

The First Mononuclear η^2 -C₆₀ Complex of Osmium: Synthesis and X-ray Crystal Structure of $[(\eta^2\text{-C}_{60})\text{Os}(\text{CO})(t\text{BuNC})(\text{PPh}_3)_2]$

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The interaction of C₆₀ fullerene with the *cis*-dihydride osmium complex $[\text{OsH}_2(\text{CO})(\text{PPh}_3)_3]$ (**I**) in the presence of *t*BuNC gives a novel metal complex $[(\eta^2\text{-C}_{60})\text{Os}(\text{CO})(t\text{BuNC})(\text{PPh}_3)_2]$ (**II**) as the first mononuclear osmium complex with an η^2 -coordinated fullerene ligand. Complex **II** was isolated and characterized by elemental analysis, UV, IR, ¹H and ³¹P NMR spectroscopy. An X-ray diffraction study of **II**

as its dichlorobenzene solvate revealed a distorted trigonal bipyramidal coordination of the Os atom, with a 6/6 bond of C₆₀ and two PPh₃ ligands in the equatorial plane and CO and *t*BuNC as axial ligands.

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A large number of mononuclear complexes of fullerenes with transition metals, with general formula $(\eta^2\text{-C}_n)\text{ML}$ (where L stands for any ligand environment of M metal), with an olefin-like π -coordinated fullerene moiety have been obtained and structurally characterized for most metals of the platinum family, including Ru,^[1] Rh,^[2–4] Ir,^[5,6] Pd,^[7,8] and Pt.^[9–11] Based on their structures and spectroscopic properties, $(\eta^2\text{-C}_n)$ fullerene ligands in such mononuclear complexes are believed to be analogues of acceptor η^2 -olefins with electron-withdrawing substituents (e.g. tetrafluoroethylene or tetracyanoethylene).^[12,13] However, no mononuclear η^2 -derivatives of fullerenes with osmium have been reported to date, notwithstanding the fact that an exopolyhedrally coordinated osmate complex of C₆₀, $(\sigma, \sigma\text{-C}_{60})\text{O}_2\text{OsO}_2(4\text{-}t\text{ert-butylpyridine})_2$, was the first fullerene derivative studied by single-crystal X-ray diffraction.^[14] Meanwhile, a number of osmium tri-^[15–17] and pentanuclear clusters,^[17,18] with the C₆₀ moiety connected to a cluster core in an η^2 - [in $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-C}_{60})$]^[15], $\eta^1\text{:}\eta^2\text{:}\eta^1$ -,^[16] $\eta^2\text{:}\eta^2$ -,^[17] or $\eta^2\text{:}\eta^2\text{:}\eta^2$ -mode,^[15,17,18] have been obtained and structurally characterised by X-ray methods.

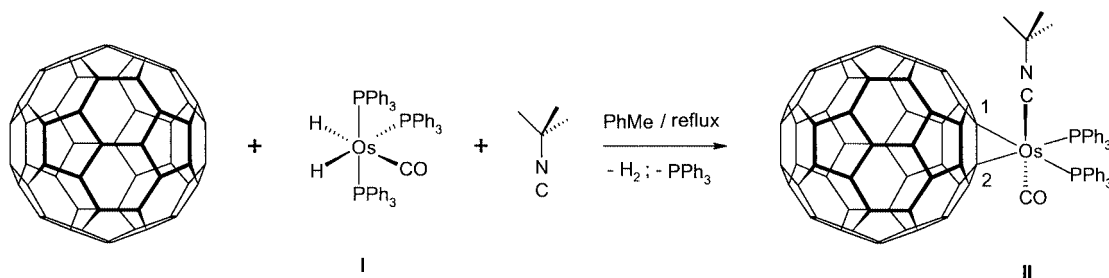
In this paper we report the synthesis of the first mononuclear π -complex of osmium with buckminsterfullerene as an η^2 -ligand and its structural characterization by single-crystal X-ray diffraction. To reach this goal, we have used the method recently developed by us for a synthesis of the mixed-ligand $\eta^2\text{-C}_{60}$ and σ -carboranyl derivative of iridium $[(\eta^2\text{-C}_{60})\text{Ir}(o\text{-HCB}_{10}\text{H}_9\text{CCH}_2\text{PPh}_2\text{-}B,P)(t\text{BuNC})_2]$.^[6] This approach is based on the interaction of the C₆₀ molecule with a coordinatively unsaturated reactive intermediate,

