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Reactions of the alkylidyne tungsten complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4) with the dirhodium compound $[Rh_2(\mu\text{-}SPh)_2(cod)_2]$; crystal structure of $[W_2Rh_2(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}SPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$

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Abstract

In THF (tetrahydrofuran) the alkylidynetungsten complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4) react with $[Rh_2(\mu\text{-}SPh)_2(cod)_2]$ (cod = cyclo-octa-1,5-diene) to give, respectively, the tetranuclear mixed-metal compound $[W_2Rh_2(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}SPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and the trinuclear metal species $[WRh_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}SPh)_2(CO)_3(cod)(\eta\text{-}C_5H_5)]$. The molecular structure of the former has been established by X-ray diffraction. The metal atom core is based on a 'butterfly' arrangement with the two rhodium atoms forming the body of the butterfly (Rh–Rh 2.588(1) Å) and the tungsten atoms occupying the 'wing-tip' positions (W–Rh mean 2.817 Å). The two WRh_2 triangles forming the wings of the butterfly are inclined at 20° to one another. In one triangle the W–Rh bonds are bridged, respectively, by a μ-CMe group (μ-C–W 1.88(1), μ-C–Rh 2.08(1) Å) and by two μ-SPh ligands (mean μ-S–W 2.403, mean μ-S–Rh 2.416 Å), and the tungsten atom carries a C_5H_5 ring. The other WRh_2 triangle is triply bridged by an ethylidyne group (μ_3-C–W 2.02(1), mean μ_3-C–Rh 2.09 Å), and one of the W–Rh bonds is semi-bridged by a CO ligand (W–C–O 168(1)°, W–CO 1.97(1), Rh ··· CO 2.42(1) Å). The tungsten atom is also ligated by a C_5H_5 ring and another CO group (W–C–O 171(1)°). Each rhodium atom carries an essentially terminally bound CO ligand. The NMR data (^1H and $^{13}C\{^1H\}$) for the new compounds are reported and discussed.

Introduction

We have recently employed the dirhodium compound $[Rh_2(\mu\text{-}PPh_2)_2(cod)_2]$ (**Ia**, cod = cyclo-octa-1,5-diene) as a reagent for the synthesis of complexes containing

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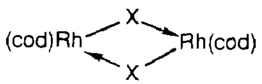
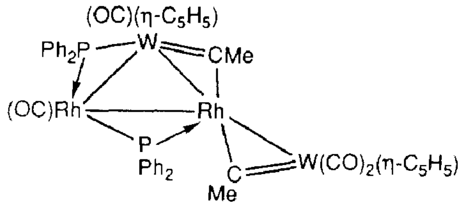
W–Rh bonds [1]. Treatment of **Ia** with two equivalents of the ethylidynetungsten compound $[\mathrm{W}(\equiv\mathrm{CMe})(\mathrm{CO})_2(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)]$ in THF (tetrahydrofuran) at ambient temperatures affords initially the tetranuclear metal complex $[\mathrm{W}_2\mathrm{Rh}_2(\mu\text{-}\mathrm{CMe})_2(\mu\text{-}\mathrm{PPh}_2)_2(\mathrm{CO})_4(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2]$ (**II**). The latter isomerises in solution to give $[\mathrm{W}_2\mathrm{Rh}_2(\mu\text{-}\mathrm{CO})\{\mu\text{-}\mathrm{C}(\mathrm{Me})\mathrm{C}(\mathrm{O})\}(\mu\text{-}\mathrm{PPh}_2)_2(\mu_3\text{-}\mathrm{CMe})(\mathrm{CO})_2(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2]$ (**III**). Moreover, this species readily adds a molecule of CO to yield $[\mathrm{W}_2\mathrm{Rh}_2(\mu\text{-}\mathrm{CO})\{\mu\text{-}\mathrm{C}(\mathrm{Me})\mathrm{C}(\mathrm{O})\}(\mu\text{-}\mathrm{PPh}_2)_2(\mu_3\text{-}\mathrm{CMe})(\mathrm{CO})_3(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2]$ (**IV**). In refluxing THF the latter isomerises to give $[\mathrm{W}_2\mathrm{Rh}_2(\mu\text{-}\mathrm{CO})_2\{\mu\text{-}\mathrm{C}(\mathrm{Me})\mathrm{PPh}_2\}(\mu\text{-}\mathrm{PPh}_2)(\mu_3\text{-}\mathrm{CMe})(\mathrm{CO})_3(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2]$ (**V**), which on further heating loses CO and affords $[\mathrm{W}_2\mathrm{Rh}_2(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{CMe})(\mu\text{-}\mathrm{PPh}_2)_2(\mu_3\text{-}\mathrm{CMe})(\mathrm{CO})_3(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)_2]$ (**VI**). The transformation of **IV** into **V** involves an unprecedented conversion of μ-PPh$_2$ and μ-C(Me)C(O) groups into μ-CO and μ-C(Me)PPh$_2$ ligands at a dimetal centre. If the reaction between **Ia** and $[\mathrm{W}(\equiv\mathrm{CMe})(\mathrm{CO})_2(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)]$ is carried out with a large excess of the tungsten reagent (4/1 mol ratio) pentanuclear metal compounds are obtained. These compounds



