

$W(\eta^2\text{-PhC}\equiv\text{CPh})_3(\eta^1\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)$ as a ligand to prepare homo- and hetero-nuclear cluster complexes

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Received 26 August 2003; accepted 25 September 2003

Abstract

Reaction of $W(\eta^2\text{-PhC}\equiv\text{CPh})_3(\text{NMe}_3)$ (**1**) and $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ (dppa) produces $W(\eta^2\text{-PhC}\equiv\text{CPh})_3(\eta^1\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)$ (**2**), which contains a pendant phosphine group. Treatment of **2** with $W(\text{CO})_4(\text{NCMe})_2$ yields $[W(\eta^2\text{-PhC}\equiv\text{CPh})_3](\mu, \eta^2\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)[W(\text{CO})_4(\text{NCMe})]$ (**3**). Compound **2** reacts with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ to afford $\text{Os}_3(\text{CO})_{10}[(\mu, \eta^2\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)W(\eta^2\text{-PhC}\equiv\text{CPh})_3]_2$ (**4**), and reacts with $\text{Ru}_3(\text{CO})_9(\text{NCMe})_3$ to afford $\text{Ru}_3(\text{CO})_9[(\mu, \eta^2\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)W(\eta^2\text{-PhC}\equiv\text{CPh})_3]_3$ (**5**). The crystal structures of **2** and **3** are determined by an X-ray diffraction study.

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Keywords: Bis(diphenylphosphino)acetylene; Tungsten; Osmium; Ruthenium; Cluster complexes

1. Introduction

The ‘coordination clusters’ assembling from mono-metallic complexes and multidentate bridging ligands currently attract much interest [1,2]. Bis(diphenylphosphino)acetylene (dppa) is a potentially trifunctional ligand. The two phosphorus centers of dppa are normally coordinated to metals in advance of the acetylene group due to stronger net donor capability of the phosphine ligand compared with alkyne [3]. However, the rigidity of the linear $-\text{C}\equiv\text{C}-$ unit between two phosphorus centers forces the dppa ligand to form bonds between different metal atoms [4–7].

We have previously prepared the complex $W(\eta^2\text{-PhC}\equiv\text{CPh})_3(\text{NMe}_3)$ (**1**) and shown the reaction of **1** with diphenylacetylene to lead to trimerization or tetramerization of the alkyne ligands depending on the solvents used [8]. In this paper we wish to report the synthesis of $W(\eta^2\text{-PhC}\equiv\text{CPh})_3(\eta^1\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)$ (**2**) from **1** and the coordination chemistry of **2** towards $W(\text{CO})_4(\text{NCMe})_2$, $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ and $\text{Ru}_3(\text{CO})_9$

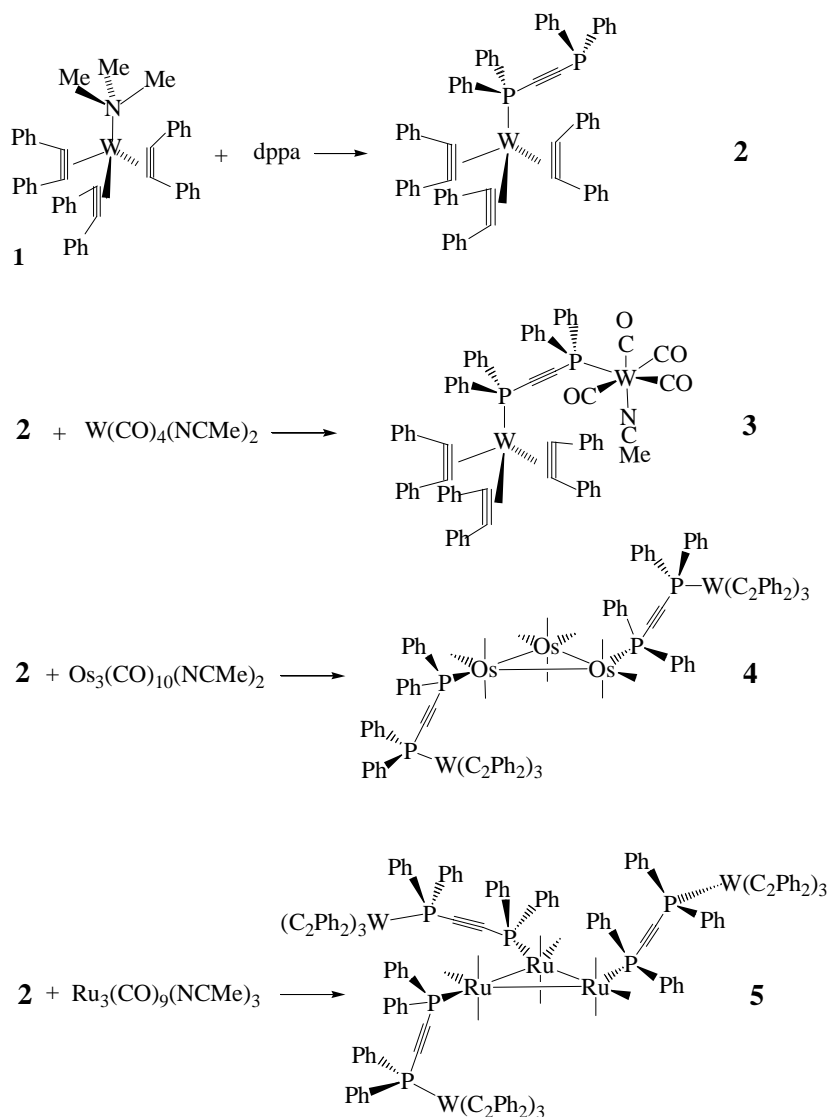
$(\text{NCMe})_3$, which contain labile acetonitrile ligands for substitution.

