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Syntheses and characterization of tricarbonyl tungsten complexes containing 1,1′-bis(diphenylphosphino)ferrocene ligand

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Abstract

Treatment of $W(CO)_3(NCCH_3)_3$ with 1,1′-bis(diphenylphosphino)ferrocene (dppf) affords $W(CO)_3(NCCH_3)(\eta^2\text{-dppf})$ (**1**) in 85%) yield. Reaction of **1** with I_2 produces a seven-coordinated complex $W(CO)_3(I)_2(\eta^2\text{-dppf})$ (**2**), which is further oxidized by H_2O_2 to give $W(CO)_3(I)_2(\eta^2\text{-dppf(=O)})$ (**3**) in 80% yield. Compound **1** reacts with PMe_3 forming *fac*-$W(CO)_3(\eta^2\text{-dppf})(PMe_3)$ (**4**) in 90% yield. However, reaction of **1** with PPh_2Cl generates *fac*-$W(CO)_3(\eta^2\text{-dppf})(PPh_2H)$ (**5**) and *fac*-$W(CO)_3(\eta^2\text{-dppf})(PPh_2OH)$ (**6**) after separation of the reaction mixture by TLC. The structures of compounds **1** and **3** have been characterized by X-ray diffraction methods.

Keywords: Tungsten

1. Introduction

The use of ferrocenylphosphines as ligands in organometallic and transition metal cluster complexes has received much attention recently owing to their varied modes of coordination towards metal atoms [1] and possible catalytic activities of many of their complexes [2]. The unique ability of this metalloligand to modify its steric bite by ring twisting and tilting make it capable of adapting to different geometric requirements of metal centers. We have been interested in the potential variability of ferrocenylphosphines compared with the bisphosphine ligands of the type $R_2P(CH_2)_nPR_2$ [3]. Here we report the syntheses and characterization of several tricarbonyl tungsten 1,1′-bis(diphenylphosphino)ferrocene (dppf) complexes (Scheme 1).

2. Results and discussion

Treatment of $W(CO)_3(NCCH_3)_3$ with dppf ligand in acetonitrile solution at 28°C affords *fac*-$W(CO)_3(NCCH_3)(\eta^2\text{-dppf})$ (**1**) in 85% yield. A closely related compound *fac*-$W(CO)_3(NCCH_3)(\eta^2\text{-dppm})$ (dppm = $(PPh_2)_2CH_2$) was previously prepared and structurally characterized by Darensbourg *et al.* [4]. The molecular structure of compound **1**, shown in Fig. 1, appears as a slightly distorted octahedron. The dppf ligand is chelated to the tungsten atom with a bite angle of 98.05(6)°, which is comparable with those reported for $Mo(CO)_4(\eta^2\text{-dppf})$ (95.28(2)°) [5] and $(\eta^5\text{-}C_5H_4Me)Mn(CO)(\eta^2\text{-dppf})$ (99.3(12)°) [6], but significantly larger than the bite angle of $(Ph_2P)_2(CH_2)_n$ ligands in *fac*-$W(CO)_3(NCCH_3)(\eta^2\text{-dppm})$ (67.5(1)°) [4], $Mo(CO)_4(\eta^2\text{-dppm})$ (67.3(1)°) [7], and $Mo(CO)_4(\eta^2\text{-dppe})$ (80.2(1)°) [8]. The two cyclopentadienyl rings are eclipsed and tilted inward by 2.7°, where the C(25)–P(1) and C(30)–P(2) vectors are twisted by 35.5°. The $^{31}P\{^1H\}$ NMR spectrum presents a single resonance at δ 22.4 with ^{183}W satellite ($^1J_{W-P} = 234$ Hz), consistent with the facial configuration for compound **1**.

Reaction of compound **1** with diiodine results in the oxidative addition of I_2 to the tungsten center to generate a seven-coordinated complex $W(CO)_3(I)_2(\eta^2\text{-dppf})$ (**2**). Compound **2** has been previously reported by Baker *et al.* [9], but prepared by a different process from the reaction of $W(CO)_3(I)_2(NCMe)_2$ with dppf ligand. Exposure of **2** in benzene solution to air leads

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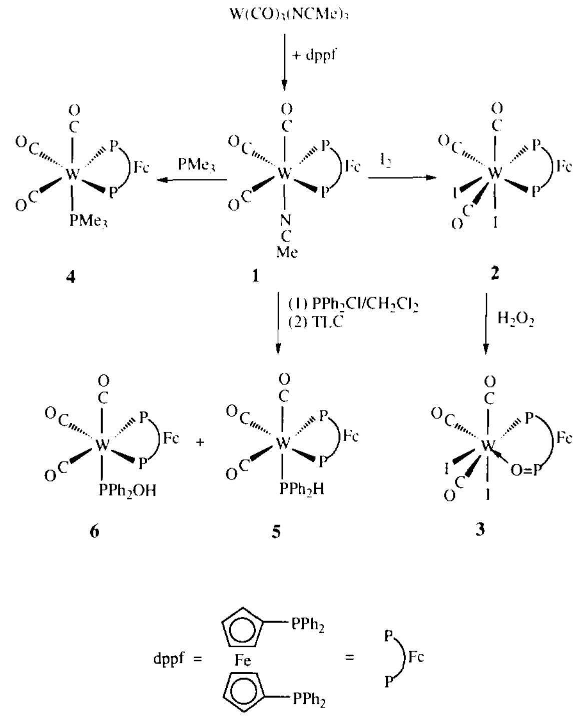

Scheme 1. Syntheses and characterization of tricarbonyl tungsten complexes.

