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Preliminary communication

SYNTHESIS OF μ-HYDRIDO-μ-PHOSPHIDO HETEROTRIMETAL ALKYLIDYNE CLUSTERS; X-RAY CRYSTAL STRUCTURE OF $[Co_2W(\mu\text{-}H)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$

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Summary

Treatment of the μ_3-alkylidyne clusters $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and $[Co_2W(\mu_3\text{-}CMe)(CO)_8(\eta\text{-}C_5H_5)]$ with PPh_2H affords a series of new μ-phosphido-μ-hydrido alkylidyne complexes which undergo protonation with $HBF_4 \cdot Et_2O$ to give cationic derivatives. The X-ray structure of $[Co_2W(\mu\text{-}H)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ has been determined.

We have recently observed that treatment of the alkylidyne clusters $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$, I, with an excess of PPh_2H in CH_2Cl_2 affords good yields of the μ_3-acyl complex $[Fe_2W(\mu_3\text{-}OCCH_2R)(\mu\text{-}PPh_2)_2(CO)_5(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) [1]. The conversion of the μ_3-alkylidyne moiety in I to a μ_3-acyl ligand formally involves migration of hydrogen from metal-bound PPh_2H ligands to the μ_3-C carbon atom in I, followed by migration of the resulting alkyl to a metal carbonyl. We now report that by varying the reaction conditions hydrogen migration may be exclusively directed to an Fe—W bond, affording new μ-hydrido-μ-phosphido alkylidyne clusters.

Treatment of I [2] with one equivalent of PPh_2H in dilute Et_2O solutions initially affords an orange brown solution of the unstable complex II, analogous to the known complex $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_6(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ and $[Co_2W(\mu_3\text{-}CR)(CO)_7(PMe_3)(\eta\text{-}C_5H_5)]$ [3]. Compound II rearranges at 20°C (Et_2O) and following chromatography on alumina good yields (ca. 70%) of the μ-hydrido-μ-phosphido cluster III [4] are obtained. The $^{31}P\text{-}\{^1H\}$ and ^1H NMR data confirm that the μ-PPh_2 and μ-H ligands bridge Fe—W bonds and the $^{13}C\text{-}\{^1H\}$ NMR spectrum shows a characteristic resonance for the μ-*C*R moiety at δ 270.5 ppm ($J(WC)$ 110 Hz) [5].

Protonation of III with $HBF_4 \cdot Et_2O$ in CH_2Cl_2 affords the bis-μ-hydrido

