Stepwise Transformation of a Terminally Bound Alkylidyne Ligand to a Bridging Acyl Group at a Bimetal Centre *via* an Asymmetrically Bridging Alkyl; *X*-Ray Crystal Structures of $[N(PPh_3)_2][ReW(\mu\text{-}CHR)(CO)_9]$ ($R = C_6H_4Me\text{-}4$), $[ReW(\mu\text{-}CH_2R)(\mu\text{-}Me_2PCH_2PMe_2)(CO)_7]$, and $[ReW(\mu\text{-}OCCH_2R)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_6\{P(OMe)_3\}]$

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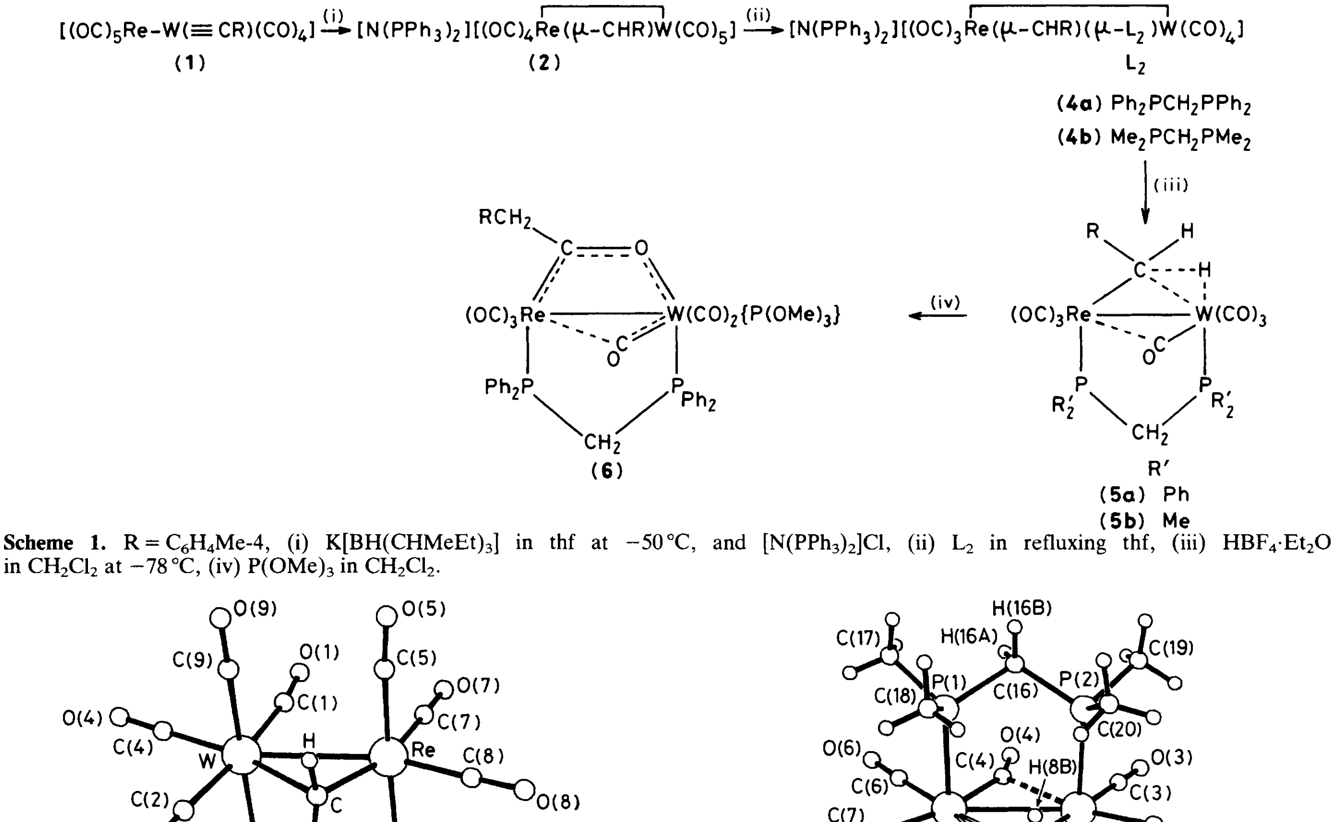
Rhenium–tungsten complexes containing bridging alkylidene, asymmetrically bridging alkyl, and bridging acyl ligands have been synthesised sequentially from the terminal alkylidyne complex $[ReW(\equiv CR)(CO)_9]$ ($R = C_6H_4Me\text{-}4$), and the structures of the complexes $[N(PPh_3)_2][ReW(\mu\text{-}CHR)(CO)_9]$, $[ReW(\mu\text{-}CH_2R)(\mu\text{-}Me_2PCH_2PMe_2)(CO)_7]$ and $[ReW(\mu\text{-}OCCH_2R)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_6\{P(OMe)_3\}]$ have been established by *X*-ray crystallography.