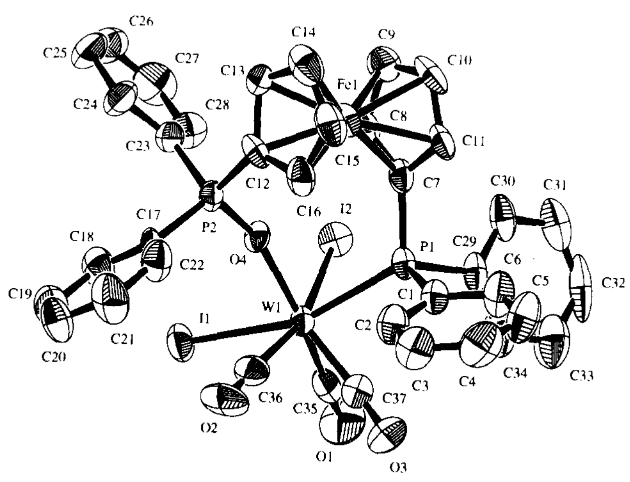

Fig. 2. Molecular structure of compound **3**, showing the atomic labeling used in the text.

to gradual decomposition and a phosphine oxide complex $W(CO)_3(I)_2(\eta^2\text{-dppf(=O)})$ (**3**) is isolated in small yield (< 5%). However, compound **3** can be obtained in 80% yield by slow addition of H_2O_2 (3% in water) in equimolar proportions to a dichloromethane solution of **2** at 25°C [10]. Oxidation of coordinated phosphines to form coordinated phosphine oxides is known. For instance, Gal and Bolder [11] showed that the reaction of $(PPh_3)_2Rh[Ph_2PC(S)NPh]$ with O_2 in the presence of additional PPh_3 gave $O{=}PPh_3$ and *cis*-$(PPh_3)_2$-$Rh(O_2)[Ph_2P(O)C(S)NPh]$, while Schmidt and Yoke [12] reported the autoxidation of $CoCl_2(PEt_3)_2$ in organic solvents to afford $CoCl_2(PEt_3)(O{=}PEt_3)$ and $CoCl_2(O{=}PEt_3)_2$.

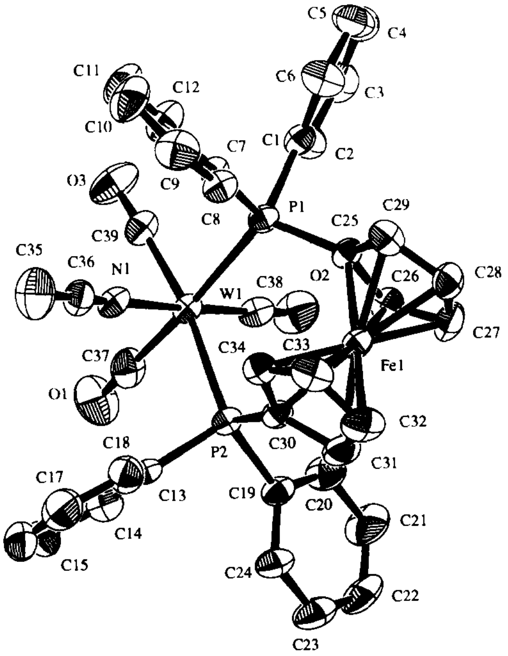

Fig. 1. Molecular structure of compound **1**, showing the atomic labeling used in the text.

The $^{31}P\{^1H\}$ NMR spectrum of **3** presents two distinct resonances at δ 50.6 and δ 14.5, assigned to the phosphoryl (P=O) and the unoxidized phosphorus atoms, respectively. The molecular structure of **3** is illustrated in Fig. 2. Based on the angles subtended at the tungsten atom, the geometry of **3** can be described as a distorted capped octahedron [13] with a carbonyl group (C37) in the capping position, two carbonyl (C35, C36) and one phosphorus atom (P1) in the capped face, and two iodine atoms (I1, I2) and the phosphoryl oxygen atom (O4) in the uncapped face. Fig. 3 shows the projection of compound **3** down the W–C(37) vector. The three carbonyl ligands are terminally bonded to the tungsten atom (∠ W–C–O = 175–178°), whereas the W–CO bond to the carbon in the capping position is shorter by 0.06 Å than the bonds to the capped face. The phosphoryl group is coordinated to the tungsten atom with distances W–O(4) = 2.131(7) Å and P(2)–O(4) = 1.509(7) Å, suggesting the presence of a phosphorus–oxygen double bond (cf. P=O = 1.521(8), 1.506(2), and 1.485(8) Å in $W(CO)_5(\eta^1\text{-(O)PPh}_2\text{CHPPh}_3)$ [14], $MoCl_3(O)(\eta^2\text{-PEt}_2CH_2CH_2P(O)Et_2)$ [15], and $CpFe(CO)I(\eta^1\text{-PPh}_2CH_2P(O)Ph_2)$ [10], respectively) and an oxygen–tungsten dative bond (cf. W–O = 2.200(7) Å in $W(CO)_5(\eta^1\text{-(O)PPh}_2\text{CHPPh}_3)$ [14]). The enlarged angle ∠ W–O(4)–P(2) = 160.2(5)° in comparison with other complexes containing η^2-dppm(O) or η^2-dppe(O) ligands (ca. 140°) [15,16] is