	X
Ia	PPh$_2$
Ib	SPh



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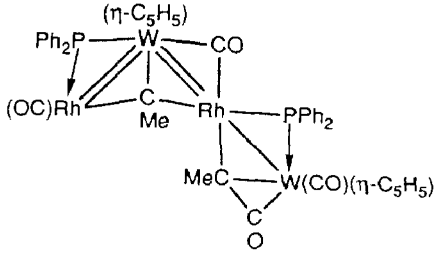

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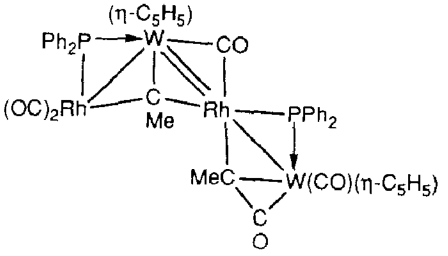

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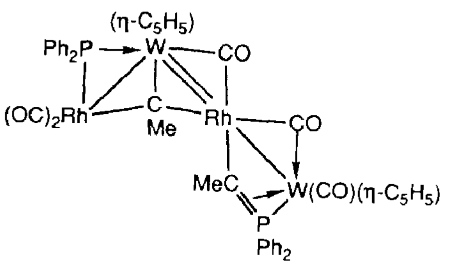

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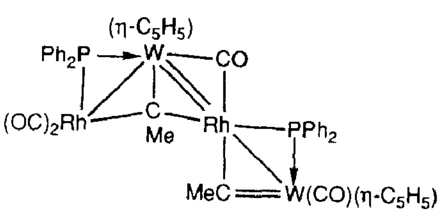


VI

have structures based on a chain of metal atoms (W · Rh · W · Rh · W) with the metal–metal bonds bridged by CO, CMe, C(Me)C(O), PPh_2, or C(Me)PPh_2 groups. Moreover, these products are formed as a result of migration and transformation of the ligands in a similar manner to that observed for the tetranuclear metal species **II**–**VI**.

The above results prompted us to investigate reactions between the μ-sulphido complex $[Rh_2(\mu\text{-}SPh)_2(cod)_2]$ (**Ib**) and the alkylidynetungsten compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4) in the expectation that a variety of new polynuclear tungsten-rhodium species would be obtained. Since **Ib** is structurally related to **Ia** it was hoped that the μ-SPh groups in the former would undergo migratory and other processes similar to those displayed by the μ-PPh_2 groups of **Ia**. In practice, as described below, compound **Ib** proved to be a much less versatile precursor than **Ia**, and only two mixed-metal complexes were isolated in reactions with the alkylidyne tungsten reagents.

Results and discussion

In THF at ca. 50–60 °C a mixture of **Ib** and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$, in 1/2 mol ratio, afforded a black crystalline cluster compound $[W_2Rh_2(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}SPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (**VII**), but only in low yield (ca. 10%). Microanalytical and spectroscopic data were in agreement with the formulation of **VII**, but the structure of the compound only became apparent following an X-ray diffraction study. The results of the latter are summarised in Table 1, and the molecule is shown in Fig. 1.