generated in situ from the corresponding metal *cis*-dihydride complex and *tert*-butyl isocyanide. The *t*BuNC ligand, having both π -acceptor and σ -donor properties, plays a dual role in the synthesis: as a strong π -acceptor it promotes the reductive elimination of a dihydrogen molecule from the initial dihydride complex after ligand substitution, to give a low-valent intermediate, whereas as a σ -donor it enhances the electron density at the metal center facilitating the effective coordination of the bulky and electron-deficient fullerene ligand.

As a starting *cis*-dihydride complex, the well-known and readily available $[\text{OsH}_2(\text{CO})(\text{PPh}_3)_3]$ ^[19] (**I**), which does not react directly with C₆₀, was chosen. However, when C₆₀ and **I** are refluxed together in toluene with *t*BuNC, a substitution of triphenylphosphane ligand for isocyanide occurs, accompanied by elimination of dihydrogen, giving rise to a new $[(\eta^2\text{-C}_{60})\text{Os}(\text{CO})(t\text{BuNC})(\text{PPh}_3)_2]$ complex (**II**) (Scheme 1).

The product **II**, obtained in analytically pure form by chromatography, was characterized by microanalysis and spectroscopy data (UV/Vis, IR, ¹H and ³¹P NMR). The UV/Vis pattern of **II** is rather typical for transition metal $\eta^2\text{-C}_{60}$ complexes.^[3,6,20] The presence of a strong $\nu(\text{CO})$ band at 1953 cm^{−1} and a strong single $\nu(\text{NC})$ band at 2153 cm^{−1} in the IR spectrum of **II** reveals both isocyanide and carbonyl ligands to be present in the molecule, pointing to a specific substitution of the triphenylphosphane ligand. According to the ¹H NMR spectroscopic data, complex **II** contains two PPh₃ and one *t*BuNC ligand, whereas the presence of only one singlet resonance at $\delta = 7.9$ ppm in the ³¹P{¹H} NMR corresponds to the existence of only one isomer, with two equivalent PPh₃ ligands, in solution. The latter may be considered as evidence of metal-fullerene coordination by the 1–2 bond (see discussion in ref.^[20]).

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Scheme 1

The analytical data for **II** (C, H P, Os) correspond unequivocally to a monoadduct such as $[(C_{60})Os(CO)(t-BuNC)(PPh_3)_2]$. However, the available spectroscopic data do not allow us to distinguish between the possible equatorial (with carbonyl and *t*BuNC as axial ligands) and *trans*-axial positions of the two equivalent PPh_3 ligands. Notwithstanding a close resemblance of the spectroscopic data for **II** with those of the related complex $[Os(C_2F_4)(CO)\{(p-Tolyl)NC\}(PPh_3)_2]$ [$\nu(CO) = 1968\text{ cm}^{-1}$, $\nu(NC) = 2160\text{ cm}^{-1}$; $\delta_P = 3.5\text{ ppm}$]^[21] with two equivalent equatorial PPh_3 ligands and strong preference of equatorial location of bulky PPh_3 and fullerene ligands due to the steric repulsion, no decisive evidence was obtained in favor of one of the two possible isomers from the spectroscopic data.

To determine the molecular geometry of **II** unequivocally and to analyze its structural features, we grew a single crystal of **II** from *o*-dichlorobenzene solution and performed an X-ray diffraction study.

