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Synthesis of the phosphino–fullerene $PPh_2(o-C_6H_4)(CH_2NMeCH)C_{60}$ and its function as an η^1 -P or η^3 -P,C₂ ligand[†]

Chia-Hsiang Chen, Chi-Shian Chen, Huei-Fang Dai and Wen-Yann Yeh*

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Following the method of Prato *et al.*, reaction of C_{60} , *N*-methylglycine and *o*-(diphenylphosphino) benzaldehyde affords PPh₂(*o*-C₆H₄)(CH₂NMeCH)C₆₀ (1) in moderate yield. Compound 1 reacts with W(CO)₄(NCMe)₂ to produce W(CO)₄(η^3 -PPh₂(*o*-C₆H₄)(CH₂NMeCH)C₆₀) (2), through coordination of the phosphine group and one 6 : 6-ring junction of fullerene. Reaction of 1 and Os₃(CO)₁₁(NCMe) affords Os₃(CO)₁₁(PPh₂(*o*-C₆H₄)(CH₂NMeCH)C₆₀) (3), which undergoes a cluster fragmentation reaction in refluxing toluene to produce Os(CO)₃(η^3 -PPh₂(*o*-C₆H₄)(CH₂NMeCH)C₆₀) (4). Thermal reaction of 1 and Os₃(CO)₁₂ affords 3 and 4. On the other hand, reaction of 1 and Ru₃(CO)₁₂ yields only the mononuclear complex Ru(CO)₃(η^3 -PPh₂(*o*-C₆H₄)(CH₂NMeCH)C₆₀) (5). The structures of 1–3 and 5 were determined by an X-ray diffraction study.

Introduction

The discovery of fullerenes in 1985 marked the beginning of a new field of chemical research.¹ Attachment of organometallic complexes to fullerenes is an important area within fullerene chemistry, due to its potential application in biological, magnetic, electronic, catalytic and optical devices.^{2,3} With the development of an extensive organic chemistry of fullerenes, it is now possible to construct a variety of modified fullerenes that incorporate metal-binding groups into their structures.⁴ The syntheses of such fullerene-containing ligands offer the potential to exploit the chemical reactivity, redox and electron acceptor characteristics, photochemical behavior, electron withdrawing properties, and novel structural features that a fullerene group provides.⁵ One of the most valuable preparative methods to functionalize fullerenes is the Prato reaction.⁶ The versatility of this reaction arises from the possibility of introducing different substituents into three different positions of the pyrrolidine ring depending on the use of aldehyde/ketone and respective amino acid.^{2a} Previously, the phosphine-functionalized fullerenes C₆₀H(PR₂) were prepared through addition of phosphide nucleophiles to C₆₀ and subsequent protonation of the resulting anion.⁷ In our continuing interest in phosphine and fullerene chemistry,8 herein we present the synthesis of a new phosphino-fullerene molecule by Prato's method and its complexation with transition metal carbonyls.

Results and discussion

Heating a toluene solution of C_{60} , *N*-methylglycine, and *o*-(diphenylphosphino)benzaldehyde (abbreviated as PCHO)

afforded PPh₂(o-C₆H₄)(CH₂NMeCH)C₆₀ (1) in 34% yield after purification by column chromatography (silica gel) and crystallization from CS_2/n -hexane (eqn (1)). Compound 1 forms a slightly air-sensitive, brown crystalline solid. The molecular ion peak at m/z 1038 agrees with the expected formula. The ¹H NMR spectrum displays multiplets in δ 8.28–7.09 for the aromatic protons, a doublet at δ 6.18 (⁴ J_{P-H} = 8 Hz) for the methynyl proton, two doublets at δ 4.94 and 4.28 ($J_{\rm H-H}$ = 9 Hz) for the diastereotopic methylene protons, and a singlet at δ 2.57 for the methyl protons. The ³¹P resonance of 1 at δ -19.47 is 8.5 ppm upfield of PCHO (δ –11.0), but is *ca*. 50 ppm shielded relative to the fullerene-bound phosphine in $(PPh_2)C_{60}H$ (δ 30.1).⁷ The molecular structure of **1** is illustrated in Fig. 1. It appears that a pyrrolidine unit is fused with one 6:6-ring junction of C_{60} molecule. The distances C21-C22 = 1.571(6) Å, C22-C23 = 1.593(6) Å and C19-C23 = 1.614(6) Å are typical C–C single bonds, while the remaining C–C lengths of C_{60} are av. 1.38 Å (6:6-junctions) and 1.45 Å (6:5-junctions). The C22 and C23 atoms are sp³ hybridized and show a distorted tetrahedral bonding, where the C-C-C angles centered on the C22 atom are in the range 102.9(3)-113.6(4)°, and on the C23 atom are 103.1(3)–111.7(3)°. The pyrrolidine ring displays an envelope shape, of which the C19, C21, C22 and C23 atoms are coplanar with the N1 atom 0.66 Å away from the plane, and the N1-C20 and C19-C18 bonds occupy the equatorial positions.

