Conversion of a μ_3-Alkylidyne into a μ_3-Acyl Group at a Trimetal Centre; *X*-Ray Crystal Structures of the Phosphido Bridged Complexes $[Fe_2W(\mu_3\text{-}OCCH_2R)(\mu\text{-}PPh_2)_2(CO)_5(\eta\text{-}C_5H_5)]$ and $[Fe_2W(\mu\text{-}OCCH_2R)(\mu\text{-}PPh_2)_2(CO)_6(PPh_2H)(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4)

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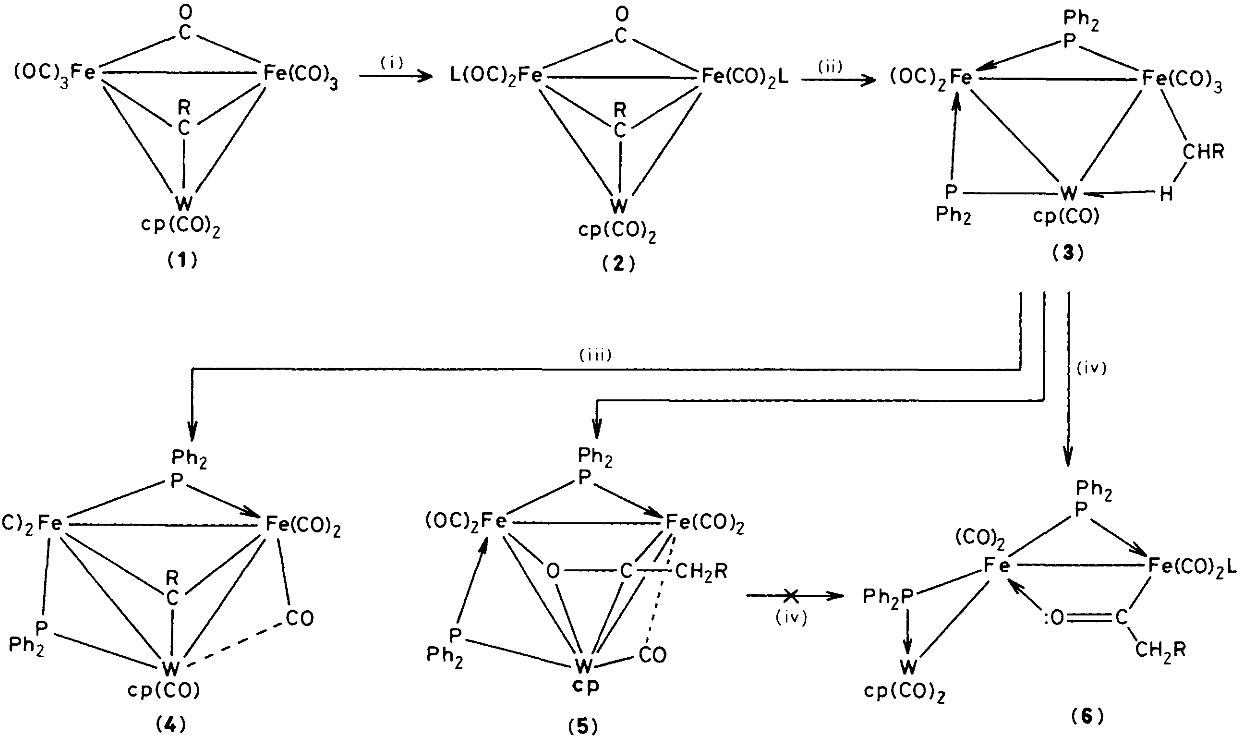
Treatment of the compound $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ with PPh_2H affords the phosphido-bridged acyl complexes $[Fe_2W(\mu_3\text{-}OCCH_2R)(\mu\text{-}PPh_2)_2(CO)_5(\eta\text{-}C_5H_5)]$ and $[Fe_2W(\mu\text{-}OCCH_2R)(\mu\text{-}PPh_2)_2(CO)_6(PPh_2H)(\eta\text{-}C_5H_5)]$, as well as the compound $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}PPh_2)_2(CO)_6(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4); the structures of the acyl species have been established by *X*-ray crystallography.

The availability of stable but reactive alkylidyne complexes such as (**1**)[1] affords a potential entry to the chemistry of organic groups attached to heterotrimetal clusters. Herein we report the synthesis of new phosphido-bridged derivatives of (**1**), and demonstrate for the first time the conversion of a μ_3-alkylidyne ligand into a μ_3-acyl group at a trimetal centre.