2. Results and discussion

Treatment of **1** with dppa in CH_2Cl_2 solvent at ambient temperature generates $W(\eta^2\text{-PhC}\equiv\text{CPh})_3(\eta^1\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)$ (**2**) in 46% yield. Compound **2** contains a pendant phosphine moiety. Attempts to attach $[W(\eta^2\text{-PhC}\equiv\text{CPh})_3]$ groups to both ends of dppa ligand by treating **2** with **1** gave no reaction. Nevertheless, compound **2** reacts with $W(\text{CO})_4(\text{NCMe})_2$ to produce $[W(\eta^2\text{-PhC}\equiv\text{CPh})_3](\mu, \eta^2\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)[W(\text{CO})_4(\text{NCMe})]$ (**3**, 57% yield), whereas only one acetonitrile ligand can be substituted by phosphine even after adding two-fold of **2**. In these reactions, it is probable the steric factors that preclude two bulky $[W(\eta^2\text{-PhC}\equiv\text{CPh})_3]$ groups being in close proximity. On the other hand, the reaction of **2** and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ in a 2:1 ratio affords $\text{Os}_3(\text{CO})_{10}[(\mu, \eta^2\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)W(\eta^2\text{-PhC}\equiv\text{CPh})_3]_2$ (**4**, 93% yield), in which the two phosphine ligands are bound to adjacent Os atoms. In addition, **2** reacts with $\text{Ru}_3(\text{CO})_9(\text{NCMe})_3$ in a 3:1 ratio to lead to the hexanuclear cluster $\text{Ru}_3(\text{CO})_9[(\mu, \eta^2\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)W(\eta^2\text{-PhC}\equiv\text{CPh})_3]_3$ (**5**).

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$\text{CPh}_3\text{]}_3$ (**5**) in 38% yield after separation by TLC. The results are summarized in Scheme 1.

Compounds **2** and **3** form slightly air-sensitive crystalline solids, while **4** and **5** are air-stable. The new complexes have been characterized by elemental analyses, IR, and NMR. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **2** presents a doublet signal at 15.83 ppm ($^3J_{\text{P-P}} = 3$ Hz) for the coordinated phosphorus atom, which is accompanied by one pair of ^{183}W satellites ($J_{\text{W-P}} = 131$ Hz), and a doublet resonance at -28.74 ppm for the free phosphine. On the other hand, the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **3** displays two signals accompanied by ^{183}W satellites at 5.61 ($J_{\text{W-P}} = 253$ Hz) and 16.88 ($J_{\text{W-P}} = 129$ Hz) ppm, and are assigned to the phosphorus atoms coordinated to $[\text{W}(\text{CO})_4(\text{NCMe})]$ and $[\text{W}(\eta^2\text{-PhC}\equiv\text{CPh})_3]$ groups, respectively. The structures of **2** and **3** were further investigated by an X-ray diffraction study.

