V in DCB) by 290 mV, due to the metal-to-C$_{60}$ π-back-donation and the electron donating nature of the triphos ligand. Comparable cathodic shifts (ca. 300 mV) have been observed previously in phosphine substituted complexes such as (Et$_3$P)$_2$M(η^2-C$_{60}$) (M = Pt, Ni) [13]. The electron donating addends to C$_{60}$ are known to raise the energy of the C$_{60}$-localized LUMO and thus decrease the electron affinity of C$_{60}$, resulting in the cathodic shift. Complex **2** shows a remarkable electrochemical stability compared to other known η^2-C$_{60}$ complexes which generally undergo easy decomposition in the reduced states [6c,13a,14].

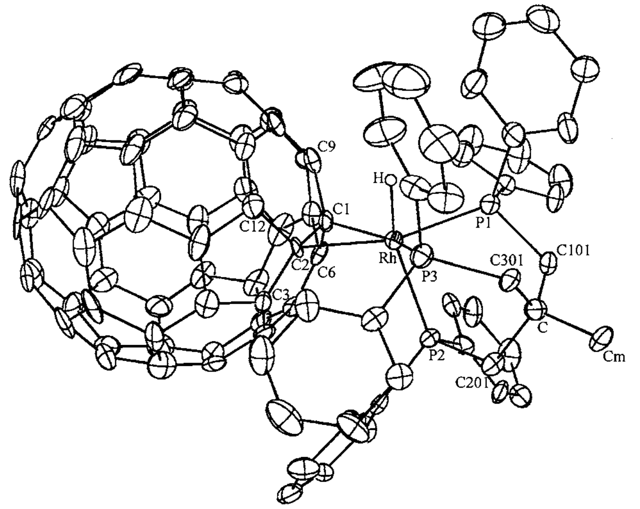

Fig. 2. Molecular geometry and atomic-labeling scheme for **2**.

3.2. Crystal structure of **2**

The crystal contains discrete (triphos)RhH(η^2-C_{60}) molecules, which are mutually separated by normal van der Waals distances. The overall geometry and atomic labeling scheme is illustrated in Fig. 2. Selected interatomic distances and angles are listed in Table 2.

The rhodium atom is coordinated to a C_{60} molecule, a hydride atom, and the triphos ligand which occupies three *fac*-positions of an octahedron. The three P–Rh–P angles are close to 90°, while the octahedron is significantly distorted due to steric interactions between the bulky C_{60} and triphos ligands. The Rh–P distances are nonequivalent. The Rh–P bond *trans* to the hydride ligand (2.394(6) Å) is significantly longer than the two Rh–P basal distances (2.281(6) and 2.290(6) Å). The hydride ligand can be directly located with an isotropic thermal parameter. The Rh–H bond length (1.5(2) Å) of **2** is comparable to the average Rh–H bond length (1.52(5) Å) found in $RhH_3(EtC(CH_2PPh_2)_3)$ [10].

Table 2
Selected interatomic distances (Å), angles (°) and estimated S.D. for **2**

Bond lengths			
Rh–P1	2.281(6)	C1–C2	1.46(3)
Rh–P2	2.394(6)	C1–C6	1.48(3)
Rh–P3	2.290(6)	C1–C9	1.47(3)
Rh–C1	2.17(2)	C2–C3	1.43(3)
Rh–C2	2.15(2)	C2–C12	1.49(3)
Rh–H	1.5(2)		
Bond angles			
Rh–C1–C2	70(1)	P2–Rh–P3	91.8(2)
Rh–C2–C1	71(1)	C1–Rh–H	98(7)
C1–Rh–P1	117.0(6)	C2–Rh–H	94(7)
C1–Rh–P2	104.0(6)	P1–Rh–H	81(7)
C1–Rh–P3	148.4(6)	P2–Rh–H	157(7)
C2–Rh–P1	155.7(5)	P3–Rh–H	68(7)
C2–Rh–P2	103.1(5)	C2–C1–C6	117(2)
C2–Rh–P3	110.6(5)	C2–C1–C9	118(2)
P1–Rh–P2	87.8(2)	C1–C2–C3	119(2)
P1–Rh–P3	90.3(2)	C1–C2–C12	115(2)

The C_{60} moiety is bound to the rhodium in an η^2-fashion through a 6–6 ring fusion, as found in other η^2-C_{60} transition metal complexes. The C1–C2 bond coordinated to the rhodium atom is 1.46(3) Å (cf. 1.48(1) Å in RhH(CO)$(PPh_3)_2$(η^2-C_{60}) and 1.50(3) Å in Rh(acac)(3,5-Me_2py)$_2$(η^2-C_{60}) [3]) and this bond is elongated due to the metal-to-C_{60} π-back-donation compared with 1.38 Å for an unperturbed (6,6)-bond. The Rh–C(C_{60}) bond distances are Rh–C1 = 2.17(2) and Rh–C2 = 2.15(2) Å. These bond distances of **2** are comparable to those of the dimethylfumarate complex, (triphos)RhH(dmfu) (1.45(2) Å for C–C(alkene) and average 2.16(1) Å for Rh–C(alkene)) [9], indicating similar amount of the metal-to-ligand π-back-donation in both complexes.

All other features of the molecular geometry are within the expected range. The average C–C bond length of the C_{60} moiety at the junction of the 5,6 ring is 1.44(4) Å and that at the junction of the 6,6 ring is 1.39(4) Å.

4. Supplementary material

Crystallographic data for the structure of **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CSD-113833. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk).

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