

Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 40.¹ Transformation of Terminally Bound Alkylidyne Ligands to μ -Alkylidene, μ -Vinyl, μ -Alkyl, and μ -Acyl Groups at a Bimetal Centre; X-Ray Crystal Structures of $[\text{N}(\text{PPh}_3)_2][\text{ReW}(\mu\text{-CHR})(\text{CO})_9]$, $[\text{ReW}(\mu\text{-CH}_2\text{R})(\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2)(\text{CO})_7]$, and $[\text{ReW}(\mu\text{-OCCH}_2\text{R})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_6\{\text{P}(\text{OMe})_3\}]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$)*

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Treatment of the complexes $[\text{ReM}(\equiv\text{CR})(\text{CO})_9]$ in tetrahydrofuran (thf) with $\text{K}[\text{BH}(\text{CHMeEt})_3]$, followed by addition of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ affords the salts $[\text{N}(\text{PPh}_3)_2][\text{ReM}(\mu\text{-CHR})(\text{CO})_9]$ ($\text{M} = \text{Cr}$, Mo , or W , $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$; $\text{M} = \text{W}$, $\text{R} = \text{Me}$). The structure of one of these species ($\text{M} = \text{W}$, $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) was determined by X-ray diffraction. In the anion, the Re-W bond [$3.033(1) \text{ \AA}$] is asymmetrically spanned by the $\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})$ group [$\mu\text{-C-Re } 2.155(8)$, $\mu\text{-C-W } 2.404(6) \text{ \AA}$]. The rhenium atom is ligated by four CO groups and the tungsten by five of these ligands. On warming in thf solution, the bridged ethylidene complex $[\text{N}(\text{PPh}_3)_2][\text{ReW}(\mu\text{-CHMe})(\text{CO})_9]$ releases CO and converts to the hydrido- and vinyl-bridged salt $[\text{N}(\text{PPh}_3)_2][\text{ReW}(\mu\text{-H})(\mu\text{-CH=CH}_2)(\text{CO})_8]$. Treatment of the compounds $[\text{N}(\text{PPh}_3)_2][\text{ReM}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$ with the bidentate phosphines $\text{R}'_2\text{PCH}_2\text{PR}'_2$ ($\text{R}' = \text{Ph}$ or Me) affords the complexes $[\text{N}(\text{PPh}_3)_2][\text{ReM}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-R}'_2\text{PCH}_2\text{PR}'_2)(\text{CO})_7]$ ($\text{M} = \text{W}$, $\text{R}' = \text{Ph}$; $\text{M} = \text{Cr}$, Mo , or W , $\text{R}' = \text{Me}$). The rhenium-tungsten species on protonation ($\text{HBF}_4 \cdot \text{Et}_2\text{O}$) afford complexes $[\text{ReW}(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-R}'_2\text{PCH}_2\text{PR}'_2)(\text{CO})_7]$ in which the *p*-tolylmethyl group asymmetrically bridges the metal-metal vector, being σ -bonded to the rhenium and co-ordinated to the tungsten by a three-centre, two-electron $\text{C-H}\rightarrow\text{W}$ bond. This result, strongly indicated by ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. data, was confirmed by an X-ray diffraction study on the $\text{Me}_2\text{PCH}_2\text{PMe}_2$ derivative [$\mu\text{-C-Re } 2.302(7)$, $\mu\text{-C-W } 2.539(7) \text{ \AA}$]. The Re-W vector [$2.950(2) \text{ \AA}$] is also spanned by the $\text{Me}_2\text{PCH}_2\text{PMe}_2$ ligand and a strongly semi-bridging carbonyl attached to the tungsten [$\text{W-C-O } 153.6(6)^\circ$]. The $\text{Me}_2\text{PCH}_2\text{PMe}_2$ and $\text{CH}_2\text{C}_6\text{H}_4\text{Me-4}$ groups are cisoid in the bridge system. The rhenium and tungsten atoms each carry three terminally bound CO ligands. Several reactions of the bridged *p*-tolylmethyl rhenium-tungsten compounds have been investigated, that between $[\text{ReW}(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_7]$ and $\text{P}(\text{OMe})_3$ affording the complex $[\text{ReW}(\mu\text{-OCCH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_6\{\text{P}(\text{OMe})_3\}]$, the structure of which was established by X-ray diffraction. In this compound the Re-W bond [$3.155(1) \text{ \AA}$] is bridged by the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligand and by the acyl group [$\text{Re-C } 2.167(8)$, $\text{W-O } 2.206(5) \text{ \AA}$]. The rhenium atom carries three terminally bound CO groups and the tungsten two. A further CO ligand on tungsten semi-bridges the Re-W bond [$\text{W-C-O } 157.0(6) \text{ \AA}$], the tungsten being also ligated by the $\text{P}(\text{OMe})_3$ group. The $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and acyl groups in the bridge system are cisoid. The n.m.r. spectra (^1H , $^{13}\text{C}\{-^1\text{H}\}$, and $^{31}\text{P}\{-^1\text{H}\}$) of the new compounds are reported and discussed.

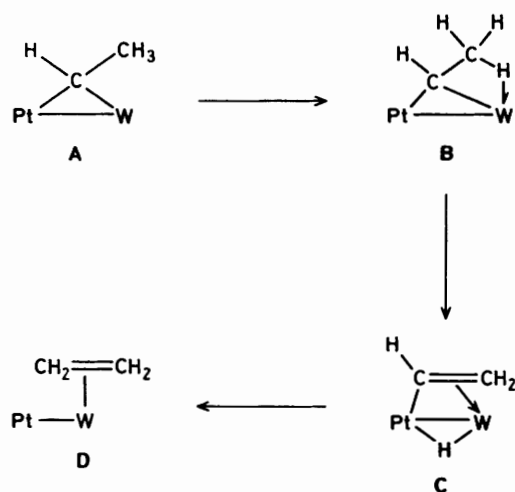
In the previous paper¹ we showed that protonation of the neutral complex $[\text{PtW}(\mu\text{-CMe})(\text{CO})_2(\text{PEt}_3)_2(\eta\text{-C}_5\text{H}_5)]$ afforded a salt $[\text{PtW}(\mu\text{-CO})_2(\text{PEt}_3)_2(\eta\text{-C}_2\text{H}_4)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ containing an ethylene ligand co-ordinated to tungsten. The transformation of a $\mu\text{-CMe}$ group into ligated ethylene in this manner was considered to proceed (Scheme 1) *via* an ethylidene-bridged platinum-tungsten species **A**. Since in the latter the tungsten has a 16- rather than an 18-electron shell,

* Bis(triphenylphosphine)iminium 1,1,1,1,2,2,2,2-nonacarbonyl- μ -*p*-tolylmethylene-rheniumtungstate (*Re-W*), μ -[bis(dimethylphosphino)methane]- μ -carbonyl-1,1,1,2,2,2-hexacarbonyl- μ -[*p*-tolylmethyl- C^α -(Re), H^β (W)]-rheniumtungsten (*Re-W*), and μ -[bis(diphenylphosphino)methane]- μ -carbonyl-1,1,1,2,2-pentacarbonyl- μ -[*p*-tolylacetyl- $\text{C}(\text{Re})$, $\text{O}(\text{W})$]-2-(trimethyl phosphite)rheniumtungsten (*Re-W*).

Supplementary data available (No. SUP 56356, 19 pp.): thermal parameters, complete bond lengths and angles, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

there might be a low-energy pathway for rearrangement to an intermediate **B** with an agostic² hydrogen. Activation of the methyl group in this way could lead to the hydrido- and vinyl-bridged species **C**, from which the final product, containing the non-bridged fragment **D**, might form *via* transfer of hydride. Although during the previous work no evidence was obtained for the intermediacy of an alkylidene-bridged dimetal species possessing a $\text{C-H}\rightarrow\text{W}$ interaction as in **B**, other studies now described have led to the successful isolation of alkyl-bridged dimetal compounds having $\text{C-H}\rightarrow\text{W}$ bonding.

The work reported in this paper was prompted by some interesting results of Kreissl and co-workers³ who found that treatment of the compounds $[\text{ReW}(\equiv\text{CR})(\text{CO})_9]$ ($\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{Me-4}$) with PMe_3 afforded the bridged ylide complexes $[\text{ReW}\{\mu\text{-CR}(\text{PMe}_3)\}(\mu\text{-CO})(\text{CO})_8]$. The conversion of a compound containing a *trans*- $\text{Re-W}\equiv\text{CR}$ arrangement into one with the bridge system $\text{Re}\{\mu\text{-CR}(\text{PMe}_3)\}\text{W}$ suggested that a similar reaction might occur with hydride anion. The latter, if it



Scheme 1. Ligands on platinum and tungsten are omitted

functioned as a nucleophile like PMe_3 , should afford alkylidene-bridged dimetal anions $[\text{ReW}(\mu\text{-CHR})(\text{CO})_9]^-$ as products. Such species would be of considerable interest, since on protonation they might yield alkyl-bridged dimetal compounds. Moreover, anionic dimetal complexes in which the metal-metal bonds are spanned by alkylidene ligands are rare, although likely to be useful in synthesis. This feature is illustrated by the salt $[\text{N}(\text{PPh}_3)_2][\text{W}_2\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$ which on treatment with $[\text{AuCl}(\text{PPh}_3)]$ or with SnPh_3Cl gives, respectively, the neutral dimetal compounds $[\text{AuW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^4$ and $[\text{W}(\text{SnPh}_3)\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^5$.

Results and Discussion

Treatment of the compound $[\text{ReW}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_9]$ with $\text{K}[\text{BH}(\text{CHMeEt})_3]$ in tetrahydrofuran (thf), followed by addition of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$, afforded an orange salt $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]^-$ (1), the formulation of which was supported by microanalytical and spectroscopic data (Tables 1 and 2). The ^1H n.m.r. spectrum had a resonance at δ 8.09, characteristic for a $\mu\text{-CHR}$ (R = alkyl or aryl) group. Moreover, a signal at δ 114.7 p.p.m. in the $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum, with ^{183}W satellite peaks [$J(\text{WC})$ 28 Hz], is diagnostic for an alkylidene carbon bridging two metal centres.⁶ Six peaks were observed in the CO region of the $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum (Table 2), and based on chemical shifts and relative intensities these could be assigned to one 'axial' and four radial CO ligands on tungsten, and four-non-equivalent CO groups attached to the rhenium.

Since (1) was intended as a key intermediate in other syntheses, an X-ray diffraction study was carried out in order to establish firmly its structure. The salient results are summarised in Table 3, and the anion is shown in Figure 1. As expected, five terminal carbonyl groups are attached to the tungsten and four to the rhenium. The metal-metal bond is bridged by the $\text{CH}(\text{C}_6\text{H}_4\text{Me-4})$ group. It is evident that the rhenium atom is in an approximately octahedral environment. This is also true of the tungsten atom, if the anion is regarded as a complex of a $\text{W}(\text{CO})_5$ fragment with a $(\text{OC})_4\text{Re}=\text{CH}(\text{C}_6\text{H}_4\text{Me-4})$ group isolobal with an alkene.^{7,8} This view of the bonding is discussed further below, in the light of other results.

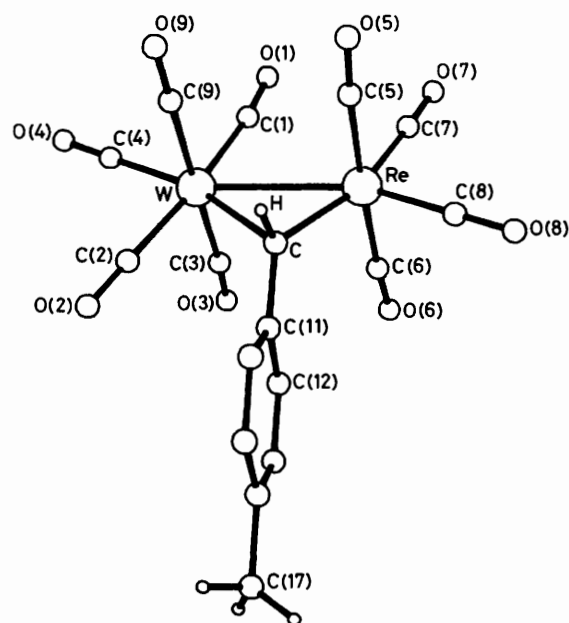


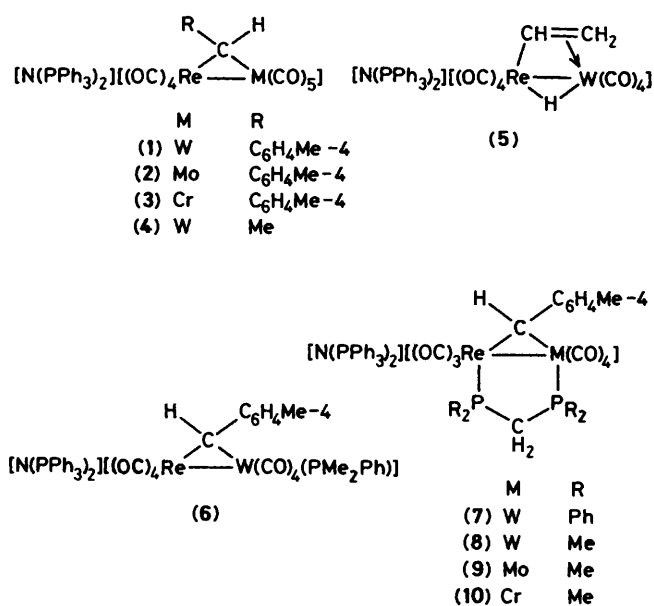
Figure 1. Molecular structure of the anion of the salt $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]^-$ (1) showing the atom labelling scheme

The Re-W separation [$3.033(1)$ Å] in (1) may be compared with that in the bridged ylide complex $[\text{ReW}\{\mu\text{-CPh}(\text{PMe}_3)\}(\mu\text{-CO})(\text{CO})_8]$ (3.00 Å), a poorly determined structure.³ The alkylidene carbon asymmetrically bridges the metal-metal bond [C-Re $2.155(8)$, C-W $2.404(6)$ Å], but this asymmetry is less marked than that in the homonuclear dimetal anion $[\text{W}_2\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]^-$ [C-W $2.436(8)$ and $2.127(7)$ Å].⁵ The $\mu\text{-C-Re}$ distance in (1) is comparable with that [$2.13(3)$ Å] in the complex $[\text{Re}_2(\mu\text{-H})_2(\mu\text{-CHBu}^t)(\eta\text{-C}_6\text{H}_6)_2]$.⁹

Although other anions (*e.g.* Me^- , OMe^- , F^- , or NMe_2^-) were found to react with $[\text{ReW}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_9]$, unfortunately no stable products could be isolated. The reagent NaBH_4 behaved in a similar manner to $\text{K}[\text{BH}(\text{CHMeEt})_3]$, affording the salt (1). A possible mechanism for the formation of the latter might involve initial formation of an octahedral alkylidenetungsten species $\text{trans}-[(\text{OC})_5\text{Re}-\text{W}=\text{CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_4]^-$ which could then undergo an intramolecular rearrangement *via* a trigonal prismatic intermediate, so as to produce a further intermediate wherein the groups $\text{Re}(\text{CO})_5$ and $\text{CH}(\text{C}_6\text{H}_4\text{Me-4})$ are *cis* in the co-ordination sphere of the tungsten. Formation of (1) could then easily occur by bridging of the alkylidene ligand, accompanied by transfer of CO from rhenium to tungsten. A trigonal twist mechanism has also been invoked to account for the *cis-trans* isomerisation of $[\text{Cr}\{\text{C}(\text{OMe})\text{Me}\}(\text{PR}_3)(\text{CO})_4]$ (R = Et or cyclo- C_6H_{11}).¹⁰

The compounds (2) and (3) were obtained by treating the complexes $[\text{ReMo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_9]$ and $[\text{ReCr}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_9]$, respectively, with $\text{K}[\text{BH}(\text{CHMeEt})_3]$, and adding $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ to precipitate the salts. Data for (2) and (3) are given in Tables 1 and 2. In the ^1H n.m.r. spectra, resonances for the $\mu\text{-CH}$ proton occur at δ 8.62 and 7.97 for (2) and (3), respectively. In the $^{13}\text{C}\{-^1\text{H}\}$ spectra, peaks due to the bridging alkylidene carbon nuclei are obscured by resonances due to the C_6H_4 and Ph groups.