The ORTEP drawing of **2** is shown in Fig. 1. Selected bond distances and bond angles are collected in Table 1. The three acetylene groups are essentially eclipsed but inclined with respect to the W–P bond by angles averaging 16.3° . This tilting angle is comparable with that measured for $\text{W}(\eta^2\text{-PhC}\equiv\text{CPh})_3(\text{PMe}_3)$ (av. 13.2°) [9] and $[\text{W}(\eta^2\text{-PhC}\equiv\text{CPh})_3(\text{SnPh}_3)]^-$ (av. 15.3°) [10]. The coordinated phosphine ligand gives rise to slightly different W–C_(acetylene) distances, where the upper W–C lengths (av. 2.10 Å) are ca. 0.04 Å longer than the lower W–C lengths (av. 2.06 Å). The coordinated acetylene C≡C distances are about equal, 1.32 ± 0.01 Å, and the phenyl groups are bent back from the C≡C axis by angles averaging 135.2° . The uncoordinated C(43)≡C(44) length is 1.199(6) Å.

The ORTEP drawing of **3** is shown in Fig. 2. Selected bond distances and bond angles are collected in Table 2.

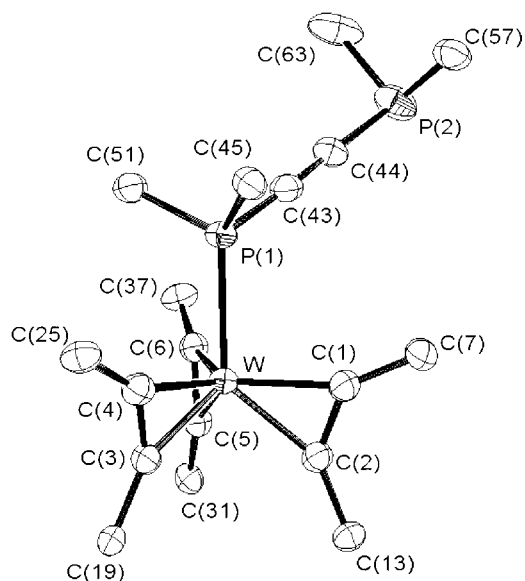


Fig. 1. Molecular structure of **2**. The phenyl groups have been artificially omitted, except the ipso carbon atom, for clarity.

The geometry of $[P-W(\eta^2\text{-PhC}\equiv\text{CPh})_3]$ part is essentially identical with that in **2**. The P(1) atom is coordinated to a $[W(\text{CO})_4(\text{NCMe})]$ unit, which is associated with four terminal carbonyls with the W–C–O angles in the range $174.8(9)$ – $178(1)^\circ$ and an acetonitrile ligand with the W(1)–N(1)–C(5) angle of $173.4(8)^\circ$. The W(1)–P(1) and W(2)–P(2) bonds are about eclipsed, as evi-

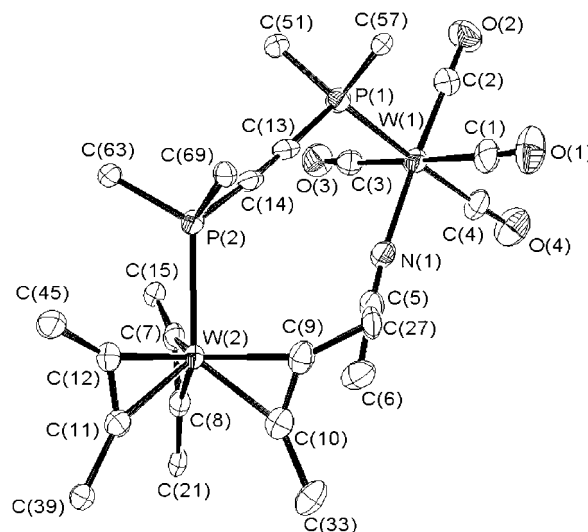


Fig. 2. Molecular structure of **3**. The phenyl groups have been artificially omitted, except the ipso carbon atom, for clarity.

denced by the torsion angle of 6.42° . The W–P–C angles in the range $112.7(3)$ – $120.8(3)^\circ$ show a significant deviation from the ideal tetrahedral, consistent with steric strains arising from *syn*-coordination of the dppa ligand, while the C–P–C bond angles are compressed, ranging from $97.3(4)^\circ$ through $103.3(4)^\circ$. The P–C≡C–P backbone is slightly bowed as indicated by the angles: P(1)–C(13)–C(14) $176.6(9)^\circ$ and P(2)–C(14)–C(13) $173.4(9)^\circ$.

