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FULL PAPER

Synthesis and skeletal isomerization of the phosphinidene acetylide cluster complexes [$Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)\{WL(CO)\}$] where L = C_5Me_5 or C_5H_5

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Reactions of the phosphinidene cluster [$Ru_4(CO)_{13}(\mu_3\text{-}PPh)$] with tungsten acetylide complexes [$WL(CO)_3(CCPh)$] (L = C_5Me_5 or C_5H_5) gave interconvertible isomers of formula [$Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)\{WL(CO)\}$]. The structures of the two C_5Me_5 derivatives were determined by X-ray diffraction, showing a novel WRu_4P octahedral core arrangement, in which the acetylide ligand is co-ordinated to a WRu_2 triangle with its C–C vector bridging the Ru–Ru edge. For one isomer the phosphinidene ligand is located at the position *trans* to the W atom, while in the second isomer it is at the *cis* position. Possible mechanisms for this rare example of skeletal isomerization are suggested.

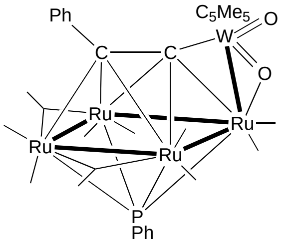
Facile addition of reactive organic and organometallic molecules to the phosphinidene cluster [$Ru_4(CO)_{13}(\mu_3\text{-}PPh)$] provides a convenient method to study the substrate–metal interaction between organic molecules and transition-metal atoms, and to obtain high-nuclearity metal cluster compounds.[1] Recently, we reported the synthesis of a heterometallic cluster complex [$Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)\{W(C_5Me_5)O_2\}$] **1** from the reaction of [$Ru_4(CO)_{13}(\mu_3\text{-}PPh)$] with the high-oxidation-state dioxo acetylide complex [$W(C_5Me_5)O_2(CCPh)$] in which the (C_5Me_5)WO_2 fragment is linked to only one Ru metal atom through the formation of a novel W=O→Ru interaction.[2] The W=O→Ru bonding was retained, with no formation of an additional W–Ru bond, even under forcing conditions. This is due to the fact that all ligands on the (C_5Me_5)WO_2(CCPh) fragment are tightly bound to the W atom; therefore, the tungsten center acts as a well protected, saturated molecular entity.

In continuation of our investigation on the factors that influence mixed-metal cluster growth,[3] we report here the reactions of [$Ru_4(CO)_{13}(\mu_3\text{-}PPh)$] with a low-oxidation-state acetylide carbonyl complex [$W(C_5Me_5)(CO)_3(CCPh)$]. In contrast to the formation of **1**, the products isolated from this reaction were two complexes with identical formula [$Ru_4(CO)_{11}(\mu_4\text{-}PPh)(CCPh)\{W(C_5Me_5)\}$] each possessing a pentametallic square-pyramidal core which is apparently obtained by removing CO ligands from the W atom. This study thus probes the properties of a low-oxidation-state transition-metal precursor, the ligands of which can dissociate in a stepwise manner. In addition, the rapid interchange between these WRu_4 cluster compounds at higher temperatures offered a challenging exploration of the mechanism for their skeletal isomerization.

Experimental

General information and materials

Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer, ^1H and ^{13}C NMR spectra on either a Bruker AM-400 or Varian Unity-400 instrument. The ^1H and ^{13}C NMR chemical shifts are quoted with respect to the internal standard tetramethylsilane, ^{31}P NMR chemical shifts with respect to the external standard 85% H_3PO_4. Mass spectra were obtained on a JEOL HX110 instrument operating in fast atom bombardment (FAB) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The phosphinidene complex [$Ru_4(CO)_{13}(\mu_3\text{-}PPh)$] was prepared according to the literature procedure.[4] The reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck) and the products were separated on preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, E. Merck). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.