Metal bound alkylidene and alkylidyne groups are believed to play a pivotal role in several catalytic reactions, and these processes may be homo- or hetero-geneous in nature.[1–3] Interest currently focuses on di- and poly-nuclear metal species where it is possible for these groups to migrate between metal centres,[4,5] a facility long known for carbonyl



Scheme 1. $R = C_6H_4Me\text{-}4$, (i) $K[BH(CHMeEt)_3]$ in thf at −50 °C, and $[N(PPh_3)_2]Cl$, (ii) L_2 in refluxing thf, (iii) $HBF_4\cdot Et_2O$ in CH_2Cl_2 at −78 °C, (iv) $P(OMe)_3$ in CH_2Cl_2.

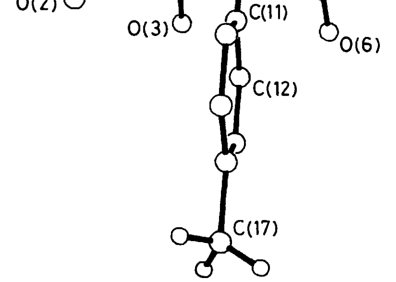


Figure 1. Molecular structure of the anion of the salt $[N(PPh_3)_2][ReW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_9]$ (**2**). Dimensions: Re–W 3.033(1), W–C 2.404(6), Re–C 2.155(8) Å. ∠ W–C–Re 83.2(3), W–C(1)–O(1) 172(1)°. Here and in Figures 2 and 3, aromatic hydrogens have been omitted for clarity.

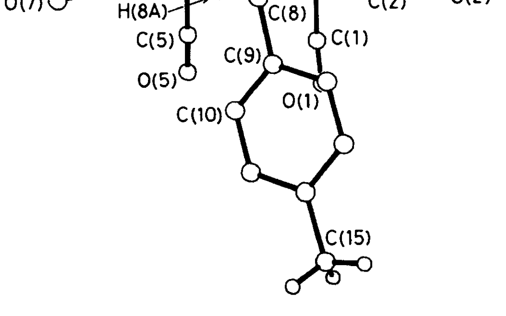


Figure 2. Molecular structure of $[ReW(\mu\text{-}CH_2C_6H_4Me\text{-}4)(\mu\text{-}Me_2PCH_2PMe_2)(CO)_7]$ (**5b**). Dimensions: Re–W 2.950(1), W–P(1) 2.510(2), Re–P(2) 2.450(2), Re–C(8) 2.302(7), W–C(8) 2.541(7), W–H(8A) 2.08(6), C(8)–H(8A) 0.86(8), W–C(4) 2.024(8), Re–C(4) 2.457(8) Å. ∠ W–C(8)–Re 74.9(2), W–H(8A)–C(8) 113(7), W–C(4)–O(4) 153.6(6)°.

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ligands, and recently demonstrated for alkyl.[6] Herein we report for the first time the stepwise conversion of an alkylidyne ligand attached to a single metal centre into a bridging acyl group, *via* an asymmetrically bridging alkyl.

Treatment of compound (**1**)[7,8] with K[BH(CHMeEt)$_3$] in thf (tetrahydrofuran) followed by [N(PPh$_3$)$_2$]Cl affords the orange salt (**2**) (86%),‡ the structure of which has been established by *X*-ray diffraction.§ The configuration of the anion is shown in Figure 1. The Re–W bond is spanned by a CH(C$_6$H$_4$Me-4) group, formed by attack of H$^-$ on the terminally bound tolylmethylidyne ligand in (**1**). It has been shown previously that the compounds [ReW($\equiv$CR)(CO)$_9$] (R = Ph or C$_6$H$_4$Me-4) react with PMe$_3$ to give the bridged ylide complexes (**3**),[8] and hence the reactions of H$^-$ and PMe$_3$ are related. The conversion of terminal alkylidyne into bridging alkylidene also occurs in the formation of the anion [W$_2$(μ-CHR)(CO)$_7$(η-C$_5$H$_5$)]$^-$ (R = C$_6$H$_4$Me-4) from the reaction between [W$_2$($\equiv$CR)(CO)$_7$(η-C$_5$H$_5$)] and H$^-$ using K[BH(CHMeEt)$_3$].[9]

