Synthesis and Characterization of Ir(H)(CO)(PEt₃)₂(η^2-C₆₀) [†]

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The title complex, Ir(H)(CO)(PEt₃)₂(η^2-C₆₀) (2), has been prepared by the reaction of excess C₆₀ (4 equiv) with a tetrairidium complex Ir₄(CO)₈(PEt₃)₄ (1) in refluxing chlorobenzene in 40% yield as green crystals. Compound 2 has been characterized by cyclic voltammetry (CV), spectroscopic methods (mass, IR, ^{1}H and ^{31}P NMR), and a single crystal X-ray diffraction study. The molecular structure reveals that the iridium atom of 2 is coordinated by two axial ligands of a hydrogen atom and a carbonyl group, and three equatorial ligands of two phosphorus atoms and an η^2-C₆₀ moiety. The CV study exhibits three reversible one-electron redox waves for the successive reductions of 2, together with additional four redox waves due to free C₆₀ reductions, which was formed by decomposition of 2 in the reduced states. The three reversible redox waves of 2 are shifted to more negative potentials by *ca.* 270 mV compared to free C₆₀, reflecting both metal-to-C₆₀ π-back-donation and the electron-donating nature of the two phosphorus ligands.

Key Words : Metallofullerene, Iridium, Crystal structure, Cyclic voltammetry

Introduction

Since the first C₆₀ transition metal complex with a direct metal-C₆₀ bond, Pt(PPh₃)₂(η^2-C₆₀)[1], has been reported, intensive studies in the field of exohedral metallofullerenes have been carried out to understand the effect of metal coordination on the chemical and physical properties of C₆₀.[2] Numerous η^2-C₆₀ monometallic transition metal complexes have been reported for Ta, Mo, W, Fe, Ru, Co, Rh, Ir, Ni, Pd, and Pt metals.[2-5] Subsequent development in C₆₀-metal π-complex chemistry has led to the syntheses of μ-η^2:η^2-C₆₀ complexes for Re, Ru, and Ir metals[6] and μ_3-η^2:η^2:η^2-C₆₀ complexes for Re, Ru, Os, Rh, and Ir metals.[7]

The hydrido iridium compound, Ir(H)(CO)(PPh₃)₃, is a well-known catalyst for both hydrogenation and isomerization catalysts of alkenes and alkynes.[8] Its fullerene-substituted compound, Ir(H)(CO)(PPh₃)₂(η^2-C₆₀) (3),[9] has been previously reported from the reaction of C₆₀ with octahedral Ir(H)₂(Cl)(CO)(PPh₃)₂ by elimination of HCl, but has not been structurally characterized, although a chloro analogue of 3 was prepared from the reaction of C₆₀ with Ir(Cl)(CO)(PPh₃)₂ and its crystal structure was reported.[10] Herein we report full details of synthetic, structural, spectroscopic, and electrochemical characterization of Ir(H)(CO)(PEt₃)₂(η^2-C₆₀) (2), a triethylphosphine analogue of 3, isolated serendipitously from the reaction of the tetrakistriethylphosphine-substituted compound Ir₄(CO)₈(PEt₃)₄ (1) with C₆₀.

Experimental Section

General Techniques. 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. C₆₀ (99.5%, SES Research) and PEt₃ (1.0 M THF solution, Aldrich) were used without further purification, and Ir₄(CO)₈(PEt₃)₄ (1) was prepared according to the literature procedure.[11] Preparative thin layer plates (tlc) were prepared with silica gel GF₂₅₄ (Type 60, E. Merck). Infrared spectra were obtained on a Bruker EQUINOX-55 FT-IR spectrophotometer. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker AVANCE-400 spectrometer and ^{31}P{^{1}H} NMR (122 MHz) spectrum were recorded on a Bruker AM-300 spectrometer. Positive ion FAB mass spectra (FAB$^+$) were obtained by the staff of the Korea Basic Science Institute and all m/z values were referenced to ^{193}Ir. Elemental analyses were provided by the staff of the Energy and Environment Research Center at KAIST.