The metal atoms of the core adopt the now well established 'butterfly' arrangement [2], with the two rhodium atoms forming the body of the butterfly and the two tungsten atoms occupying the wing-tip sites (Rh(1)–Rh(2) 2.588(1), W(1)–Rh(1) 2.764(1), W(1)–Rh(2) 2.820(1), W(2)–Rh(1) 2.886(1), W(2)–Rh(2) 2.798(1) Å). The angle between the planes defined by the atoms W(1)Rh(1)Rh(2) and W(2)Rh(1)Rh(2) is 20 °, and so the butterfly structure is relatively flat. The disposition of the various ligands renders the structure very asymmetric. In the W(1)Rh(1)Rh(2) triangle the W(1)–Rh(1) bond is bridged by two SPh groups (mean μ-S–W 2.403, μ-S–Rh 2.416 Å) while the W(1)–Rh(2) edge is asymmetrically bridged by an ethylidyne ligand [C(14)–W(1) 1.88(1), C(14)–Rh(2) 2.08(1) Å]. We have reported X-ray crystallographic studies on several complexes containing a W(μ-CR)Rh (R = alkyl or aryl) fragment [1,3] and the μ-C–W and μ-C–Rh distances are in the ranges 1.84–1.91 and 2.05–2.12 Å, respectively. Thus the μ-C–W and μ-C–Rh separations in **VII** are as expected.

The W(2)Rh(1)Rh(2) triangle is triply bridged by an ethylidyne group [C(17)–W(2) 2.02(1), C(17)–Rh(1) 2.11(1), C(17)–Rh(2) 2.07(1) Å]. Several other complexes are known [1,4] in which WRh_2 triangles are capped by CR (R = Me or C_6H_4Me-4) groups, and the μ-C–W (1.90–2.03 Å) and μ-C–Rh (1.99–2.07 Å) distances are all very close to those found in **VII**. Both rhodium atoms carry an essentially terminally bound CO ligand, although that coordinated to Rh(2) deviates somewhat from linearity (Rh(2)–C(16)–O(16) 173(1)°). Both CO groups attached to W(2) are bent (W(2)–C(19)–O(19) 168(1), W(2)–C(20)–O(20) 171(1)°), and the ligand C(19)O(19) should be regarded as semi-bridging. The IR spectrum of **VII** in the CO region shows a strong band at 1962 cm^{-1}, and two very broad absorptions

Table 1

Selected internuclear distances (Å) and angles (°) for $[W_2Rh_2(\mu\text{-CMe})(\mu_3\text{-CMe})(\mu\text{-SPh})_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **(VII)**

W(1)–Rh(1)	2.764(1)	W(1)–Rh(2)	2.820(1)	W(2)–Rh(1)	2.886(1)	W(2)–Rh(2)	2.798(1)
Rh(1)–Rh(2)	2.588(1)	W(1)–S(1)	2.414(3)	W(1)–S(2)	2.391(2)	Rh(1)–S(1)	2.460(2)
Rh(1)–S(2)	2.372(3)	W(1)–C(14)	1.88(1)	Rh(2)–C(14)	2.08(1)	W(2)–C(17)	2.02(1)
Rh(1)–C(17)	2.11(1)	Rh(2)–C(17)	2.07(1)	W(2)–C(19)	1.97(1)	Rh(2)–C(19)	2.42(1)
W(2)–C(20)	1.97(1)	S(1)–C(1)	1.81(1)	S(2)–C(7)	1.79(1)	C(14)–C(15)	1.53(2)
C(17)–C(18)	1.49(1)	Rh(1)–C(13)	1.92(1)	Rh(2)–C(16)	1.88(1)	C(13)–O(13)	1.13(1)
C(16)–O(16)	1.12(2)	C(19)–O(19)	1.17(1)	C(20)–O(20)	1.16(2)	W(1)–C(cp) [a]	2.34(1)
W(2)–C(cp) [a]	2.34(1)						
Rh(1)–W(1)–Rh(2)	55.2(1)	Rh(1)–W(2)–Rh(2)	54.1(1)	W(1)–Rh(1)–W(2)	121.5(1)	W(2)–Rh(2)–W(1)	122.6(1)
Rh(1)–W(1)–C(14)	101.9(3)	Rh(1)–W(2)–C(17)	47.1(3)	W(1)–Rh(1)–Rh(2)	63.5(1)	W(2)–Rh(2)–Rh(1)	64.7(1)
Rh(1)–W(1)–S(1)	56.2(1)	C(19)–W(2)–Rh(1)	86.3(3)	W(1)–Rh(1)–S(1)	54.7(1)	W(2)–Rh(2)–C(17)	46.1(3)
Rh(1)–W(1)–S(2)	54.2(1)	C(19)–W(2)–Rh(2)	57.9(3)	W(1)–Rh(1)–S(2)	54.9(1)	W(2)–Rh(2)–C(16)	101.2(4)
W(1)–S(1)–Rh(1)	69.1(1)	C(20)–W(2)–Rh(1)	62.7(3)	W(2)–Rh(1)–S(1)	97.4(1)	W(2)–Rh(2)–C(19)	43.6(2)
W(1)–S(1)–C(1)	108.0(3)	C(20)–W(2)–Rh(2)	106.8(3)	W(2)–Rh(1)–S(2)	131.6(1)	W(2)–Rh(2)–C(14)	163.1(3)
Rh(1)–S(1)–C(1)	116.6(3)	W(1)–C(14)–Rh(2)	90.6(5)	W(2)–Rh(1)–Rh(2)	61.2(1)	W(2)–C(17)–C(18)	137.8(7)
W(1)–S(2)–Rh(1)	70.9(1)	W(1)–C(14)–C(15)	143.6(8)	W(2)–Rh(1)–C(17)	44.4(3)	Rh(1)–C(17)–C(18)	126.4(6)
W(1)–S(2)–C(7)	116.8(3)	Rh(2)–C(14)–C(15)	125.7(8)	W(2)–Rh(1)–C(13)	105.9(3)	Rh(2)–C(17)–C(18)	121.0(8)
Rh(1)–S(2)–C(7)	113.2(4)	Rh(1)–C(13)–O(13)	177(1)	Rh(2)–C(16)–O(16)	173(1)	W(2)–C(19)–O(19)	168(1)
W(2)–C(20)–O(20)	171(1)	Rh(2)–C(19)–O(19)	114(1)				