Compound (4) was similarly prepared from $[\text{ReW}(\equiv\text{CMe})(\text{CO})_9]$ and $\text{K}[\text{BH}(\text{CHMeEt})_3]$. The ^1H n.m.r. spectrum (Table 2) showed a quartet signal at δ 7.91 [$J(\text{HH})$ 8 Hz] ascribed to the $\mu\text{-CH}$ proton, while the $\mu\text{-CMe}$ group protons are observed as a doublet resonance at δ 3.21 [$J(\text{HH})$ 8 Hz]. In the $^{13}\text{C}\{-^1\text{H}\}$



n.m.r. spectrum, the signal for the μ -C nucleus occurs at δ 118.8 p.p.m. [$J(\text{WC})$ 24 Hz]. Although (4) is stable at room temperature, in refluxing thf it loses a CO ligand, and affords a new complex, (5). Data for the latter are given in Tables 1 and 2, from which the salt is formulated as a vinyl- and hydrido-bridged rhenium-tungsten species. The presence of the μ -H ligand is confirmed by the ^1H n.m.r. spectrum which shows a high-field resonance at δ -12.48 [$J(\text{WH})$ 42 Hz]. The μ -CH=CH₂ group gives rise to three resonances with the expected coupling constants (Table 2). The ^{13}C - $\{^1\text{H}\}$ n.m.r. spectrum of (5) is also in accord with the structure proposed. There are eight CO resonances, and peaks at δ 119.9 and 78.0 p.p.m. due to the CH and CH₂ groups, respectively. The compound $[\text{Re}_2(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)(\text{CO})_8]$, which is structurally similar to (5), has recently been prepared.¹¹ The ^1H n.m.r. spectrum of the dirhenium compound is very similar to that of (5). There is a hydride ligand resonance at δ -14.72, and signals for the μ -CH=CH₂ group appearing as three doublet of doublets at δ 4.46, 6.26, and 7.18 with $J(\text{HH})$ values of 17, 11, and 3, identical with those of (5) (Table 2). Compound (5) was found to be relatively inert. It did not react with $\text{P}(\text{OMe})_3$ (reflux in thf) or with CO (*ca.* 1.0×10^7 Pa).

Unlike (4), complex (1) is stable in refluxing thf. However, in the latter solvent it reacts with PMe_2Ph to give (6), characterised in the usual manner (Tables 1 and 2). The presence of the PMe_2Ph ligand in (6) is confirmed by the ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum (Table 4). A resonance at δ -34.5 p.p.m. with ^{183}W - ^{31}P coupling (229 Hz) shows that a direct P-W bond is present.

Attempts to protonate the complexes (1)–(3) in order to obtain alkyl-bridged dimetal complexes resulted only in decomposition. It was therefore decided to use a different approach to alkyl dimetal compounds, based on a strategy used earlier. We have previously shown¹² that heteronuclear metal-metal bonds bridged by alkylidene groups can be stabilised if these bonds are also bridged by the bidentate ligand $\text{Ph}_2\text{PCH}_2\text{PPh}_2$. In this manner reactions at the alkylidene carbon centre can be explored with less chance of cleavage of the metal-metal bond. Accordingly, (1) in thf was treated with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ thereby affording complex (7). Compounds (8)–(10) were prepared under milder conditions using $\text{Me}_2\text{PCH}_2\text{PMe}_2$ and the salts (1)–(3), respectively.

The synthesis of (7) required several hours reflux of the reactants in thf for completion. Monitoring the reaction by ^{31}P - $\{^1\text{H}\}$ n.m.r. spectroscopy revealed the presence of an intermediate, probably involving $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ acting as a unidentate ligand being bonded to the tungsten only, and therefore structurally similar to (6). The suggested intermediate $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me}-4)\}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_8]$ had a singlet resonance in the ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum at 21.1 p.p.m. [$\text{N}(\text{PPh}_3)_2^+$] and doublet signals at 27.5 and -28.2 p.p.m. [$J(\text{PP})$ 50 Hz]. The ^{31}P chemical shift for the latter peak may be compared with those observed for the uncoordinated PPh_2 group in the complexes $[\text{PtW}\{\mu\text{-C}(\text{OMe})\text{R}\}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me}-4$, δ -22.3 p.p.m.; $\text{R} = \text{Me}$, δ -27.6 p.p.m.).¹²

Compounds (7)–(10) were characterised by the data given in Tables 1, 2, and 4. The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum of (7) consists of an AB pattern [δ 7.1 and 9.5 p.p.m., $J(\text{AB})$ 101 Hz]. Both ^{31}P nuclei of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligand couple with ^{183}W . The one bound to tungsten (resonance at δ 7.1 p.p.m.) has $J(\text{WP}) = 216$ Hz, a value similar to that (229 Hz) observed for the ^{183}W - ^{31}P coupling in the spectrum of (6). As expected, the PRe group (signal at 9.5 p.p.m.) shows weaker ^{183}W - ^{31}P coupling (4 Hz). The ^1H n.m.r. spectrum of (7) is consistent with the structure proposed. The resonance for the proton attached to the alkylidene carbon nucleus is observed as a doublet of doublets at δ 6.52 [$J(\text{PH})$ 20 and 14 Hz], with multiplet signals for the inequivalent protons of the PCH_2P group appearing at δ 2.23–2.34 and 3.38–3.57. The ^{13}C - $\{^1\text{H}\}$ n.m.r. spectrum was particularly informative. There are seven distinct CO resonances (Table 2), and these can be assigned as being co-ordinated to the tungsten or to the rhenium atoms on the basis of the presence or absence of ^{183}W satellite peaks, and the fact that carbonyl groups attached to rhenium tend to give broader signals, a feature common to all the dimetal compounds herein described. The observation of relatively large ^{31}P - ^{13}C couplings on the resonances at δ 209.5 and 200.6 p.p.m., 35 and 70 Hz, respectively, indicates that one CO group on each metal centre is *trans* to a phosphorus nucleus. It is likely, therefore, that the ligands $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and $\text{CH}(\text{C}_6\text{H}_4\text{Me}-4)$ adopt a *cisoid* arrangement about the Re-W bond. In the ^{13}C - $\{^1\text{H}\}$ n.m.r. spectrum of (7) resonances for the μ -C and the PCH_2P groups occur as a doublet at δ 110.0 [$J(\text{PC})$ 6, $J(\text{WC})$ 33 Hz] and an apparent triplet at δ 21.7 [$J(\text{PC})$ 15 Hz], respectively.

The n.m.r. data for (8)–(10) have been assigned as shown in Tables 2 and 4. In the ^1H spectra, resonances for the PCH_2P groups occur in the region δ 1.2–2.0 as broad unresolved multiplets due to ^1H and ^{31}P coupling.

As mentioned earlier, the salts (7)–(10) were prepared in the hope that on protonation they would give stable alkyl-bridged species. With this objective the salts were treated with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. Compounds (9) and (10) decomposed on addition of the acid, but with (7) and (8) novel products could be isolated.

In dichloromethane at -78°C , compound (7) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ afforded a neutral complex (11). The latter was unstable at room temperature, and hence the n.m.r. data (Tables 2 and 4) were measured at -20°C . The ^{31}P - $\{^1\text{H}\}$ spectrum showed the pattern expected for two coupled inequivalent phosphorus nuclei with one of the signals (Table 4) having ^{183}W satellite peaks, corresponding to the presence of a P-W bond. It was thus apparent that the $\text{Re}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{W}$ system had remained in the molecule. Aspects of the ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. spectra of (11) were especially revealing. In the ^1H spectrum there was a doublet signal at δ -3.69. Selective decoupling experiments showed that this resonance was coupled with another proton signal, which overlapped that due to one of the protons of the PCH_2P moiety in the region δ 3.06–3.44. When decoupled, the resonance at δ -3.69 had

Table 1. Analytical^a and physical data for the dimetal compounds

Compound ^b	$\nu_{\max}(\text{CO})^c/\text{cm}^{-1}$	Yield (%)	Analysis (%)		
			C	H	N
(1) $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$	2 060w, 2 019s, 1 950vs, 1 933s, 1 914s, 1 903 (sh), 1 883m	86	49.3 (50.3)	3.1 (3.0)	0.8 (1.1)
(2) $[\text{N}(\text{PPh}_3)_2][\text{ReMo}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$	2 060w, 2 018s, 1 951vs, 1 933s, 1 917s, 1 883m	89	53.7 (54.1)	3.7 (3.3)	1.1 (1.2)
(3) $[\text{N}(\text{PPh}_3)_2][\text{ReCr}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$	2 059w, 2 007s, 1 954vs, 1 935s, 1 913s, 1 861w	70	55.3 (56.2)	3.4 (3.4)	1.2 (1.2)
(4) $[\text{N}(\text{PPh}_3)_2][\text{ReW}(\mu\text{-CHMe})(\text{CO})_9]$	2 060w, 2 013s, 1 949vs, 1 929s, 1 909s, 1 828m	82	47.7 (47.5)	3.2 (2.9)	0.8 (1.2)
(5) $[\text{N}(\text{PPh}_3)_2][\text{ReW}(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)(\text{CO})_8]$	2 074w, 2 002m, 1 967vs, 1 916s, 1 879s, 1 847m	95	48.3 (47.6)	2.9 (3.0)	1.2 (1.2)
(6) $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_8(\text{PMe}_2\text{Ph})]$	2 041w, 1 980m, 1 966w, 1 938s, 1 915m, 1 892s, 1 864m	93	52.5 (52.4)	4.1 (3.6)	0.8 (1.0)
(7) $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-dppm})(\text{CO})_7]$	1 993m, 1 956vs, 1 901m, 1 887s, 1 860m, 1 845m	70	57.7 (57.3)	4.5 (3.8)	0.6 (0.9)
(8) $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-dmpm})(\text{CO})_7]$	1 988m, 1 949vs, 1 893s, 1 876s, 1 859m, 1 837m	88	49.8 (50.0)	4.4 (3.9)	0.9 (1.0)
(9) $[\text{N}(\text{PPh}_3)_2][\text{ReMo}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-dmpm})(\text{CO})_7]$	1 989m, 1 949vs, 1 898s, 1 876, 1 860 (sh), 1 842m	81	53.5 (53.5)	4.1 (4.2)	1.1 (1.1)
(10) $[\text{N}(\text{PPh}_3)_2][\text{ReCr}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-dmpm})(\text{CO})_7]$	1 999m, 1 982s, 1 936s, 1 883vs, 1 877 (sh), 1 860 (sh), 1 835m	69	54.4 (55.4)	5.2 (4.3)	0.9 (1.2)
(11) $[\text{ReW}(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-dppm})(\text{CO})_7]^d$	^e 2 040s, 2 002vs, 1 943s, 1 908m, 1 799w	85			
(12) $[\text{ReW}(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-dmpm})(\text{CO})_7]$	^e 2 040s, 1 999vs, 1 937s, 1 902m, 1 800w	76	^f 28.0 (28.3)	2.6 (2.8)	
(13) $[\text{ReW}(\mu\text{-OCCH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-dppm})(\text{CO})_6\{\text{P}(\text{OMe})_3\}]$	^e 2 027vs, 1 956s, 1 942s, 1 901m, 1 864m, 1 755w	68	^f 43.9 (43.8)	3.5 (3.4)	
(14) $[\text{ReW}(\text{CH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-dmpm})(\text{CO})_7\{\text{P}(\text{OMe})_3\}_2]$	^e 2 023m, 2 014m, 1 921 (sh), 1 899s	57	29.0 (29.6)	4.0 (3.9)	
(15) $[\text{N}(\text{PPh}_3)_2][\text{ReW}(\mu\text{-H})\{\mu\text{-PPh}(\text{C}_6\text{H}_4)\text{CH}_2\text{PPh}_2\}(\text{CO})_7]$	2 010s, 1 985m, 1 914s, 1 890s, 1 870s, 1 836m	82	54.1 (54.9)	3.9 (3.5)	0.9 (0.9)

^a Calculated values are given in parentheses. ^b All compounds are orange in colour, except for (13) and (15) (yellow), and (14) (white); dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, dmpm = $\text{Me}_2\text{PCH}_2\text{PMe}_2$. ^c Measured in tetrahydrofuran, unless otherwise stated. ^d Satisfactory microanalytical data not obtained: compound thermally unstable, see text. ^e In dichloromethane. ^f Crystallises with a molecule of CH_2Cl_2 .