Preparation of Ir(H)(CO)(PEt₃)₂(η^2-C₆₀) (2). A chlorobenzene solution (30 mL) of Ir₄(CO)₈(PEt₃)₄ (1, 30 mg, 0.020 mmol) and an excess of C₆₀ (58 mg, 0.080 mmol, 4 equiv) was heated to reflux for 10 h with stirring and the color changed to a green solution. The solvent was evaporated and the residue was purified by preparative tlc with a CS₂ eluent. Recrystallization in CS₂ with EtOH as a layering solvent afforded compound 2 (9 mg, 0.008 mmol, 40%, R_f = 0.56) as black crystals. IR (CH₂Cl₂) ν_{Ir-H} 2091(m), ν_{CO} 2091 (m); ^{1}H NMR (CDCl₃, 298 K) δ 2.23 (m, 12H, P(CH₂CH₃)₃), 1.34 (dt, J_{HH} = 7.8 Hz; $^3J_{PH}$ = 15.9 Hz, 18H, P(CH₂CH₃)₃), −9.70 (t, $^2J_{PH}$ = 18.8 Hz, 1H, Ir-H); ^{13}C{^{1}H}NMR (CS₂/THF-d₄, 298 K, CO region) δ 179.1 (br, 1CO), ^{13}C{^{1}H} NMR (CS₂/THF-d₄, 298 K, C₆₀ region) δ 167.1(2C), 165.4(2C), 148.3(2C), 148.0(2C), 147.0(1C), 146.8(1C), 145.8(2C), 145.7(2C), 145.3(2C), 145.0(2C), 144.9(2C), 144.8(6C), 144.3(1C), 144.2(1C), 143.8(2C), 143.7(2C), 143.6(2C), 143.5(2C), 143.3(2C), 142.7(2C), 142.6(2C), 142.4(2C), 142.3(2C), 142.0(2C), 141.9(2C), 141.6(2C),

141.5(2C), 134.7(2C), 134.3(2C), 60.3 (t, J_{PC} = 12.5 Hz, 2C, sp^3 carbon). ^{31}P{^{1}H} NMR (CDCl₃, 298 K) δ −6.9 (s, 2P, PEt₃). MS (FAB$^+$): m/z: 1178 [M^+]. Anal. Calc. for C₇₃H₃₁P₂OIr·0.5CS₂:C, 72.6; H 2.57, Found:C, 73.2; H, 2.58.

Electrochemical Measurements. Cyclic voltammetry was carried out on a AUTOLAB (PGSTAT 10, Eco Chemie, Netherlands) electrochemical analyzer using the conventional three electrode system of a platinum working electrode (1.6 mm diameter disk, Bioanalytical Systems, Inc.), a platinum counter wire electrode (5 cm length of 0.5 mm diameter wire), and a Ag/Ag$^+$ reference electrode (0.1 M AgNO₃/Ag in acetonitrile with a Vycor^{TM} salt bridge). All the measurements were performed at ambient temperature under nitrogen atmosphere in a dry deoxygenated 0.1 M chlorobenzene solution of [(n-Bu)₄N]ClO₄. The concentrations of compounds were ca. 3 × 10^{-4} M. All potentials were referenced to the standard ferrocene/ferrocenium (Fc/Fc$^+$) scale. Relative number of electrons involved in each reduction process was obtained from the graph of current vs. (time)$^{-1/2}$ according to the Cottrell equation.

X-ray Data Collection and Structure Determination of 2. Crystals of **2** suitable for an X-ray diffraction study were obtained by slow diffusion of ethanol into CS₂ solution. Data collection was carried out on a Bruker SMART diffracto-meter/CCD area detector at 293 K. Preliminary orientation matrix and cell constants were determined from three series of ω scans at different start angles. The hemisphere of reflection data were collected at scan interval of 0.5° ω

Table 1. Crystal and structure determination data for **2**·0.5CS₂

	Ir(H)(CO)(PEt₃)₂(η²-C₆₀)
formula	C₇₃H₃₁P₂OIr·0.5CS₂
fw	1216.18
cryst system	monoclinic
space group	$P2_1/n$
a, Å	14.9465(4)
b, Å	16.5758(4)
c, Å	18.8214(5)
α, deg.	90
β, deg.	108.448(1)
γ, deg.	90
V, Å^3	4423.4(2)
Z	4
D_{calcd}, g cm^{-3}	1.826
temp, K	293(2)
λ (Mo Kα), Å	0.71073
μ, mm^{-1}	3.197
θ range for collection	1.53° < θ < 28.30°
no. of rflns measd	40047
no. of unique rflns	10898
R_{int}	0.0312
goodness of fit	1.055
$R_1{}^a$	0.0407
wR2^b	0.1102