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Preparation of phosphinidene acetylide clusters

To a reaction flask (100 cm^3), [$Ru_4(CO)_{13}(\mu_3\text{-}PPh)$] (100 mg, 0.111 mmol), [$W(C_5Me_5)(CO)_3(CCPh)$] (112 mg, 0.222 mmol) and toluene (60 cm^3) were added. The solution was then heated to reflux and heating continued for 50 min, during which time the mixture changed from dark red to black. The solution was allowed to cool to room temperature and the solvent removed under vacuum. The residue was separated by thin-layer chromatography (CH_2Cl_2–hexane 1:6), from which 31 mg of green [$Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)\{W(C_5Me_5)(CO)\}$] **2a** (0.025 mmol, 26%) and 70 mg of black [$Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)\{W(C_5Me_5)(CO)\}$] **3a** (0.057 mmol, 60%) were isolated as the

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major isolable products. Crystals of both complexes suitable for X-ray diffraction study were obtained from a mixture of CH_2Cl_2 and methanol at room temperature. Similarly, the reaction of [$Ru_4(CO)_{13}(\mu_3$-PPh)] and [$W(C_5H_5)(CO)_3(CCPh)$] in refluxing toluene for 15 min afforded the corresponding complexes **2b** and **3b** in 55 and 36% yield, respectively.

Compound **2a**: mass spectrum (FAB, ^{184}W, ^{102}Ru) *m*/*z* 1244 (M^+); IR (C_6H_{12}) ν(CO) 2064m, 2025vs, 2002s, 1988w (sh), 1975m, 1964w (sh), 1946w (br) and 1834w (br) cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) δ 7.60–7.48 (m, 4 H), 7.35–7.25 (m, 6 H) and 2.11 (s, 15 H); ^{13}C NMR (100 MHz, CD_2Cl_2, 293 K) δ 247.4 (J_{WC} = 150), 205.7 (d, J_{PC} = 34), 202.1 (d, J_{PC} = 9, 3C), 199.4 (d, J_{PC} = 3), 199.0, 198.2 (d, J_{PC} = 37), 192.4 (J_{WC} = 141, *C*CPh), 149.1 (d, J_{PC} = 18, *ipso*-C of C_6H_5), 140.2 (*ipso*-C of C_6H_5), 133.8 (d, J_{PC} = 15, 2C, *o*-C of C_6H_5), 131.9 (*p*-C of C_6H_5), 131.3 (2C, *o*-C of C_6H_5), 129.6 (2C, *m*-C of C_6H_5), 129.2 (*p*-C of C_6H_5), 128.6 (d, J_{PC} = 12, 2C, *m*-C of C_6H_5), 119.0 (d, J_{PC} = 7 Hz, C*C*Ph), 106.8 (*C*$_5$Me$_5$) and 13.0 (C$_5$*Me*$_5$) (Found: C, 33.82; H, 2.13. Calc. for $C_{35}H_{25}O_{11}PRu_4W$: C, 33.88; H, 2.03%).