Compound 1 has the tertiary phosphine linked to a rigid fullerene backbone. Treatment of 1 with a slight excess of $W(CO)_4(NCMe)_2$ in hot toluene resulted in displacement of the labile acetonitrile ligands to afford $W(CO)_4(\eta^3-PPh_2(o-C_6H_4))$ $(CH_2NMeCH)C_{60}$ (2) in 51% yield, after purification by column chromatography (silica gel) and crystallization from CS_2/n -hexane (eqn(2)). The IR spectrum of 2 in the carbonyl region displays an absorption pattern similar to the starting

Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, 804, Taiwan

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Fig. 1 ORTEP diagram of 1 with 30% probability ellipsoids. Selected bond distances (Å): C1–P1 1.839(5), C7–P1 1.843(5), C13–P1 1.855(5), C18–C19 1.500(6), C19–C23 1.614(6), C19–N1 1.473(6), C20–N1 1.488(6), C21–N1 1.452(6), C21–C22 1.571(6), C22–C23 1.593(6), C22–C27 1.533(6), C22–C30 1.521(6), C23–C24 1.547(6), C23–C33 1.510(6). Selected bond angles (°): C1–P1–C7 100.9(2), C1–P1–C13 104.5(2), C7–P1–C13 100.3(2), P1–C13–C18 120.2(4), C13–C18–C19 123.7(4), C18–C19–C23 115.3(3), C18–C19–N1 112.0(4), C19–N1–C20 111.4(4), C19–N1–C21 104.3(4), C19–C23–C22 103.1(3), C19–C23–C24 109.5(3), C19–C23–C33 111.7(3), C20–N1–C21 110.8(4), N1–C21–C22 104.6(4), C21–C22–C23 102.9(3), C21–C22–C27 112.0 (4), C21–C22–C30 113.6(4).

compound, indicating retention of the *cis*-L₂W(CO)₄ configuration. The ¹H NMR of **2** closely resembles **1**, except the separation between the two methylene proton resonances (δ 4.51 and 4.30) is 0.45 ppm less than that observed for **1**. The molecular structure for **2** is depicted in Fig. 2, where the W(CO)₄ moiety is *cis*-chelated by the phosphine ligand and one 6 : 6-ring junction of the fullerene, with P1–W1 = 2.563(2) Å, C28–W1 = 2.422(6) Å and C29–W1 = 2.376(6) Å. The W1–C1 bond (1.965(9) Å) is

Fig. 2 ORTEP diagram of **2** with 30% probability ellipsoids. Selected bond distances (Å): C1–W1 1.965(9), C2–W1 2.042(8), C3–W1 2.016 (7), C4–W1 2.013(8), P1–W1 2.563(2), C28–W1 2.422(6), C29–W1 2.376(6), C23–C27 1.590(9), C25–C26 1.563(9), C26–C27 1.613(9), C26–C34 1.51(1), C27–C28 1.55(1), C28–C29 1.412(9), C29–C33 1.496(9), C33–C34 1.371(9). Selected bond angles (°): P1–W1–C1 163.2(2), P1–W1–C2 92.9(2), P1–W1–C3 80.9(2), P1–W1–C4 89.3(2), P1–W1–C28 88.6(2), P1–W1–C29 122.4(2), C1–W1–C2 85.9(3), C1–W1–C3 82.3(3), C1–W1–C4 91.3(3), C28–W1–C29 34.2(2), C5–P1–C17 105.0(3), C11–P1–C17 100.3(3), C5–P1–W1 111.2(3), C11–P1–W1 115.0(2), C17–P1–W1 120.7(2), C25–C26–C27 103.7(5), C25–C26–C34 116.5(6).