Treatment of (**1**) with an excess of PPh_2H in CH_2Cl_2 initially affords a solution in which the predominant species present is the bis-phosphine complex (**2**), analogous to the known complexes $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_6L_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 and L = PMe_2Ph or L_2 = $Ph_2PCH_2PPh_2$).[1] Solutions of (**2**) rearrange (CH_2Cl_2, 8 h, 20 °C) and afford



Scheme 1. R = C_6H_4Me-4, L = PPh_2H, cp = η-C_5H_5; (i) 2 × L in CH_2Cl_2, $-2CO$, (ii) $-CO$, (iii) $-H_2$, (iv) CO + L.

after chromatography on alumina the complexes (**4**) (*ca.* 20%) and (**5**) (>50%), together with small quantities of a μ_2-acyl complex (**6**) (*ca.* 10%). Spectroscopic data† for the new complexes (**4**)—(**6**) are consistent with the structures established by *X*-ray diffraction.‡

In (**5**) (Figure 1) the μ_3-acyl ligand acts as a five-electron donor. The $RCH_2C–O$ moiety is η^2-bound to tungsten with σ-attachments to the two iron atoms. The acyl C(5)–O(5) distance of 1.43(1) Å is characteristic of a C–O single bond, and is substantially longer than found in the related homonuclear tri-iron complexes $[NEt_4][Fe_3(\mu_3\text{-}OCMe)(CO)_9]$ [1.32(2) Å] and $[Fe_3(\mu\text{-}H)(\mu_3\text{-}OCMe)(CO)_9]$ [1.325(5)Å].[2] The marked reduction of the acyl C–O bond order found in (**5**), and to a lesser extent in $[WOs_3(\mu_3\text{-}OCCH_2R)(CO)_{11}(\eta\text{-}C_5H_5)]$ [$RCH_2C–O$ 1.37(2) Å],[3] may well reflect a strong interaction between the acyl oxygen atoms and the oxophilic tungsten centres in these clusters. The conversion of a μ_3-alkylidyne group into an activated μ_3-acyl ligand may be relevant to the chemistry of CO reduction on metal surfaces.[4,5]

The structure of (**6**) (Figure 2) shows a W–Fe–Fe chain of metal atoms which evidently arises *via* cleavage of an Fe–W bond in (**1**). The Fe–Fe bond is spanned by a μ-acyl ligand which now formally acts as a three-electron donor. In contrast with (**5**), the acyl C(10)–O(10) bond in (**6**) [1.255(6) Å] retains appreciable multiple bond character, a feature which is also apparent in the related phosphido-bridged complex $[Fe_2(\mu\text{-}OCMe)(\mu\text{-}PPh_2)(CO)_5(PPh_2Me)]$ [MeC–O 1.244(8) Å].[6]

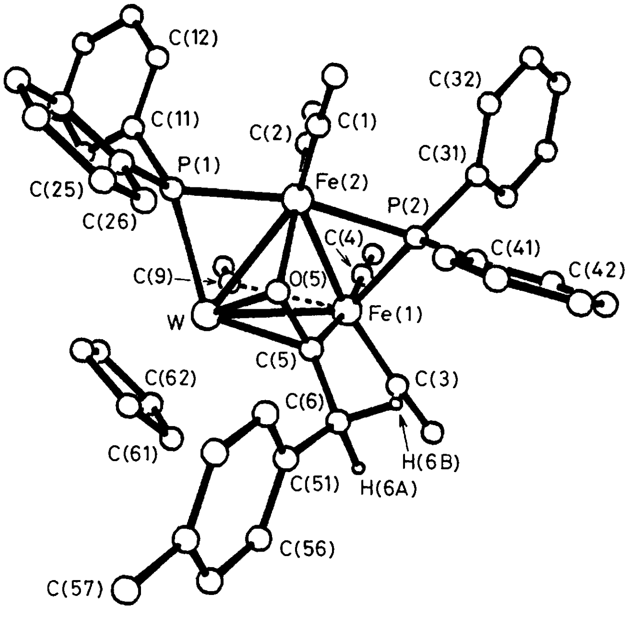


Figure 1. Molecular structure of $[Fe_2W(\mu_3\text{-}OCCH_2R)(\mu\text{-}PPh_2)_2(CO)_5(\eta\text{-}C_5H_5)]$ (**5**). Dimensions: W–Fe(1) 2.723(1), W–Fe(2) 2.712(1), Fe(1)–Fe(2) 2.616(2), W–C(5) 2.155(7), Fe(1)–C(5) 1.913(10), W–O(5) 2.129(6), Fe(2)–O(5) 2.011(6), C(5)–O(5) 1.431(10), C(5)–C(6) 1.551(13) Å, W–C(9)–O(9) 161.9(7) °.