The molecular structure of $II \cdot 2.5C_6H_4Cl_2$ with selected geometric parameters (bond lengths and bond angles) is shown in Figure 1. The molecule $[(\eta^2-C_{60})Os(CO)(t-BuNC)(PPh_3)_2]$ has an ordered C_{60} moiety with a normal olefin-type π -coordination to the osmium atom. A trigonal bipyramidal ligand environment of Os in **II** is completed by two equatorial PPh_3 ligands, with one isocyanide and one CO ligand in the axial positions. Most of the bond lengths and angles (see Figure 1) have their normal values. However, the bond angles $P(1)-Os-P(2)$ [$109.58(5)^\circ$], $P(1)-Os-C_{60}$ [$120.3(1)^\circ$] and $P(2)-Os-C_{60}$ [$130.1(1)^\circ$] in the equatorial plane of the trigonal bipyramid (where C_{60} denotes a center of the coordinated 6/6 bond) display a substantial asymmetry due to intramolecular $C-H \cdots C$ steric repulsion between one Ph substituent at $P(2)$ and C_{60} (shortest $H \cdots C$ distances at 2.64–2.87 Å are slightly less than the sum of their van der Waals radii). Metal-fullerene bonding leads to elongation of η^2 -coordinated 6/6 bonds to 1.498(7) Å from the normal value of 1.39 Å in pristine C_{60} and a more pyramidal environment of the C atoms [the spherical excess (spherical excess is $360^\circ - \Sigma(\text{all CCC bond angles})$) of the carbon environment, which is a good quantitative measure of pyramidalization,^[22] is 12° in pristine C_{60} ,

23.2 and 24.0° at these atoms of **II**, 7.4 – 8.6° at their neighbors and 10.5 – 13.5° at all other C atoms].

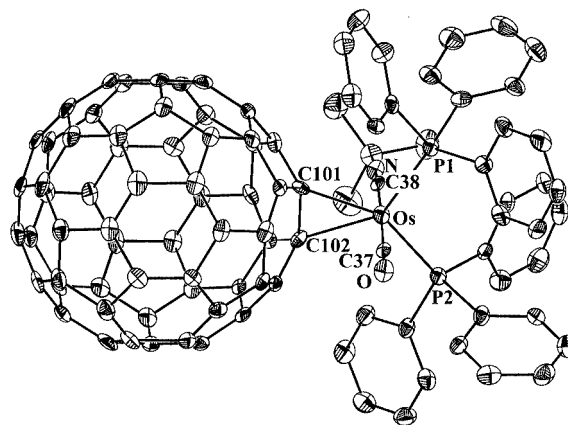


Figure 1. Molecule **II** with atomic numbering in the coordination environment of the Os atom (hydrogen atoms not shown); bond lengths (Å): Os–P(1) 2.347(2), Os–P(2) 2.351(1), Os–C(37) 1.898(2), Os–C(38) 2.011(2), Os–C(101) 2.193(5), Os–C(102) 2.193(5), C(37)–O(1) 1.146(4), C(38)–N(1) 1.169(6), C(101)–C(102) 1.479(7); bond angles ($^\circ$): P(1)–Os–P(2) 109.58(5), P(1)–Os–C(37) 88.52(8), P(2)–Os–C(37) 92.41(7), P(1)–Os–C(38) 96.13(8), P(2)–Os–C(38) 84.26(7), C(37)–Os–C(38) 175.0(1), Os–C(37)–O 178.0(2), Os–C(38)–N 173.9(2)

It is interesting to note that only two mononuclear phosphane π -complexes of osmium with η^2 -coordinated olefins having electron acceptor substituents, viz. $[(Ph_3P)_2Os(CO)_2(\eta^2-C_4H_2O_3)]$ ^[21] (with maleic anhydride) and $[(iPr_3P)_2OsH(OH)(CO)(\eta^2-CH_2=CHCOOMe)]$ ^[23] (with methylmetacrylate) are found in the last (2002) version of the Cambridge Structural Database (CSD). Mononuclear π -complexes of Ru with electron-accepting olefins, which have been studied in more detail, include derivatives of tetrafluoroethylene $[(Ph_3P)_2Ru(CO)_2(\eta^2-C_2F_4)]$,^[21] maleic anhydride $[(Ph_3P)_2Ru(CO)\{(p-Tolyl)NC\}(\eta^2-C_4H_2O_3)]$,^[24] and buckminsterfullerene $[(Ph_3P)_2RuCl(NO)(\eta^2-C_{60})]$.^[1] The main geometric molecular parameters of these complexes are compared with the corresponding parameters of **II** in Table 1.