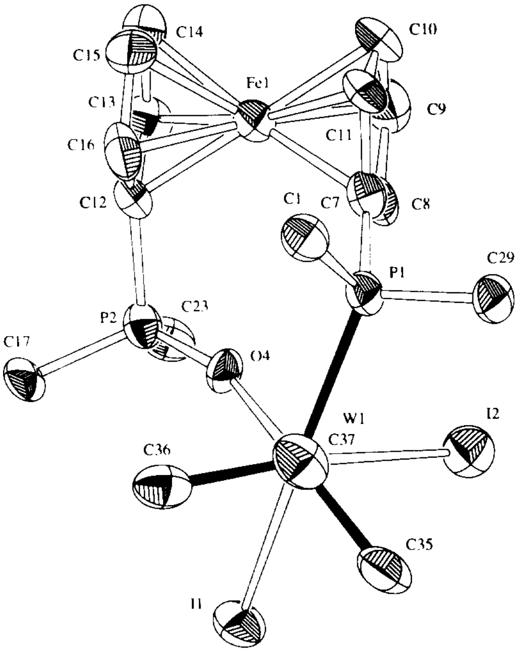

Fig. 3. Projection of compound 3 down the W–C(37) bond, showing the capped octahedral coordination about the tungsten atom.

likely due to the steric demand of the ferrocene group.

The acetonitrile moiety in **1** can be readily replaced by the phosphine ligands. For example, compound **1** reacts with PMe_3 at 28°C affording *fac*-$W(CO)_3(\eta^2$-dppf)(PMe_3) (**4**) in 90% yield. The facial geometry is indicated by the IR band pattern observed in the CO stretching region [4,17], which is comparable with that recorded for compound **1**. The $^{31}P\{^1H\}$ NMR spectrum of **4** is also consistent with the formation of the facial isomer, showing a doublet signal at δ 18.3 ($^2J_{P-P} = 25$ Hz) and a triplet signal at $\delta - 48.38$, assigned to the η^2-dppf and PMe_3 ligands, respectively. The meridional isomer, which should display three sets of multiplet signals, is not observed.

Treating compound **1** with PPh_2Cl and subsequent separation of the reaction mixture by thin layer chromatography (TLC (silica gel)), however, leads to *fac*-$W(CO)_3(\eta^2$-dppf)(PPh_2H) (**5**) and *fac*-$W(CO)_3(\eta^2$-dppf)(PPh_2OH) (**6**) in 34% and 32% yield, respectively. Since the $^{31}P\ \{^1H\}$ NMR of compound **1** in CD_2Cl_2 following addition of PPh_2Cl under nitrogen affords a triplet (δ 98.02) and a doublet (δ 17.16, $^2J_{P-P} = 22$ Hz) signal, both accompanied by ^{183}W satellites, the complex *fac*-$W(CO)_3(\eta^2$-dppf)(PPh_2Cl) (**7**) is probably formed initially, although attempts to isolate **7** in pure form have been unsuccessful. After adding a trace amount of water to the NMR tube, the signals corresponding to **6** are observed. It appears that **6** is derived from hydrolysis of **7**, whereas the mechanism leading to **5** remains unclear. The IR spectra of compounds **5** and **6** in the CO stretching region are almost identical and in close agreement with the pattern expected for the facial form. The ^1H NMR spectrum of **5** shows a multiplet in the range δ 7.70–7.10 for the phenyl protons, four broad signals between δ 4.49 and 4.01 for the Cp protons, and a doublet at δ 5.75 with $^1J_{P-H} = 317$ Hz for the proton bonded to the phosphorus atom. The ^{31}P NMR spectrum of **5** presents a doublet of triplet at δ 9.04 with $^2J_{P-P} = 19.5$ Hz and $^1J_{P-H} = 317$ Hz, assigned to the PPh_2H group, and a doublet at δ 18.79, assigned to the dppf group. The ^1H NMR spectrum of **6** resembles that of **5** in the phenyl and Cp protons resonance regions, but the POH signal is not found, presumably due to fast exchange with moisture in the solvent. However, the fast atom bombardment (FAB) mass spectrum of **6** does show the molecular ion signals at $m/z = 1024$ (^{184}W), and a strong broad IR band at 3500 cm^{-1}, assigned to ν(O–H), is observed, consistent with the proposed formulation. The downfield ^{31}P shift of PPh_2OH ligand (δ 101.8) in comparison with PPh_2H (δ 9.04) may be attributed to the more electron-withdrawing hydroxyl group [18].