significantly shorter than the other W–CO distances (2.013(8)– 2.042(8) Å), consistent with enhancement of W→CO back donation with the carbonyl group *trans* to a better σ -donating phosphorus atom. Meanwhile, the distance C28–C29 = 1.412(9) Å is elongated (*ca.* 0.03 Å) in comparison with other unperturbed (6:6)-double bonds, and may be attributed to π back donation from the tungsten atom. Apparently, steric constraints of the pyrrolidine group forces the tungsten atom to bind the C=C bond of the same hexagonal ring, causing a substantial distortion surrounding the tungsten atom. Such that the bond angles P1–W1–C3 = 80.9(2)° and C1–W1–C3 = 82.3(3)° are acute, and the *trans* P1–W1–C1 angle becomes 163.2(2)°.



Scheme 1 Reaction of 1 and Os₃(CO)₁₁(NCMe).



We previously described the reaction of $Os_3(CO)_{11}(NCMe)$ and (PPh₂)C₆₀H to give Os₃(CO)₁₁(PPh₂C₆₀H),⁹ which carried out a decarbonylation reaction to produce Os₃(CO)₁₀(PPh₂C₆₀₋ H), with the C=C bond from the adjacent hexagonal ring coordinated to a separate osmium atom (eqn (3)). It is therefore of interest to compare the reactivity of 1 towards Os₃ clusters. Thus, $Os_3(CO)_{11}(NCMe)$ reacted with 1 in hot toluene solution to yield a brown crystalline solid of $Os_3(CO)_{11}(PPh_2(o-C_6H_4))$ (CH₂NMeCH)C₆₀) (3; 33%) after purification by TLC (silica gel) and crystallization from CS₂/n-hexane. On thermolysis in refluxing toluene, 3 underwent a cluster fragmentation reaction to produce the mononuclear complex $Os(CO)_3(\eta^3 - PPh_2(o-C_6H_4))$ (CH₂NMeCH)C₆₀) (4) in 17% yield, together with Os₃(CO)₁₂ and the free ligand 1. There is no evidence for the formation of Os₃(CO)₁₀(PPh₂(o-C₆H₄)(CH₂NMeCH)C₆₀). Alternatively, treating 3 with one equivalent of Me₃NO (to remove a CO ligand) under milder conditions (toluene solution at 60 °C) also produced 4 and $Os_3(CO)_{12}$. These results are summarized in Scheme 1. Direct thermal reaction of $Os_3(CO)_{12}$ and 1 in refluxing toluene solution afforded a mixture of 3 and 4.

The structure of 3 was determined by a single-crystal X-ray diffraction study. There are two independent but structurally similar complexes in the asymmetric unit, with the ORTEP diagram of one shown in Fig. 3. It is derived from the mother molecule $Os_3(CO)_{12}$ by replacing an equatorial carbonyl group with a phosphine ligand. The Os1-P1 bond is slightly tilted from the trimetallic plane by 2.2°. The Os₃ unit forms an isosceles triangle with the Os1–Os2 distance (2.923(1) Å) being slightly longer (ca. 0.03 Å) than the other two Os-Os bonds. The average Os–Os distance for 3 (2.902 Å) is ca. 0.03 Å longer than that determined for $Os_3(CO)_{11}(\eta^2-C_{60})$,¹⁰ and may be attributed to the stronger net donor but weaker acceptor capability of phosphine compared with olefin. The Os1, Os2 and Os3 atoms are each linked to three, four and four terminal carbonyl groups. Individual Os–CO distances range from 1.78(3) Å to 2.05(3) Å, C-O distances range from 1.08(3) Å to 1.24(3) Å, and the Os-C-O angles are in the range 166(2)-178(2)°. The axial carbonyls are roughly orthogonal to the Os₃ surface and eclipsed to each other.