$^a R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|.$ $^b wR2 = [\Sigma \omega(F_o{}^2 - F_c{}^2)^2 / \Sigma \omega(F_o{}^2)^2]^{1/2}.$

within a exposure time of 20 seconds per frame. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Absorption corrections were performed using SADABS.^{12} Relevant crystallographic data are summarized in Table 1. Structure was solved by direct^{13} and difference 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. The metal hydride was located from the difference electron density map and refined with an isotropic thermal parameter.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-656226). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis and Characterization of 2. In our previous work, reaction of Ir₄(CO)₈(PMe₃)₄ (**4**) with excess (4 equiv) C₆₀ in refluxing 1,2-dichlorobenzene, followed by treatment with CNCH₂Ph at 70 °C, affords a square-planar tetrairidium complex with two C₆₀ ligands and a face-capping methylidyne ligand, Ir₄(CO)₃(μ₄-CH)(PMe₃)₂(μ-PMe₂)(CNCH₂Ph)-(μ-η²:η²-C₆₀)(μ₄-η¹:η¹:η²:η²-C₆₀) (**5**) as the major product as shown in the bottom of Scheme 1.^{15} In order to prepare a μ₄-CCH₃ analogue of **5**, a similar reaction of tetrakistriethylphosphine-substituted compound Ir₄(CO)₈(PEt₃)₄ (**1**) with C₆₀ was carried out, unexpectedly, to give a hydrido mono-iridium fullerene complex Ir(H)(CO)(PEt₃)₂(η²-C₆₀) (**2**) by fragmentation of the tetrairidium cluster framework (the top of Scheme 1).

Formulation of **2** is supported by elemental analysis and by the molecular ion (M$^+$) multiplet in the positive ion FAB mass spectrum (MS). The M$^+$ multiplet in the MS of **2** matches perfectly the calculated pattern: the highest peaks in the M$^+$ multiplet (m/z, found, calcd) are 1178, 1178. Compound **2** is soluble in common solvents such as THF, dichloromethane, chloroform, and carbon disulfide to form a green solution. This new compound decomposes slowly in solution at room temperature and must be kept in the refrigerator.

The IR spectrum of **2** shows an Ir-H stretching band at 2091 cm^{-1}, which compares with those at 2082 (Rh-H) and 2102 (Ir-H) cm^{-1} in analogous complexes such as Rh(H)(CO)(PPh₃)₂(η²-C₆₀)^{3a} and Ir(H)(CO)(PPh₃)₂(η²-C₆₀),^{9} respectively.