3. Experimental section

3.1. General procedures

All manipulations were performed on a double-manifold Schlenk line under an atmosphere of dry nitrogen, or in a nitrogen-filled glove box. Solvents were distilled over appropriate drying agents under a nitrogen atmosphere. $W(CO)_3(NCCH_3)_3$ [19] and dppf [20] were prepared by literature methods. PMe_3 (1.0 M in toluene) and PPh_2Cl were purchased from Aldrich and were used without further purification. Thin-layer chromatographic plates were prepared from silica gel (Merck). Infrared spectra were recorded in a 0.10 mm CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. ^1H and $^{31}P\ \{^1H\}$ NMR spectra were obtained on a Varian VXR-300 spectrometer at 300 MHz and 121.4 MHz, respectively. FAB mass spectra were recorded by using a VG-5022 mass spectrometer. Elementary analyses were performed at the National Science Council Regional Instrumentation Center, National Chung-Hsing University, Taichung.

3.2. Preparation of *fac*-$W(CO)_3(NCCH_3)(\eta^2$-*dppf*) (*1*)

$W(CO)_3(NCCH_3)_3$ (0.554 g, 1.42 mmol) and dppf (0.79 g, 1.43 mmol) were placed in a 50 ml Schlenk flask containing a magnetic stirring bar. The flask was capped with a rubber septum stopper, evacuated, and backfilled with a nitrogen atmosphere. 15 ml of dry acetonitrile was added to the flask and the mixture was stirred for 5 h at ambient temperature, forming a yellow precipitate. The supernatant was removed via a cannula, and the product washed with 50 ml of diethyl ether and then dried under vacuum, affording *fac*-W(CO)$_3$(NCCH$_3$)(η^2-dppf) (**1**) (1.041 g, 1.20 mmol) in 85% yield. Mass spectroscopy (FAB) m/z: 863 (M$^+$, ^{184}W), 822 (M$^+$-CH$_3$CN), 822 − 28n (n = 1–3). IR (1,2-C$_2$H$_4$Cl$_2$): ν(CO) 1930vs, 1836s, 1812s cm^{-1}. ^{31}P {^{1}H} NMR (CD$_2$Cl$_2$, 20°C): 22.40 (s, J_{W-P} = 234 Hz) ppm. ^{1}H NMR (CD$_2$Cl$_2$, 20°C): 1.99 (s, 3H, NCMe), 4.32 (s, 2H), 4.37 (s, 2H), 4.40 (s, 2H), 4.43 (s, 2H, C$_5$H$_4$), 7.30–7.70 (m, 20H, Ph) ppm. Anal. found N, 1.87; C, 53.67; H, 3.67. C$_{39}$H$_{31}$NO$_3$P$_2$FeW calc. N, 1.62; C, 54.26; H, 3.62.

3.3. Reaction of W(CO)$_3$(NCCH$_3$)(η^2-dppf) (1) with I$_2$

W(CO)$_3$(NCCH$_3$)(η^2-dppf) (**1**) (0.05 g, 0.058 mmol) and dichloromethane (10 ml) were added to a 50 ml Schlenk flask equipped with a magnetic stirring bar and a rubber serum stopper. The flask was placed in an ice bath, and a solution of iodine (0.015 g, 0.059 mmol) in benzene (5 ml) was added dropwise over a period of 2 h. Hexane (50 ml) was then introduced into the flask, giving an orange–red solid of the known W(CO)$_3$-(I)$_2$(η^2-dppf) (**2**) [9] (0.058 g, 0.054 mmol, 93%).

3.4. Reaction of W(CO)$_3$(I)$_2$(η^2-dppf) (2) with H$_2$O$_2$

W(CO)$_3$(I)$_2$(η^2-dppf) (**2**) (0.058 g, 0.054 mmol) and dichloromethane (10 ml) were placed in a 50 ml Schlenk flask equipped with a magnetic stirring bar and a rubber serum stopper. An aqueous H$_2$O$_2$ solution (3%, 50 μl) was then added with a micro-syringe. The resulting mixture was stirred at 25°C for 10 h. After adding 30 ml of dry hexane, the reaction mixture was allowed to stand at −20°C for 2 h, forming air-stable greenish-red crystals of W(CO)$_3$(I)$_2$(η^2-dppf(=O)) (**3**) (0.049 g, 0.045 mmol, 84%). Mass spectroscopy (FAB) m/z: 1036 (M$^+$-CO). IR (CH$_2$Cl$_2$): ν(CO) 2020m, 1954s, 1892s cm^{-1}. ^{31}P {^{1}H} NMR (CD$_2$Cl$_2$, 20°C): 50.63 (s), 14.5 (br, J_{W-P} = 210 Hz) ppm. ^{1}H NMR (CD$_2$Cl$_2$, 20°C): 3.72 (br, 2H), 4.15 (br, 2H), 4.56 (br, 2H), 4.83 (br, 2H, C$_5$H$_4$), 7.00–8.20 (m, 20H, Ph) ppm.