[a] Mean W–C(η-C_5H_5) distance.

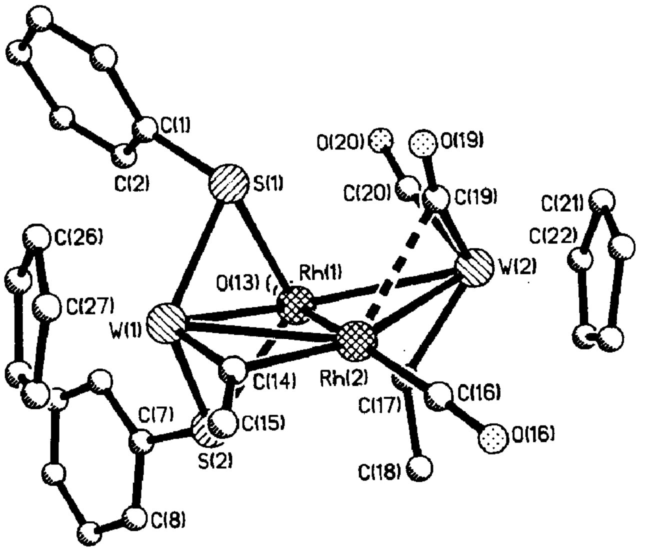


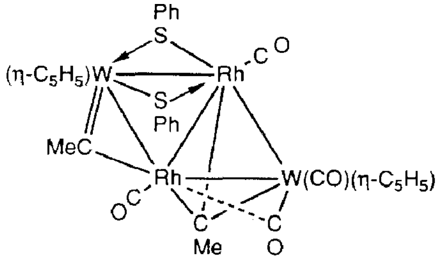
Fig. 1. The molecular structure of $[W_2Rh_2(\mu\text{-CMe})(\mu_3\text{-CMe})(\mu\text{-SPh})_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (**VII**) showing the crystallographic numbering scheme.

at 1853 and 1783 cm^{-1}. These last two peaks are in the region for semi-bridging or asymmetrically bridging CO groups. Each tungsten atom, as expected, carries a C_5H_5 ligand.