The ^{1}H NMR spectrum of **2** exhibit a hydride resonance at −9.70 ppm as a triplet ($^2J_{PH}$ = 18.8 Hz), which is typical for a hydride cis to two equivalent phosphorus atoms. The hydride resonances of Rh(H)(CO)(PPh₃)₂(η²-C₆₀) and Ir(H)(CO)(PPh₃)₂(η²-C₆₀) appeared at −9.33 ppm with $^2J_{PH}$ = 8.4 Hz and −9.02 ppm with $^2J_{PH}$ = 17.3 Hz, respectively.^{3a,9} The ethyl proton resonances appear at 2.23 (m, 12H) for the
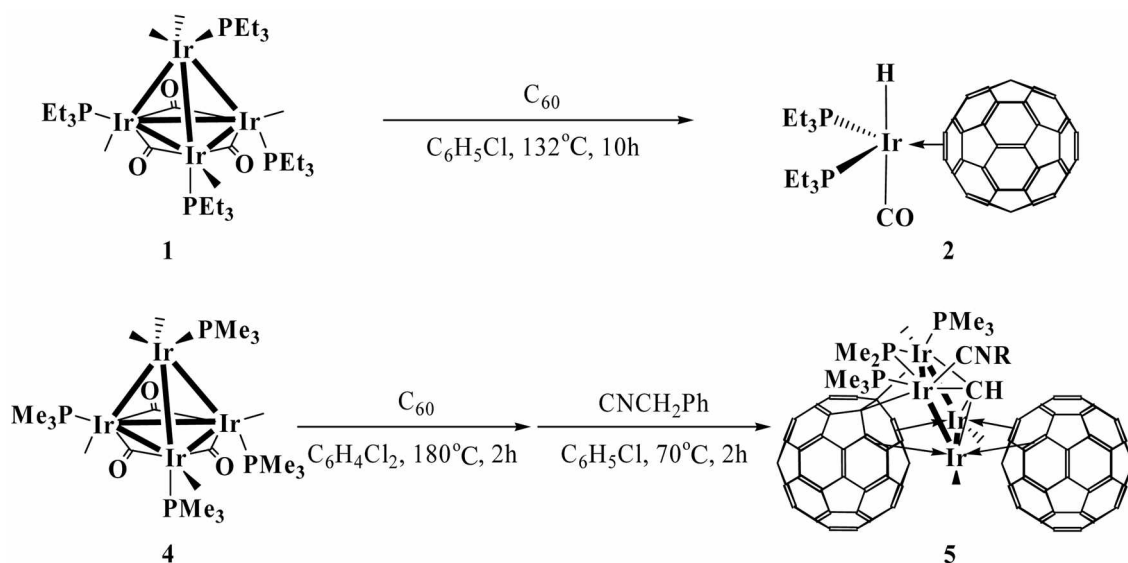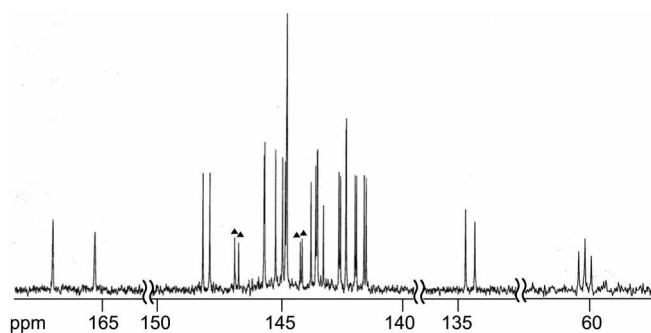
Scheme 1

Figure 1. ^{13}C NMR spectrum (100 MHz, CS_2/THF-d_4, 298 K, C_{60} region) of **2**.

methylene moieties and 1.34 (dt, 18H, J_{HH} = 7.8 Hz, $^3J_{PH}$ = 15.9 Hz,) for the methyl groups. The ^{31}P{^{1}H} NMR spectrum reveals a singlet at −6.9 ppm which is shifted to the higher field compared to that at 8.3 ppm of Ir(H)(CO)-$(PPh_3)_2(\eta^2$-$C_{60})$.[9]

The ^{13}C NMR spectrum of **2** reveals a broad signal at 179.1 ppm for the carbonyl carbon of the one carbonyl ligand. 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 (denoted as ▲), 24 × 2C, 1 × 6C (accidental coincidence of three resonances)] in the region of δ 170-130 and one sp^3 carbon resonance due to the two sp^3 carbons bonded to the metal center exhibits a triplet at δ 60.3 (Figure 1). The chemical shifts of the C_{60} sp^2 and sp^3 carbon atoms for exohedral metallofullerenes are typically in the regions δ 175-135 and 85-50, respectively. In particular, 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, whereas those adjacent to the C2 atoms (referred to as C3 atoms) typically appear in the high field region below *ca.* 140 ppm.[2b] Therefore, the two low field resonances at δ 167.1(2C) and 165.4(2C) of **2** can be assigned to C2 type carbons and two high field resonances at δ 134.7(2C) and 134.3(2C) can be assigned to the C3 type
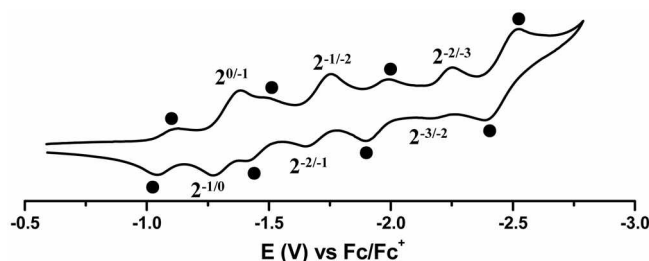

Figure 2. Cyclic voltammogram of **2** in dry deoxygenated chlorobenzene (0.1 M [(n-Bu)$_4$N]ClO$_4$). Scan rate = 50 mV/s.