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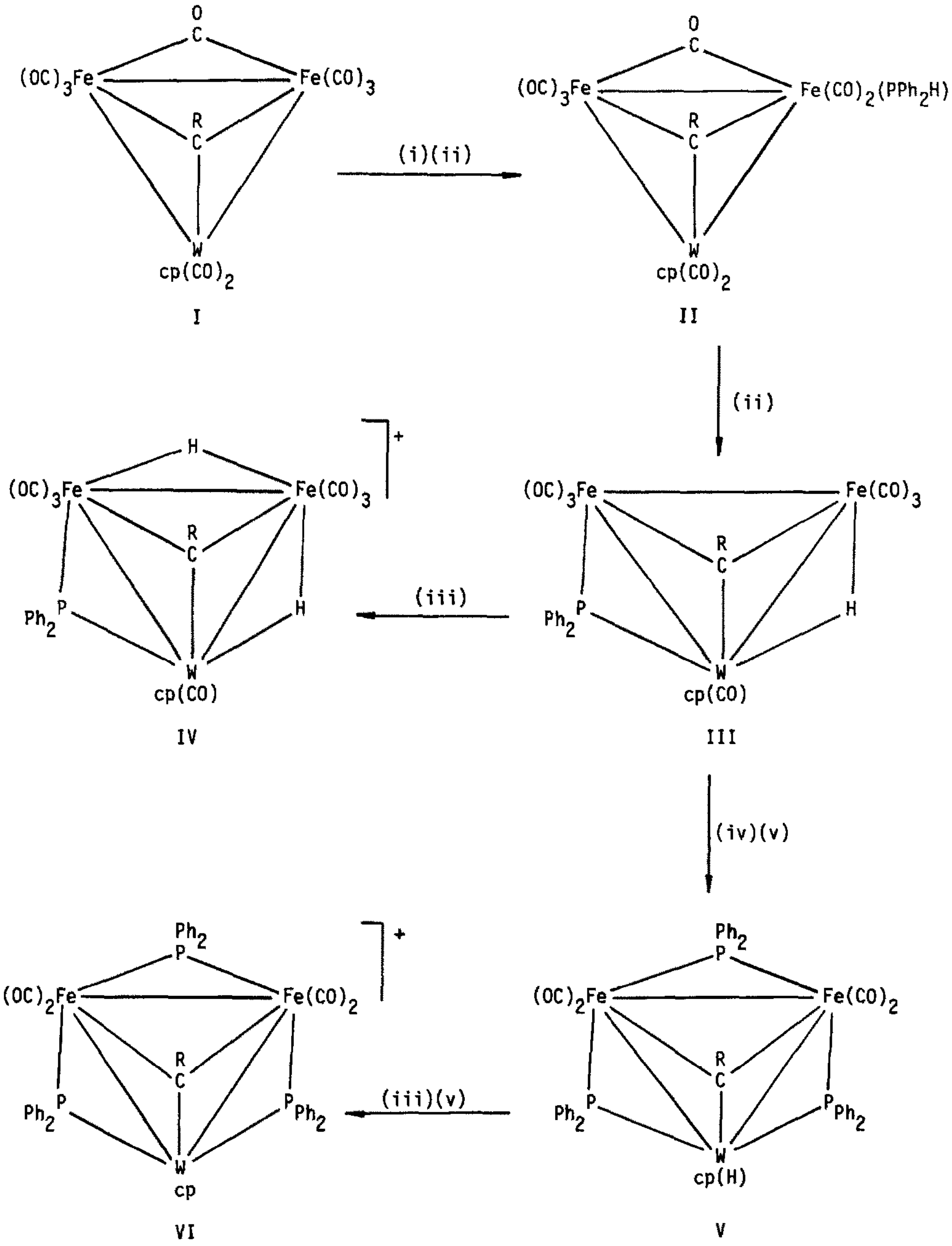
complex IV [6]. This reaction is readily reversible and attempts to isolate IV in the absence of $HBF_4 \cdot Et_2O$ led to quantitative recovery of III. The ^1H NMR spectrum of IV shows two bridging hydride resonances and the absence of ^{183}W satellites on the signal at δ −26.69 ppm indicates that protonation has occurred at the Fe—Fe bond (Scheme 1).