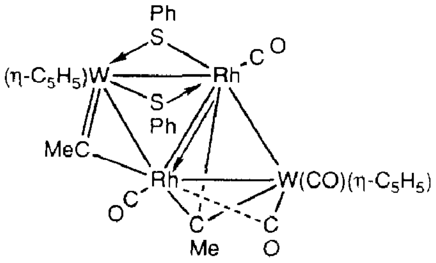
Compound **VII** has 60 metal-plus-ligand valence electrons. In terms of the polyhedral skeletal electron pair theory a butterfly configuration is regarded as an arachno structure associated with 62 valence electrons. However, electron counts less than 62 are not uncommon when atoms of one or other of the platinum metals are incorporated into the cluster. For example, the butterfly clusters $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ and $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ have 60 and 58 valence electrons, respectively [5]. In contrast, the anionic complex $[Rh_4(\mu\text{-}PPh_2)_5(CO)_5]^-$ conforms with skeletal electron pair theory in having 62 metal-plus-ligand electrons [6]. Moreover, this species is similar to **VII** in having a (OC)RhRh(CO) fragment forming the body of the butterfly core. The Rh–Rh separation [3.02(1) Å], however, is appreciably longer than that in **VII** (2.588(1) Å), a feature perhaps reflecting the electronic unsaturation of the latter complex. Indeed, the Rh(1)–Rh(2) distance in **VII** is similar to that found (2.564(1) Å) in the electronically unsaturated compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ [7]. Addition of a CO molecule to the latter affords the electronically saturated complex $[Rh_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)_2]$ wherein the Rh–Rh distance is increased to 2.743(1) Å [8]. However, the Rh(1)–Rh(2) separation in **VII** is likely to be influenced by the stereochemical requirements of the various groups ligating the rhodium atoms as well as by the electronic effects.

Although a precise allocation of electron pairs to metal–metal connectivities in clusters is often unrewarding two representations for **VII** are depicted. In **VIIa** one rhodium atom (Rh(2) of Fig. 1) has a 16 electron valence shell, and the other (Rh(1)) has a filled 18 electron shell. In **VIIb** by invoking a donor bond from Rh(1) to Rh(2) both of these atoms attain 18 electron configurations.

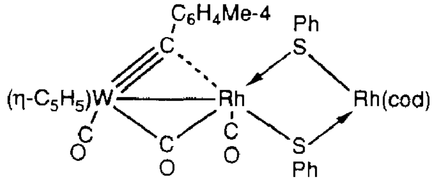
The structure of **VII** having been established, the NMR data are readily interpretable and are in agreement with the X-ray crystallographic results. The ^1H NMR



VII(a)



VII(b)



VIII

spectrum shows two C_5H_5 resonances and two CMe signals, as expected. In the $^{13}C\{^1H\}$ NMR spectrum there are four peaks in the CO region. Those at δ 230.6 and 223.4 ppm have chemical shifts diagnostic for WCO groups. Moreover, the resonance at 230.6 ppm is a doublet, displaying weak $^{103}Rh-^{13}C$ coupling (7 Hz). It is likely that this signal is due to the semi-bridging C(19)O(19) ligand (Fig. 1). The terminal RhCO groups give rise to doublet resonances at δ 196.9 and 193.2 ppm, with *J*(RhC) 75 and 86 Hz, respectively. Of interest are the resonances displayed by the bridging ethylidyne groups at δ 325.5 and 319.2 ppm. The former appears as a doublet (*J*(RhC) 29 Hz) and the latter as an apparent triplet (*J*(RhC) 28 Hz), resulting from overlap of two doublets arising through coupling with two non-equivalent ^{103}Rh nuclei. It is thus evident that the resonance at δ 325.5 ppm is due to the edge-bridging μ-*C*Me group and that at δ 319.2 ppm to the μ_3-*C*Me nucleus. The latter signal is relatively deshielded for a triply bridging alkylidyne group bridging a WRh_2 triangle. Thus in the $^{13}C\{^1H\}$ NMR spectra of the complexes $[WRh_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ and $[WRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(acac)_2(\eta\text{-}C_5H_5)]$ (acac = acetylacetonato) the μ_3-C nuclei resonate at δ 299.7 and 302.0 ppm, respectively [4]. In the spectra of the compounds III–VI the resonances due to the μ_3-*C*Me nuclei occur in the range 292.9–305.3 ppm [1]. In the $^{13}C\{^1H\}$ NMR spectrum of **VII** the chemical shift for the μ-*C*Me nucleus at 325.5 ppm may be compared with those observed in the spectra of compound **II** at δ 346.5 and 349.1 ppm, compound **VI** at δ 332.7 and 335.8 ppm (two isomers) [1], and $[WRh(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (C_9H_7 = indenyl) at δ 323.4 ppm [9].