$$[(\mathrm{OC})_4\overline{\mathrm{Re}\{\mu\text{-}\mathrm{CR(PMe_3)}\}(\mu\text{-}\mathrm{CO})\mathrm{W}}(\mathrm{CO})_4]$$

(**3**) R = Ph or C$_6$H$_4$Me-4

Refluxing (**2**) in thf with the bidentate ligands R$'_2$PCH$_2$PR$'_2$ (R$'$ = Ph or Me) affords the complexes (**4**) (80%), which are more robust than (**2**), and can be successfully protonated to give the compound (**5**) (80%). The latter are the first heterometallic complexes to be reported with asymmetrically bridging alkyl groups, a structural feature confirmed for (**5b**) by an *X*-ray diffraction study (Figure 2).§ The Re–W separation [2.950(1) Å] is appropriate for a formal bond order of unity, and the metal–metal bond is bridged asymmetrically by the CH$_2$C$_6$H$_4$Me-4 moiety and by a CO group, and symmetrically by the Me$_2$PCH$_2$PMe$_2$ ligand. The bridging *p*-xylyl group can be regarded as a four-electron anionic ligand contributing two electrons to the rhenium *via* the usual σ-alkyl bond, and two *via* the interaction of a C–H bond with the tungsten. Alternatively, the three-centre two-electron W–H(8A)–C(8) interaction in (**5b**) could be viewed as resulting from the protonation of the μ-C–W bond in (**4b**). In this context, three-centre two-electron M–H–M bonds have been described[10] as protonated M–M bonds.

The ^{13}C-{^{1}H} n.m.r. spectra of the compounds (**5**)‡ show signals corresponding to seven CO ligand environments. Hence these groups are not undergoing site-exchange on the n.m.r. time-scale. Resonances for the μ-*C*H$_2$R nuclei occur at δ 18.2 and 16.4 p.p.m. for (**5a**) and (**5b**), respectively. In a ^{13}C spectrum of (**5a**) the resonance at δ 18.2 p.p.m. is a doublet of doublets [*J*(HC) 131 and 81 Hz]. The smaller ^{13}C–^{1}H coupling is characteristic for the 'agostic' bridging hydrogen atom.[11] The ^{1}H n.m.r. spectrum of (**5b**)‡ has signals for the μ-C*H*$_2$R group at δ 2.41 and at −3.89; the latter resonance has a

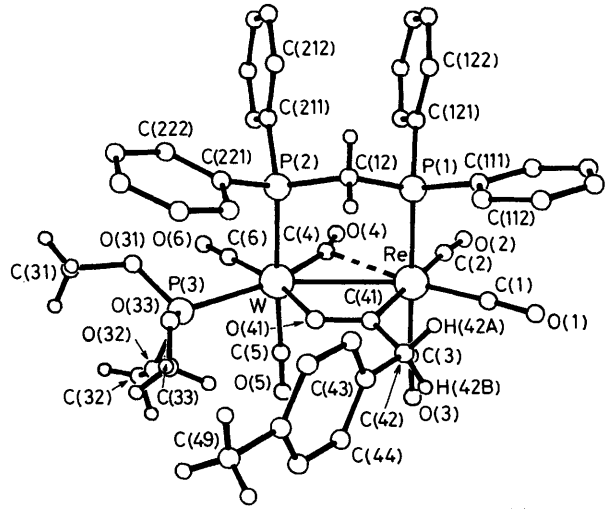

Figure 3. Molecular structure of [ReW(μ-OCCH$_2$C$_6$H$_4$Me-4)(μ-Ph$_2$PCH$_2$PPh$_2$)(CO)$_6${P(OMe)$_3$}] (**6**). Dimensions: Re–W 3.155(1), Re–P(1) 2.452(2), W–P(2) 2.558(2), W–P(3) 2.489(2), Re–C(41) 2.167(8), W–O(41) 2.206(5), C(41)–O(41) 1.248(7), W–C(4) 1.995(8), Re–C(4) 2.605(7) Å. ∠ Re–C(41)–O(41) 119.8(5), W–O(41)–C(41) 111.9(5), W–C(4)–O(4) 157.0(6)°.