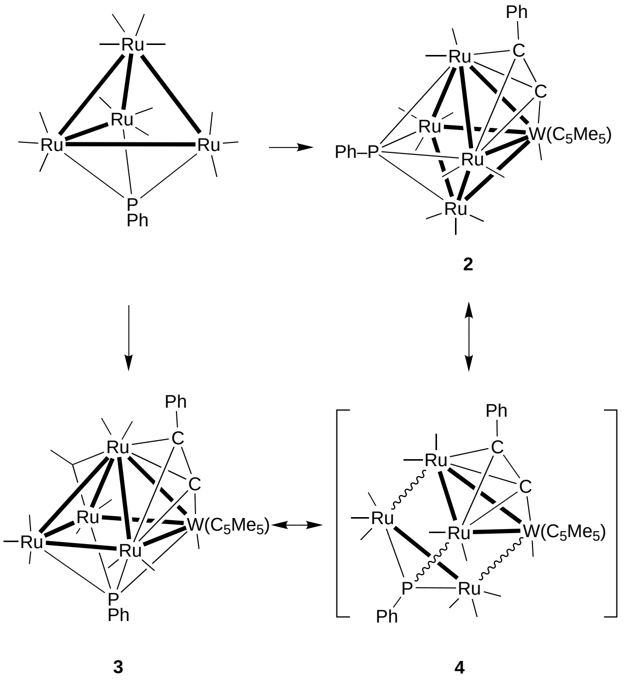
Compound **2b**: mass spectrum (FAB, ^{184}W, ^{102}Ru) *m*/*z* 1174 (M^+); IR (C_6H_{12}) ν(CO) 2067m, 2030vs, 2006s, 1992w (sh), 1978m, 1967w (sh), 1952w (br) and 1869w (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ 7.72–7.27 (m, 10 H) and 5.33 (s, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, 293 K) δ 237.6 (d, J_{PC} = 2), 203.2 (d, J_{PC} = 35), 200.2 (d, J_{PC} = 12, 3C), 197.6 (d, J_{PC} = 5), 197.4 (d, J_{PC} = 6), 197.0 (d, J_{PC} = 36), 186.5 (*C*CPh), 148.1 (d, J_{PC} = 17, *ipso*-C of C_6H_5), 148.9 (*ipso*-C of C_6H_5), 132.4 (d, J_{PC} = 14, 2C, *o*-C of C_6H_5), 131.2 (*p*-C of C_6H_5), 130.4 (2C, *o*-C of C_6H_5), 128.7 (2C, *m*-C of C_6H_5), 128.6 (*p*-C of C_6H_5), 127.8 (d, J_{PC} = 12, 2C, *m*-C of C_6H_5), 118.8 (d, J_{PC} = 7 Hz, C*C*Ph) and 88.9 (C_5H_5) (Found: C, 30.14; H, 1.48. Calc. for $C_{30}H_{15}O_{11}PRu_4W$: C, 30.78; H, 1.29%).

Compound **3a**: mass spectrum (FAB, ^{184}W, ^{102}Ru) *m*/*z* 1244 (M^+); IR (C_6H_{12}) ν(CO) 2069vs, 2024vs, 2015vs, 2004s, 1985m, 1959m, 1933m and 1889w (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ 7.49–7.12 (m, 10 H) and 2.12 (s, 15 H); ^{13}C NMR (75 MHz, CD_2Cl_2, 293 K) δ 225.9 (d, J_{PC} = 5, J_{WC} = 165), 213.3 (d, J_{PC} = 15), 206.2 (br, 3C), 205.1, 200.2, 196.7, 195.2 (d, J_{PC} = 12, 3C), 187.6 (*C*CPh), 145.4 (d, J_{PC} = 6 Hz, *ipso*-C of C_6H_5), 137.4 (*ipso*-C of C_6H_5), 133.5 (br, *o*-C of C_6H_5), 131.4 (br, *o*-C of C_6H_5), 131.2 (2C, *o*-C of C_6H_5), 130.7 (*p*-C of C_6H_5), 129.6 (*p*-C of C_6H_5), 129.5 (2C, *m*-C of C_6H_5), 128.9 (br, 2C, *m*-C of C_6H_5), 112.4 (C*C*Ph), 106.1 (*C*$_5$Me$_5$) and 11.9 (C$_5$*Me*$_5$) (Found: C, 33.85; H, 2.07. Calc. for $C_{35}H_{25}O_{11}PRu_4W$: C, 33.88; H, 2.03%).