3.5. Reaction of fac-W(CO)$_3$(NCCH$_3$)(η^2-dppf) (1) with PMe$_3$

Fac-W(CO)$_3$(NCCH$_3$)(η^2-dppf) (**1**) (0.03 g, 0.035 mmol) and 10 ml of dichloromethane were added to a 50 ml Schlenk flask equipped with a magnetic stirring bar and a rubber serum stopper. PMe$_3$ (132 μl, 0.132 mmol) was added with a micro-syringe, and the mixture was stirred at 25°C for 1 h, giving a yellow precipitate. The supernatant was removed by pipette, and the product was washed with fresh hexanes (3 × 3 ml) and then dried under vacuum for 5 h. *Fac*-W(CO)$_3$-(PMe$_3$)(η^2-dppf) (**4**) (0.029 g, 0.032 mmol) was isolated in 90% yield. Mass spectroscopy (FAB) m/z: 898 (M$^+$, ^{184}W), 869 (M$^+$-CO), 822 (M$^+$-PMe$_3$), 822 − 28n (n = 1–3). IR (1,2-C$_2$H$_4$Cl$_2$): ν(CO) 1932 vs, 1836s, 1824s cm^{-1}. ^{31}P {^{1}H} NMR (CD$_2$Cl$_2$, 20°C): −48.38 (t, J_{P-P} = 25 Hz, J_{W-P} = 232 Hz), 18.3 (d, J_{P-P} = 25 Hz, J_{W-P} = 214 Hz) ppm. ^{1}H NMR (CD$_2$Cl$_2$, 20°C): 1.01 (d, 9H, J_{P-H} = 7 Hz, PMe$_3$), 4.1–4.4 (m, 8H, C$_5$H$_4$), 7.30–7.70 (m, 20H, Ph) ppm. Anal. found C, 52.31; H, 4.28. C$_{40}$H$_{37}$O$_3$P$_3$FeW calc. C, 53.48; H, 4.15.

3.6. Reaction of fac-W(CO)$_3$(NCCH$_3$)(η^2-dppf) (1) with PPh$_2$Cl

Fac-W(CO)$_3$(NCCH$_3$)(η^2-dppf) (**1**) (0.03 g, 0.035 mmol) and dichloromethane (10 ml) were added into a 50 ml Schlenk flask equipped with a magnetic stirring bar and a rubber serum stopper. PPh$_2$Cl (0.088 g, 0.4 mmol) was added with a micro-syringe. The mixture was stirred at room temperature for 10 h. The volatile materials were removed under vacuum, and the residue subjected to TLC, eluting with dichloromethane/hexane (1:1, v/v). *Fac*-W(CO)$_3$(η^2-dppf)(PPh$_2$H) (**5**) (0.012 g, 0.012 mmol, 34%) and *fac*-W(CO)$_3$(η^2-dppf)(PPh$_2$OH) (**6**) (0.011 g, 0.011 mmol, 32%) were isolated from the first and second yellow bands, respectively.

Compound **5**: mass spectroscopy (FAB) m/z: 1008 (M$^+$, ^{184}W), 980 (M$^+$-CO), 822 (M$^+$-PPh$_2$H), 822 − 28n (n = 1–3). IR (KBr): ν(CO) 1936vs, 1846s, 1838sh cm^{-1}. ^{31}P {^{1}H} NMR (CD$_2$Cl$_2$, 20°C): 9.04 (t, J_{P-P} =

Table 1
Crystal data and refinement details for compound **1** and compound **3**

	1	**3**
Formula	C$_{39}$H$_{31}$NO$_3$P$_2$FeW	C$_{37}$H$_{28}$I$_2$O$_4$P$_2$FeW
Crystal system	monoclinic	monoclinic
Space group	P2$_1$/n	P2$_1$/c
a (Å)	12.015(9)	10.219(3)
b (Å)	21.497(5)	18.539(4)
c (Å)	13.383(3)	22.424(7)
β (deg)	97.11(3)	98.94(3)
V (Å^3)	3546(2)	4196(2)
Z	4	4
D_{calc} (g cm^{-3})	1.617	1.728
F(000)	1704.00	2072.00
Radiation λ (Å)	Mo Kα 0.71069	Mo Kα 0.71069
T (K)	297	297
μ (cm^{-1})	38.44	46.69
Scan parameter	1.21 + 0.30 tan θ	1.10 + 0.30 tan θ
$2\theta_{max}$ (deg)	50.0	50.0
No. of unique data	5577	5868
No. of data with $I > 3\sigma(I)$	4365	4028
R_F ^{a}	0.032	0.041
R_w ^{a}	0.029	0.055
Goodness of fit	1.96	1.41

[a] $R_F = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$; $R_w = \{\Sigma[\omega(| F_0 | - | F_c |)^2] / \Sigma \omega | F_0 |^2\}^{1/2}$.

19.5 Hz, $J_{W-P} = 224$ Hz), 18.79 (d, $J_{P-P} = 19.5$ Hz, $J_{W-P} = 229$ Hz) ppm. ^{1}H NMR (CD_2Cl_2, 20°C): 4.01 (s, 2H), 4.20 (s, 2H), 4.30 (s, 2H), 4.50 (s, 2H, C_5H_4), 5.75 (d, 1H, $J_{P-H} = 317$ Hz), 7.10–7.70 (m, 30H, Ph) ppm.