¹⁸³W satellite peaks [$J(\text{WH})$ 48 Hz]. This observation provides strong evidence for the presence of a C-H \rightarrow W interaction, involving an asymmetrically bridging *p*-tolymethyl ligand and the tungsten atom. The observed chemical shift is similar to those observed for protons engaged in three-centre two-electron C-H \rightarrow M bonding in the two unsymmetrically bridging alkyl complexes $[\text{Fe}_2(\mu\text{-Me})(\mu\text{-CO})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ (δ -2.84)¹³ and $[\text{Os}_3(\mu\text{-H})(\mu\text{-Me})(\text{CO})_{10}]$ (δ -3.68).¹⁴ In the ¹³C-¹H n.m.r. spectrum of (11), the $\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4}$ resonance occurs at 18.2 p.p.m., and in a ¹³C spectrum this signal becomes a doublet of doublets [$J(\text{HC})$ 131 and 81 Hz] as expected for a carbon-13 nucleus attached to two chemically inequivalent protons. The larger coupling constant is typical for a normal C(*sp*³)-H bond, but the diminished value of 81 Hz is in the region (75-100 Hz) generally found for a C-H \rightarrow M bridged system.²

In all known examples of alkyl groups asymmetrically bridging homonuclear metal-metal bonds, the hydrogen atoms on the ligated carbon centre undergo site exchange between C-H and C-H \rightarrow M.² The marked asymmetry revealed in the solid-state structure of (12), and by comparison likely to exist in (11) also, causes the two $\mu\text{-CH}_2\text{R}$ hydrogen atoms to be fundamentally inequivalent irrespective of any fluxional processes which are likely to occur. Thus although the data just discussed strongly imply that the dominant species present in solution has a C-H \rightarrow W interaction, it does not rule out the possibility of

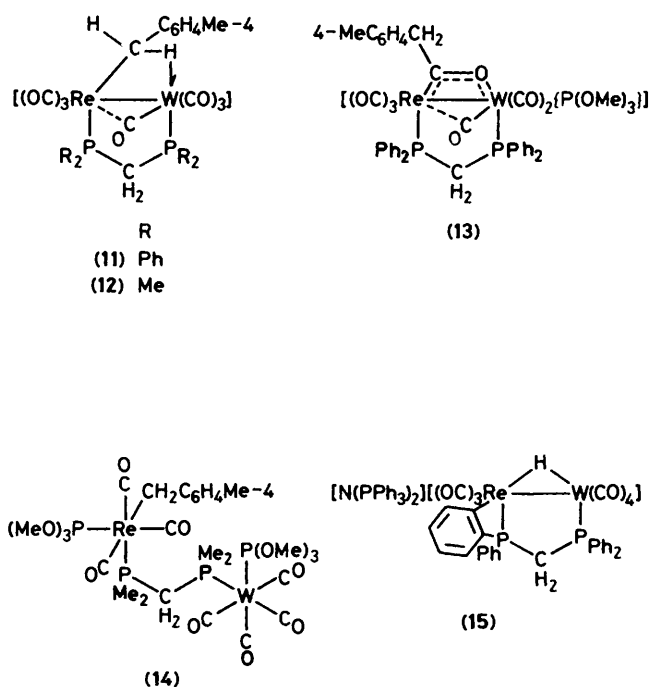


Table 2. Hydrogen-1 and carbon-13 n.m.r. data^a for the dimetal compounds

Compd.	¹ H (δ)	¹³ C ^b (δ)
(1) ^c	2.15 (s, 3 H, Me-4), 6.84 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.17 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.3—7.7 (m, 30 H, Ph), 8.09 (s, 1 H, μ-CH)	205.9 [WCO, <i>J</i> (WC) 145], 203.4 [4 × WCO, <i>J</i> (WC) 121], 200.5, 198.2, 197.9, 196.7 (ReCO), 161.1 [C ¹ (C ₆ H ₄)], 134.9—127.5 (Ph), 130.5 [C ⁴ (C ₆ H ₄)], 128.4 [C ² and C ⁶ (C ₆ H ₄)], 126.3 [C ³ and C ⁵ (C ₆ H ₄)], 114.7 [μ-C, <i>J</i> (WC) 28], 20.9 (Me-4)
(2)	2.14 (s, 3 H, Me-4), 6.82 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.22 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.4—7.7 (m, 30 H, Ph), 8.62 (s, 1 H, μ-CH)	216.3 (MoCO), 212.6 (4 × MoCO), 200.9, 199.4, 198.5, 198.0 (ReCO), 161.0 [C ¹ (C ₆ H ₄)], 133.9—125.5 (C ₆ H ₄ , Ph, and μ-C), 21.0 (Me-4)
(3)	2.17 (s, 3 H, Me-4), 6.86 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.24 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.4—7.6 (m, 30 H, Ph), 7.97 (s, 1 H, μ-CH)	229.4 (CrCO), 223.7 (4 × CrCO), 198.6, 196.1, 195.0 (ReCO), 159.7 [C ¹ (C ₆ H ₄)], 134.0—125.1 (C ₆ H ₄ , Ph, and μ-C), 21.0 (Me-4)
(4)	3.21 [d, 3 H, μ-CMe, <i>J</i> (HH) 8], 7.4—7.7 (m, 30 H, Ph), 7.91 [q, 1 H, μ-CH, <i>J</i> (HH) 8]	206.7 [WCO, <i>J</i> (WC) 145], 204.2 [4 × WCO, <i>J</i> (WC) 121], 201.0, 200.2, 198.7, 198.5 (ReCO), 135—126 (Ph), 118.8 [μ-C, <i>J</i> (WC) 24], 41.4 (μ-CMe)
(5)	−12.48 [s, 1 H, μ-H, <i>J</i> (WH) 42], 4.33 [d of d, 1 H, CH ₂ , <i>J</i> (HH) 17 and 3], 5.55 [d of d, 1 H, CH ₂ , <i>J</i> (HH) 11 and 3], 6.78 [d of d, 1 H, CH, <i>J</i> (HH) 17 and 11], 7.4—7.7 (m, 30 H, Ph)	210.3 [WCO, <i>J</i> (WC) 156], 203.0, 202.3, 201.6 (WCO), 192.1, 188.5, 187.6, 187.0 (ReCO), 135—126 (Ph), 119.9 [CH, <i>J</i> (WC) 11], 78.0 [CH ₂ , <i>J</i> (WC) 7]
(6) ^{c,d}	1.44 [d, 3 H, MeP, <i>J</i> (PH) 7], 1.68 [d, 3 H, MeP, <i>J</i> (PH) 8], 2.14 (s, 3 H, Me-4), 6.68 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 7], 7.06 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 7], 7.2—7.6 (m, 36 H, Ph and μ-CH)	222.8 [d, CO, <i>J</i> (PC) 5], 207.2 [d, CO, <i>J</i> (PC) 7], 203.8—193.3 (m, CO), 165.3 [d, C ¹ (C ₆ H ₄), <i>J</i> (PC) 5], 136—126 (C ₆ H ₄ and Ph), 96.3 [d, μ-C, <i>J</i> (PC) 7], 20.8 (Me-4), 18.2 [d, MeP, <i>J</i> (PC) 29], 16.7 [d, MeP, <i>J</i> (PC) 27]
(7) ^d	2.18 (s, 3 H, Me-4), 2.23—2.34 (m, 1 H, CH ₂), 3.38—3.57 (m, 1 H, CH ₂), 6.52 [d of d, 1 H, μ-CH, <i>J</i> (PH) 20 and 14], 6.8—7.6 (m, 54 H, C ₆ H ₄ and Ph)	225.7 [d, WCO, <i>J</i> (PC) 4], 214.9 [d, WCO, <i>J</i> (PC) 4, <i>J</i> (WC) 147], 210.2 [d, WCO, <i>J</i> (PC) 7, <i>J</i> (WC) 129], 209.5 [d of d, WCO, <i>J</i> (PC) 35 and 7], 204.9, 203.6 (ReCO), 200.6 [d, ReCO, <i>J</i> (PC) 70], 165.0 [C ¹ (C ₆ H ₄)], 139.3—126.5 (Ph and C ₆ H ₄), 110.0 [d, μ-C, <i>J</i> (PC) 6, <i>J</i> (WC) 33], 21.7 [t, CH ₂ , <i>J</i> (PC) 15], 20.4 (Me-4)
(8) ^e	1.37 [d, 3 H, MeP, <i>J</i> (PH) 6], 1.46 [d, 3 H, MeP, <i>J</i> (PH) 6], 1.55 [d, 3 H, MeP, <i>J</i> (PH) 7], 1.62 [d, 3 H, MeP, <i>J</i> (PH) 7], 2.11 (s, 3 H, Me-4), 6.19 [d of d, 1 H, μ-CH, <i>J</i> (PH) 21 and 11], 6.75 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.16 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 6.7—7.7 (m, 30 H, Ph)	223.9 [d, WCO, <i>J</i> (PC) 7, <i>J</i> (WC) 107], 216.7 [d, WCO, <i>J</i> (PC) 6, <i>J</i> (WC) 143], 211.3 [d, WCO, <i>J</i> (PC) 7], 210.3 [d of d, WCO, <i>J</i> (PC) 37 and 6], 206.8 [d, ReCO, <i>J</i> (PC) 7], 203.8 (ReCO), 201.2 [d, ReCO, <i>J</i> (PC) 78], 164.5 [C ¹ (C ₆ H ₄)], 134.7—126.3 (Ph and C ₆ H ₄), 110.1 (μ-C), 20.9 (Me-4), 20.7—19.5 (m, MeP and PCH ₂ P)
(9) ^e	1.2—1.6 (m, 12 H, MeP), 2.10 (s, 3 H, Me-4), 6.63 [d of d, 1 H, μ-CH, <i>J</i> (PH) 25 and 11], 6.74 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.19 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.5—7.7 (m, 30 H, Ph)	230.0 [d, MoCO, <i>J</i> (PC) 9], 225.1 [d, MoCO, <i>J</i> (PC) 7], 220.0 [d, MoCO, <i>J</i> (PC) 11], 218.3 [d of d, MoCO, <i>J</i> (PC) 41 and 5], 207.3 [d, ReCO, <i>J</i> (PC) 7], 204.0 (ReCO), 202.3 [d, ReCO, <i>J</i> (PC) 79], 164.3 [d, C ¹ (C ₆ H ₄), <i>J</i> (PC) 4], 134.5—125.5 (C ₆ H ₄ and Ph), 123.2 [d, μ-C, <i>J</i> (PC) 7], 20.9 (Me-4), 20.4—18.7 (m, MeP and PCH ₂ P)
(10) ^e	1.2—1.6 (m, 12 H, MeP), 2.13 (s, 3 H, Me-4), 5.83 [d of d, 1 H, μ-CH, <i>J</i> (PH) 20 and 12], 6.78 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.20 [AB, 2 H, C ₆ H ₄ , <i>J</i> (AB) 8], 7.0—7.7 (m, 30 H, Ph)	241.9 [d, CrCO, <i>J</i> (PC) 15], 236.8 [d, CrCO, <i>J</i> (PC) 15], 232.5 [d, CrCO, <i>J</i> (PC) 17], 230.0—229.3 (m, CrCO), 204.8 [d, ReCO, <i>J</i> (PC) 9], 201.6 [d, ReCO, <i>J</i> (PC) 7], 199.6 [d of d, ReCO, <i>J</i> (PC) 75 and 71], 163.5 [C ¹ (C ₆ H ₄)], 135.4—126.1 (C ₆ H ₄ and Ph), 118.3 (μ-C), 21.0 (Me-4), 20.6—14.0 (m, MeP and PCH ₂ P)
(11) ^{f,g}	−3.69 [d, 1 H, μ-C-H-W, <i>J</i> (HH) 13, <i>J</i> (WH) 48], 2.28 (s, 3 H, Me-4), 2.37—2.49 (m, 1 H, PCH ₂ P), 3.06—3.44 (m, 2 H, μ-CH and PCH ₂ P), 6.7—7.5 (m, 24 H, C ₆ H ₄ and Ph)	221.0 [μ-CO, <i>J</i> (WC) 101], 206.0 [d, WCO, <i>J</i> (PC) 6, <i>J</i> (WC) 145], 201.4 [d of d, W(CO), <i>J</i> (PC) 42 and 7, <i>J</i> (WC) 135], 195.1 [d, WCO, <i>J</i> (PC) 6, <i>J</i> (WC) 136], 191.0 [d, ReCO, <i>J</i> (PC) 7], 189.8 [d, ReCO, <i>J</i> (PC) 8], 187.7 [d of d, ReCO, <i>J</i> (PC) 72 and 7], 153.1 [C ¹ (C ₆ H ₄)], 147.4 [C ⁴ (C ₆ H ₄)], 135—123 (C ₆ H ₄ and Ph), 20.4 [q, Me-4, <i>J</i> (HC) 127], 18.2 [d of d, μ-C, <i>J</i> (HC) 81 and 131], 15.2 [t of t, PCH ₂ P, <i>J</i> (HC) 132, <i>J</i> (PC) 19]
(12) ^e	−3.90 [d, 1 H, μ-C-H-W, <i>J</i> (HH) 13, <i>J</i> (WH) 41], 1.53 [d, 3 H, MeP, <i>J</i> (PH) 7], 1.65 [d, 3 H, MeP, <i>J</i> (PH) 7], 1.68 [d, 3 H, MeP, <i>J</i> (PH) 8], 1.85 [d, 3 H, MeP, <i>J</i> (PH) 8], 2.26 (s, 3 H, Me-4), 2.48 [d of d of d, μ-CH, <i>J</i> (HH) 13, <i>J</i> (PH) 9 and 4], 6.9—7.1 (m, 4 H, C ₆ H ₄)	219.2 (μ-CO), 208.2 [d, WCO, <i>J</i> (PC) 4], 202.5 [d of d, WCO, <i>J</i> (PC) 42 and 9], 196.1 (WCO), 192.8 [d, ReCO, <i>J</i> (PC) 7], 190.5 [d, ReCO, <i>J</i> (PC) 7], 189.2 [d of d, ReCO, <i>J</i> (PC) 70 and 9], 147.5 [d, C ¹ (C ₆ H ₄), <i>J</i> (PC) 2], 132.5 [C ⁴ (C ₆ H ₄)], 128.8, 127.1 (C ₆ H ₄), 20.9 (Me-4), 19.5—17.1 (m, MeP), 16.4 (μ-C), 13.3 [d of d, PCH ₂ P, <i>J</i> (PC) 21 and 17]
(13) ^h	2.36 (s, 3 H, Me-4), 3.32 [d, 9 H, OMe, <i>J</i> (PH) 11], 3.5—3.6 (m, 2 H, PCH ₂ P), 4.04 [AB, 1 H, CH ₂ C ₆ H ₄ Me-4, <i>J</i> (AB) 17], 4.22 [AB, 1 H, CH ₂ C ₆ H ₄ Me-4, <i>J</i> (AB) 17], 6.9—7.5 (m, 24 H, C ₆ H ₄ and Ph)	284.5 [d, μ-C(O)CH ₂ , <i>J</i> (PC) 10], 219.4 [d, μ-CO, <i>J</i> (PC) 17], 211.5 [d, WCO, <i>J</i> (PC) 15], 208.7 [d of d, WCO, <i>J</i> (PC) 47 and 11], 194.5 [d, ReCO, <i>J</i> (PC) 7], 193.0 [d, ReCO, <i>J</i> (PC) 59], 191.8 (ReCO), 138—127 (C ₆ H ₄ and Ph), 71.9 (μ-CCH ₂), 28.1—27.2 (m, PCH ₂ P), 21.2 (Me-4)
(14)	1.6—2.1 (m, 14 H, MeP and PCH ₂ P), 2.22 (s, 3 H, Me-4), 2.50—2.70 (m, 2 H, CH ₂ C ₆ H ₄ Me-4), 3.63 [d, 9 H, OMe, <i>J</i> (PH) 11], 3.73 [d, 9 H, OMe, <i>J</i> (PH) 16], 6.87—6.91 (m, 4 H, C ₆ H ₄)	205.6—204.6 (m, WCO), 201.7—201.3 (m, WCO), 196.6 [d of d, ReCO, <i>J</i> (PC) 90 and 10], 194.7 [d of d, ReCO, <i>J</i> (PC) 53 and 13], 191.8—191.4 (m, ReCO), 155.2 [C ¹ (C ₆ H ₄)], 134.1, 128.2, 126.0 (C ₆ H ₄), 53.1 [d, OMe, <i>J</i> (PC) 7], 52.3 (OMe), 34.0—33.6 (m, PCH ₂ P), 21.2 [d, Me ₂ PW, <i>J</i> (PC) 30], 20.8 (Me-4), 17.0 [d, MePRE, <i>J</i> (PC) 29], 16.7 [d, MePRE, <i>J</i> (PC) 27], 4.0—3.6 (m, CH ₂ C ₆ H ₄ Me-4)
(15) ^{c,d}	−12.59 [d of d, 1 H, μ-H, <i>J</i> (PH) 18 and 11, <i>J</i> (WH) 39], 2.9—3.0 (m, 1 H, PCH ₂ P), 4.1—4.4 (m, 1 H, PCH ₂ P), 6.2—8.0 (m, 49 H, C ₆ H ₄ and Ph)	212.9 [d, WCO, <i>J</i> (PC) 28], 212.2 [d, WCO, <i>J</i> (PC) 6], 205.7 [d, WCO, <i>J</i> (PC) 7, <i>J</i> (WC) 121], 205.2 [d, WCO, <i>J</i> (PC) 7, <i>J</i> (WC) 125], 199.7 [d, ReCO, <i>J</i> (PC) 57], 198.0 [t, ReCO, <i>J</i> (PC) 6], 196.5 [d, ReCO, <i>J</i> (PC) 9], 161.7 [d of d, C(C ₆ H ₄), <i>J</i> (PC) 44 and 15], 153.4 [d, C(C ₆ H ₄), <i>J</i> (PC) 55], 148.5 [d, CH(C ₆ H ₄), <i>J</i> (PC) 18], 140—126 (C ₆ H ₄ and Ph), 121.8 [d, CH(C ₆ H ₄), <i>J</i> (PC) 8], 35.1 [d of d, PCH ₂ P, <i>J</i> (PC) 26 and 22]