Compound **3b**: mass spectrum (FAB, ^{184}W, ^{102}Ru) *m*/*z* 1174 (M^+); IR (C_6H_{12}) ν(CO) 2071vs, 2028vs, 2016vs, 2006vs, 1988s, 1968m, 1952w, 1940m and 1918w (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ 7.45–7.23 (m, 10 H) and 5.51 (s, 5 H); ^{13}C NMR (75 MHz, CD_2Cl_2, 293 K) δ 220.2 (d, J_{PC} = 5), 212.9 (d, J_{PC} = 14), 206.1, 203.5 (br, 3C), 201.4 (d, J_{PC} = 3), 196.6, 195.2 (d, J_{PC} = 13, 3C), 184.3 (*C*CPh), 149.0 (d, J_{PC} = 10, *ipso*-C of C_6H_5), 137.1 (*ipso*-C of C_6H_5), 131.7 (d, J_{PC} = 15, 2C, *o*-C of C_6H_5), 131.4 (2C, *m*-C of C_6H_5), 131.3 (*p*-C of C_6H_5), 129.8 (*p*-C of C_6H_5), 129.7 (d, J_{PC} = 12, 2C, *m*-C of C_6H_5), 129.5 (2C, *o*-C of C_6H_5), 111.7 (d, J_{PC} = 4 Hz, C*C*Ph) and 92.6 (C_5H_5) (Found: C, 30.53; H, 1.43. Calc. for $C_{30}H_{15}O_{11}PRu_4W$: C, 30.78; H, 1.29%).

X-Ray crystallography

The X-ray diffraction measurements were carried out on a Nonius CAD-4 diffractometer. Lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections were monitored every 3600 s. No significant change in intensities, due to crystal decay, was observed over the course of all data collection. Intensities of the diffraction signals were corrected for Lorentz, polarization and absorption effects (ψ scans). The structure was solved by using the NRCC-SDP-VAX package.[5] All the non-hydrogen atoms had anisotropic thermal parameters. The hydrogen atoms were placed at idealized positions with $U_H = U_C + 0.1$. The crystallographic refinement parameters of complexes **2a** and **3a** are given in Table 1, while selected bond distances and angles are presented in Tables 2 and 3, respectively.



Scheme 1

CCDC reference number 186/854.

See http://www.rsc.org/suppdata/dt/1998/1053/ for crystallographic files in .cif format.

Results and Discussion

Synthesis and characterization

The generation of phosphinidene cluster complexes **2a** and **3a** was effected by the reaction of [$Ru_4(CO)_{13}(\mu_3$-PPh)] with [$W(C_5Me_5)(CO)_3(CCPh)$] in refluxing toluene solution (Scheme 1). Similarly, treatment of [$Ru_4(CO)_{13}(\mu_3$-PPh)] with [$W(C_5H_5)(CO)_3(CCPh)$] afforded the corresponding pentametallic complexes **2b** and **3b** in 55 and 36% yields, respectively. All complexes were purified by routine thin-layer chromatography, followed by recrystallization. They were fully characterized using FAB mass spectrometry, IR, ^{1}H and ^{13}C NMR spectroscopies and single-crystal X-ray diffraction.

Complex **2a** crystallizes in monoclinic space group $P2_1/c$ with two crystallographically independent, but structurally identical molecules in the unit cell. As indicated in Fig. 1 it possesses a square-pyramidal core arrangement with the W atom located at the apical position. In addition the metal skeleton is coordinated by 11 terminal CO ligands, one μ_4-PPh fragment and one μ_3-η^2-CCPh fragment. The metal–metal distances are somewhat irregular, with the W–Ru distances [3.000(1)–2.927(1) Å] being slightly longer than the Ru–Ru distances [2.958(1)–2.699(1) Å]. The acetylide ligand forms a σ bond to the W atom and two π interactions with Ru atoms in a bonding mode similar to that observed in the acetylide complexes [$Ru_2(CO)_8(CCR)(WL)$] (L = C_5Me_5 or C_5H_5; R = Ph, Bu^t, *etc.*[6]). The phosphinidene ligand is found to link to four Ru atoms, and the Ru–P distances fall in the range 2.333(2)–2.380(2) Å which are in agreement with the structural data of other Ru_5 phosphinidene complexes.[7] If we consider that the μ_4-PPh ligand is a part of the cluster core, then the molecule appears to adopt a WRu_4P octahedral geometry. This geometry has also been observed in related cluster compounds containing a