Table 1

Selected bond distances and bond angles for **2**

Bond distances (Å)			
W–C(3)	2.054(4)	W–C(2)	2.057(4)
W–C(5)	2.063(5)	W–C(6)	2.089(4)
W–C(4)	2.096(5)	W–C(1)	2.104(5)
W–P(1)	2.4977(11)	P(1)–C(43)	1.763(5)
P(1)–C(45)	1.833(5)	P(1)–C(51)	1.834(5)
P(2)–C(44)	1.767(5)	P(2)–C(57)	1.825(6)
P(2)–C(63)	1.839(7)	C(1)–C(2)	1.330(6)
C(1)–C(7)	1.460(7)	C(2)–C(13)	1.472(6)
C(3)–C(4)	1.320(6)	C(3)–C(19)	1.462(6)
C(4)–C(25)	1.471(7)	C(5)–C(6)	1.324(6)
C(5)–C(31)	1.459(6)	C(6)–C(37)	1.471(6)
C(43)–C(44)	1.199(6)		
Bond angles (°)			
C(5)–W–C(6)	37.20(17)	C(3)–W–C(4)	37.07(17)
C(2)–W–C(1)	37.26(17)	C(3)–W–P(1)	123.22(12)
C(2)–W–P(1)	128.45(13)	C(5)–W–P(1)	118.16(13)
C(6)–W–P(1)	80.97(12)	C(4)–W–P(1)	86.90(13)
C(1)–W–P(1)	91.19(13)	C(43)–P(1)–C(45)	98.0(2)
C(43)–P(1)–C(51)	99.8(2)	C(45)–P(1)–C(51)	105.1(2)
C(43)–P(1)–W	113.82(15)	C(45)–P(1)–W	121.18(15)
C(51)–P(1)–W	115.61(16)	C(44)–P(2)–C(57)	99.4(2)
C(44)–P(2)–C(63)	98.9(3)	C(57)–P(2)–C(63)	102.6(3)
C(2)–C(1)–C(7)	135.1(4)	C(1)–C(2)–C(13)	137.5(4)
C(4)–C(3)–C(19)	136.0(4)	C(3)–C(4)–C(25)	134.7(4)
C(6)–C(5)–C(31)	134.8(4)	C(5)–C(6)–C(37)	133.0(4)
P(1)–C(43)–C(44)	173.2(4)	P(2)–C(44)–C(43)	177.8(5)