^a Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature unless otherwise stated. Hydrogen-1 spectra recorded in CD₂Cl₂ and carbon-13 in CD₂Cl₂-CH₂Cl₂, unless otherwise indicated. ^b Hydrogen-1 decoupled, unless otherwise stated, with chemical shifts to high frequency of SiMe₄. ^c Hydrogen-1 spectrum in CD₃CN. ^d Carbon-13 spectrum in CD₃CN-MeCN. ^e Signals for PCH₂P group are broad multiplets in region ca. 1.2—2.0. ^f Spectra measured at −20 °C. ^g Carbon-13 spectrum fully ¹H-coupled. ^h In ¹³C-¹H spectrum OMe resonance is masked by solvent peak.

Table 3. Selected internuclear distances (Å) and angles (°) for $[N(PPh_3)_2][ReW\{\mu-CH(C_6H_4Me-4)\}(CO)_9]$ (1)

W-Re	3.033(1)	W-C	2.404(6)	W-C(1)	2.052(10)	W-C(2)	2.025(10)
W-C(3)	2.060(7)	W-C(4)	1.981(8)	W-C(9)	2.049(8)	Re-C	2.155(8)
Re-C(5)	1.979(7)	Re-C(6)	1.994(8)	Re-C(7)	1.960(10)	Re-C(8)	1.888(8)
C-C(11)	1.495(11)	C-H	1.01(7)	C(1)-O(1)	1.15(1)	C(2)-O(2)	1.14(1)
C(3)-O(3)	1.125(9)	C(4)-O(4)	1.15(1)	C(5)-O(5)	1.135(9)	C(6)-O(6)	1.12(1)
C(7)-O(7)	1.15(1)	C(8)-O(8)	1.16(1)	C(9)-O(9)	1.13(1)	N-P(1)	1.570(7)
N-P(2)	1.573(7)						
Re-W-C	44.9(2)	Re-W-C(1)	69.9(2)	C-W-C(1)	114.2(2)	Re-W-C(2)	118.3(2)
C-W-C(2)	74.2(3)	C(1)-W-C(2)	171.4(3)	Re-W-C(3)	86.9(2)	C-W-C(3)	95.0(3)
C(1)-W-C(3)	88.0(3)	C(2)-W-C(3)	90.1(3)	Re-W-C(4)	154.2(3)	C-W-C(4)	160.5(4)
C(1)-W-C(4)	84.3(4)	C(2)-W-C(4)	87.4(4)	C(3)-W-C(4)	91.4(3)	Re-W-C(9)	93.2(2)
C-W-C(9)	86.5(3)	C(1)-W-C(9)	90.2(4)	C(2)-W-C(9)	91.5(4)	C(3)-W-C(9)	178.0(4)
C(4)-W-C(9)	87.6(3)	W-Re-C	51.9(2)	W-Re-C(5)	88.0(2)	C-Re-C(5)	86.4(3)
W-Re-C(6)	94.3(3)	C-Re-C(6)	96.0(4)	C(5)-Re-C(6)	177.4(4)	W-Re-C(7)	110.6(2)
C-Re-C(7)	162.4(3)	C(5)-Re-C(7)	90.8(4)	C(6)-Re-C(7)	87.2(4)	W-Re-C(8)	153.4(3)
C-Re-C(8)	101.5(4)	C(5)-Re-C(8)	90.6(3)	C(6)-Re-C(8)	88.0(3)	C(7)-Re-C(8)	95.9(4)
W-C-Re	83.2(3)	W-C-C(11)	120.2(4)	Re-C-C(11)	128.2(5)	W-C-H	101(4)
Re-C-H	109(5)	C(11)-C-H	110(5)	P(1)-N-P(2)	146.6(4)		

dynamic processes occurring on the n.m.r. time-scale involving minor isomers which might, for example, include species with a C-H \rightarrow Re interaction. Although cooling to -80°C did not reveal obvious additional peaks in the ^1H n.m.r. spectrum due to isomers, it did show that the proton signal at high field was temperature dependent, changing from $\delta -3.54$ at ambient temperature to $\delta -3.94$ at -80°C . Over the same temperature range the resonance for the Me-4 group changes by only *ca.* 0.02 p.p.m. This behaviour is consistent with a shift in equilibrium between isomers with the species with the C-H \rightarrow W interaction becoming increasingly dominant at lower temperatures.

The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum of (11) has seven distinct CO resonances. The most deshielded at 221.0 p.p.m. is assigned to a bridging or semi-bridging ligand, in agreement with the appearance of a band in the i.r. spectrum (Table 1) at 1799 cm^{-1} . This absorption shifts to 1806 cm^{-1} when measured in thf. The remaining six CO resonances in the $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum (Table 2) all show ^{31}P coupling, and the pattern suggests that the $\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2$ ligand is transoid to CO groups on tungsten and on rhenium, and cisoid to the $\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4}$ moiety.

Since (11) was the first example of a heterodinuclear metal complex with an asymmetrically bridging alkyl, confirmation of its structure by an X-ray diffraction study would have been desirable. Unfortunately, the thermal instability of the complex precluded this possibility. However, protonation of (8) afforded a much more stable species (12), suitable crystals of which could be obtained. The spectroscopic data for (12) (Tables 1, 2, and 4) establish that it was structurally analogous to (11).

The results of the X-ray study are summarised in Table 5. The compound crystallises with CH_2Cl_2 , and the structure consists of isolated molecules of (12) and CH_2Cl_2 separated by normal van der Waals contacts. The molecular geometry is shown in Figure 2, with the hydrogens on the tolyl and methyl groups omitted for clarity. It is immediately evident that the rhenium-tungsten bond is bridged by the $\text{Me}_2\text{PCH}_2\text{PMe}_2$ ligand, and also by a $\mu\text{-}p\text{-tolylmethyl}$ group. The tungsten atom carries four carbonyl ligands and the rhenium atom three of these groups. The $\text{CH}_2\text{C}_6\text{H}_4\text{Me-4}$ moiety is bound asymmetrically, acting as a $\sigma\text{-alkyl}$ ligand to the rhenium [Re-C(8) 2.302(7) Å with Re-C(8)-X [X = H(8a), H(8b), and C(9)] near tetrahedral], and binding to the tungsten *via* a three-centre W-H(8a)-C(8) bond [W-C(8) 2.539(7), W-H(8a) 2.08(8), C(8)-H(8a) 0.86(8)

Å]. A similar bridging mode for a methyl ligand has been characterised in $[\text{Fe}_2(\mu\text{-Me})(\mu\text{-CO})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ by X-ray¹³ and neutron diffraction.¹⁵ In this mode the alkyl ligand can be regarded as acting formally as either a three-electron or an anionic four-electron donor to the dimetal. In either formalism the electron count is 34 for (12), giving an Re-W bond order of unity, consistent with the observed separation [2.950(2) Å].

The structural effects of replacing two CO ligands in (1) by $\text{Me}_2\text{PCH}_2\text{PMe}_2$ and protonating the system to give (12) are considerable. The $\mu\text{-C-Re}$ and $\mu\text{-C-W}$ distances are markedly

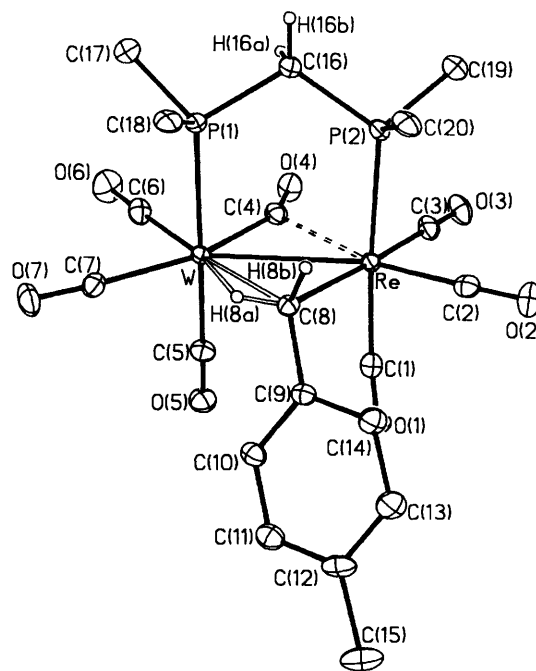
**Figure 2.** Molecular structure of $[\text{ReW}(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2)(\mu\text{-CO})(\text{CO})_6]$ (12) showing the atom labelling scheme. Hydrogen atoms on $\text{C}_6\text{H}_4\text{Me-4}$ and PMe_2 groups are omitted for clarity

Table 4. Phosphorus-31 n.m.r. data^a

Compound	³¹ P (δ)
(6) ^b	21.0 [s, N(PPh ₃) ₂] -34.5 [s, PMe ₂ Ph, J(WP) 229]
(7) ^b	20.9 [s, N(PPh ₃) ₂] 9.5 [AB, PRe, J(AB) 101, J(WP) 4] 7.1 [AB, PW, J(AB) 101, J(WP) 216]
(8) ^c	21.1 [s, N(PPh ₃) ₂] -21.8 [AB, PRe, J(AB) 106, J(WP) 3] -26.1 [AB, PW, J(AB) 106, J(WP) 211]
(9) ^c	21.2 [s, N(PPh ₃) ₂] 0.4 [d, PMo, J(PP) 105] -23.2 [d, PRe, J(PP) 105]
(10) ^c	29.5 [d, CrP, J(PP) 104] 21.2 [s, N(PPh ₃) ₂] -22.1 [d, PRe, J(PP) 104]
(11) ^{c,d}	20.8 [AB, PW, J(AB) 121, J(WP) 230] 9.1 [AB, PRe, J(AB) 121] -5.1 [AB, PW, J(AB) 116, J(WP) 220] -11.9 [AB, PRe, J(AB) 116]
(13) ^c	131.9 [d of d, P(OMe) ₃ , J(PP) 29 and 4, J(WP) 378] 12.2 [d of d, PW, J(PP) 71 and 29, J(WP) 219] 5.4 [d of d, PRe, J(PP) 71 and 4]
(14) ^c	142.5 [d, (MeO) ₃ PW, J(PP) 32, J(WP) 376] 118.8 [d, (MeO) ₃ PRe, J(PP) 44] -21.2 [d of d, PW, J(PP) 32 and 28] -27.3 [d of d, PRe, J(PP) 44 and 28]
(15) ^b	21.0 [s, N(PPh ₃) ₂] 13.3 [d, PW, J(PP) 56, J(WP) 225] -2.1 [d, PRe, J(PP) 56]

^a Hydrogen-1 decoupled, chemical shifts (δ) in p.p.m. to high frequency of 85% H₃PO₄ (external), coupling constants in Hz. Measurements at room temperature unless otherwise stated. ^b Measured in CD₃CN. ^c Measured in CD₂Cl₂. ^d Spectrum measured at -20 °C.

increased, being 2.302(7) and 2.539(7) Å, respectively, in (12), and 2.155(8) and 2.404(6) Å in (1). The reasons for the extension of the μ-C-W distance are presumably the same as those for the lengthening of other metal-metal bonds on protonation. The formation of a three-centre, two-electron bond in place of a two-centre, two-electron bond leads to an increase in internuclear separation whether in H₃⁺, M-H-M, or C-H-M systems, and probably in C-H-C also. The origin of the lengthening of the μ-C-Re distance is less obvious. Replacement of CO by Me₂PCH₂PMe₂ *cis* to this bond might influence its length. However, a more likely explanation is that the μ-C-Re distance in (1) is relatively short, due to a degree of multiple-bond character. We referred earlier to a bonding model for (1) wherein the anion is regarded as a complex of a W(CO)₅ fragment with the (OC)₄Re=CH(C₆H₄Me-4) moiety. Hence protonation at the alkylidene carbon centre would remove any partial multiple bonding and hence lengthen the μ-C-Re vector to a value appropriate for a C(sp³)-Re single bond. It is interesting to compare the μ-C-Re separations in (1) and (12) with carbon-rhenium distances in other organo-rhenium compounds. That in (1) [2.155(8) Å] is similar to those found in the species [Re₂(μ-CHCHCMe₂)(CO)₈] [μ-σ-C-Re 2.109(11) Å]¹⁶ and [MnRe{C(OMe)Me}(CO)₉] [2.094(7) Å]¹⁷ wherein a degree of C=Re bond character occurs. In contrast, the μ-C-Re distance in (12) [2.302(7) Å] is comparable with those found (*ca.* 2.30 Å) in species having C(sp³)-Re bonds, *e.g.* [ReH(CH₂Ph)(CO)₂(η-C₅H₅)] [2.29(1) Å].¹⁸

Other effects of substitution of CO groups in (1) by Me₂PCH₂PMe₂, followed by protonation, are more subtle. As indicated by the ¹³C-{¹H} n.m.r. data [Table 2, and discussed above for (11)], the bridging diphosphine ligand occupies a pair

of pseudo-axial sites *cis* to the μ-CH₂C₆H₄Me-4 ligand. This configuration ensures that the two hydrogen atoms H(8a) and H(8b) in (12) are fundamentally inequivalent, and moreover, cannot become equivalent by rotation of the *p*-tolylmethyl group about the C(8)-Re bond. The metal-C(O) lengths [Re-C(1) 1.964(8), W-C(5) 2.001(7) Å] for the carbonyls *trans* to P in (12) are marginally shorter than the comparable distances in (1) [Re-C(6) 1.994(8), W-C(3), 2.060(7) Å] despite the loss of negative charge in passing from the latter to the former.