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‡ Selected spectroscopic data (unless otherwise stated, i.r. measured in CH$_2$Cl$_2$, ^{1}H n.m.r. in CD$_2$Cl$_2$, and ^{13}C-{^{1}H} and ^{31}P-{^{1}H} n.m.r. in CD$_2$Cl$_2$–CH$_2$Cl$_2$; coupling constants in Hz): compound (**2**), n.m.r., ^{1}H (CD$_3$CN), δ 8.09 (s, 1 H, μ-C*H*R); ^{13}C-{^{1}H}, δ 115.0 p.p.m. (μ-C). Compound (**4a**), n.m.r.: ^{1}H, δ 6.52 [d of d, 1 H, μ-C*H*R, *J*(PH) 20 and 14]; ^{13}C-{^{1}H} (CD$_3$CN), δ 110.0 p.p.m. [d, μ-C, *J*(PC) 6, *J*(WC) 33]; ^{31}P-{^{1}H} (CD$_3$CN, positive shifts to high frequency of H$_3$PO$_4$), δ 9.5 [d, PRe, *J*(PP) 101, *J*(WP) 4] and 7.1 p.p.m. [d, PW, *J*(PP) 101, *J*(WP) 216]. Compound (**5a**) i.r., ν_{CO} (max) at 2 040s, 2 002vs, 1 943s, 1 908m, and 1 799 cm^{-1}; n.m.r. (−20 °C): ^{1}H, δ 3.25 (m,br, 2 H, μ-CH$_2$R and PCH$_2$P), 2.43 (m,br, 1 H, PCH$_2$P), and −3.69 [d, 1 H, μ-C–H–W, *J*(HH) 13, *J*(WH) 48]; ^{13}C (fully coupled), δ 221.0 [μ-CO, *J*(WC) 101], 206.0 [d, WCO, *J*(PC) 6, *J*(WC) 145], 201.4 [d of d, WCO, *J*(PC) 42 and 7, *J*(WC) 135], 195.1 [d, WCO, *J*(PC) 6, *J*(WC) 136], 191.0 [d, ReCO, *J*(PC) 7], 189.8 [d, ReCO, *J*(PC) 7], 187.7 [d of d, ReCO, *J*(PC) 72 and 7], and 18.2 p.p.m. [d of d, *C*H$_2$R, *J*(HC) 131 and 81]. Compound (**5b**), n.m.r.: ^{1}H (−20 °C), δ 2.41 [d of d of d, 1 H, μ-CH$_2$R, *J*(HH) 13, *J*(PH) 9 and 4] and −3.89 [d, 1 H, μ-C–H–W, *J*(HH) 13, *J*(WH) 41]. Compound (**6**), i.r. ν_{CO} (max) at 2 027vs, 1 956s, 1 942s, 1 901m, 1 864m, and 1 755w cm^{-1}; n.m.r.: ^{1}H, δ 4.22 and 4.04 [(AB), 2 H, μ-CH$_2$R, *J*(AB) 17]; ^{13}C-{^{1}H}, δ 284.5 [d, O*C*CH$_2$R, *J*(PC) 10], 219.4 [d, μ-CO, *J*(PC) 17], 211.5 [d, WCO, *J*(PC) 15], 208.7 [d of d, WCO, *J*(PC) 47 and 11], 194.5 [d, ReCO, *J*(PC) 7], 193.0 [d, ReCO, *J*(PC) 59], and 191.8 p.p.m. (ReCO); ^{31}P-{^{1}H}, δ 131.9 [d of d, P(OMe)$_3$, *J*(PP) 29 and 4, *J*(WP) 378], 12.2 [d of d, WPPh$_2$, *J*(PP) 71 and 29, *J*(WP) 219], and 5.4 p.p.m. [d of d, RePPh$_2$, *J*(PP) 71 and 4].