Table 2
Selected bond distances and bond angles for **3**

Bond distances (Å)			
W(1)–C(2)	1.949(11)	W(1)–C(4)	2.003(10)
W(1)–C(3)	2.016(11)	W(1)–C(1)	2.037(11)
W(1)–N(1)	2.172(8)	W(1)–P(1)	2.491(2)
W(2)–C(8)	2.052(10)	W(2)–C(10)	2.053(9)
W(2)–C(11)	2.059(9)	W(2)–C(12)	2.061(9)
W(2)–C(7)	2.069(9)	W(2)–C(9)	2.086(9)
W(2)–P(2)	2.509(2)	P(1)–C(13)	1.768(10)
P(1)–C(57)	1.829(11)	P(1)–C(51)	1.836(9)
P(2)–C(14)	1.789(10)	P(2)–C(69)	1.811(10)
P(2)–C(63)	1.817(9)	C(7)–C(8)	1.313(13)
C(7)–C(15)	1.490(13)	C(8)–C(21)	1.487(13)
C(9)–C(10)	1.289(13)	C(9)–C(27)	1.494(13)
C(10)–C(33)	1.477(13)	C(11)–C(12)	1.284(13)
C(11)–C(39)	1.475(13)	C(12)–C(45)	1.488(13)
C(13)–C(14)	1.189(13)		
Bond angles (°)			
C(3)–W(1)–C(1)	178.1(4)	C(2)–W(1)–N(1)	176.9(4)
C(4)–W(1)–P(1)	176.7(3)	C(11)–W(2)–C(12)	36.3(4)
C(8)–W(2)–C(7)	37.2(4)	C(10)–W(2)–C(9)	36.3(4)
C(8)–W(2)–P(2)	122.5(3)	C(10)–W(2)–P(2)	125.1(3)
C(11)–W(2)–P(2)	121.2(3)	C(12)–W(2)–P(2)	85.1(3)
C(7)–W(2)–P(2)	85.4(3)	C(9)–W(2)–P(2)	88.9(3)
C(13)–P(1)–C(57)	100.4(5)	C(13)–P(1)–C(51)	100.6(4)
C(57)–P(1)–C(51)	103.3(4)	C(13)–P(1)–W(1)	116.9(3)
C(57)–P(1)–W(1)	112.7(3)	C(51)–P(1)–W(1)	120.2(3)
C(14)–P(2)–C(69)	97.3(4)	C(14)–P(2)–C(63)	99.7(4)
C(69)–P(2)–C(63)	102.0(4)	C(14)–P(2)–W(2)	114.1(3)
C(69)–P(2)–W(2)	120.8(3)	C(63)–P(2)–W(2)	119.0(3)
C(8)–C(7)–C(15)	134.6(9)	C(7)–C(8)–C(21)	136.0(9)
C(10)–C(9)–C(27)	135.0(9)	C(9)–C(10)–C(33)	137.1(9)
C(12)–C(11)–C(39)	134.0(9)	C(11)–C(12)–C(45)	131.2(9)
C(14)–C(13)–P(1)	176.6(9)	C(13)–C(14)–P(2)	173.4(9)

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **4** show that it is a mixture of two isomers in an approximate ratio of 3:1 at room temperature, which become fast exchanged above 90 °C (in d_8 -toluene). The major isomer has two equal intense signals at -27.67 and -30.44 ppm (bound to Os atoms) and two signals at 16.76 and 16.49 ppm (bound to W atoms), while the minor isomer displays one set of signals at -30.02 (P–Os) and 17.12 (P–W) ppm. It has been illustrated that bulky ligands, like phosphines and phosphite, generally adopt equatorial positions in trinuclear clusters, while small ligands such as H and CH_3CN are normally found in axial sites [11]. Four possible isomers for the cluster $\text{M}_3(\text{CO})_{10}(\text{phosphine})_2$ with phosphines occupying the equatorial sites are depicted in Fig. 3(a). For compound **4**, the isomers 1,1-A and 1,2-A are space-congested and can be excluded for steric reasons. Thus, the major isomer of **4** likely has the configuration 1,2-B, which contains nonequivalent phosphorus nuclei, and the minor isomer has the configuration 1,2-C with equivalent phosphorus nuclei. The isomerism of phosphine-substituted triosmium clusters is well documented in the literature [11–14].

On the other hand, the tri-substituted cluster **5** presents only two ^{31}P resonances at 13.13 (P–Ru) and 16.67 (P–W, $J_{\text{W-P}} = 126$ Hz) ppm, in agreement with the configuration 1,2,3-A shown in Fig. 3(b), where the three phosphorus nuclei are equilibrated through C_3 rotations.

In summary, compound **2** is an attractive metal-containing ligand to construct homo- and heteronuclear complexes **3–5**. Since the acetylene groups of dppa ligands remain free in these compounds, it is promising to assemble higher nuclearity clusters through coordination of $\text{C}\equiv\text{C}$ units with other metal species. The investigation is in progress in our laboratory.

3. Experimental

3.1. General methods

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. $\text{W}(\eta^2\text{-PhC}\equiv\text{CPh})_3(\text{NMe}_3)$ (**1**) [8], $\text{W}(\text{CO})_4(\text{NCMe})_2$ [15], $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ [16] and $\text{Ru}_3(\text{CO})_9$