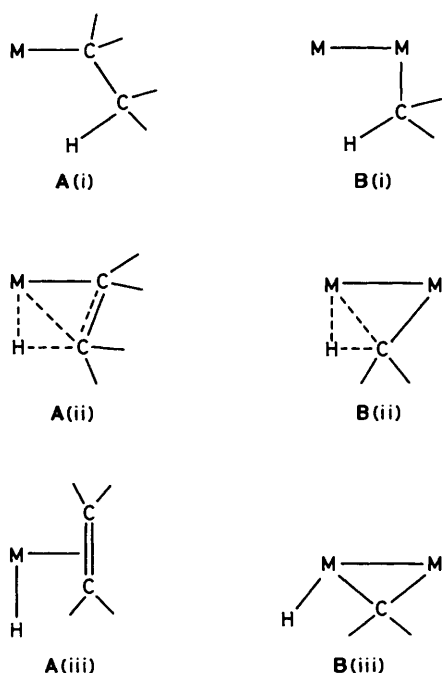
Ignoring the metal-metal bonds, the tungsten atoms in (1) and (12) can be regarded as approximately octahedrally coordinated; in (1) by five CO groups and the Re=CH(C₆H₄Me-4) unit, and in (12) by four CO ligands, the Me₂PCH₂PMe₂ group, and the C(8)-H(8a) bond pair. This approximation is better for (1), as reflected in OC-W-CO angles near 90 and 180°. Moreover, with C-W-C(2) 74.2(3)° and C(1)-W-Re 69.9(2)°, the sixth site lies near the mid-point of the μ-C-Re bond. The effect of protonation seems to be to increase the crowding in the pseudo-equatorial plane in (12), *i.e.* that containing Re, W, μ-C, and the five carbonyl ligands. This leads to reduced *cis* OC-W-CO angles, as the three equatorial carbonyls on W [C(4)O(4), C(6)O(6), and C(7)O(7)] are displaced away from H(8a). As a consequence of this feature, C(4)O(4) becomes markedly semi-bridging and non-linear [W-C(4)-O(4) 153.6(6), Re-W-C(4) 55.3(2)°; C(4)-Re 2.457(8) Å]. In compound (1) the C(1)O(1) group is only marginally semi-bridging [W-C(1)-O(1) 171.8(7), Re-W-C(1) 69.9(2)°]. The co-ordination geometry at rhenium in the two structures is less clear cut, but is probably best viewed as being derived from trigonal bipyramidal in (1) and octahedral in (12). Thus ignoring the metal-metal bond, rhenium is ligated by four terminal CO groups and the μ-C-W unit in (1), and by three terminal CO ligands, the semi-bridging CO, the μ-*p*-tolylmethyl, and the phosphorus ligand in (12). The compression of *cis* C-Re-C angles towards *ca.* 90° on going from (1) to (12) is most noticeable, and as a corollary the *trans* μ-C-Re-CO angle increases from 162.4(3)° in (1) to 177.2(3)° in (12). Moreover, in (12) the semi-bridging carbonyl becomes more exactly *trans* to C(2) [C(2)-Re-C(4) 165.1(3)°].

Several aspects of the μ-*p*-tolylmethyl ligand geometry are of interest. Thus alternative co-ordination modes for this ligand are possible, but are evidently disfavoured either for mechanistic or thermodynamic reasons. The most likely alternative¹⁹ would be a μ-allyl-like mode using two carbon atoms of the aryl ring to co-ordinate to the tungsten rather than the C-H group. If this is thermodynamically disfavoured, it means that in these special circumstances a C-H bond pair is a better ligand than an arene ring π-electron pair. This is presumably at least partly because of steric crowding in the *pseudo*-equatorial plane of complex (12). In this context it is worth noting that other potential ligands are also less favoured than C-H. Thus there are no four-electron CO groups as in, for example, [Mn₂(μ-Ph₂PCH₂PPh₂)₂(μ-CO)(CO)₄].²⁰

The ReCHW four-centre system in (12) is near planar [H(8a) lies 0.11(8) Å from the C(8)ReW plane]. This feature corresponds to the planar geometry postulated and found²¹ for the β-elimination of hydrogen in mononuclear metal complexes [Scheme 2, A(i)-A(iii)]. The bridging alkyl group in (12) can be viewed as initially co-ordinated to Re [Scheme 2, B(i)] but being in the process of having a hydrogen abstracted from it [B(ii)] by a neighbouring metal (W). Conversely, the bridged CH₂C₆H₄Me-4 system in (12) can be viewed as an intermediate in the insertion of a μ-alkylidene ligand into a neighbouring metal-hydrogen bond [B(iii) → B(ii)]. These processes linking the various intermediates in Scheme 2 are clearly of major importance in the chemistry of alkyl ligands at dimetal centres,

Table 5. Selected internuclear distances (Å) and angles (°) for [ReW(μ-CH₂C₆H₄Me-4)(μ-Me₂PCH₂PMe₂)(CO)₇] (12)

Re-W	2.950(2)	Re-P(2)	2.450(2)	P(1)-C(18)	1.813(9)	P(2)-C(16)	1.825(8)
Re-C(1)	1.964(8)	Re-C(2)	1.900(8)	P(2)-C(19)	1.810(8)	P(2)-C(20)	1.841(8)
Re-C(3)	1.923(8)	Re-C(4)	2.457(8)	C-Cl(1)	1.733(13)	C-Cl(2)	1.766(12)
Re-C(8)	2.302(7)	W-P(1)	2.510(2)	O(1)-C(1)	1.125(9)	O(2)-C(2)	1.150(10)
W-C(4)	2.074(8)	W-C(5)	2.001(7)	O(3)-C(3)	1.139(10)	O(4)-C(4)	1.158(10)
W-C(6)	1.965(8)	W-C(7)	2.024(8)	O(5)-C(5)	1.145(9)	O(6)-C(6)	1.142(10)
W-C(8)	2.539(7)	W-H(8a)	2.08(8)	O(7)-C(7)	1.142(9)	C(8)-H(8a)	0.86(8)
P(1)-C(16)	1.839(7)	P(1)-C(17)	1.813(9)	C(8)-H(8b)	0.99(8)	C(8)-C(9)	1.506(10)
				C(16)-H(16b)	0.96(8)	C(16)-H(16a)	1.21(8)
W-Re-P(2)	92.2(1)	W-Re-C(1)	91.8(2)	Re-W-H(8a)	66.9(21)	P(1)-W-H(8a)	82(2)
P(2)-Re-C(1)	174.1(2)	W-Re-C(2)	150.4(2)	C(4)-W-H(8a)	122(2)	C(5)-W-H(8a)	100(2)
P(2)-Re-C(2)	85.6(2)	C(1)-Re-C(2)	88.8(3)	C(6)-W-H(8a)	161(2)	C(7)-W-H(8a)	82(2)
W-Re-C(3)	121.0(2)	P(2)-Re-C(3)	91.0(2)	C(8)-W-H(8a)	18(2)	W-P(1)-C(16)	114.5(2)
C(1)-Re-C(3)	90.7(3)	C(2)-Re-C(3)	88.6(3)	W-P(1)-C(17)	117.0(3)	C(16)-P(1)-C(17)	100.7(4)
W-Re-C(4)	43.9(2)	P(2)-Re-C(4)	90.3(2)	W-P(2)-C(18)	115.3(3)	C(16)-P(1)-C(18)	105.0(4)
C(1)-Re-C(4)	95.6(3)	C(2)-Re-C(4)	165.1(3)	Re-P(2)-C(16)	116.2(2)	Re-P(2)-C(19)	115.3(3)
C(3)-Re-C(4)	77.2(3)	W-Re-C(8)	56.2(2)	C(16)-P(2)-C(19)	102.2(4)	Re-P(2)-C(20)	115.4(3)
P(2)-Re-C(8)	89.2(2)	C(1)-Re-C(8)	89.3(3)	C(16)-P(2)-C(20)	104.5(4)	Cl(1)-C-Cl(2)	113.5(7)
C(2)-Re-C(8)	94.2(3)	C(3)-Re-C(8)	177.2(3)	Re-C(1)-O(1)	174.4(7)	Re-C(2)-O(2)	178.2(7)
C(4)-Re-C(8)	100.1(2)	Re-W-P(1)	90.3(1)	Re-C(3)-O(3)	178.5(6)	Re-C(4)-W	80.8(3)
Re-W-C(4)	55.3(2)	P(1)-W-C(4)	91.2(2)	Re-C(4)-O(4)	125.6(6)	W-C(4)-O(4)	153.6(6)
Re-W-C(5)	90.5(2)	P(1)-W-C(5)	178.2(2)	W-C(5)-O(5)	175.7(7)	W-C(6)-O(6)	178.4(7)
C(4)-W-C(5)	87.9(3)	Re-W-C(6)	130.5(2)	W-C(7)-O(7)	172.5(7)	Re-C(8)-W	74.9(2)
P(1)-W-C(6)	89.5(2)	C(4)-W-C(6)	75.2(3)	Re-C(8)-H(8a)	123(5)	W-C(8)-H(8a)	49(5)
C(5)-W-C(6)	88.7(3)	Re-W-C(7)	147.7(2)	Re-C(8)-H(8b)	99(5)	W-C(8)-H(8b)	119(5)
P(1)-W-C(7)	91.7(2)	C(4)-W-C(7)	156.8(3)	H(8a)-C(8)-H(8b)	101(7)	Re-C(8)-C(9)	112.2(4)
C(5)-W-C(7)	88.5(3)	C(6)-W-C(7)	81.8(3)	W-C(8)-C(9)	126.3(4)	H(8a)-C(8)-C(9)	109(5)
Re-W-C(8)	48.9(2)	P(1)-W-C(8)	86.1(2)	H(8b)-C(8)-C(9)	112(5)	W-H(8a)-C(8)	113(6)
C(4)-W-C(8)	104.1(3)	C(5)-W-C(8)	95.7(3)	C(8)-C(9)-C(10)	121.6(6)	C(8)-C(9)-C(14)	121.1(6)
C(6)-W-C(8)	175.5(3)	C(7)-W-C(8)	99.1(3)	P(1)-C(16)-P(2)	113.1(4)		

**Scheme 2.**

and by inference also at polynuclear metal centres and on metal surfaces.

The Re-C(8)-W angle [74.9(2)°] in (12) is considerably smaller than the Re-C-W angle [83.2(3)°] in (1). The μ-Me ligand in the cation [Fe₂(μ-CO)(μ-Me)(μ-Ph₂PCH₂PPh₂)(η-C₅H₅)₂]⁺

shows ¹³ a similar metal-μ-C-metal angle [75.7(1)°] to that in (12). The more acute angles in the alkyl species compared with the alkylidene are partly due to longer μ-C-metal distances, and for (1) and (12) the shorter Re-W distance in the latter. However, the Re-W distances spanned may be a consequence rather than a cause of the angle at μ-C. Finally, the conformation adopted by (12) is sterically satisfactory in that if H(8b) and the C₆H₄Me-4 substituent at C(8) were interchanged there would be unfavourable contacts between the Me₂PCH₂PMe₂ and *p*-tolyl moieties.

In compound (12) the ReWP(1)C(16)P(2) ring is substantially folded across the P...P vector. The atom C(16) lies 0.59(1) Å out of the ReWP₂ plane, away from the *p*-tolylmethyl group (r.m.s. deviation of the ReWP₂ atoms is 0.032 Å). We referred earlier to the large temperature dependence of chemical shift for the C-H→W proton in the ¹H n.m.r. spectrum of (11), and proposed that it might be due to isomerism involving a species with a C-H→Re bonding mode. However, the isomerism may be related to a change in the conformation of the C(16)P₂ReW ring in these species.