§ *Crystal data for* (**2**): C$_{53}$H$_{38}$NO$_9$P$_2$ReW, $M = 1\,265.0$, triclinic, space group $P\bar{1}$, $a = 11.380(7)$, $b = 13.594(5)$, $c = 16.711(6)$ Å, $\alpha = 76.93(3)$, $\beta = 74.51(4)$, $\gamma = 82.41(4)°$, $U = 2\,420(2)$ Å^3, $Z = 2$, $D_x = 1.74$ g cm^{-3}, $F(000) = 1\,228$, Mo-K_α *X*-radiation, graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 50.8 cm^{-1}. Current *R* 0.039 (*R*$'$ 0.040) for 6 305, absorption corrected reflections [293 K, ω-scans, $2\theta \leqslant 50°$, $I \geqslant 2.5\sigma(I)$]; for (**5b**)·CH$_2$Cl$_2$: C$_{21}$H$_{25}$O$_7$-P$_2$ReW·CH$_2$Cl$_2$, $M = 892.3$, monoclinic, space group $P2_1/n$, $a = 9.488(4)$, $b = 16.903(7)$, $c = 17.119(7)$ Å, $\beta = 90.37(4)°$, $U = 2\,745(2)$ Å^3, $Z = 4$, $D_x = 2.33$ g cm^{-3}, $F(000) = 1\,664$, μ(Mo-K_α) = 90.9 cm^{-1}. Current *R* 0.034 (*R*$'$ 0.037) for 4 362, absorption corrected reflections [200 K, θ–2θ scans, $2\theta \leqslant 50°$, $I \geqslant 2\sigma(I)$]; for (**6**)·CH$_2$Cl$_2$: C$_{43}$H$_{40}$O$_{10}$P$_3$ReW·CH$_2$Cl$_2$, $M = 1\,264.7$, triclinic, space group $P\bar{1}$, $a = 9.955(4)$, $b = 12.438(6)$, $c = 19.868(12)$ Å, $\alpha = 98.66(5)$, $\beta = 89.55(4)$, $\gamma = 105.51(3)°$, $U = 2\,342(2)$ Å^3, $Z = 2$, $D_x = 1.79$ g cm^{-3}, $F(000) = 1\,228$, μ(Mo-K_α) = 119.5 cm^{-1}. Current *R* 0.036 (*R*$'$ 0.037) for 5 918, absorption corrected reflections [293 K, θ–2θ scans, $2\theta \leqslant 50°$, $I \geqslant 2.5\sigma(I)$].

Intensity data were collected on Nicolet *P3m* diffractometers. The structures were solved by conventional heavy atom (Patterson and Fourier) methods and were refined using a blocked-cascade full matrix least-squares procedure. The important μ-C*H*R (**2**), μ-C*H*$_2$R (**5b**), and μ-C(O)C*H*$_2$R (**6**), hydrogen atoms were located from final electron-density difference syntheses. The positional parameters of these hydrogen atoms in (**2**) and (**5b**) were refined, whilst all remaining hydrogen atoms in complexes (**2**), (**5b**), and (**6**) were included in calculated positions.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

chemical shift as expected for the bridging hydride and, in confirmation of this, shows ^{183}W satellite peaks [J(WH) 41 Hz]. The appearance of two distinct signals for the μ-CH_2R group in spectra measured from −50 to +30 °C shows that the two protons are not undergoing site exchange on the n.m.r. time-scale in this temperature range, in contrast with the rapid exchange observed in a related asymmetric μ-CH_3 di-iron complex.[12]

Addition of excess of $P(OMe)_3$ to (**5a**), followed by chromatography of the mixture on alumina, gave the yellow complex (**6**) (68%).‡ The molecular structure (Figure 3), established by X-ray diffraction,§ is one in which a Re–W bond [3.155(1) Å] is spanned by an acyl moiety resulting from CO insertion into the asymmetrically bridging CH_2R group present in (**5a**). Acyl group bridging of this kind has been observed previously in the species [M_2{μ-OCCHC(Ph)NRR′}(μ-PPh_2)$(CO)_6$] (M = Fe, R = Ph, R′ = H; M = Ru, R = R′ = Et),[13] and [MoZr(μ-OCMe)(μ-CO)(CO)(η-C_5H_5)$_3$].[14] The bridge-bonding in these related species has been described in terms of resonance between oxycarbene and acyl forms.[14] The acyl ligand in (**6**) acts as a four-electron anionic donor giving 34 valence electrons around the dimetal unit in accord with a formal Re–W bond order of unity, its bonding to the Re–W fragment being delocalised in nature, as indicated in Scheme 1.

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