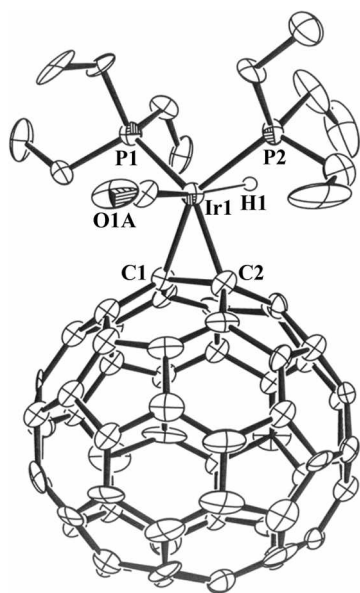carbons of C_{60} ligand. The C_s symmetric complex, Rh(NO)-$(PPh_3)_2(\eta^2$-$C_{60})$, has been previously reported to show 31 sp^2 and one sp^3 resonance including the two low field C2 resonances around 160 ppm and the two high field C3 resonances around 136 ppm by Green and coworkers.[2b]

Electrochemical Study of 2. The electrochemical property of **2** has been examined by cyclic voltammetry in chlorobenzene (CB) solution with tetrabutylammonium perchlorate as the supporting electrolyte. The cyclic voltammogram (CV) of **2** is shown in Figure 2 and reveals seven reversible redox couples in the CB potential window. Their half-wave potentials are provided, together with free C_{60}[16] and other known Group 9 and 10 transition metal η^2-C_{60} complexes with phosphine ligands for comparison in Table 2.

The three redox waves at −1.33, −1.70, and −2.16 V are due to three successive one-electron reductions localized at C_{60} of **2** corresponding to formation of 2^-, 2^{2-}, and 2^{3-}. The other four waves (denoted as ●) at −1.08, −1.44, −1.94, and −2.45 V are assigned to redox reactions of free C_{60} formed by decomposition of **2** in the reduced states during cyclic voltammetry. It is well documented that most of the known η^2-C_{60} transition metal complexes are unstable in the reduced states to release metal fragment and formations of the anions C_{60}^-, C_{60}^{2-}, and C_{60}^{3-}, respectively, although Rh(H)(CH$_3$C-(CH$_2$PPh$_2$)$_3$)(η^2-C_{60}) complexes display exceptional stability

Table 2. Half-wave potentials ($E_{1/2}$ *vs* E^o_{Fc/Fc^-}) of C_{60}, free C_{60} with **2**, and **2**

compound	$E_{1/2}^{0/-1}$	$E_{1/2}^{-1/-2}$	$E_{1/2}^{-2/-3}$	$E_{1/2}^{-3/-4}$	solvent	ref
C_{60}	−1.06	−1.43	−1.91	−2.38	CB	16
a mixture of C_{60} with **2** (denoted as •)	−1.08	−1.44	−1.94	−2.45	CB	This work
Ir(H)(CO)(PEt₃)₂(η²-C₆₀) (**2**)	−1.33	−1.70	−2.16		CB	This work
Rh(H)(CH₃C(CH₂PPh₂)₃)(η²-C₆₀)	−1.37	−1.75			DCB	17
Co(NO)(PPh₃)(η²-C₆₀)	−1.17	−1.72	−2.25		THF	6c
Pt(PEt₃)₂(η²-C₆₀)	−1.20	−1.73	−2.27		THF	18a
Pd(PEt₃)₂(η²-C₆₀)	−1.18	−1.69	−2.23		THF	18a
Ni(PEt₃)₂(η²-C₆₀)	−1.20	−1.74	−2.32		THF	18a

Figure 3. Molecular geometry and atomic-labeling scheme for **2**.