During our studies [1] on reactions of **Ia** with the alkylidynetungsten compounds we failed to isolate products when the *p*-tolylmethylidyne reagent $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ was employed. However, we have found in the present work that **Ib** reacts slowly with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in THF at room temperature to give the trimetal complex $[WRh_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}SPh)_2(CO)_3(cod)(\eta\text{-}C_5H_5)]$ (**VIII**). The formulation and structure of this species is based on microanalytical and spectroscopic data.

The IR spectrum shows three bands in the CO region at 1968, 1857 and 1790 cm^{-1}, and the latter may be ascribed to a bridging ligand. The ^1H NMR spectrum shows resonances for the C_5H_5, Ph, C_6H_4Me-4 and cod groups with the expected relative intensity for the structure proposed. In the $^{13}C\{^1H\}$ NMR spectrum there are diagnostic signals for the CO ligands at δ 224.0, 223.2 (WCO) and 183.2 ppm (RhCO, d, J(RhC) 72 Hz). Other peaks in the spectrum agree with the structure indicated. In particular, the resonance for the $\mu\text{-}CC_6H_4Me$-4 nucleus at δ 301.2 ppm (d, J(RhC) 24 Hz) has a chemical shift close to that observed for the precursor $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (δ 300 ppm). This suggests that the p-tolylmethylidyne group in **VIII** interacts only weakly with the rhodium atoms. In the spectrum of the dimetal compound $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ the μ-C resonance is appreciably more deshielded at δ 322.9 ppm [10]. We have previously reported other complexes in which an alkylidyne ligand only weakly bridges a metal–metal bond, and have confirmed this by X-ray diffraction studies [11]. In these compounds also the resonances for the alkylidyne-carbon nuclei in the $^{13}C\{^1H\}$ NMR spectra have chemical shifts which are very close to those observed in the spectra of the alkylidynetungsten complex from which they are derived.

The pathways by which compounds **VII** and **VIII** are formed are obscure, and their formation in relatively low yield makes any speculation of little value. The isolation of **VIII** suggests that an initial step in the formation of **VII** is the displacement of a cod ligand from **Ib** by a molecule of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$. Subsequent steps must involve migration of CO and SPh groups and addition of another molecule of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$.

Experimental

All experiments were carried out under nitrogen by Schlenk tube techniques. Light petroleum refers to the fraction of b.p. 40–60 °C. The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4 [12]) and $[Rh_2(\mu\text{-}SPh)_2(cod)_2]$ [13] were prepared by methods previously described. Aluminium oxide used for chromatography was Brockman Activity II alumina. NMR spectra were recorded with JEOL JNM FX90, GX270 and GX400 spectrometers, and IR spectra with a Perkin Elmer 1600 FT instrument. NMR spectra were measured in CD_2Cl_2, and IR spectra in THF.

Reactions of $[Rh_2(\mu\text{-}SPh)_2(cod)_2]$

(i). A mixture of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.11 g, 0.32 mmol) and $[Rh_2(\mu\text{-}SPh)_2(cod)_2]$ (0.10 g, 0.16 mmol) in THF (20 cm^3) was stirred at ca. 50–60 °C for 1 h, during which period the mixture changed from orange to dark brown. Solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (5 cm^3) and adsorbed onto alumina (ca. 3 g). The latter was transferred to the top of an alumina chromatography column (ca. 2 × 10 cm) which was first eluted with light petroleum to remove unreacted $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$. Subsequent elution with CH_2Cl_2/light petroleum (1/1) removed traces of unidentified compounds followed by a dark brown fraction. Removal of solvent in vacuo and crystallisation of the residue from

CH_2Cl_2/light petroleum (6 cm^3, 1/5) afforded black crystals of $[W_2Rh_2(\mu\text{-}CMe)(\mu_3\text{-}CMe)(\mu\text{-}SPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (**VII**) (0.02 g, 9%) (Found: C, 33.0; H, 2.5, $C_{30}H_{26}O_4S_2Rh_2W_2$ calc.: C, 33.1; H, 2.4%); IR: ν_{max} at 1962s, 1853m br, and 1783w br cm^{-1}. NMR: ^1H, δ 3.14 (s, 3 H, CMe), 4.01 (s, 3 H, CMe), 5.15 (s, 5 H, C_5H_5), 5.25 (s, 5 H, C_5H_5), and 7.25–7.42 (m, 10 H, Ph); $^{13}C\{H\}$, δ 325.5 (d, μ-C, J(RhC) 29), 319.2 (apparent t, μ_3-C, J(RhC) 28), 230.6 (d, μ-CO, J(RhC) 7), 223.4 (WCO), 196.9 (d, RhCO, J(RhC) 75), 193.2 (d, RhCO, J(RhC) 86 Hz) 133.8–126.2 (Ph), 97.9, 90.7 (C_5H_5), 48.5, 45.8 ppm. (C*Me*).