The Os–C(C_{60}) bond lengths [2.193(5) Å] in **II** are typical for mononuclear complexes with π -coordinated acceptor

Table 1. Geometric parameters of the pentacoordinate metal environment in **II** and several closely related complexes

Complex	M–P (Å)	M–CO (Å)	M–C(π) (Å)	P–M–P (deg.)	C ₂ (π)–M–L (deg.)	Ref.
[(Ph ₃ P) ₂ Os(CO)(<i>t</i> BuNC)(η^2 -C ₆₀)] (II)	2.35	1.90	2.19	109.6	120.3 130.3	[a]
[(Ph ₃ P) ₂ Os(CO) ₂ (η^2 -C ₄ H ₂ O ₃)] ^[b]	2.43	1.91	2.18	99.3 ^[c]	86.1 117.4 ^[c]	[21]
[(<i>i</i> Pr ₃ P) ₂ OsH(OH)(CO)(η^2 -CH ₂ =CHCO ₂ Me)] ^[d]	2.40	1.84	2.19	144.3 ^[e]	104.3 109.0	[23]
[(Ph ₃ P) ₂ RuCl(NO)(η^2 -C ₆₀)]	2.45	–	2.22	113.2	122.3 124.3	[1]
[(Ph ₃ P) ₂ Ru(CO)[(<i>p</i> -Tolyl)NC](η^2 -C ₄ H ₂ O ₃)] ^[b]	2.37	1.85	2.19	107.0	117.3 135.6	[24]
[(Ph ₃ P) ₂ Ru(CO) ₂ (η^2 -C ₂ F ₄)]	2.43	1.92	2.09	101.4	127.5 131.1	[21]

[a] Two PPh₃ and two CO ligands in equatorial and axial positions, respectively. [b] η^2 -Methyl methacrylate. [c] Hydride H atom between two equatorial PPh₃ ligands. [d] η^2 -Methyl methacrylate. [e] Hydride H atom between two equatorial PPh₃ ligands.

olefins (see Table 1), and are almost identical to the Os–C(olefin) distances in [(Ph₃P)₂Os(CO)(η^2 -C₂H₄)] (2.15–2.19 Å).^[25] In a disordered structure of [Os₃(CO)₁₁(η^2 -C₆₀)], η^2 -coordination to one of three Os atoms in a triangular cluster is accompanied by larger distances (2.22–2.27 Å)^[15] that lie within the usual range (2.21–2.32 Å) for a multicenter Os₃–(η^2 : η^2 : η^2 -C₆₀) coordination.^[15,17,18] A planar trigonal arrangement of two phosphanes and the center of the coordinated 6/6 bond of the η^2 -C₆₀ ligand in the equatorial plane around the Os atom in **II** is similar to other mononuclear fullerene derivatives like [(PPh₃)₂Pd(η^2 -C₆₀)],^[7] [(PPh₃)₂Pd(η^2 -C₇₀)],^[8] [(DIOP)₂-Pt(η^2 -C₆₀)],^[11] [(PPh₃)₂RuCl(NO)(η^2 -C₆₀)],^[11] [(PPh₃)₂RhH(CO)(η^2 -C₆₀)],^[2] and [L₂IrCl(CO)(η^2 -C_n)] (where L is a phosphane ligand).^[13] Unlike the symmetric L₂M–(6/6 bond) fragment in all these complexes, the P–Os–C₆₀ angles in **II** differ by 10°. However, in the related pentacoordinate complex [(PPh₃)₂Ru(CO)[(*p*-tolyl)NC](η^2 -malonic anhydride)] with carbonyl and isocyanide axial ligands,^[24] which is the closest non-fullerene analogue of **II**, the P–Ru(olefin) angles in the equatorial plane differ by 18.3° (see Table 1). Even the large angle difference in mononuclear [(Ph₃P)₂Os(CO)₂(η^2 -C₄H₂O₃)] is due to the axial position of one PPh₃ ligand,^[21] whereas in [(*i*Pr₃P)₂OsH(OH)(CO)(η^2 -CH₂=CHCOOMe)] a hydride ligand is situated between two *i*PPR₃ groups in the equatorial plane.^[23] Such asymmetry of the flexible metal coordination probably refers to an interplay of interligand repulsion and molecular packing forces in the crystal.