Compound **6**: mass spectroscopy (FAB) m/z: 1024 (M^+, ^{184}W), 996 (M^+-CO), 822 (M^+-Ph_2OH), 822–28n (n = 1–3). IR (KBr): ν(O–H) 3500br, ν(CO) 1936vs, 1842s, 1834sh cm^{-1}. ^{31}P {^{1}H} NMR (CD_2Cl_2; 20°C): 17.2 (d, $J_{P-P} = 28$ Hz, $J_{W-P} = 230$ Hz), 101.8 (t, $J_{P-P} =$ 28 Hz, $J_{W-P} = 265$ Hz) ppm. ^{1}H NMR (CD_2Cl_2, 20°C): 4.03 (s, 2H), 4.22 (s, 2H), 4.36 (s, 2H), 4.49 (s, 2H, C_5H_4), 7.10–7.60 (m, 30H, Ph) ppm. Anal. found C, 57.86; H, 4.36. $C_{49}H_{39}O_4P_3FeW$ calc. C, 57.45; H, 3.84.

Table 2
Selected atomic coordinates of compound **1**

Atom	x	y	z	B_{eq}
W(1)	0.22666(2)	0.15117(1)	−0.17112(2)	2.384(6)
Fe(1)	−0.13759(8)	0.11166(4)	−0.25139(7)	2.67(2)
P(1)	0.0543(1)	0.20570(8)	−0.1215(1)	2.41(4)
P(2)	0.1254(1)	0.07654(8)	−0.2985(1)	2.52(4)
O(1)	0.4548(4)	0.0893(3)	−0.1999(4)	5.9(2)
O(2)	0.2445(5)	0.0644(2)	0.0101(3)	5.1(1)
O(3)	0.3839(4)	0.2412(3)	−0.0405(4)	5.4(2)
O(4)	0.5497(7)	0.0343(4)	1.0102(6)	6.0(0)
N(1)	0.2071(4)	0.2145(2)	−0.2974(4)	2.8(1)
C(1)	0.0573(5)	0.2301(3)	0.0066(4)	2.7(2)
C(2)	0.1289(6)	0.2027(3)	0.0792(5)	3.5(2)
C(3)	0.1249(6)	0.2200(4)	0.1761(5)	4.3(2)
C(4)	0.0546(7)	0.2636(4)	0.2004(5)	4.3(2)
C(5)	−0.0189(6)	0.2921(4)	0.1287(5)	4.5(2)
C(6)	−0.0168(6)	0.2751(4)	0.0322(5)	4.0(2)
C(7)	0.0236(5)	0.2810(3)	−0.1827(4)	2.6(1)
C(8)	−0.0600(6)	0.2919(3)	−0.2601(5)	3.2(2)
C(9)	−0.0712(7)	0.3498(4)	−0.3039(5)	4.6(2)
C(10)	−0.0001(7)	0.3967(4)	−0.2731(6)	5.2(2)
C(11)	0.0845(7)	0.3866(4)	−0.1983(6)	5.0(2)
C(12)	0.0965(6)	0.3286(3)	−0.1541(5)	4.1(2)
C(13)	0.1907(6)	0.0824(3)	−0.4129(4)	2.8(2)
C(14)	0.2983(6)	0.0596(3)	−0.4147(5)	4.2(2)
C(15)	0.3510(7)	0.0663(4)	−0.4963(7)	5.4(2)
C(16)	0.2992(9)	0.0955(5)	−0.5776(6)	6.1(3)
C(17)	0.1923(8)	0.1176(4)	−0.5769(6)	5.8(3)
C(18)	0.1376(6)	0.1113(4)	−0.4944(5)	4.0(2)
C(19)	0.1288(5)	−0.0075(9)	−0.2780(5)	2.8(2)
C(20)	0.1331(6)	−0.0313(3)	−0.1841(5)	3.9(2)
C(21)	0.1284(8)	−0.0945(4)	−0.1685(6)	5.3(2)
C(22)	0.1202(7)	−0.1348(3)	−0.2460(6)	4.7(2)
C(23)	0.1172(6)	−0.1126(3)	−0.3393(6)	4.3(2)
C(24)	0.1190(6)	−0.0500(3)	−0.3558(5)	3.5(2)
C(25)	−0.0736(5)	0.1602(3)	−0.1325(4)	2.4(1)
C(26)	−0.0699(6)	0.0951(3)	−0.1117(4)	3.0(2)
C(27)	−0.1808(6)	0.0721(3)	−0.1257(5)	3.8(2)
C(28)	−0.2534(6)	0.1211(4)	−0.1540(5)	3.6(2)
C(29)	−0.1896(6)	0.1753(3)	−0.1568(5)	3.3(2)
C(30)	−0.0230(5)	0.0884(3)	−0.3413(4)	2.5(1)
C(31)	−0.1117(6)	0.0435(3)	−0.3496(5)	3.8(2)
C(32)	−0.2128(6)	0.0749(4)	−0.3805(5)	4.3(2)
C(33)	−0.1886(6)	0.1384(4)	−0.3923(5)	3.8(2)
C(34)	−0.0723(5)	0.1458(3)	−0.3693(4)	3.0(2)
C(35)	0.1687(7)	0.2881(4)	−0.4454(5)	5.6(2)
C(36)	0.1910(6)	0.2472(3)	−0.3623(5)	3.3(2)
C(37)	0.3677(6)	0.1133(4)	−0.1959(5)	3.8(2)
C(38)	0.2355(6)	0.0962(3)	−0.0587(5)	3.2(2)
C(39)	0.3231(6)	0.2094(3)	−0.0893(5)	3.2(2)