(ii). Similarly, $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.14 g, 0.36 mmol) and $[Rh_2(\mu\text{-}SPh)_2(cod)_2]$ (0.11 g, 0.18 mmol) in THF (20 cm^3) after 3 days at ambient temperatures, and work-up as described above, gave brown microcrystals of $[WRh_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}SPh)_2(CO)_3(cod)\eta\text{-}C_5H_5)]$ (**VIII**) (0.02 g, 13%) (Found: C, 39.7; H, 3.2. $C_{30}H_{30}O_3S_2Rh_2W$ calc.: C, 40.4; H, 3.4%); IR: ν_{max} at 1968s, 1857m br, and 1790w br cm^{-1}. NMR: ^1H, 1.70–2.50 (m, 8 H, CH_2) 2.34 (s, 3 H, Me-4), 3.65–4.18 (m, 4 H, CH), 5.48 (s, 5 H, C_5H_5), 6.95–7.28 (m, 10 H, SPh), and 7.64, 8.29 ((AB_2), 4 H, C_6H_4, J(AB) 8 Hz); $^{13}C\{^1H\}$, δ 301.2 (d, μ-C, J(RhC) 24), 224.0, 223.2 (WCO), 183.2 (d, RhCO, J(RhC) 72 Hz), 153.3 ($C^1(C_6H_4)$), 137.9–125.1 (C_6H_4 and Ph), 91.5 (C_5H_5), 83.6–79.7 (CH), 30.9–27.0 (CH_2), and 21.0 ppm (Me-4).

Crystal structure determination

Crystals of **VII** were grown by diffusion of light petroleum into a CH_2Cl_2 solution of the complex. The crystal chosen for study (ca. 0.20 × 0.25 × 0.20 mm) was sealed under nitrogen in a Lindemann tube. Data were collected (θ-2θ scans) at 293 K on a Nicolet $P2_1$ four-circle diffractometer. Of the 5578 intensities measured ($2\theta \leqslant 50°$), 3945 unique data had $F \geqslant 6\sigma(F)$ and only these were used in the structural solution and refinement, after correction for Lorentz and polarisation effects and for X-ray absorption, the latter by a semi-empirical method based on azimuthal scan data [14].

Crystal data. $C_{30}H_{26}O_4S_2Rh_2W_2$, $M = 1088.1$, triclinic, space group $P\bar{1}$, a 9.435(2), b 11.121(2), c 15.806(6) Å, α 72.60(2), β 83.28(3), γ 74.31(2)°, U 1523(1) $Å^3$, $Z = 2$, D_c 2.37 g cm^{-3}, $F(000) = 1016$, Mo-K_α X-radiation (graphite monochromator) $\lambda = 0.71069$ Å, μ(Mo-K_α) 89.1 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and successive difference-Fourier syntheses were used to locate all the non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters ca. $1.2 \times U_{equiv}$ of the parent carbon atoms. Refinement by blocked-cascade least squares led to $R = 0.034$ ($R' = 0.040$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005 | F_o |^2]$ giving a satisfactory analysis of variance. The final electron density difference synthesis showed no peaks $\geqslant 0.78$ or $\leqslant -1.30$ $eÅ^{-3}$. All calculations were performed with the SHELXTL system of programs [14]. Scattering factors with corrections for anomalous dispersion were taken from ref. 15. The atom coordinates are given in Table 2. Full listing of bond distances and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Structure factors are available from the authors.

Table 2

Atomic positional parameters (fractional coordinates $\times 10^4$) for compound **VII** with estimated standard deviations in parentheses.