Table 1 X-Ray structural data * for complexes **2a** and **3a**

	2a	**3a**
Formula	$C_{35}H_{25}O_{11}PRu_4W$	$C_{35}H_{25}O_{11}PRu_4W$
M	1240.67	1240.67
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a/Å	32.487(4)	10.856(2)
b/Å	10.295(3)	16.522(1)
c/Å	22.624(2)	20.453(2)
β/°	96.06(1)	
U/Å^3	7524(3)	3668.2(8)
Z	8	4
D_c/g cm^{-3}	2.190	2.247
F(000)	4652	2326
$2\theta_{max}$/°	45.0	55.0
hkl Ranges	−34 to 34, 0–11, 0–24	0–14, 0–21, 0–26
Crystal size/mm	0.05 × 0.10 × 0.55	0.10 × 0.15 × 0.40
μ(Mo-Kα)/cm^{-1}	47.51	48.73
Maximum, minimum transmission	1.000, 0.816	1.000, 0.778
No. data in refinement [$I \geqslant 2\sigma(I)$]	7136	3674
No. atoms and parameters	154, 938	77, 470
Weight modifier, g	0.000 02	0.000 01
Maximum Δ/σ ratio	0.004	0.009
R, R'	0.027, 0.024	0.030, 0.030
Goodness of fit	1.32	1.08
Maximum, minimum electron density peaks/e Å^{-3}	0.69, −0.61	0.67, −0.74

* Common features: λ(Mo-Kα) = 0.7107 Å; function minimized $\Sigma(w|F_o - F_c|^2)$, weighting scheme $w^{-1} = \sigma^2(F_o) + |g|F_o^2$; goodness of fit $= [\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{\frac{1}{2}}$ (N_o = number of observations, N_v = number of variables).

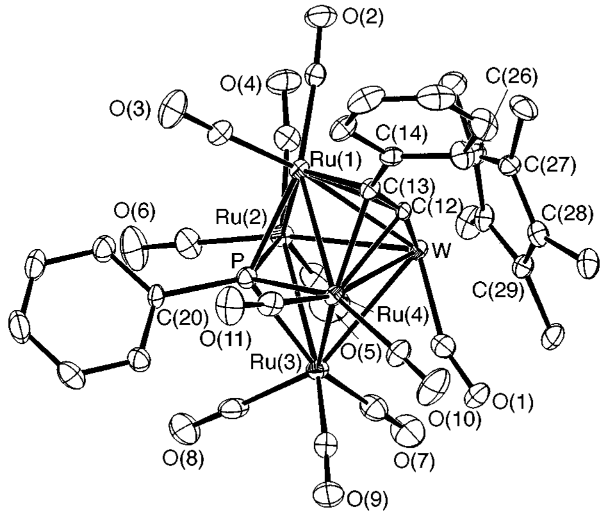


Fig. 1 Molecular structure and atomic labelling scheme of the green complex $[Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)\{W(C_5Me_5)(CO)\}]$ **2a** with thermal ellipsoids at the 30% probability level

bridging sulfide ligand.[8] Finally, assuming that the acetylide ligand serves as a five-electron donor, complex **2a** contains a total of 74 valence electrons, which is compatible with the electron counting for pentametallic cluster compounds with eight M–M bonds.

An X-ray diffraction study of compound **3a** was also undertaken in an attempt to compare its structure and bonding. As indicated in Fig. 2, the core arrangement is nominally similar to that of the previously discussed **2a**, comprising a square-pyramidal WRu_4 metal core and a μ_3-η^2-acetylide ligand co-ordinated to the WRu_2 triangle. A noteworthy distinction between **2a** and **3a** is that the W atom now resides in a basal position, while the μ_4-PPh phosphinidene ligand is co-ordinated to the WRu_3 square face with W–P and Ru–P distances in the range 2.447(3)–2.380(3) Å, analogous to those of W–Ru heterometallic phosphinidene cluster compounds.[9] Compound **3a** is hence related to **2a** by moving the W atom from the apical vertex to the basal position. Associated with this change of the cluster skeleton, a unique CO(2) ligand, which spans the Ru(1)–Ru(3) edge and adopts a semibridging mode with Ru(1)–C(2)–O(2) 151.6(9) and Ru(3)–C(2)–O(2) 126.4(8)°, was observed together with 10 other terminal CO ligands.