Different reactivity of $(PPh_2)C_{60}H$ and **1** towards the Os₃ clusters can be rationalized by the configurations shown in Fig. 4. Apparently, the P–Os bond of Os₃(CO)₁₁(PPh₂C₆₀H) can rotate to place an adjacent osmium atom nearby one 6 : 6-junction of the fullerene and facilitate their ligation. In contrast, the Os₃ cluster of **3** is far away from the fullerene surface, and only the osmium atom bonded to the phosphine group can interact with fullerene, likely generating a sterically congested intermediate, which then carries out a cluster fragmentation reaction to release the strains and form **4**.

We then investigated the reaction of 1 and $Ru_3(CO)_{12}$, which proceeded in benzene solvent at 80 °C to produce only the





Fig. 3 ORTEP diagram of **3** with 30% probability ellipsoids. Selected bond distances (Å): C23–P1 1.86(3), C29–P1 1.85(2), C35–P1 1.83(2), P1–Os1 2.393(6), Os1–Os2 2.923(1), Os1–Os3 2.893(2), Os2–Os3 2.890(2), C44–C45 1.55(3). Selected bond angles (°): Os1–Os2–Os3 59.68(4), Os1–Os3–Os2 60.72(4), Os2–Os1–Os3 59.60(4), P1–Os1–Os2 101.8(1), P1–Os1–Os3 161.3(1), Os1–P1–C23 114.4(9), Os1–P1–C29 117(1), Os1–P1–C35 112.3(7), C23–P1–C29 101(1), C23–P1–C35 104(1), C29–P1–C35 107(1), P1–C35–C40 136(2), C41–C45–C44 103(2), C43–C44–C45 105(2).



Fig. 4 Comparison for the structures of 3 and $Os_3(CO)_{11}(PPh_2HC_{60})$.

mononuclear complex Ru(CO)₃(η^3 -PPh₂(*o*-C₆H₄)(CH₂NMeCH) C₆₀) (**5**) in 45% yield (eqn (4)). Compound **5** forms an airstable, dark green solid. Its IR spectrum in the carbonyl region displays three absorptions at 2076, 2004 and 1981 cm⁻¹. The molecular structure of **5** (Fig. 5) contains a ruthenium atom in a distorted trigonal bipyramidal geometry, where the phosphorus atom and one 6 : 6-junction of the fullerene are bonded to two equatorial sites, with P1–Ru1 = 2.417(4) Å, C27–Ru1 = 2.24(2) Å and C28–Ru1 = 2.18(1) Å, and the C27 and C28 atoms are displaced from the (P1, Ru1, C2) plane oppositely by 0.1 Å. The equatorial P1–Ru1–C2 angle (108.1(6)°) and the axial C1–Ru1– C3 angle (169.1(9)°) are 12° deviated from the ideal value of 120° and 180°, respectively, apparently arising from steric constraints of the ligands.



Fig. 5 ORTEP diagram of 5 with 30% probability ellipsoids. Selected bond distances (Å): C1–Rul 1.89(3), C2–Rul 1.93(2), C3–Rul 1.93(2), P1–Rul 2.417(4), C27–Rul 2.24(2), C28–Rul 2.18(1), C22–C26 1.59 (2), C24–C25 1.55(2), C25–C26 1.64(2), C26–C27 1.55(2), C27–C28 1.42(2), N1–C22 1.44(2), N1–C23 1.47(2), N1–C24 1.48(2). Selected bond angles (°): P1–Ru1–C1 95.2(6), P1–Ru1–C2 108.1(6), P1–Ru1–C3 91.2(6), P1–Ru1–C27 97.9(4), P1–Ru1–C28 135.0(4), C1–Ru1–C2 84.1(9), C1–Ru1–C3 169.1(9), C2–Ru1–C3 85.6(9), C27–Ru1–C28 37.5(6), C4–P1–C10 101.4(7), C4–P1–C16 103.0(7), C10–P1–C16 102.7(7).



Table 1UV-Vis data of C_{60} and 1–5

Compound	λ_{\max} , nm (ε , 10 ⁻³ M ⁻¹ cm ⁻¹)			
C ₆₀ 1 2 3	230 (190), 257 (352), 330 (92), 406(5) 228 (160), 256 (180), 308 (60), 326 (56) 229 (195), 253 (190), 349 (45), 415(22), 438(21) 231 (239), 256 (258), 312 (96), 330 (85), 407(20), 431			
4 5	(15) 228 (256), 255 (203), 330 (72) 235 (176), 255 (166), 330 (60)			



Fig. 6 Absorption spectra of C_{60} and 1–5 in dichloromethane.