The di-iron cation [Fe₂(μ-CO)(μ-Me)(μ-Ph₂PCH₂PPh₂)(η-C₅H₅)₂]⁺ can be readily deprotonated,¹³ but treatment of (11) or (12) with NaH, LiMe, or NET₃ failed to reform the alkylidene precursors (7) and (8), respectively. Since the agostic hydrogen atoms in (11) and (12) are functioning as two-electron donors to the tungsten centres, it was thought that addition of CO might possibly transform the bridging CH₂C₆H₄Me-4 group into a ligand terminally bonded to rhenium. Bubbling CO through dichloromethane solutions of (11) or (12) produced no change, and the use of high pressures was precluded by the instability of the compounds. However, addition of excess P(OMe)₃ to a dichloromethane solution of (11) afforded a new complex (13). The i.r. spectrum of the latter (Table 1) had six CO absorptions, one of which at 1755 cm⁻¹ indicated the presence of a bridging

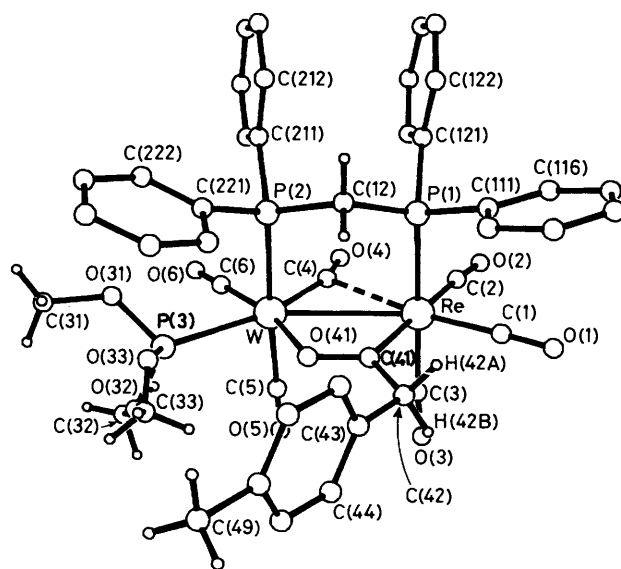
Table 6. Selected internuclear distances (Å) and angles (°) for $[\text{ReW}(\mu\text{-OCCH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_6\{\text{P}(\text{OMe})_3\}]$ (13)

Re-W	3.155(1)	Re-P(1)	2.452(2)	Re-C(41)	2.167(8)	Re-C(1)	1.915(7)
Re-C(2)	1.957(9)	Re-C(3)	1.944(8)	Re-C(4)	2.605(7)	W-P(2)	2.558(2)
W-P(3)	2.489(2)	W-O(41)	2.206(5)	W-C(4)	1.995(8)	W-C(5)	1.963(8)
W-C(6)	1.964(8)	C(1)-O(1)	1.145(9)	C(2)-O(2)	1.16(1)	C(3)-O(3)	1.12(1)
C(4)-O(4)	1.18(1)	C(5)-O(5)	1.13(1)	C(6)-O(6)	1.16(1)	C(41)-O(41)	1.248(7)
C(41)-C(42)	1.51(1)						
W-Re-P(1)	89.5(1)	W-Re-C(41)	63.2(2)	P(1)-Re-C(41)	86.4(2)	W-Re-C(1)	154.8(2)
P(1)-Re-C(1)	90.0(2)	C(41)-Re-C(1)	91.6(3)	W-Re-C(2)	116.0(2)	P(1)-Re-C(2)	95.0(3)
C(41)-Re-C(2)	178.4(3)	C(1)-Re-C(2)	89.1(3)	W-Re-C(3)	89.9(2)	P(1)-Re-C(3)	175.5(3)
C(41)-Re-C(3)	89.3(3)	C(1)-Re-C(3)	88.6(3)	C(2)-Re-C(3)	89.3(4)	W-Re-C(4)	39.1(2)
P(1)-Re-C(4)	91.6(2)	C(41)-Re-C(4)	102.3(2)	C(1)-Re-C(4)	166.1(3)	C(2)-Re-C(4)	77.0(3)
C(3)-Re-C(4)	90.7(3)	Re-W-P(2)	88.7(1)	Re-W-P(3)	149.7(1)	P(2)-W-P(3)	91.3(1)
Re-W-O(41)	65.0(1)	P(2)-W-O(41)	81.6(1)	P(3)-W-O(41)	85.1(1)	Re-W-C(4)	55.4(2)
P(2)-W-C(4)	94.8(2)	P(3)-W-C(4)	154.4(2)	O(41)-W-C(4)	120.4(2)	Re-W-C(5)	87.9(2)
P(2)-W-C(5)	174.4(2)	P(3)-W-C(5)	89.3(2)	O(41)-W-C(5)	93.0(3)	C(4)-W-C(5)	87.0(4)
Re-W-C(6)	128.9(3)	P(2)-W-C(6)	99.4(3)	P(3)-W-C(6)	80.9(3)	O(41)-W-C(6)	165.9(3)
C(4)-W-C(6)	73.6(3)	C(5)-W-C(6)	86.2(3)	W-O(41)-C(41)	111.9(5)	Re-C(41)-O(41)	119.8(5)
Re-C(41)-C(42)	124.8(5)	O(41)-C(41)-C(42)	115.3(6)	C(41)-C(2)-C(43)	116.8(6)	Re-C(4)-W	85.5(3)
Re-C(41)-O(4)	117.3(5)	W-C(4)-O(4)	157.0(6)				

carbonyl ligand. The n.m.r. data (Tables 2 and 4) did not resolve the structure of (13), although the $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectrum indicated the presence of a $\text{WP}(\text{OMe})_3$ group [δ 131.9 p.p.m., d of d, $J(\text{PP})$ 29 and 4, $J(\text{WP})$ 378 Hz], while the ^1H spectrum showed no high-field resonance due to a C-H \rightarrow W linkage. In order to establish the nature of (13) a single-crystal X-ray diffraction study was undertaken. The results are summarised in Table 6 and the structure is shown in Figure 3, but without the associated CH_2Cl_2 molecule of crystallisation.

It is evident that as a consequence of the reaction between (11) and $\text{P}(\text{OMe})_3$ a carbonyl insertion process has taken place to produce an acyl ligand which bridges the Re-W bond. The latter is also bridged by the bidentate phosphorus ligand, and semi-bridged by a carbonyl group [W-C(4)-O(4) 157.0(6)°]. The Re-W separation [3.155(1) Å] is longer than those observed in (1) [3.033(1) Å] and in (12) [2.950(2) Å], and since in all three species a formal single bond exists between the two metal centres the differences in length reflect the 'softness' of metal-metal bonds in general. The length seems likely to be at least partly determined by the 'bite' of the bridging ligands $\mu\text{-CHR}$, $\mu\text{-CH}_2\text{R}$, or $\mu\text{-OCR}$ ($\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{Me-4}$). The 'softness' of homonuclear Re-Re or W-W single bonds is evident from previous data: Re-Re, 3.058(1) Å in $[\text{Re}_2(\mu\text{-CHCHCMe}_2)(\text{CO})_8]^{16}$ and 2.957(1) Å in $[\text{Re}_2(\mu\text{-CO})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]^{22}$; W-W 3.111(1) Å in $[\text{W}_2\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_7(\eta\text{-C}_5\text{-H}_5)]^{-5}$ and 2.987(1) Å in $[\text{W}_2(\mu\text{-HC}_2\text{H})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]^{23}$.

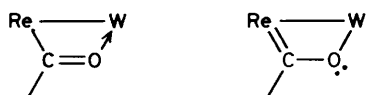
A bridging acyl group, as found in (13), has been previously observed in the species $[\text{M}_2\{\mu\text{-OCCHC}(\text{Ph})\text{NRR}'\}(\mu\text{-PPh}_2)(\text{CO})_6]$ ($\text{M} = \text{Fe}$, $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$; $\text{M} = \text{Ru}$, $\text{R} = \text{R}' = \text{Et}$)²⁴ and $[\text{MoZr}(\mu\text{-OCMe})(\mu\text{-CO})(\text{CO})(\eta\text{-C}_5\text{H}_5)_3]^{25}$. The bridge system in the latter has been described²⁵ in terms of resonance between oxyalkylidene and acyl bonding modes, and evidently the two canonical forms shown below contribute to the bonding in (13) also. Thus the C(41)-Re separation [2.167(8) Å] is intermediate between the rhenium-alkylidene carbon distance [1.92(2) Å] in $[\text{Re}\{\text{=CH}(\text{SiPh}_3)\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^{26}$ and the rhenium-alkyl carbon distance [C(8)-Re, 2.302(7) Å] in (12). The C(41)-O(41) distance [1.248(7) Å] in (13) is shorter than

**Figure 3.** Molecular structure of $[\text{ReW}(\mu\text{-OCCH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_6\{\text{P}(\text{OMe})_3\}]$ (13) showing the atom numbering scheme

those previously observed for such distances in complexes wherein an acyl group spans two transition element centres, e.g. $[\text{MoZr}(\mu\text{-OCMe})(\mu\text{-CO})(\text{CO})(\eta\text{-C}_5\text{H}_5)_3]$ [1.285(3) Å],²⁵ $[\text{Ir-Mn}(\mu\text{-OCMe})_2(\mu\text{-PPh}_2)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ [1.257(10) Å],²⁷ $[\text{Fe}_2(\mu\text{-OCPh})_2(\text{CO})_6]$ [1.262(8) Å],²⁸ and $[\text{N}(\text{PPh}_3)_2][\text{Mn}(\mu\text{-H})\{\mu\text{-OCC}(\text{Ph})\text{=CHPh}\}(\mu\text{-PPh}_2)(\text{CO})_6]$ [1.264(5) Å].²⁹

The P-Re and P-W distances in (13) are similar to those in (12). However, in the former, the W-PPh₂ separation [2.558(2) Å] is longer than the W-P(OMe)₃ distance [2.489(2) Å], an effect which is probably due to the greater π -acceptor characteristics of $\text{P}(\text{OMe})_3$ versus $\text{Ph}_2\text{PCH}_2\text{PPh}_2$. Ignoring the Re-W bond in (13), the two metal centres are in essentially octahedral co-ordination environments, taking C(4) as ligated to the rhenium (Figure 3). However, it may be noted that the W-C(4)-O(4) angle in (13) is less bent (ca. 4°) than the corresponding angle in (12).

Having established the molecular structure of (13), the n.m.r.



data (Tables 2 and 4) for the complex are seen to be in agreement with the results of the X-ray diffraction study. In the ^1H n.m.r. spectrum the two protons of the $\text{CH}_2\text{C}_6\text{H}_4\text{Me}$ -4 group give rise to an AB pattern [δ 4.04 and 4.22, with $J(\text{AB})$ 17 Hz]. In the $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum, the deshielded doublet signal at δ 284.5 p.p.m. [$J(\text{PC})$ 10 Hz] can be ascribed to the μ -acyl carbon. There are six CO resonances, as expected; that at 219.4 p.p.m. [d, $J(\text{PC})$ 17 Hz] can be assigned to the semi-bridging carbonyl group. As in (11) and (12), the *cisoid* arrangement of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and organo-ligand bridge system places two CO groups *trans* to phosphorus, leading to relatively strong $^{31}\text{P}\text{-}^{13}\text{C}$ coupling. Consequently, resonances in the $^{13}\text{C}\{-^1\text{H}\}$ spectrum of (13) at δ 208.7 [d of d, $J(\text{PC})$ 47 and 11 Hz] and at 193.0 [d, $J(\text{PC})$ 59 Hz] can be attributed to C(5)O(5) and C(3)O(3), respectively. A peak in the spectrum at 71.9 p.p.m. is assigned to the CH_2 group of the $\mu\text{-OCCH}_2\text{C}_6\text{H}_4\text{-Me}$ -4 ligand.

Monitoring (i.r. and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r.) of the reaction between (11) and $\text{P}(\text{OMe})_3$ revealed that a species was initially formed which was structurally very different from that of (13). Attempts to isolate this intermediate were unsuccessful. However, some insight into the complicated reaction pathways followed was gained by a study of the reaction between (12) and $\text{P}(\text{OMe})_3$.

Treatment of a dichloromethane solution of (12) with excess of $\text{P}(\text{OMe})_3$ afforded a yellow solution, the i.r. spectrum of which showed carbonyl stretching bands [2 023m, 2 014m, 1 921(sh), and 1 899s cm^{-1}] very similar to those of the unidentified species mentioned above. It was found, however, that the reaction mixture decomposed on chromatography (alumina or Florisil). Nevertheless, crystallisation of the mixture afforded white crystals of a complex (14), the i.r. spectrum of which was the same as that of the complete reaction mixture. Suitable crystals of (14) for an X-ray diffraction study could not be obtained, and hence the structure shown for the compound is proposed on the basis of the n.m.r. data discussed below.

The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of (14) (Table 4) showed that the complex contained two $\text{P}(\text{OMe})_3$ groups in different chemical environments, as well as a $\text{Me}_2\text{PCH}_2\text{PMe}_2$ ligand. The ^{31}P spectrum is relatively simple, the $\text{P}(\text{OMe})_3$ groups giving rise to two doublets at δ 142.5 [$J(\text{PP})$ 32, $J(\text{WP})$ 376 Hz] and 118.8 p.p.m. [$J(\text{PP})$ 44 Hz]. The presence of the $^{183}\text{W}\text{-}^{31}\text{P}$ satellite peaks on the former signal allow it to be assigned to a $\text{WP}(\text{OMe})_3$ group, with the latter ascribed to a $\text{ReP}(\text{OMe})_3$ fragment. The $\text{Me}_2\text{PCH}_2\text{PMe}_2$ group shows peaks at δ -21.2 [$J(\text{PP})$ 32 and 28 Hz] and -27.3 p.p.m. [$J(\text{PP})$ 44 and 28 Hz]. The lack of coupling between the two phosphite ^{31}P nuclei, or coupling between phosphine and phosphite ^{31}P nuclei bonded to different metals, implies that no Re-W bond is present in (14). The magnitude of the phosphite-phosphine coupling constants at the two metal centres suggest *cisoid* configurations of these groups.

The ^1H n.m.r. spectrum of (14) (Table 2) shows resonances for a $\text{C}_6\text{H}_4\text{Me}$ -4 group and two inequivalent $\text{P}(\text{OMe})_3$ ligands. The methyl substituents of the $\text{Me}_2\text{PCH}_2\text{PMe}_2$ group appear as an unresolved multiplet (δ 1.6-2.1) which may mask the signals due to the PCH_2P moiety. Another multiplet (δ 2.50-2.70), corresponding in intensity to two protons, is ascribed to the CH_2 fragment of a $\text{CH}_2\text{C}_6\text{H}_4\text{Me}$ -4 group. The $^{13}\text{C}\{-^1\text{H}\}$ spectrum is more revealing. No resonance near 280 p.p.m. ascribable to a bridging acyl group as in (13), is seen. The CO ligand region of the spectrum is complicated with resonances due to carbonyl groups attached to rhenium well resolved, and those bonded to tungsten less so. The WCO signals occur as two multiplets (205.6-204.6, and 201.7-201.3 p.p.m.). The former consists of six peaks and can be assigned to two CO groups *trans* to phosphorus nuclei. The latter pattern is a poorly resolved doublet of doublets [$J(\text{PC})$ ca. 7 Hz] suggesting the

presence of two mutually *trans* CO ligands made nearly equivalent by an approximate mirror plane through the tungsten. There are three rhenium-carbonyl resonances (Table 2), and on the basis of the $^{31}\text{P}\text{-}^{13}\text{C}$ couplings can be assigned to two CO groups which are *trans* to ^{31}P nuclei and one that is *cis*. The latter, centred at δ 191.6 p.p.m. [$J(\text{PC})$ ca. 10 Hz], appears as an unresolved doublet of doublets. Other resonances in the $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum are as expected. The CH_2 group of the $\text{CH}_2\text{C}_6\text{H}_4\text{Me}$ -4 fragment gives a poorly resolved doublet of doublets signal at δ 3.8 p.p.m. [$J(\text{PC})$ ca. 9 Hz], the magnitude of the coupling indicating its *cis* configuration with respect to ^{31}P nuclei, as shown. Resonances due to the Me_2PW group are coincident at δ 21.2 p.p.m., while two separate signals are seen for the Me_2PRe group (δ 17.0 and 16.7 p.p.m.), demonstrating that no mirror plane runs through the rhenium centre. Taken together the various n.m.r. data support the structure shown for (14).