Table 2 Selected bond distances (Å) and angles (°) of complex **2a** with estimated standard deviations (e.s.d.s) in parentheses

W–Ru(1)	3.000(1)	W–Ru(2)	2.927(1)
W–Ru(3)	2.966(1)	W–Ru(4)	2.993(1)
Ru(1)–Ru(2)	2.930(1)	Ru(2)–Ru(3)	2.845(1)
Ru(1)–Ru(4)	2.699(1)	Ru(3)–Ru(4)	2.958(1)
Ru(1)–P	2.333(2)	Ru(2)–P	2.341(2)
Ru(3)–P	2.380(2)	Ru(4)–P	2.361(2)
W–C(12)	1.898(8)	Ru(1)–C(12)	2.180(7)
Ru(4)–C(12)	2.164(7)	Ru(1)–C(13)	2.119(7)
Ru(4)–C(13)	2.173(7)	C(12)–C(13)	1.37(1)
W–C(12)–C(13)	160.5(6)	C(12)–C(13)–C(14)	136.1(7)
W–C(1)–O(1)	160.8(7)		

Table 3 Selected bond distances (Å) and angles (°) of complex **3a** with e.s.d.s in parentheses

W–Ru(1)	2.929(1)	W–Ru(2)	2.950(1)
W–Ru(3)	2.988(1)	W–P	2.447(3)
Ru(1)–Ru(3)	2.820(1)	Ru(1)–Ru(4)	2.897(1)
Ru(2)–Ru(3)	2.699(1)	Ru(2)–Ru(4)	2.782(1)
Ru(3)–Ru(4)	2.879(1)	Ru(1)–P	2.380(3)
Ru(2)–P	2.399(3)	Ru(4)–P	2.403(3)
W–C(12)	1.959(9)	Ru(2)–C(12)	2.188(9)
Ru(3)–C(12)	2.199(9)	Ru(2)–C(13)	2.182(9)
Ru(3)–C(13)	2.186(9)	C(12)–C(13)	1.31(1)
Ru(1)–C(2)	1.96(1)	Ru(3)–C(2)	2.32(1)
W–C(12)–C(13)	158.5(7)	C(12)–C(13)–C(14)	140.0(9)
W–C(1)–O(1)	167.5(8)	Ru(1)–C(2)–O(2)	151.6(9)
Ru(3)–C(2)–O(2)	126.4(8)		

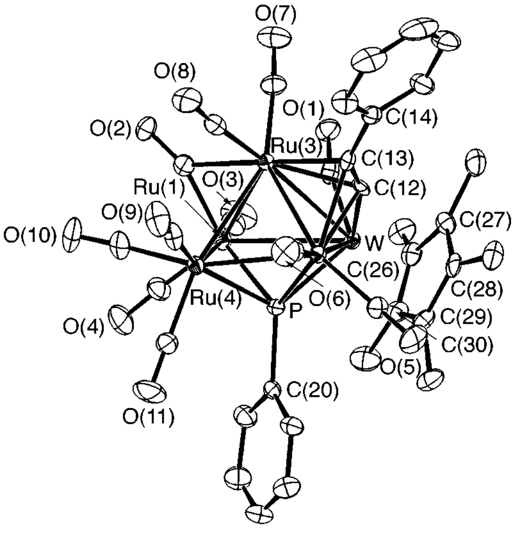
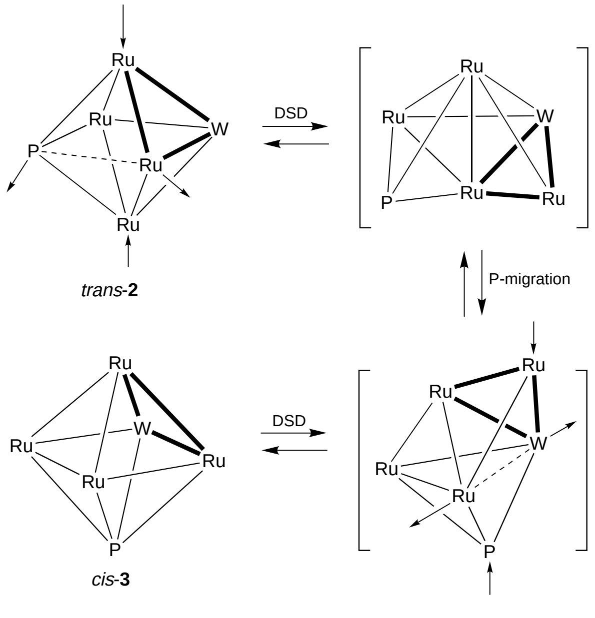