Compound **4** forms an air-stable, green solid. The molecular ion peak at m/z 1314 (¹⁹²Os) is the combination of **1** and one Os(CO)₃ moiety. The IR spectrum in the carbonyl region displays three peaks at 2076, 1996 and 1973 cm⁻¹, with an absorption pattern almost identical to that of **5**. The ³¹P resonance at δ -16.03 is 21 ppm upfield of **3** (δ 5.05). Though the structure of **4** was not determined, the Os(CO)₃ unit is presumed to link to the phosphine ligand and one 6:6-junction of fullerene, in a fashion similar to **5**.

The UV-Vis spectra of C₆₀ and **1–5** in dichloromethane (10⁻⁵ M) are displayed in Fig. 6, with the data summarized in Table 1. The spectral features are similar where the absorptions between 250 and 410 nm are due to $\pi \rightarrow \pi^*$ transitions of fullerene and phenyl groups,¹¹ whereas those between 410 and 500 nm are mainly arising from MLCT transitions. These compounds contain a redox-active fullerene core, and their electrochemical properties were measured by cyclic voltammetry in dry, oxygen-free CS₂/CH₂Cl₂ (3 : 2, v/v) solution at 27 °C (Fig. 7). CS₂ was added as the co-solvent to improve the solubility of the complexes. Under these conditions, C₆₀ has three consecutive reduction waves within the solvent cutoff, corresponding to the C₆₀^{-/2-/3-} states.¹² The first reduction potential for the free ligand **1** is shifted cathodically by 182 mV compared to C₆₀.



Fig. 7 Cyclic voltammograms for C₆₀, **1**, **2**, **3** and **5** in carbon disulfide/dichloromethane (3 : 2, v/v). The potential was scanned at 10 mV s⁻¹ at 27 °C, with arrows indicating the direction of current. The potentials are *vs.* the Fc/Fc⁺ couple.

This can be attributed to the added pyrrolidine that decreases the electron affinity of the C_{60} sphere.^{2a} The first reduction potentials for **2** and **3** are comparable, *ca.* 70 mV more positive than **1**, and can be ascribed to donation of electrons to the metal carbonyl moieties. Compound **5** exhibits an irreversible two-electron reduction at -1315 mV, which is likely associated with reduction of the ruthenium metal.¹³

In conclusion, we have synthesized a new phosphine-functionalized fullerene molecule 1 by Prato's method. Compound 1 can act as an η^1 -P ligand in 3, or as an η^3 -P,C₂ chelating agent in 2, 4 and 5 (bite angle 90–120°), demonstrating a flexible binding capacity. The latter bonding mode is contrary to the (PPh₂)C₆₀H molecule, which prefers an η^3 -P,C₂ bridging mode in coordination to Os₃ clusters. The versatile bonding properties of 1 are applicable to split polynuclear complexes, or serve as a hemilabile chelating agent to alter the activity of the bound metal centers and may find an application in homogeneous catalytic systems.

Experimental section

General methods

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. $W(CO)_4(NCMe)_2^{14}$ and $Os_3(CO)_{11}(NCMe)^{15}$ were prepared as described in the literature. *N*-methyl glycine (TCI), PCHO (Aldrich), C₆₀ (99%; Bucky USA), Os₃(CO)₁₂ and Ru₃(CO)₁₂ (Strem) were used as received. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded on a Jasco FT/IR-4100 IR spectrometer. ¹H and ³¹P spectra were obtained on a Bruker AVANCE-300 spectrometer at 300 and 121.5 MHz. UV-Vis spectra were recorded from 200 to 700 nm in dichloromethane

by using a 1.0 cm quartz cell with an Agilent 8452 spectrophotometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded on a Bruker Microflex-LT mass spectrometer. High-resolution mass spectra (HRMS) were measured with Finnigan/Thermo Quest MAT and JMS-700 HRMS mass spectrometers. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chung-Hsing University, Taichung, Taiwan.