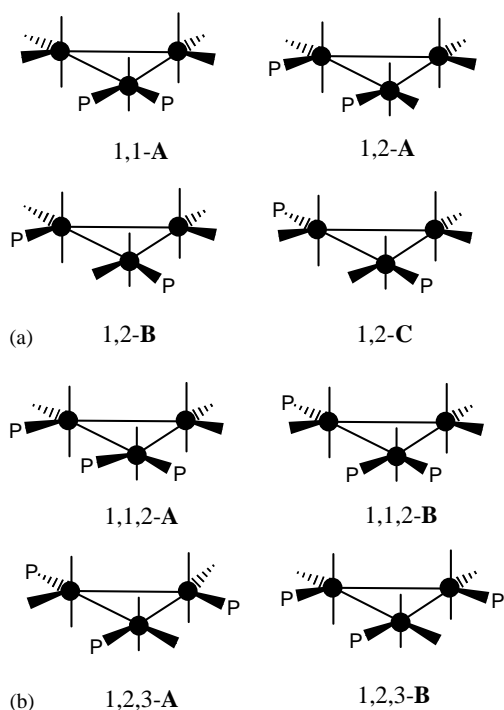


Fig. 3. Possible isomers for $M_3(CO)_{10}(phosphine)_2$ (a) and $M_3(CO)_9(phosphine)_3$ (b), with phosphine ligands occupying the equatorial sites.

(NCMe)₃ [17] were prepared as described in the literature. $Ph_2PC\equiv CPh_2$ (dppa) was purchased from Aldrich and used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Kieselgel, DGF₂₅₄). Infrared spectra were recorded with a 0.1 mm-path CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. ¹H and ³¹P NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer. Elemental analyses were performed at the National Chen-Kung University, Tainan, Taiwan.

3.2. Preparation of 2

$W(\eta^2-PhC\equiv CPh)_3(NMe_3)$ (**1**) (365 mg, 0.47 mmol) and $Ph_2PC\equiv CPh_2$ (185 mg, 0.47 mmol) were placed in a 50 ml Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper. Dichloromethane (15 ml) was introduced into the flask via a syringe through the serum stopper. The solution was stirred at room temperature for 24 h to result in a yellow cloudy mixture. The mixture was filtered, and the filtrate was evaporated to dryness on a rotary evaporator. The residue was subjected to TLC, with *n*-hexane/dichloromethane (1:1, *vv*⁻¹) as eluant. Crystallization of the material forming the first colorless band from *n*-hexane/dichloromethane afforded slightly air-sensitive, white crystals of

$W(\eta^2-PhC\equiv CPh)_3(\eta^1-Ph_2PC\equiv CPh_2)$ (**2**; 240 mg, 0.22 mmol, 46%). ¹H-NMR ($CDCl_3$, 20 °C): 7.40–6.55 (m, Ph) ppm. ³¹P{¹H}-NMR ($CDCl_3$, 20 °C): -28.74 (d, $J_{P-P} = 3$ Hz), 15.83 (d, $J_{P-P} = 3$ Hz; with ¹⁸³W satellites, $J_{W-P} = 131$ Hz) ppm. Anal. found: C, 73.08; H, 4.60. $C_{68}H_{50}P_2W$ Anal. Calc.: C, 73.39; H, 4.52%.

3.3. Preparation of 3

Compound **2** (180 mg, 0.16 mmol), $W(CO)_4(NCMe)_2$ (60 mg, 0.16 mmol) and dichloromethane (20 ml) were introduced into a Schlenk flask under dinitrogen, and the mixture was stirred at room temperature for 12 h. The solution was filtered, concentrated to ca. 5 ml, and carefully layered with *n*-hexane (15 ml). Slightly air-sensitive, yellow crystals of $[W(\eta^2-PhC\equiv CPh)_3](\mu, \eta^2-Ph_2PC\equiv CPh_2)[W(CO)_4(NCMe)]$ (**3**; 130 mg, 57%) were obtained. IR (CH_2Cl_2 , ν_{CO}): 2016w, 1908s, 1868m cm^{-1} . ¹H-NMR (C_6D_6 , 20 °C): 7.90–6.74 (m, Ph) ppm. ³¹P{¹H}-NMR (C_6D_6 , 20 °C): 5.61 (s, with ¹⁸³W satellites, $J_{W-P} = 253$ Hz), 16.88 (s, with ¹⁸³W satellites, $J_{W-P} = 129$ Hz) ppm. Anal. found: C, 60.79; H, 3.75; N, 0.90. $C_{74}H_{53}NO_4P_2W_2$ Anal. Calc.: C, 61.30; H, 3.68; N, 0.97%.