Table 3. Selected interatomic distances (Å), angles (deg), and Esd's for **2**

Bond Lengths (Å)			
Ir-P1	2.281(6)	Ir-P2	2.394(6)
Ir-C1	2.17(2)	Ir-C2	2.15(2)
Ir-H	1.5(2)	C1-C2	1.46(3)
Angles (deg)			
Ir-C1-C2	70(1)	P1-Ir-P2	87.8(2)
Ir-C2-C1	71(1)	C1-Ir-H	98(7)
C1-Ir-P1	117.0(6)	C2-Ir-H	94(7)
C1-Ir-P2	104.0(6)	P1-Ir-H	81(7)
C2-Ir-P1	155.7(5)	P2-Ir-H	157(7)
C2-Ir-P2	103.1(5)		

both thermally and electrochemically.[17] The three redox waves of **2** are shifted to more negative potentials than those of free C_{60} by 270, 270, and 250 mV, respectively, because of both the metal-to-C_{60} π-back-donation and the electron donating nature of the phosphine ligands. Comparable cathodic shifts have been observed previously in other phosphine-substituted complexes such as (Et₃P)₂M(η²-C₆₀) (M = Ni, Pd, Pt),[18] and Rh(H)(CH₃C(CH₂PPh₂)₃)(η²-C₆₀)[17] as listed in Table 2. The electron donating addenda to C_{60} are known to raise the C_{60}-localized LUMO energy and thus decrease the electron affinity of C_{60}, resulting in the observed cathodic shift. Complex **2**, however, is relatively electrochemically stable compared to other known η²-C₆₀ complexes, which generally undergo fast decomposition in the reduced states.

Molecular Structure of 2. The overall geometry and atomic labeling scheme of **2** are illustrated in Figure 3, and selected interatomic distances and angles are listed in Table 3. The iridium atom of **2** is coordinated by two axial ligands of a hydrogen atom and a carbonyl group, and three equatorial ligands of two phosphorus atoms and an η²-C₆₀ moiety. The C_{60} ligand is bound to the iridium atom in an η² fashion at the 6-6 ring junction, as generally found in other

η²-C₆₀ metallofullerens. The general structural features of **2** are similar to those of the structurally characterized Ir(Cl)(CO)(PPh₃)₂(η²-C₆₀) and Rh(H)(CO)(PPh₃)₂(η²-C₆₀) complexes. The Ir-C(carbonyl) bond length (1.932(6) Å) of **2** compares with the Rh-C(carbonyl) bond length (1.934(9) Å) of Rh(H)(CO)(PPh₃)₂(η²-C₆₀).[3a] The Ir-H bond length (1.57(6) Å) is comparable to the Rh-H bond length (1.5(2) Å) observed in Rh(H)(CH₃C(CH₂PPh₂)₃)(η²-C₆₀).[17] The hydride ligand is directly located from the crystallographic study at the opposite axial position of the carbonyl ligand. The distance of the C1-C2 bond coordinated to the iridium atom is 1.507(8) Å (cf. 1.53(3) Å in Ir(Cl)(CO)(PPh₃)₂(η²-C₆₀),[10] 1.46(3) Å in Rh(H)(CH₃C(CH₂PPh₂)₃)(η²-C₆₀),[17] and 1.48(1) Å in Rh(H)(CO)(PPh₃)₂(η²-C₆₀)[3a]). This bond is elongated due to the metal-to-C_{60} π-back-donation relative to 1.38 Å for an unperturbed (6,6)-bond. The Ir-C(C_{60}) bond distances are Ir-C1 = 2.146(5) Å and Ir-C2 = 2.164(5) Å, which are comparable to those of average 2.19(2) Å for Ir(Cl)(CO)(PPh₃)₂(η²-C₆₀),[10] and 2.16(2) Å for Rh(H)-(CH₃C(CH₂PPh₂)₃)(η²-C₆₀).[17]

All other features of the molecular geometry are within the expected ranges. The average C-C bond length of the C_{60} moiety at the junction of the 5,6 ring is 1.536(8) Å and that at the junction of the 6,6 ring is 1.37(1) Å.

Conclusion

Hydrido monoiridium fullerene complex Ir(H)(CO)-(PEt₃)₂(η₂-C₆₀) (**2**) has been prepared by the reaction of tetrakistriethylphosphine-substituted compound Ir₄(CO)₈-

$(PEt_3)_4$ (**1**) with C_{60} in refluxing chlorobenzene. Compound **2** has been fully characterized by various spectroscopic (IR, MS, ^1H and ^{13}C-NMR) methods, cyclic voltammetry, and X-ray diffraction study. Compound **2** is, to our knowledge, the first example of structurally characterized hydrido iridium η^2-C_{60} complex.

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