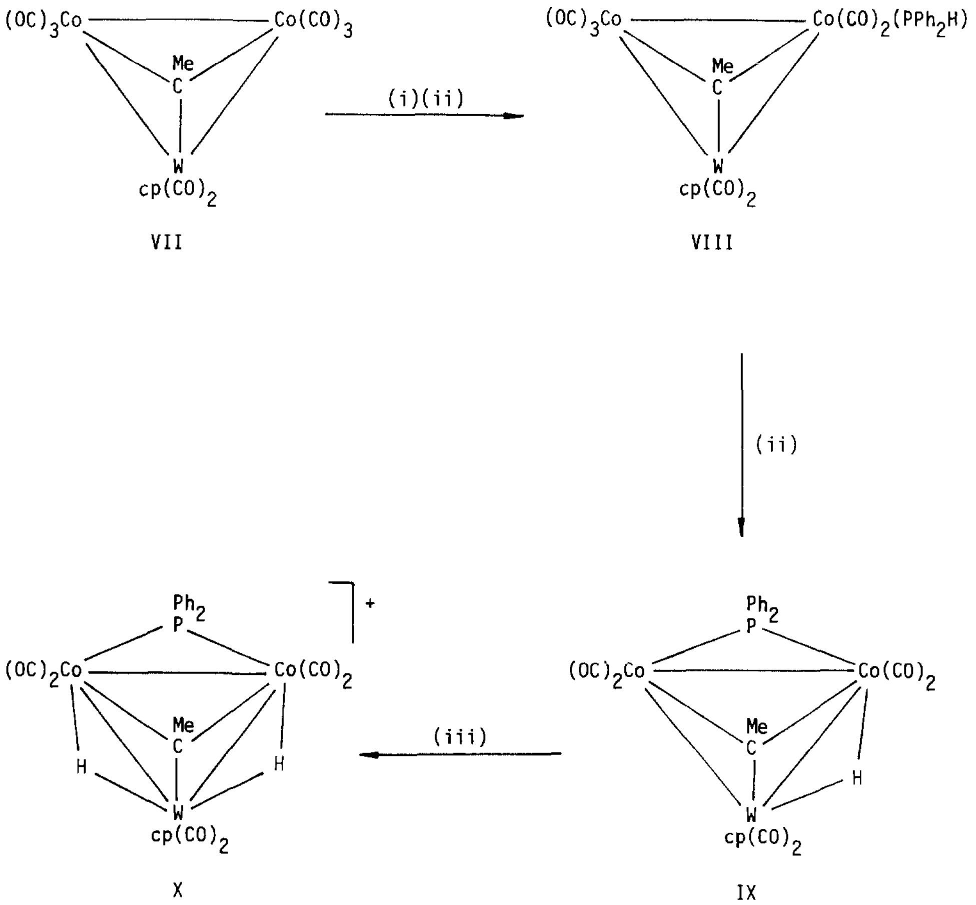


Scheme 1. (i) PPh_2H; (ii) —CO; (iii) $HBF_4 \cdot Et_2O$; (iv) 2 × PPh_2H; —3 CO, 111°C; (v) $-H_2$; R = C_6H_4Me-4.

Compound III does not react further with PPh_2H at 20°C but on refluxing in toluene good yields (ca. 70%) of the tris-μ-phosphido cluster V [7] are obtained. The ^{31}P-$\{^1H\}$ NMR data confirm that all three edges of the Fe_2W triangle of metal atoms are now bridged by μ-PPh_2 ligands and the ^1H NMR spectrum has a resonance at δ −4.55 ppm which may be assigned to a terminal hydride ligand on tungsten.

Complex V is more nucleophilic than III and protonation with $HBF_4 \cdot Et_2O$ results in irreversible loss of dihydrogen affording the cationic coordinatively unsaturated, 46 cluster valence electron species VI [8]. In the ^{13}C-$\{^1H\}$ NMR spectrum the μ_3-C resonance is unusually deshielded (δ 312.2 ppm) suggesting that the positive charge in this cation may be at least partially localised on the μ_3-C carbon atom.

The closely related Co_2W cluster VII (Scheme 2) also reacts with PPh_2H to give high yields (> 80%) of the μ-hydrido-μ-phosphido species IX [9]. The presumed intermediated VIII is not detected under the more vigorous reaction conditions (111°C) employed in this reaction. The molecular structure of IX



Scheme 2. (1) PPh_2H; (ii) —CO; (iii) $HBF_4 \cdot Et_2O$.