3.4. Preparation of 4

Compound **2** (21 mg, 0.018 mmol), $Os_3(CO)_{10}(NCMe)_2$ (8 mg, 0.009 mmol) and dichloromethane (5 ml) were introduced into a Schlenk flask under dinitrogen, and the mixture was stirred at room temperature for 4 h, at which point the IR spectrum showed no absorptions due to the starting cluster. The solution was then layered with *n*-hexane (10 ml) and left to settle at ambient temperature. Air-stable, orange needle crystals of $Os_3(CO)_{10}[(\mu, \eta^2-Ph_2PC\equiv CPh_2)W(\eta^2-PhC\equiv CPh)_3]_2$ (**4**; 26 mg, 93%) were obtained. IR (CH_2Cl_2 , ν_{CO}): 2088w, 2028s, 1996vs, 1964m cm^{-1} . ¹H-NMR ($CDCl_3$, 20 °C): 7.34–6.49 (m, Ph) ppm. ³¹P{¹H}-NMR($CDCl_3$, 20 °C): 17.12, 16.76, 16.49 (P–W), -27.67, -30.02, -30.44 (P–Os) ppm. Anal. found: C, 55.89; H, 3.48. $C_{147}H_{102}Cl_2O_{10}Os_3P_4W_2$ (including a CH_2Cl_2 crystal solvent) Anal. Calc.: C, 55.85; H, 3.25%.

3.5. Preparation of 5

Compound **2** (52 mg, 0.047 mmol), $Ru_3(CO)_9(NCMe)_3$ (10 mg, 0.0015 mmol) and dichloromethane (5 ml) were introduced into a Schlenk flask under dinitrogen, and the mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum and the residue subjected to TLC, with *n*-hexane/dichloromethane (1:1, *vv*⁻¹) as eluant. Isolation of the material forming the second orange band afforded an air stable solid of $Ru_3(CO)_9[(\mu, \eta^2-Ph_2PC\equiv CPh_2)W(\eta^2-PhC\equiv CPh)_3]_3$

Table 3
Crystal data and refinement details for **2** and **3**

	2	3
Formula	C ₆₈ H ₅₀ P ₂ W	C ₇₄ H ₅₃ NO ₄ P ₂ W ₂
<i>T</i> (K)	150(1)	150(1)
Crystal system	Monoclinic	Triclinic
Space group	P2 ₁ /c	P1
Unit cell dimensions		
<i>a</i> (Å)	13.5626(1)	12.1741(5)
<i>b</i> (Å)	18.8354(2)	14.0302(6)
<i>c</i> (Å)	21.3692(3)	18.5850(8)
α (°)		81.010(1)
β (°)	108.1515(5)	73.505(1)
γ (°)		89.496(1)
<i>V</i> (Å ³)	5187.3(1)	3004.3(2)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.425	1.603
<i>F</i> (0 0 0)	2248	1428
Radiation λ (Å)	0.71073	0.71073
μ (mm ⁻¹)	2.331	3.931
θ range (°)	1.47–27.50	1.16–27.50
<i>R</i> ₁	0.0410	0.0653
w <i>R</i> ₂	0.0889	0.1415
GOF on <i>F</i> ²	1.060	1.097

(**5**; 22 mg, 38%). IR (CH₂Cl₂, ν_{CO}): 2056w, 1994s, 1982s, 1960m cm⁻¹. ¹H-NMR (CDCl₃, 20 °C): 7.38–6.53 (m, Ph) ppm. ³¹P{¹H}-NMR(CDCl₃, 20 °C): 16.67 (s, with ¹⁸³W satellites, *J*_{W-P} = 126 Hz) 13.13 (s, P–Ru) ppm. Anal. found: C, 65.20; H, 3.99. C₂₁₃H₁₅₀O₉P₆Ru₃W₃ Anal. Calc.: C, 65.70; H, 3.88%.

3.6. Structure determination for **2** and **3**

Crystals of **2** and **3** suitable for X-ray diffraction studies were each mounted in a thin-walled glass capillary and aligned on the Bruker Smart ApexCCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The data were collected at 150 K. All data were corrected for the effects of absorption. The structures were solved by the direct method and refined by full-matrix least-square on *F*². The program used was the SHELXTL package [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included but not refined. A summary of relevant crystallographic data is provided in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis of **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 217851 and 217850, respectively. Copy of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44(12 23)336033 or E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We are grateful for support of this work by the National Science Council of Taiwan.

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