Synthesis of 1

C₆₀ (120 mg, 0.167 mmol), N-methyl glycine (16 mg, 0.18 mmol) and PCHO (240 mg, 0.828 mmol) were placed in an oven-dried 250 mL Schlenk flask, under a dinitrogen atmosphere. Toluene (90 mL) was introduced into the flask via a syringe, and the solution was heated to reflux for 4 h. The solution was cooled to room temperature, dried under vacuum, and the residue was subjected to column chromatography (silica gel). with toluene/n-hexane (3:2, v/v) as eluant. Isolation of the material forming the second brown band gave brown crystals of PPh₂(o-(C₆H₄)(CH₂NMeCH)C₆₀ (1; 59 mg, 34% based on C₆₀) after crystallization from CS₂/n-hexane. ¹H NMR (CD₂Cl₂, 25 °C): δ 8.28 (m, 1H, C₆H₄), 7.09-7.54 (m, 13H, Ph, C₆H₄), 6.18 (d, 1H, $J_{P-H} = 8.1$ Hz, CH), 4.94 (d, 1H, $J_{H-H} = 9.3$ Hz, CH₂), 4.28 (d, 1H, J_{H-H} = 9.3 Hz, CH₂), 2.57 (s, 3H, CH₃). ³¹P {¹H} NMR (CD₂Cl₂, 25 °C): δ –19.47 (s). HRMS (FAB) Calcd for $C_{81}H_{21}N_1P_1$ (MH⁺): 1038.1412. Found: 1038.1426.

Reaction of 1 and W(CO)₄(NCMe)₂

Compound 1 (37 mg, 0.036 mmol), W(CO)₄(NCMe)₂ (26 mg, 0.069 mmol) and toluene (6 mL) were introduced into a 25 ml Schlenk flask under a dinitrogen atmosphere. The flask was placed in an oil bath at 100 °C for 1 h. The solvent was removed under vacuum and the residue subjected to column chromatography (silica gel), with carbon disulfide/dichloromethane/nhexane (2:1:1, v/v) as eluant. Isolation of the material forming the second green band afforded dark green crystals of $W(CO)_4(\eta^3 - PPh_2(o-C_6H_4)(CH_2NMeCH)C_{60})$ (2; 24 mg, 51%) based on C₆₀) after crystallization from CS₂/n-hexane. MS (MALDI) m/z 1277 (M⁺ – 2CO, ¹⁸⁴W); IR (CS₂) ν (CO) 2039 s, 1946 s, 1919 s cm⁻¹; ¹H NMR (CD₂Cl₂+CS₂, 25 °C) δ 7.33–8.03 (m, 14H, Ph, C₆H₄), 6.27 (d, 1H, $J_{P-H} = 6$ Hz, CH), 4.51 (d, 1H, J_{H-H} = 9.3 Hz, CH₂), 4.30 (d, 1H, J_{H-H} = 9.3 Hz, CH₂), 2.30 (s, 3H, CH₃); ³¹P{¹H} NMR (CD₂Cl₂+CS₂, 25 °C) δ 0.76 (s, with ¹⁸³W satellites, $J_{W-P} = 224.2$ Hz). Anal. Calcd for C₈₅H₂₀O₄NPW: C, 76.54; H, 1.51; N, 1.05. Found: C, 76.50; H, 2.01; N, 1.00%.

Reaction of 1 and Os₃(CO)₁₁(NCMe)

Compound 1 (13 mg, 0.013 mmol), $Os_3(CO)_{11}(NCMe)$ (11 mg, 0.012 mmol) and toluene (5 mL) were introduced into a 25 ml Schlenk flask under a dinitrogen atmosphere. The flask was placed in an oil bath at 85 °C for 66 h. The solvent was removed under vacuum and the residue subjected to TLC, eluting with carbon disulfide. Isolation of the material forming the first yellow band gave $Os_3(CO)_{12}$ (1.7 mg, 16%). Isolation of the