Table 3
Selected bond distances and bond angles for **1**

Bond distance (Å)			
W–P(1)	2.547(2)	W–P(2)	2.576(2)
W–N(1)	2.204(5)	W–C(37)	1.948(8)
W–C(38)	1.946(7)	W–C(39)	1.966(7)
N(1)–C(36)	1.139(8)	C(37)–O(1)	1.175(8)
C(38)–O(2)	1.166(7)	C(39)–O(3)	1.156(8)
C(36)–C(35)	1.446(9)	Fe–C(25)	2.018(6)
Fe–C(26)	2.034(6)	Fe–C(27)	2.060(7)
Fe–C(28)	2.063(7)	Fe–C(29)	2.043(7)
Fe–C(30)	2.029(6)	Fe–C(31)	2.048(7)
Fe–C(32)	2.058(7)	Fe–C(33)	2.053(7)
Fe–C(34)	2.033(6)		
Bond angle (deg)			
P(1)–W–P(2)	98.05(6)	P(1)–W–C(37)	173.6(2)
P(1)–W–C(38)	91.7(2)	P(1)–W–C(39)	89.6(2)
P(1)–W–N(1)	85.4(1)	P(2)–W–C(37)	88.1(2)
P(2)–W–C(38)	98.2(2)	P(2)–W–C(39)	170.3(2)
P(2)–W–N(1)	81.2(1)	W–P(1)–C(25)	116.0(2)
W–P(2)–C(30)	119.7(2)	N(1)–W–C(37)	97.3(2)
N(1)–W–C(38)	176.9(2)	N(1)–W–C(39)	93.5(2)
N(1)–C(36)–C(35)	178.9(8)	C(37)–W–C(38)	85.7(3)
C(37)–W–C(39)	84.5(3)	C(38)–W–C(39)	87.5(3)
W–C(37)–O(1)	172.5(6)	W–C(38)–O(2)	177.4(6)
W–C(39)–O(3)	176.4(6)	W–P(1)–C(1)	118.0(2)
W–P(1)–C(7)	113.8(2)	W–P(2)–C(13)	109.1(2)
W–P(2)–C(19)	120.6(2)	W–N(1)–C(36)	176.4(6)

3.7. *Structure determination for 1*

A crystal of *fac*-W(CO)$_3$($NCCH_3$)(η^2-dppf) (**1**), with appropriate dimensions 0.48 × 0.5 × 0.5 mm^3, was mounted on a glass fiber and aligned on the Rigaku AFC7S diffractometer. Diffraction data were collected with graphite monochromated Mo-Kα radiation using $\theta/2\theta$ scan mode. Lattice parameters were determined from 24 randomly selected reflections with 2θ ranging from 10.6° to 17.9°. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method [21] and refined by least-square cycles. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included but not refined. The calculation was performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation [22]. The data collection and refinement parameters are collected in Table 1. Atomic positional parameters are given in Table 2. Selected bond lengths and angles are included in Table 3.

3.8. Structure determination for 3

A brown prism crystal of $W(CO)_3(I)_2(\eta^2\text{-dppf(=O)})$ (3), with approximate dimensions $0.20 \times 0.20 \times 0.16$ mm^3, was mounted on a glass fiber and aligned on the Rigaku AFC7S diffractometer. Diffraction data were collected with graphite monochromated Mo–Kα radiation using $\theta/2\theta$ scan mode. Lattice parameters were determined from 25 randomly selected reflections with 2θ ranging from 11.3° to 28.6°. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-square cycles; all non-hydrogen atoms were refined anisotropically. The calculation was performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation. The data collection and refinement parameters are collected in Table 1. Atomic positional parameters are given in Table 4. Selected bond lengths and angles are included in Table 5.