Treatment of (12) with one equivalent of $\text{P}(\text{OMe})_3$, in an attempt to obtain a product analogous to (13), only afforded (14) in lower yield. Interestingly, the intermediate detected in the synthesis of (13) had a $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum with a pattern very similar to that of (14), but with one resonance partially obscured by a signal due to the final product (13). The following assignment was made for the observed resonances due to the intermediate: 142.5 [d, $\text{WP}(\text{OMe})_3$, $J(\text{PP})$ 32], 118.4 [d, $\text{ReP}(\text{OMe})_3$, $J(\text{PP})$ 39], 18.9 [d of d, WPPH_2 , $J(\text{PP})$ 32 and 24], and 7.2 p.p.m. [d of d, RePPh_2 , $J(\text{PP})$ 39 and 24 Hz]. That a compound structurally similar to (14) is an intermediate in the formation of (13) is surprising, since formation of an Re-W bond and CO migration to produce the bridging acyl group must be accompanied by displacement of the rhenium-bound $\text{P}(\text{OMe})_3$ ligand. Clearly this interesting reaction merits further study.

We referred earlier to unsuccessful attempts to deprotonate compounds (11) and (12) with LiMe or NaH , a process which if it had occurred with these reagents would have yielded anionic complexes with release of CH_4 or H_2 , respectively. This negative result prompted a study of reactions of (11) with the more reactive hydride sources $\text{K}[\text{BH}(\text{CHMeEt})_3]$ and NaBH_4 . Both boron reagents react with (11) to afford the same product (15), a salt isolated by addition of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$. Data for this new compound are given in Tables 1, 2, and 4, and the structure proposed for (15) is based on the n.m.r. properties.

The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum confirms the presence of the $[\text{N}(\text{PPh}_3)_2]^+$ cation, and the bridging $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligand. The ^1H n.m.r. spectrum clearly reveals the presence of a bridging hydrido-ligand with a resonance at δ -12.59 p.p.m., appearing as a doublet of doublets [$J(\text{PH})$ 18 and 11] with ^{183}W satellite peaks [$J(\text{WH})$ 39 Hz]. The chemical shift is very similar to that [δ -12.48, $J(\text{WH})$ 42 Hz] observed for the bridging hydrido-ligand in (5). No resonance occurs in the ^1H n.m.r. spectrum of (15) ascribable to a Me-4 group, suggesting that in the formation of the salt from (11) the $\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me}$ -4 group has been lost. However, the aromatic region of the spectrum is considerably broadened towards high field, indicating the presence of an *ortho*-metallated phenyl group.³⁰

The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum of (15) showed seven distinct CO group resonances which could be assigned to a $\text{W}(\text{CO})_4$ and an $\text{Re}(\text{CO})_3$ group as indicated in Table 2. The aromatic region of the spectrum was dominated by phenyl group resonances (δ 140-126 p.p.m.). However, four of the six resonances expected for a unique C_6H_4 group could be identified, and by recording a partially proton-coupled ^{13}C spectrum signals at δ 161.7 and 153.4 p.p.m. could be assigned to carbon atoms not bonded to hydrogen. The former resonance in a $^{13}\text{C}\{-^1\text{H}\}$ spectrum is a doublet of doublets [$J(\text{PC})$ 44 and 15], while the latter is a doublet [$J(\text{PC})$ 55 Hz], and neither showed ^{183}W peaks. This latter observation indicates orthometallation

Table 7. Data for crystal structure analyses^a

	(1)	(12)	(13)
Molecular formula	C ₅₃ H ₃₈ NO ₉ P ₂ ReW	C ₂₀ H ₂₃ O ₇ P ₂ ReW·CH ₂ Cl ₂	C ₄₃ H ₄₀ O ₁₀ P ₃ ReW·CH ₂ Cl ₂
<i>M</i>	1 264.9	892.3	1 264.7
Crystal shape and colour	Yellow parallelepiped	Red sphere (ground)	Yellow prism
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	11.380(7)	9.488(4)	9.955(4)
<i>b</i> /Å	13.594(5)	16.903(7)	12.438(6)
<i>c</i> /Å	16.711(6)	17.119(7)	19.868(12)
α /°	76.93(3)	90	98.66(5)
β /°	74.51(4)	90.37(4)	89.55(4)
γ /°	82.41(4)	90	105.51(3)
<i>U</i> /Å ³	2 420(2)	2 745(2)	2 342(2)
<i>Z</i>	2	4	2
<i>D_c</i> /g cm ⁻³	1.74	2.16	1.79
<i>F</i> (000)	1 288	1 680	1 228
μ (Mo- <i>Kα</i>)/cm ⁻¹	50.8	90.9	119.5
<i>T</i> /K	293	200	293
Method	ω (Wyckoff)	θ -2 θ	θ -2 θ
2 θ range/°	3 \leq 2 θ \leq 50	4 \leq 2 θ \leq 50	3 \leq 2 θ \leq 50
Approx. crystal size (mm)	0.25 \times 0.20 \times 0.10	diam. 0.35 mm	—
No. of unique data	8 541	4 866	7 764
No. of observed data	6 305	4 362	5 918
Criterion for observed, <i>n</i>	2.5	2.0	2.5
[<i>I</i> \geq <i>n</i> σ (<i>I</i>)]			
Refinement			
Solution method	Patterson	Patterson	Patterson
Anisotropic atoms	C, N, O, P, Re, W	C, O, P, Re, W, Cl	C, O, P, Re, W, Cl
Isotropic atoms	H	H	H
H atoms refined	μ -CHR	μ -CH ₂ R, PCH ₂ P	none
Final <i>R</i> (<i>R'</i>) ^b	0.039 (0.041)	0.034 (0.036)	0.036 (0.037)
<i>g</i>	0.001	0.0005	0.001
Largest final difference	+2.0, -2.0	+1.3, -1.8	+2.0, -0.7
electron-density features (e Å ⁻³)			

^a Common to all: data collected using graphite-monochromated Mo-*K α* X-radiation, $\lambda = 0.710 69$ Å; diffractometer *P3m*. ^b $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$; $R' = \Sigma w^{\frac{1}{2}} |F_o| - |F_c| / \Sigma w^{\frac{1}{2}} |F_o|$; $w = [\sigma_c^2(F_o) + g F^2]$, $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics; *g* was chosen so as to minimise variation in $\Sigma w(|F_o| - |F_c|)^2$ with $|F_o|$.

at the rhenium centre, a type of reaction recently observed by others.³¹ The other two C₆H₄ resonances appear at δ 148.5 [*J*(PC) 18 Hz] and 121.8 p.p.m. [*J*(PC) 8 Hz]. Finally, the PCH₂P group signal is a doublet of doublets at δ 35.1 [*J*(PC) 26 and 22 Hz].

It is, therefore, proposed that attack by hydride on (11) results in the elimination of *p*-xylene and the resulting unsaturated ReW species undergoes *ortho*-metallation at the rhenium centre to form (15). This is supported by the observation that the only residue obtained after treating (11) with NaBH₄ contained *p*-xylene (detected by mass spectrometry). Treatment of (11) with NaBD₄ afforded (15) and not a Re(μ -D)W species, the doublet of doublets signal at high field in the ¹H n.m.r. spectrum being retained. Thus the hydride ligand in (15) is not derived from tetrahydroborate. Unfortunately the mass spectrum of the residues was weak, and the formation of deuteriated xylene could not be confirmed.

The results described in this paper are of considerable interest in relation to C₁ chemistry in a heteronuclear dimetal complex. Formation of the complexes (1)–(4) represents the hitherto unrecognised conversion of a terminally bound alkylidyne group into bridging alkylidene. Synthesis of the vinyl-bridged compound (5) from (4) provides a model for the intermediate proposed in the preceding paper¹ for the important transformation of a bridging μ -CHMe group into ligated η -C₂H₄ in a heteronuclear dimetal complex. The preparation of the complexes (11) and (12) demonstrates the formation of

unsymmetrically bridging alkyl groups from bridging alkylidene ligands. Moreover, the *p*-tolylmethyl bridge system in (11) undergoes a novel CO insertion with C–C bond formation to yield (13), while hydride reduction releases *p*-xylene. The latter result completes a reaction path from terminally metal-bound alkylidyne in [ReW(\equiv CC₆H₄Me-4)(CO)₉] to release of alkane in the formation of (15).

Experimental

Light petroleum refers to that fraction of b.p. 40–60 °C. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere. The n.m.r. measurements were made with JNM-FX 90Q and FX 200 instruments, and i.r. spectra were recorded with a Nicolet 10-MX FT spectrophotometer. The compounds [ReM(\equiv CR)(CO)₉] (M = Cr, Mo, or W, R = C₆H₄Me-4; M = W, R = Me) were prepared by the method described elsewhere for the CPh analogues.³² Analytical and other data for the new compounds are given in Table 1.

Preparation of the Compounds [N(PPh₃)₂][ReM(μ -CHR)(CO)₉] (M = Cr, Mo, or W, R = C₆H₄Me-4; M = W, R = Me).—A similar procedure was used for the synthesis of complexes (1)–(4), and hence only that for (1) is given in detail. A thf solution (20 cm³) of [ReW(\equiv CC₆H₄Me-4)(CO)₉] (0.29 g, 0.40 mmol) at -50 °C was treated with a solution of K[BH(CHMeEt)₃] (0.40 cm³, 0.40 mmol) in the same solvent.

Table 8. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for complex (1)

Atom	x	y	z	Atom	x	y	z
W	252(1)	4 711(1)	2 971(1)	C(114)	8 476	2 326	183
Re	193(1)	7 004(1)	2 555(1)	C(115)	8 827	1 454	715
C	-76(6)	6 009(5)	1 793(4)	C(116)	8 138	1 188	1 548
C(1)	847(7)	5 220(6)	3 851(5)	C(121)	7 188(4)	820(3)	3 571(3)
O(1)	1 219(6)	5 386(5)	4 376(4)	C(122)	7 273	-231	3 838
C(2)	-358(7)	4 009(5)	2 229(5)	C(123)	7 961	-683	4 420
O(2)	-746(6)	3 612(4)	1 836(4)	C(124)	8 564	-85	4 736
C(3)	-1 503(7)	4 877(7)	3 705(5)	C(125)	8 479	965	4 470
O(3)	-2 459(5)	4 899(6)	4 123(4)	C(126)	7 792	1 418	3 888
C(4)	531(7)	3 352(7)	3 664(6)	C(131)	5 353(4)	2 462(3)	3 270(3)
O(4)	702(7)	2 572(5)	4 070(5)	C(132)	5 891	3 369	3 135
C(5)	1 950(7)	6 870(6)	1 975(5)	C(133)	5 235	4 171	3 493
O(5)	2 950(5)	6 867(5)	1 621(4)	C(134)	4 041	4 066	3 987
C(6)	-1 564(8)	7 197(7)	3 151(6)	C(135)	3 503	3 158	4 122
O(6)	-2 538(6)	7 352(6)	3 497(5)	C(136)	4 159	2 357	3 763
C(7)	580(8)	7 512(7)	3 455(5)	C(211)	3 273(3)	493(3)	2 342(3)
O(7)	842(6)	7 810(6)	3 970(4)	C(212)	2 259	-80	2 590
C(8)	9(7)	8 286(7)	1 853(6)	C(213)	1 119	380	2 501
O(8)	-76(6)	9 064(5)	1 400(5)	C(214)	992	1 414	2 162
C(9)	2 021(8)	4 542(6)	2 277(5)	C(215)	2 006	1 987	1 914
O(9)	3 007(6)	4 441(6)	1 919(5)	C(216)	3 147	1 527	2 003
C(11)	-1 152(6)	6 010(5)	1 438(4)	C(221)	5 744(4)	-219(4)	1 465(2)
C(12)	-2 386(7)	6 077(6)	1 892(5)	C(222)	5 686	502	732
C(13)	-3 327(7)	6 099(6)	1 511(5)	C(223)	6 510	406	-37
C(14)	-3 111(7)	6 058(6)	668(5)	C(224)	7 391	-411	-73
C(15)	-1 900(7)	5 976(7)	221(5)	C(225)	7 449	-1 131	660
C(16)	-944(6)	5 956(5)	589(4)	C(226)	6 625	-1 035	1 428
C(17)	-4 153(9)	6 080(10)	245(7)	C(231)	4 507(4)	-1 309(2)	3 122(2)
N	5 272(5)	568(4)	2 958(4)	C(232)	4 308	-2 105	2 786
P(1)	6 184(2)	1 373(1)	2 887(1)	C(233)	4 085	-3 053	3 307
P(2)	4 748(2)	-71(1)	2 474(1)	C(234)	4 061	-3 206	4 165
C(111)	7 097(4)	1 795(3)	1 847(2)	C(235)	4 260	-2 410	4 502
C(112)	6 745	2 667	1 315	C(236)	4 483	-1 461	3 980
C(113)	7 436	2 933	482	H	712(67)	5 903(58)	1 353(49)

The solution changed in colour from yellow to red-orange, and was stirred (5 min) before addition of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (0.23 g, 0.40 mmol). After warming to room temperature, solvent was removed *in vacuo*. The residue was treated with thf-diethyl ether (10 cm³, 1:1) and filtered through a Celite pad (*ca.* 1.5 \times 3 cm). Removal of solvent *in vacuo* and washing the product with light petroleum (2 \times 20 cm³) afforded orange microcrystals of $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$ (1) (0.43 g).

Preparation of the Compound $[\text{N}(\text{PPh}_3)_2][\text{ReW}(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)(\text{CO})_8]$.—A thf (15 cm³) solution of (4) (0.33 g, 0.28 mmol) was refluxed for 1 h. Solvent was removed *in vacuo* and the residue treated with thf-diethyl ether (10 cm³, 1:1) and filtered through a Celite pad. Removal of solvent *in vacuo* and washing with light petroleum (2 \times 20 cm³) afforded orange microcrystals of $[\text{N}(\text{PPh}_3)_2][\text{ReW}(\mu\text{-H})(\mu\text{-CH}=\text{CH}_2)(\text{CO})_8]$ (5) (0.31 g).

Reaction between $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_9]$ and PMe_2Ph .—A mixture of (1) (0.20 g, 0.16 mmol) and PMe_2Ph (0.027 g, 0.20 mmol) in thf (20 cm³) was refluxed for 0.5 h. After cooling, and filtering through a Celite pad, solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 \times 20 cm³) yielding orange microcrystals of $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_8(\text{PMe}_2\text{Ph})]$ (6) (0.20 g).