Fig. 2 Molecular structure and atomic labelling scheme of the black complex $[Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)\{W(C_5Me_5)(CO)\}]$ **3a** with thermal ellipsoids at the 30% probability level

Skeletal isomerization

A delicate equilibrium between compounds **2a** and **3a** at higher temperature is implicated because heating a toluene solution of **2a** provided a mixture of both complexes. Similarly, the isomerization is established from the opposite direction by heating a



Scheme 2

pure sample of **3a** in refluxing toluene under nitrogen. In addition, no retardation of the relative rate of isomerization was observed when the reactions were conducted under an atmosphere of carbon monoxide. Based on these experimental findings, the involvement of CO dissociation as the initial step is eliminated, which leaves the intramolecular process as the most likely reaction pathway.

Among the many possibilities, two mechanisms have been proposed to account for these skeletal isomerization reactions. The first involves a direct twisting of a Ru_2P face with respect to the opposite WRu_2 metal triangle which is capped by the acetylide ligand (Scheme 1). In this case an intermediate possessing a trigonal-prismatic core structure (**4**) is envisioned. It is interesting that this formally contains only six M–M bonds; therefore, it is electron deficient and some partial bonding interactions between the non-bonded metal atoms are required to stabilize it.

Alternatively, the isomerization may proceed through a combination of the diamond–square–diamond (DSD) rearrangement[10] and concomitant phosphinidene migration. One possible pathway is shown in Scheme 2, in which the direction of motion for the metal atoms is shown by the arrows, the chemical bond being broken is indicated by the dashed line, and the WRu_2 face supporting the acetylide ligand is shown by the solid triangle. The transformation from compound **2** to **3** may be accomplished *via* the first DSD process to give a trigonal-bipyramidal intermediate with the phosphinidene ligand moved to a Ru_3 triangle. The transformation of the phosphinidene ligand from the μ_4 to the μ_3 mode is energetically feasible, and this is supported by the isolation of many μ_3-phosphinidene cluster compounds.[11] After the phosphinidene ligand further migrates to a nearby WRu_2 triangle, the application of a second DSD process, but in a reverse direction, would lead to the formation of **3** with the phosphinidene ligand co-ordinated *cis* to the W atom. Interestingly, the trigonal-bipyramidal intermediates proposed in this DSD process contain nine instead of the eight M–M bonds which are associated with the square-pyramidal structures of both **2** and **3**. Hence, the activation energy for phosphinidene migration may be lowered by the increase in electron density through the formation of this extra M–M bond in the trigonal-bipyramidal intermediates.

Finally, extensive heating of the corresponding C_5H_5 derivative **3b** in toluene at reflux afforded the isomeric complex **2b** in 93% yield, while heating a toluene solution of **2b** under similar conditions failed to regenerate **3b** in significant quantity. This observation suggests that the isomer **3** with a *cis* arrangement of the W and the μ_4-PPh fragment could be the initial product of these cluster-growth reactions. Moreover, the *trans* arrangement is a thermodynamically more favorable structure for the C_5H_5 derivatives. Unfortunately, the preference of the metal framework, caused by changing the ancillary ligand on the W atom, is not clear at present. Thus, further examination is required before we can delineate an unambiguous explanation for such selectivity.

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