Table 4
Selected atomic coordinates of compound **3**

Atom	*x*	*y*	*z*	B_{eq}
W(1)	0.41787(5)	0.10338(3)	0.75131(2)	2.75(1)
I(1)	0.47452(9)	0.17747(5)	0.86440(3)	4.14(2)
I(2)	0.53830(9)	0.22419(4)	0.70102(4)	4.18(2)
Fe(1)	0.7562(2)	−0.03249(4)	0.66754(7)	3.20(4)
P(1)	0.4436(3)	0.0511(2)	0.6478(1)	2.92(7)
P(2)	0.7241(3)	0.0137(2)	0.8060(1)	2.79(6)
O(1)	0.198(1)	0.2234(6)	0.7365(5)	6.8(3)
O(2)	0.3387(9)	−0.0114(5)	0.8410(5)	5.8(3)
O(3)	0.1423(1)	0.0395(6)	0.7022(5)	6.3(3)
O(4)	0.6108(7)	0.0579(4)	0.7737(3)	2.8(2)
C(1)	0.360(1)	−0.0354(6)	0.6288(5)	3.5(3)
C(2)	0.344(1)	−0.0846(7)	0.6735(6)	4.3(3)
C(3)	0.284(1)	−0.1497(8)	0.6597(7)	5.3(4)
C(4)	0.239(2)	−0.1660(8)	0.6000(8)	6.3(5)
C(5)	0.253(2)	−0.1189(9)	0.5548(7)	6.2(4)
C(6)	0.314(1)	−0.0534(8)	0.5708(6)	5.1(4)
C(7)	0.607(1)	0.0361(6)	0.6303(5)	3.3(3)
C(8)	0.724(1)	0.0750(7)	0.6501(5)	3.5(3)
C(9)	0.827(1)	0.0512(7)	0.6200(6)	4.3(3)
C(10)	0.771(1)	−0.0054(8)	0.5808(5)	4.7(4)
C(11)	0.640(1)	−0.0163(7)	0.5866(5)	3.7(3)
C(12)	0.772(1)	−0.0531(6)	0.7569(5)	3.3(3)
C(13)	0.901(1)	−0.0584(7)	0.7373(5)	3.5(3)
C(14)	0.891(2)	−0.1136(8)	0.6932(6)	5.1(4)
C(15)	0.764(2)	−0.1400(7)	0.6580(6)	4.5(3)
C(16)	0.690(1)	−0.1057(7)	0.7230(5)	4.0(3)
C(17)	0.685(1)	−0.0315(7)	0.8722(4)	3.1(3)
C(18)	0.683(1)	0.0085(7)	0.9238(6)	4.6(3)
C(19)	0.650(2)	−0.0236(9)	0.9755(6)	5.4(4)
C(20)	0.622(2)	−0.095(1)	0.9745(7)	7.0(5)
C(21)	0.620(2)	−0.1346(8)	0.9227(7)	6.2(4)
C(22)	0.651(1)	−0.1039(7)	0.8719(6)	4.5(3)
C(23)	0.865(1)	0.0702(7)	0.8293(5)	3.5(3)
C(24)	0.976(1)	0.0442(8)	0.8646(6)	5.0(4)
C(25)	1.087(1)	0.089(1)	0.8812(7)	6.5(5)
C(26)	1.082(2)	0.158(1)	0.8626(8)	6.0(5)
C(27)	0.971(2)	0.1854(8)	0.8285(7)	6.1(4)
C(28)	0.861(1)	0.1423(7)	0.8104(6)	4.5(3)
C(29)	0.368(1)	0.1082(7)	0.5847(5)	3.7(3)
C(30)	0.447(1)	0.1403(6)	0.5469(5)	4.4(3)
C(31)	0.390(2)	0.1843(8)	0.5003(6)	6.0(4)
C(32)	0.253(2)	0.1969(9)	0.4922(6)	7.3(5)
C(33)	0.178(2)	0.1667(9)	0.5302(8)	6.9(5)
C(34)	0.237(2)	0.1224(9)	0.5768(6)	5.9(4)
C(35)	0.278(1)	0.1800(8)	0.7427(5)	4.4(3)
C(36)	0.370(1)	0.0297(8)	0.8093(6)	4.2(3)
C(37)	0.247(1)	0.0629(8)	0.7182(6)	4.5(3)

Table 5
Selected bond distances and bond angles for **3**

Bond distance (Å)			
W–I(1)	2.8629(9)	W–I(2)	2.869(1)
W–P(1)	2.566(3)	W–O(4)	2.131(7)
W–C(35)	2.01(1)	W–C(36)	2.00(1)
W–C(37)	1.94(1)	O(4)–P(2)	1.509(7)
C(35)–O(1)	1.14(1)	C(36)–O(2)	1.12(1)
C(37)–O(3)	1.16(1)	Fe–C(7)	2.06(1)
Fe–C(8)	2.05(1)	Fe–C(9)	2.08(1)
Fe–C(10)	2.04(1)	Fe–C(11)	2.03(1)
Fe–C(12)	2.02(1)	Fe–C(13)	2.04(1)
Fe–C(14)	2.06(1)	Fe–C(15)	2.03(1)
Fe–C(16)	2.03(1)		
Bond angle (deg)			
I(1)–W–I(2)	86.19(3)	I(1)–W–P(1)	161.32(7)
I(1)–W–O(4)	85.9(2)	I(1)–W–C(35)	77.8(4)
I(1)–W–C(36)	77.7(4)	I(1)–W–C(37)	124.7(4)
I(2)–W–P(1)	80.15(7)	I(2)–W–O(4)	87.9(2)
I(2)–W–C(35)	75.7(4)	I(2)–W–C(36)	162.3(4)
I(2)–W–C(37)	124.6(4)	P(1)–W–O(4)	80.9(2)
P(1)–W–C(35)	110.7(3)	P(1)–W–C(36)	113.6(4)
P(1)–W–C(37)	73.8(4)	O(4)–W–C(35)	157.5(4)
O(4)–W–C(36)	83.6(4)	O(4)–W–C(37)	133.1(4)
C(35)–W–C(36)	107.6(5)	C(35)–W–C(37)	69.4(6)
C(36)–W–C(37)	71.8(5)	W–O(4)–P(2)	160.2(5)
W–C(35)–O(1)	178(1)	W–C(36)–O(2)	177(1)
W–C(37)–O(3)	175(1)	W–P(1)–C(1)	115.5(4)
W–P(1)–C(7)	119.1(4)		

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