Synthesis of the Complexes $[\text{N}(\text{PPh}_3)_2][\text{ReM}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)(\text{CO})_7]$ (M = W, R = Ph; M = Cr, Mo, or W, R = Me).—All the syntheses were carried out in a

similar manner, that for (7) is described in detail. A thf (20 cm³) solution of (1) (0.24 g, 0.19 mmol) and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (0.07 g, 0.19 mmol) was refluxed for 5 h. After cooling to room temperature, the mixture was filtered through a Celite pad (*ca.* 3 \times 1.5 cm). Solvent was removed *in vacuo*, and the residue washed with diethyl ether (2 \times 20 cm³) to give orange microcrystals of $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_7]$ (7) (0.19 g). The compound $[\text{N}(\text{PPh}_3)_2][\text{ReW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2)(\text{CO})_7]$ (8) (0.46 g) was prepared from (1) (0.49 g, 0.39 mmol) and $\text{Me}_2\text{PCH}_2\text{PMe}_2$ (0.06 g, 0.47 mmol) after refluxing in thf (20 cm³) for 1 h. The complex $[\text{N}(\text{PPh}_3)_2][\text{ReMo}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2)(\text{CO})_7]$ (9) (0.63 g) was obtained from (2) (0.71 g, 0.61 mmol) and $\text{Me}_2\text{PCH}_2\text{PMe}_2$ (0.13 g, 0.92 mmol) in thf (20 cm³) after stirring at room temperature (10 h). Solvent was removed *in vacuo* and the residue treated with thf-diethyl ether (10 cm³, 1:1), prior to filtration through a Celite pad. The product was washed with light petroleum (2 \times 30 cm³). The same technique was used to obtain $[\text{N}(\text{PPh}_3)_2][\text{ReCr}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2)(\text{CO})_7]$ (10) (1.11 g) from (3) (1.49 g, 1.32 mmol) and $\text{Me}_2\text{PCH}_2\text{PMe}_2$ (0.27 g, 1.97 mmol), with stirring in thf (30 cm³) for 3 h.

Synthesis of the Complex $[\text{ReW}(\mu\text{-CH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2)(\text{CO})_7]$.—A CH_2Cl_2 (20 cm³) solution of (8) (0.81 g, 0.60 mmol) at -78°C was treated with six drops of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (from BDH, 54% HBF_4 solution), and the mixture was stirred for 5 min. Solvent was removed at reduced pressure at *ca.* -20°C , and the residue was dissolved in light petroleum- CH_2Cl_2 (5 cm³, 1:1) and chromatographed on a Florisil

Table 9. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for complex (12)-CH₂Cl₂

Atom	x	y	z	Atom	x	y	z
Re	1 596(1)	7 314(1)	5 411(1)	C(6)	-2 245(8)	5 929(5)	6 070(4)
W	-1 325(1)	6 950(1)	5 868(1)	C(7)	-3 250(8)	7 365(5)	6 164(4)
P(1)	-2 032(2)	6 845(1)	4 456(1)	C(8)	-163(8)	8 247(4)	5 494(4)
P(2)	1 041(2)	7 148(1)	4 021(1)	C(9)	220(7)	8 913(4)	6 040(4)
C	5 195(12)	9 836(10)	6 178(7)	C(10)	-320(8)	8 954(5)	6 798(4)
Cl(1)	6 668(3)	9 490(2)	5 691(2)	C(11)	94(8)	9 557(5)	7 307(4)
Cl(2)	5 405(5)	9 855(3)	7 203(2)	C(12)	1 080(9)	10 107(4)	7 109(4)
O(1)	2 536(6)	7 716(4)	7 093(3)	C(13)	1 547(9)	10 078(5)	6 327(5)
O(2)	3 835(6)	8 477(4)	4 859(4)	C(14)	1 148(8)	9 502(4)	5 817(4)
O(3)	3 827(6)	6 007(4)	5 345(3)	C(15)	1 597(11)	10 732(5)	7 674(5)
O(4)	690(6)	5 474(3)	5 722(4)	C(16)	-578(7)	6 611(5)	3 790(4)
O(5)	-478(6)	6 973(4)	7 647(3)	C(17)	-3 278(8)	6 073(6)	4 200(5)
O(6)	-2 765(7)	5 329(4)	6 173(4)	C(18)	-2 856(8)	7 721(5)	4 047(4)
O(7)	-4 370(6)	7 516(4)	6 354(4)	C(19)	2 341(8)	6 611(5)	3 463(5)
C(1)	2 136(8)	7 548(4)	6 496(4)	C(20)	900(9)	8 072(5)	3 456(4)
C(2)	2 980(8)	8 048(5)	5 073(4)	H(8a)	-1 035(82)	8 128(46)	5 562(45)
C(3)	3 002(8)	6 496(5)	5 359(4)	H(8b)	-183(79)	8 419(47)	4 943(44)
C(4)	249(8)	6 113(4)	5 718(4)	H(16a)	-488(81)	5 918(51)	3 963(46)
C(5)	-776(8)	6 996(4)	6 998(4)	H(16b)	-878(84)	6 680(51)	3 258(49)

Table 10. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for complex (13)-CH₂Cl₂

Atom	x	y	z	Atom	x	y	z
Re	1 202(1)	298(1)	1 987(1)	C(114)	-3 726(10)	-869(9)	201(5)
W	2 310(1)	2 412(1)	3 126(1)	C(115)	-3 532(10)	-1 609(8)	609(5)
P(1)	-1 196(2)	357(1)	2 233(1)	C(116)	-2 803(9)	-1 239(8)	1 237(4)
P(2)	-209(2)	2 503(1)	3 299(1)	C(121)	-2 292(8)	-465(9)	2 822(4)
P(3)	3 201(2)	4 494(2)	3 461(1)	C(122)	-3 726(8)	-557(7)	2 817(4)
C(12)	-1 332(7)	1 792(5)	2 535(3)	C(123)	-4 555(11)	-1 119(8)	3 280(5)
O(41)	1 884(5)	2 813(4)	2 119(2)	C(124)	-3 959(12)	-1 571(9)	3 760(5)
C(41)	1 496(7)	1 946(6)	1 685(3)	C(125)	-2 591(11)	-1 465(8)	3 775(5)
C(42)	1 313(9)	2 152(6)	965(3)	C(126)	-1 723(10)	-913(7)	3 309(4)
C(43)	1 522(8)	3 359(6)	862(3)	C(211)	-1 174(8)	1 928(6)	4 012(3)
C(44)	2 811(10)	4 014(7)	719(4)	C(212)	-2 585(8)	1 851(6)	4 062(4)
C(45)	2 995(12)	5 155(8)	663(5)	C(213)	-3 313(9)	1 390(8)	4 605(4)
C(46)	1 923(12)	5 640(8)	729(4)	C(214)	-2 642(10)	1 050(7)	5 088(4)
C(47)	637(11)	4 997(8)	860(5)	C(215)	-1 258(9)	1 132(7)	5 045(4)
C(48)	435(10)	3 843(8)	920(4)	C(216)	-515(8)	1 565(7)	4 508(4)
C(49)	2 158(17)	6 892(9)	663(7)	C(221)	-483(7)	3 915(6)	3 377(3)
C(1)	612(8)	-444(6)	1 080(4)	C(222)	-536(8)	4 530(6)	4 020(4)
O(1)	324(7)	-918(5)	538(3)	C(223)	-565(10)	5 658(7)	4 076(5)
C(2)	992(10)	-1 180(7)	2 266(4)	C(224)	-570(11)	6 172(7)	3 513(6)
O(2)	915(10)	-2 067(5)	2 404(4)	C(225)	-569(11)	5 551(7)	2 885(5)
C(3)	3 111(8)	342(7)	1 748(4)	C(226)	-515(10)	4 443(7)	2 809(4)
O(3)	4 178(7)	324(7)	1 565(4)	C(31)	3 102(12)	6 075(8)	4 514(6)
C(4)	1 937(8)	809(7)	3 276(4)	C(32)	5 764(11)	4 875(12)	3 889(7)
O(4)	1 931(8)	58(5)	3 573(3)	C(33)	3 120(17)	5 855(15)	2 566(7)
C(5)	4 211(8)	2 343(7)	2 900(4)	O(31)	2 764(7)	4 898(5)	4 199(3)
O(5)	5 315(7)	2 305(7)	2 782(4)	O(32)	4 807(7)	5 074(6)	3 447(4)
C(6)	2 879(8)	2 457(7)	4 077(4)	O(33)	2 664(9)	5 295(7)	3 045(5)
O(6)	3 235(7)	2 452(6)	4 628(3)	C	6 062(16)	4 408(13)	1 827(7)
C(111)	-2 288(7)	-71(6)	1 453(3)	Cl(1)	6 282(5)	3 342(5)	1 219(3)
C(112)	-2 249(8)	649(7)	1 037(4)	Cl(2)	6 706(6)	5 702(5)	1 524(4)
C(113)	-3 219(8)	231(9)	406(4)				

column (*ca.* 15 \times 2 cm) held at -20°C . Elution with the same solvent mixture gave an orange band, and by removal of solvent *in vacuo* orange microcrystals of [ReW(μ -CH₂C₆H₄Me-4)(μ -Me₂PCH₂PMe₂)(CO)₇]-CH₂Cl₂ (12) (0.41 g) were obtained.

The compound [ReW(μ -CH₂C₆H₄Me-4)(μ -Ph₂PCH₂-PPh₂)(CO)₇] (11) (0.44 g) was similarly prepared from (7) (0.78 g, 0.49 mmol). However, unless stored at *ca.* -20°C it is unstable, and suitable microanalytical data were not obtained. The compound is characterised by the data in Tables 2 and 4, and the close similarity of its i.r. spectrum in the carbonyl stretching region with that of (12) (Table 1).

Reaction between [ReW(μ -CH₂C₆H₄Me-4)(μ -Ph₂PCH₂-PPh₂)(CO)₇] and Trimethyl Phosphite.—A CH₂Cl₂ (20 cm³) solution of (11) (0.50 g, 0.44 mmol) at -20°C was treated with excess of P(OMe)₃ (*ca.* 0.6 cm³). The mixture was warmed to room temperature and stirred for 1 h. Solvent was removed *in vacuo*, and the residue dissolved in light petroleum-CH₂Cl₂ (5 cm³, 1:1) and chromatographed on an alumina column (*ca.* 15 \times 2 cm), eluting with the same solvent mixture. Removal of solvent at reduced pressure from the yellow eluate afforded yellow microcrystals of [ReW(μ -OCCH₂C₆H₄Me-4)(μ -Ph₂P-CH₂PPh₂)(CO)₆{P(OMe)₃}] (13) (0.38 g).

Reaction between [ReW(μ -CH₂C₆H₄Me-4)(μ -Me₂PCH₂-PMe₂)(CO)₇] and Trimethyl Phosphite.—A CH₂Cl₂ (20 cm³) solution of (12) (0.75 g, 0.84 mmol) was treated with P(OMe)₃ (0.23 cm³, 1.86 mmol), and the mixture stirred at 0 °C for 1 h. The mixture was filtered through Celite (ca. 3 × 1.5 cm), and solvent removed *in vacuo*. The residue was washed with Et₂O (2 × 20 cm³) and the pale yellow powder obtained was crystallised from CH₂Cl₂-light petroleum (1:5) at ca. -20 °C to give white crystals of [(MeO)₃P](OC)₃(4-MeC₆H₄CH₂)-Re(μ -Me₂PCH₂PMe₂)W(CO)₄{P(OMe)₃} (14) (0.50 g).

Reaction between the Complex [ReW(μ -CH₂C₆H₄Me-4)(μ -Ph₂PCH₂PPh₂)(CO)₇] and K[BH(CHMeEt)₃].—A thf (20 cm³) solution of (11) (0.37 g, 0.35 mmol) at ca. -30 °C was treated with a solution of K[BH(CHMeEt)₃] (0.35 cm³, 0.35 mmol) and the mixture stirred for 1.5 h. The compound [N(PPh₃)₂]Cl (0.20 g, 0.36 mmol) was added, and the solution warmed to room temperature before addition of Et₂O (20 cm³) to precipitate KCl and excess [N(PPh₃)₂]Cl. The mixture was filtered through a Celite pad (ca. 3 × 1.5 cm), and solvent was removed *in vacuo*. The residue was washed with light petroleum (2 × 20 cm³) yielding yellow microcrystals of [N(PPh₃)₂]-[ReW(μ -H){ μ -PPh(C₆H₄)CH₂PPh₂}(CO)₇] (15).

Crystal Structure Determinations and Refinements.—Details of the data collection procedures, and structure solution and refinement are given in Table 7. Data were collected on single crystals mounted under nitrogen in thin-walled glass capillaries and were corrected for crystal decay (small in all cases), Lorentz, and polarisation effects. For (1), which had well developed faces (1 0 0), (-1 0 0), (1 1 0), (-1 -1 0), (0 0 1), and (0 0 -1), an analytical absorption correction was applied. For (12)·CH₂Cl₂ the crystal was ground to a sphere to minimise absorption effects, whilst for (13)·CH₂Cl₂ the correction was by an empirical method based upon azimuthal scan data.³³

The structures were solved by conventional heavy-atom and difference-Fourier methods and were refined by blocked-cascade least squares. For (1) the μ -CHR hydrogen atom was refined with a fixed isotropic thermal parameter. All other hydrogen atoms were included in calculated positions, with chemically related groups of hydrogen atoms being given common refined isotropic thermal parameters. The aryl rings of the [N(PPh₃)₂]⁺ cation were treated as rigid groups. For (12)·CH₂Cl₂, all hydrogen atoms were given fixed isotropic thermal parameters ca. 1.2 times those of their parent carbon atoms. The μ -CH₂R and PCH₂P hydrogen atoms were refined without positional constraints, with all remaining hydrogen atoms included in calculated positions. For (13)·CH₂Cl₂, all hydrogen atoms were included in calculated positions. The methylene, C₆H₄Me-4 and P(OMe)₃ hydrogen atoms were given common refined isotropic thermal parameters, whilst the aryl hydrogen atoms were given fixed isotropic values as for (12)·CH₂Cl₂. For (12) and (13), the hydrogen atoms of the CH₂Cl₂ molecules of crystallisation were not included in the refinements. Scattering factors were from ref. 34. All calculations were carried out on an 'Eclipse' (Data General) computer with the 'SHELXTL' system of programs.³³ Atomic co-ordinates for (1), (12)·CH₂Cl₂, and (13)·CH₂Cl₂, are given in Tables 8, 9, and 10, respectively.

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