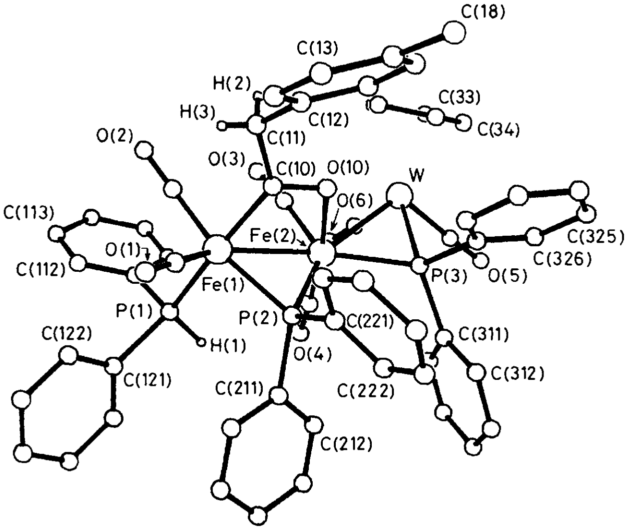


Figure 2. Molecular structure of $[Fe_2W(\mu_2\text{-}OCCH_2R)(\mu\text{-}PPh_2)_2(CO)_6(PPh_2H)(\eta\text{-}C_5H_5)]$ (**6**). Dimensions: W–Fe(2) 2.940(1), Fe(1)–Fe(2) 2.667(1), Fe(1)–C(10) 1.936(4), Fe(2)–O(10) 2.038(3), C(10)–O(10) 1.255(6), C(10)–C(11) 1.512(7) Å, Fe(1)–Fe(2)–W 147.7(1) °.

A possible mechanism for the synthesis of (**4**)—(**6**) is shown (Scheme 1) and involves an intermediate (**3**) with an asymmetrically bridging alkyl ligand.[7] Formation of (**5**) involves migration of two hydrogen atoms from terminal PPh_2H ligands in (**2**) to the μ_3-alkylidyne carbon atom, followed by migration of the resulting alkyl to metal-bound CO. Competitive loss of dihydrogen prior to alkyl migration would give (**4**), whereas attack of PPh_2H and CO on the alkyl intermediate

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† Selected spectroscopic data (i.r. measured in CH_2Cl_2; ^1H n.m.r. in CD_2Cl_2, and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ n.m.r. in $CD_2Cl_2–CH_2Cl_2$; coupling constants in Hz). Compound (**4**), i.r., ν_{CO}(max.) 2 018s, 1 972s, 1 950s, 1 930s, and 1 884w cm^{-1}; n.m.r.: $^{31}P\{^1H\}$, δ 186.8 [d, $FeW(\mu\text{-}PPh_2)$, *J*(PP) 20, *J*(WP) 332], and 199.4 p.p.m. [d, $Fe_2(\mu\text{-}PPh_2)$, *J*(PP) 20]; $^{13}C\{^1H\}$, δ 220.6 [t, μ_3-C, *J*(PC) 20], 214.0 [br., $Fe(CO)_3$], 212.6 [t, FeCO, *J*(PC) 9], 211.8 [d, WCO, *J*(PC) 15], and 210.4 [t, FeCO, *J*(PC) 9]. Compound (**5**), i.r., ν_{CO}(max.) 2 007s, 1 970s, 1 951m, 1 916m, and 1 785w cm^{-1}; n.m.r.: ^1H, δ 2.23 (s, 3 H, C_6H_4Me-4), 3.18 and 3.68 [2 × d, 2 H, $CH_2C_6H_4Me$-4, *J*(HH) 16], and 4.85 (s, 5H, C_5H_5); $^{31}P\{^1H\}$, δ 120.2 [d, $FeW(\mu\text{-}PPh_2)$, *J*(PP) 58, *J*(WP) 308] and 227.4 p.p.m. [d, $Fe_2(\mu\text{-}PPh_2)$, *J*(PP) 58]; $^{13}C\{^1H\}$, δ 258.5 [s, $W(\mu\text{-}CO)$], 218.8 [d, FeCO, *J*(PC) 7], 217.1 (s, μ_3-$OCCH_2R$), 216.5 [t, FeCO, *J*(PC) 12], 208.7 [t, FeCO, *J*(PC) 13], 197.3 [d, FeCO, *J*(PC) 12], and 53.5 (s, CH_2R). Compound (**6**), i.r., ν_{CO}(max.) 1 992s, 1 961s, 1 933s, 1 915m, 1 904m, and 1 835m cm^{-1}; n.m.r.: ^1H, δ 2.07 (s, 3 H, C_6H_4Me-4), 4.22 and 4.36 [2 × d, 2 H, $CH_2C_6H_4Me$-4, *J*(HH) 17], 4.45 [d of d, 1H, PPh_2H, *J*(PH) 354 and 11], and 4.61 (s, 5H, C_5H_5); $^{31}P\{^1H\}$, δ 44.0 [d of d, $FePPh_2H$, *J*(PP) 27 and 5], 154.4 [d of d, $FeW(\mu\text{-}PPh_2)$, *J*(PP) 29 and 5, *J*(WP) 303], and 192.1 p.p.m. [d of d, $Fe_2(\mu\text{-}PPh_2)$, *J*(PP) 27 and 29].