material forming the third brown band yielded brown crystals of $Os_3(CO)_{11}(PPh_2(o-C_6H_4)(CH_2NMeCH)C_{60})$ (**3**; 7.5 mg, 33% based on Os atoms) after crystallization from CS₂/n-hexane. MS (MALDI) *m/z* 1837 (M⁺ – 3CO, ¹⁹²Os); IR (cyclohexane) *v*(CO) 2106 m, 2084 vw, 2055 s, 2035 s, 2019 vs, 1999 w(sh), 1992 m, 1979 m, 1955 w cm⁻¹; ¹H NMR (CDCl₃, 25 °C) δ 8.49 (m, 1H, C₆H₄), 7.48–7.85 (m, 13H, Ph, C₆H₄), 5.04 (s, 1H, CH), 4.69 (d, 1H, *J*_{H–H} = 9.3 Hz, CH₂), 3.65 (d, 1H, *J*_{H–H} = 9.3 Hz, CH₂), 2.69 (s, 3H, CH₃); ³¹P{¹H} NMR (CDCl₃, 25 °C) δ 5.05 (s). Anal. Calcd for C₉₂H₂₀O₁₁NOs₃P: C, 57.65; H, 1.05; N, 0.73. Found: C, 58.03; H,1.25; N, 0.69%.

Thermolysis of 3

Compound 3 (12 mg, 0.0063 mmol) and toluene (10 mL) were placed in a 50 mL Schlenk tube under a dinitrogen atmosphere, and the solution was refluxed for 12 h. The solvent was removed under vacuum, and the residue was subjected to TLC, eluting with carbon disulfide/dichloromethane/n-hexane (4:1:1, v/v). The first yellow band gave $Os_3(CO)_{12}$ (1 mg, 18%), the second brown band yielded the free ligand 1 (2.4 mg, 37%), and the green band afforded $Os(CO)_3(\eta^3 - PPh_2(o - C_6H_4))$ third (CH₂NMeCH)C₆₀) (4; 1.4 mg, 17%). MS (ESI) *m*/*z* 1314 (MH⁺, ¹⁹²Os); IR (methylcyclohexane) v(CO) 2076 m, 1996 s, 1973 s cm⁻¹; ¹H NMR (CD₂Cl₂, 25 °C) δ 7.13–7.96 (m, 14H, Ph, C_6H_4), 5.68 (d, 1H, J_{P-H} = 3.6 Hz, CH), 4.45 (d, 1H, J_{H-H} = 9.6 Hz, CH₂), 3.91 (d, 1H, J_{H-H} = 9.6 Hz, CH₂), 2.28 (s, 3H, CH₃);³¹P{¹H} NMR (CD₂Cl₂, 25 °C): δ -16.03 (s). HRMS (ESI) Calcd for $C_{84}H_{21}O_3NOsP$ (MH⁺): 1314.0868. Found: 1314.0889.

Reaction of 1 and Os₃(CO)₁₂

Compound 1 (50 mg, 0.048 mmol), $Os_3(CO)_{12}$ (43 mg, 0.048 mmol) and toluene (15 mL) were introduced into a 50 ml Schlenk flask under a dinitrogen atmosphere. The solution was heated to reflux for 3 h. The solvent was removed under vacuum and the residue subjected to TLC, eluting with carbon disulfide. Isolation of the material forming the yellow band recovered $Os_3(CO)_{12}$ (29.4 mg, 68%), the brown band gave compound 3 (23.7 mg, 26%), and the green band gave compound 4 (10 mg, 16%).

Reaction of 1 and Ru₃(CO)₁₂

Compound **1** (51 mg, 0.049 mmol), $\text{Ru}_3(\text{CO})_{12}$ (31 mg, 0.049 mmol) and benzene (14 mL) were introduced into a 50 ml Schlenk flask under a dinitrogen atmosphere. The flask was placed in an oil bath at 80 °C for 1 h. The solvent was removed under vacuum and the residue subjected to TLC, eluting with carbon disulfide/dichloromethane/n-hexane (4 : 1 : 1, v/v). Isolation of the material forming the first yellow band recovered $\text{Ru}_3(\text{CO})_{12}$ (12.9 mg, 25%), and the third green band afforded $\text{Ru}(\text{CO})_3(\eta^3-\text{PPh}_2(o-\text{C}_6\text{H}_4)(\text{CH}_2\text{NMeCH})\text{C}_{60})$ (**5**; 26.4 mg, 45%). MS (MALDI) *m/z* 1167 (M⁺ – 2CO, ¹⁰²Ru); IR (methyl-cyclohexane) *v*(CO) 2076 m, 2004 s, 1981 s cm⁻¹; ¹H NMR (CDCl₃ + CS₂, 25 °C) δ 7.12–7.94 (m, 14H, Ph, C₆H₄), 5.72 (d, 1H, *J*_{P-H} = 4.5 Hz, CH), 4.44 (d, 1H, *J*_{H-H} = 9.3 Hz, CH₂), 3.88