Thus, we have shown that the interaction of fullerene with *cis*-dihydride transition metal complexes in the presence of isocyanide gives a rather convenient and general synthetic route to (η^2 -C₆₀) metal complexes. It allowed us to obtain the first mononuclear osmium fullerene complex [(η^2 -C₆₀)Os(CO)(*t*BuNC)(PPh₃)₂] whose crystal and molecular structure was completely characterized by single-crystal X-ray diffraction.

Experimental Section

General: All manipulations were performed under oxygen-free argon in dry degassed solutions. IR spectra were obtained on a Specord M80 spectrometer. ¹H NMR spectra (400.3 MHz) and ³¹P{¹H} NMR spectra (160.02 MHz) were recorded on a Bruker AMX-400 spectrometer and are quoted relative to residual signals of the solvent (internal standard) and 85% H₃PO₄ (external standard), respectively. [OsH₂(CO)(PPh₃)₃] was prepared by a standard literature procedure.^[19b]

Synthesis of [(η^2 -C₆₀)Os(CO)(*t*BuNC)(PPh₃)₂] (II**):** [OsH₂(CO)(PPh₃)₃] (**I**) (0.0699 g, 0.069 mmol) and *t*BuNC (17.2 μ L, 0.153 mmol) were added to a solution of C₆₀ (0.050 g, 0.069 mmol) in toluene (50 mL), with stirring, and the reaction mixture was refluxed for 24 h. After cooling the reaction mixture to room temperature, a small quantity (0.013 g) of insoluble precipitate (not further unidentified) was filtered off, and the solution was concentrated to 5 mL and then diluted with pentane. The precipitate was filtered, washed with pentane, dissolved in 1 mL of CHCl₃ and chromatographed on a short column packed with alumina, eluting with a CHCl₃/hexane mixture (1:1). A green fraction was collected, solvents were removed under reduced pressure and the residue was washed with pentane, and dried in vacuo at 60 °C to give 41 mg (38%) of **II**. C₁₀₂H₃₉NOOsP₂ (1546.6): calcd. C 79.21, H 2.54, Os 12.30, P 4.00; found C 78.47, H 2.64, Os 12.77, P 4.35. UV/Vis (THF): λ = 259, 333, 394 (sh), 444, 671 nm. IR (KBr pellet): $\tilde{\nu}$ = 2153 cm^{−1} (NC), 1953 (CO). ¹H NMR (CDCl₃): δ = 0.86 (s, 9 H, *t*Bu), 7.32 (m, 18 H, Ph), 7.58 (m, 12 H, Ph) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 7.9 ppm.

X-ray Structure Determination of **II:** Dark green crystals of **II**·2.5(*o*-C₆H₄Cl₂) were grown by slow diffusion of heptane into an *o*-dichlorobenzene solution of complex **II** at room temperature. The crystals are triclinic, space group P $\bar{1}$, *a* = 13.254(3), *b* = 16.753(4), *c* = 18.642(4) Å, α = 87.575(5)°, β = 74.626(5)°, γ = 73.672(5)°, *V* = 3828(1) Å³, *Z* = 2, *d*_{calcd.} = 1.661 g/cm³, and μ (Mo-*K* α) = 19.52 mm^{−1}. The intensities of 21936 unique reflections (*R*_{int} = 0.063) were measured at 110(2) K on a Bruker SMART 1000 CCD diffractometer (graphite monochromated Mo-*K* α radiation, λ = 0.71073 Å, ω and θ scan technique with a 0.3° step in ω and 10 s per frame exposure, $\theta \leq 30.15^\circ$). Reflection intensities were integrated using the SAINT software^[26] and corrected for absorption

semiempirically (SADABS program)^[26] based on multiple measurements of identical reflections and equivalents. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 . Two molecules of *o*-dichlorobenzene were located in general positions, and one more such molecule, disordered about the inversion center, was found in the difference Fourier map. One of the two *o*-dichlorobenzene molecule appeared to be disordered. All disordered atoms in the crystal structure of **II** were refined with isotropic thermal parameters. All H atoms were placed geometrically and included in the refinement using a riding model. The refinement converged to $wR_2 = 0.1074$ and $GOF = 0.733$ for all independent reflections ($R_1 = 0.0543$ was calculated against F for a total of 10492 observed reflections with $I > 2\sigma(I)$); the number of refined parameters was 1127. All calculations were performed with SHELXTL-97.^[27]

CCDC-202941 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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