‡ *Crystal data.* (**5**): $C_{43}H_{34}Fe_2O_6P_2W$, M = 1 003.6, triclinic, space group $P\bar{1}$, a = 10.430(7), b = 10.767(9), c = 19.372(20) Å, α = 77.37(8), β = 78.83(7), γ = 103.74(6) °, U = 1 992(3) $Å^3$, Z = 2, D_x = 1.67 g cm^{-3}, $F(000)$ = 992, $\mu(Mo\text{-}K_\alpha)$ = 39.9 cm^{-1}. Current R = 0.045 (R_w 0.045) for 4 189 absorption-corrected reflections [293 K, θ—2θ scans, 2$\theta \leqslant$ 50 °, $I \geqslant$ 2.5 $\sigma(I)$, Nicolet $P2_1$ diffractometer, Mo-K_α ($\bar{\lambda}$ = 0.710 69 Å)]. For (**6**)·CH_2Cl_2: $C_{56}H_{45}Fe_2O_7P_3W\cdot CH_2Cl_2$, M = 1 303.4, triclinic, space group $P\bar{1}$, a = 11.120(4), b = 13.289(4), c = 19.083(5) Å, α = 90.96(2), β = 99.59(2), γ = 80.88(3) °, U = 2 745(1) $Å^3$, Z = 2, D_x = 1.58 g cm^{-3}, $F(000)$ = 1 300, $\mu(Mo\text{-}K_\alpha)$ = 28.90 cm^{-1}. Current R = 0.036 (R_w 0.038) for 7 114 absorption-corrected reflections [293 K, θ—2θ scans, 2$\theta \leqslant$ 50 °, $I \geqslant$ 2.5 $\sigma(I)$, Nicolet $P3$ diffractometer, Mo-K_α ($\bar{\lambda}$ = 0.71069 Å)]. The structure of (**4**) shows no unusual features and is not included here.

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.

(**3**), followed by Fe–W bond cleavage and insertion, could give (**6**). The potential involvement of alkyl intermediates in the formation of (**5**) and (**6**) finds support in the recent observation of the phosphite-promoted conversion of an asymmetrically bridging alkyl into a bridging acyl at a Re–W heterodimetal centre.[7]

We have recently observed that Ph_2PH reacts with the related cluster $[Co_2W(\mu_3\text{-CMe})(CO)_8(\eta\text{-}C_5H_5)]$ to give high yields of the μ-hydrido-μ-phosphido cluster $[Co_2W(\mu\text{-H})(\mu_3\text{-CMe})(\mu\text{-PPh}_2)(CO)_6(\eta\text{-}C_5H_5)]$.[8] It therefore seems probable that attack of R_2PH (R = Ph or alkyl) on pre-formed alkylidyne, or related alkylidene clusters, may offer a general approach for the synthesis of new phosphido-bridged derivatives.

Received, 17th September 1984; Com. 1319

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