Atom	x	y	z
W(1)	−2558(1)	1912(1)	3309(1)
W(2)	1962(1)	2198(1)	1433(1)
Rh(1)	−748(1)	3385(1)	2241(1)
Rh(2)	−429(1)	1091(1)	2056(1)
S(1)	−274(3)	2048(2)	3778(1)
S(2)	−3248(3)	3625(2)	1981(2)
O(13)	−691(11)	6204(7)	1989(5)
O(16)	113(12)	−870(9)	1031(7)
O(19)	2403(9)	−211(7)	3101(5)
O(20)	2387(8)	3758(8)	2690(6)
C(1)	−712(10)	2898(10)	4627(6)
C(2)	−1301(11)	4224(9)	4429(6)
C(3)	−1691(14)	4829(12)	5100(8)
C(4)	−1485(13)	4098(13)	5966(8)
C(5)	−822(14)	2780(13)	6158(8)
C(6)	−457(12)	2178(11)	5495(6)
C(7)	−4435(10)	5120(9)	2110(7)
C(8)	−5471(13)	5756(10)	1494(7)
C(9)	−6428(14)	6931(13)	1500(9)
C(10)	−6283(15)	7488(13)	2125(10)
C(11)	−5283(15)	6889(14)	2763(10)
C(12)	−4339(13)	5692(12)	2752(8)
C(13)	−704(12)	5165(10)	2058(6)
C(14)	−2199(11)	501(9)	2823(7)
C(15)	−2773(14)	−650(11)	2807(9)
C(16)	−61(14)	−195(10)	1460(7)
C(17)	−160(10)	2745(8)	1087(6)
C(18)	−992(12)	3233(10)	259(6)
C(19)	2073(11)	686(10)	2485(7)
C(20)	2109(11)	3190(10)	2251(7)
C(21)	4430(14)	2025(16)	963(9)
C(22)	3634(18)	3171(15)	444(10)
C(23)	2745(16)	2966(17)	−54(8)
C(24)	2880(17)	1684(18)	98(9)
C(25)	3978(16)	1059(13)	769(9)
C(26)	−3188(13)	1269(15)	4825(7)
C(27)	−3710(13)	552(13)	4414(8)
C(28)	−4802(12)	1439(12)	3812(8)
C(29)	−4951(12)	2675(13)	3868(8)
C(30)	−3964(13)	2594(14)	4504(7)

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References

1 S.J. Davies, J.A.K. Howard, M.U. Pilotti, and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1989) 190; J. Chem. Soc., Dalton Trans., (1989) 1855; S.J. Davies and F.G.A. Stone, ibid., (1989) 1865.

2 E. Sappa, A. Tiripicchio, A.J. Carty, and G.E. Toogood, Progr. Inorg. Chem., 35 (1987) 437.

3 J.C. Jeffery, C. Sambale, M.F. Schmidt, and F.G.A. Stone, Organometallics, 1 (1982) 1597; M. Green, J.A.K. Howard, A.P. James, C.M. Nunn, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1987) 61.

4 M.J. Chetcuti, P.A.M. Chetcuti, J.C. Jeffery, R.M. Mills, P. Mitrprachachon, S.J. Pickering, F.G.A. Stone, and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 699; J.C. Jeffery, C. Marsden, and F.G.A. Stone, ibid., (1985) 1315; M. Green, J.A.K. Howard, A.P. James, C.M. Nunn, and F.G.A. Stone, ibid., (1986) 187;

5 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone, and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 162, 1274.

6 P.F. Kreter, D.W. Meek, and G.G. Cristoph, J. Organomet. Chem., 188 (1980) C27.

7 R.D. Barr, M. Green, J.A.K. Howard, T.B. Marder, and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1983) 759.

8 W.A. Herrman, J. Plank, C.H. Bauer, M.L. Ziegler, E. Guggolz, and R. Alt, Z. Anorg. Allg. Chem., 487 (1982) 85.

9 J.A. Abad, L.W. Bateman, J.C. Jeffery, K.A. Mead, H. Razay, F.G.A. Stone, and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 2075.

10 M. Green, J.C. Jeffery, S.J. Porter, H. Razay, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1982) 2475.

11 D.D. Devore, J.A.K. Howard, J.C. Jeffery, M.U. Pilotti, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1989) 303.

12 W. Uedelhoven, K. Eberl, and F.R. Kreissl, Chem. Ber., 112 (1979) 3376; E.O. Fischer, T.L. Lindner, G. Huttner, P. Friedrich, F.R. Kreissl, and J.O. Besenhard, ibid., 110 (1977) 3397.

13 R.H. Crabtree, A. Gautier, G. Giordano, and T. Khan, J. Organomet. Chem., 141 (1977) 113.

14 G.M. Sheldrick, SHELXTL programs for use with the Nicolet X-ray system, Revision 5.1, 1986.

15 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4.