Table 2Crystallographic data for compounds 1–3 and 5

	1	2	3	5
Formula	C ₈₁ H ₂₀ NP	C ₁₇₀ H ₄₀ N ₂ O ₈ P ₂ W ₂	C ₉₂ H ₂₀ NO ₁₁ Os ₃ P	C ₁₆₈ H ₄₂ N ₂ O ₆ P ₂ Ru ₂
Cryst solvent		CS_2		$3CS_2 + H_2O$
Formula weight	1037.95	2743.81	1916.66	2692.51
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a/Å	23.620(3)	10.0412(13)	17.4180(16)	10.0828(13)
b/Å	14.2383(18)	16.747(2)	19.6754(19)	16.351(2)
c/Å	30.475(4)	17.295(2)	23.140(2)	16.5332(19)
$\alpha/^{\circ}$	90	62.545(2)	106.174(6)	84.296(7)
$\beta / ^{\circ}$	109.428(8)	76.825(2)	95.677(6)	77.770(7)
$\gamma/^{\circ}$	90	89.449(2)	90.006(7)	77.840(9)
$U/Å^3$	9665(2)	2497.5(5)	7575.8(12)	2599.8(6)
T/K	200(2)	200(2)	200(2)	200(2)
Ζ	8	1	4	1
μ , mm ⁻¹	0.114	2.457	5.103	0.521
R_1, wR_2	0.0915, 0.2671	0.0504, 0.0903	0.1668, 0.3611	0.1196, 0.3090
GOF on F^2	1.086	0.847	1.053	1.059

(d, 1H, $J_{H-H} = 9.6$ Hz, CH₂), 2.29 (s, 3H, CH₃); ³¹P{¹H} NMR (CDCl₃ + CS₂, 25 °C) δ 17.41 (s). Anal. Calcd for C₁₇₁H₄₂O₇N₂P₂Ru₂S₆: C, 76.28; H, 1.57; N, 1.04. Found: C, 75.90; H, 2.48; N, 0.95%.

Electrochemical measurements

Electrochemical measurements were taken with a CV 50 W system. Cyclic voltammetry was performed with a Pt button working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode. The experiments were carried out with 1 mM solution of **1–3** and **5**, respectively, in dry carbon disulfide/dichloromethane (3 : 2, v/v) solvents containing 0.1 M $(n-C_4H_9)_4$ NPF₆ as the supporting electrolyte. Potential was scanned at 10 mV s⁻¹ at 27 °C. Under these conditions, ferrocene shows a reversible one-electron redox wave with $E_{1/2} = 420$ mV.

Structure determination for 1–3 and 5

The crystals of 1-3 and 5 suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 1.42 to 25.00° for 1, 2.20 to 25.04° for $2 \cdot CS_2$, 1.57 to 25.03° for **3** and 1.26 to 25.04° for $5 \cdot 1.5 \text{CS}_2 \cdot 0.5 \text{H}_2 \text{O}$. Of the 25 609, 20 007, 53 527 and 23 286 reflections collected, 8395, 8757, 25085 and 8638 reflections were independent for 1, $2 \cdot CS_2$, 3 and $5 \cdot 1.5CS_2 \cdot 0.5H_2O$, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. Heavily disordered solvent molecules were removed from the diffraction data for 1 (maybe $2 \sim 3 \text{ H}_2\text{O}$) and 3 (maybe 2 H₂O) using the SQUEEZE program.¹⁶ The structures were solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package. The data collection and refinement parameters are presented in Table 2. Although the structure determinations for 1, 3 and 5 were based on poor quality data sets, the bonding features for these compounds should be unambiguous. Attempts to grow better crystals, however, were not successful.

CCDC reference number 843722 for **1**, 843720 for **2**, 843721 for **3** and 843723 for **5**.

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