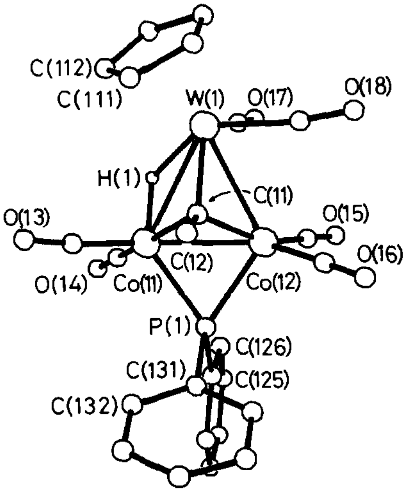


Fig. 1. Molecular structure of $[Co_2W(\mu\text{-}H)(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ (IX). The unit cell contains two very similar crystallographically independent molecules of the complex of which only one is shown. W(1)—Co(11) 2.792(1), W(1)—Co(12) 2.730(1), W(1)—C(11) 2.085(9), W(1)—H(1) 1.80(10), Co(11)—Co(12) 2.470(1), Co(11)—P(1) 2.176(2), Co(11)—C(11) 1.954(8), Co(11)—H(1) 1.48(12), Co(12)—P(1) 2.172(2), Co(12)—C(11) 1.907(8) Å; Co(11)—W(1)—Co(12) 53.1(1), W(1)—Co(11)—Co(12) 62.1(1), W(1)—Co(12)—Co(11) 64.7(1), Co(11)—P(1)—Co(12) 69.2(1), W(1)—H(1)—Co(11) 116(7)°.

[10] (Fig. 1) shows a Co_2W triangle of metal atoms capped by a μ_3-CMe ligand and in contrast with III the μ-PPh_2 ligand bridges the homonuclear (Co—Co) metal—metal bond. One of the two Co—W bonds is bridged by an hydride ligand which is consistent with the ^1H NMR spectrum, which shows a doublet at δ −13.92 ppm (J(PH) 25, J(WH) 44 Hz) with ^{183}W satellites.

Protonation of IX with $HBF_4 \cdot Et_2O$ occurs at the Co—W bond affording the mirror symmetric bis-μ-hydrido complex X [11] which shows a doublet resonance in the ^1H NMR spectrum for the two chemically equivalent μ-H ligands. Like IV, compound X readily deprotonates in the absence of $HBF_4 \cdot Et_2O$.

It is apparent that PPh_2H ligands bound to small alkylidyne clusters will undergo facile, thermally induced, oxidative addition of P—H to a metal—metal bond. In contrast, complexes such as $[Ru_3(CO)_9(PPh_2H)_3]$ require photolysis to induce hydrogen migration from phosphorus, a process which is characterised by the formation of a complex mixture of products [12].

The results described herein together with our previous observation of hydrogen migration from metal-bound PPh_2H ligands to an alkylidyne carbon atom [1], suggest that attack of PPh_2H on preformed homo- or heteronuclear alkylidyne or alkylidene clusters may offer a useful approach for the synthesis of new phosphido-bridged derivatives.

References and notes

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4 For Compound III, ν_{max}(CO) at 2051s, 2012s, 1992s, 1977m, 1967m, and 1944m cm^{-1} (cyclohexane). NMR (CD_2Cl_2): ^{1}H, δ −15.90 ppm (d, 1 H, μ-H, J(PH) 33, J(WH) 33 Hz); ^{31}P-$\{^1H\}$, δ 156.3 ppm (s, μ-PPh_2, J(WP) 298 Hz); ^{13}C-$\{^1H\}$, δ 270.5 (s, μ_3-C, J(WC) 110 Hz), 213.5 (s, $Fe(CO)_3$), 212.4 (s, br, $Fe(CO)_3$), and 211.1 ppm (d, WCO, J(PC) 9, J(WC) 164 Hz).

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6 For Compound IV, ν_{max}(CO) at 2099(s), 2076s, 2048m, 2033s, and 1996m cm^{-1} (CH_2Cl_2). NMR (CD_2Cl_2): ^{1}H, δ −26.69 (d of d, 1 H, Fe_2(μ-H), J(PH) 11, J(HH) 6 Hz), and −16.27 ppm (d of d, 1 H, WFe(μ-H), J(PH) 24, J(HH) 6, J(WH) 29 Hz); ^{31}P-$\{^1H\}$, δ 171.7 ppm (s, μ-PPh_2, J(WP) 325 Hz).

7 For Compound V, ν_{max}(CO) at 1973m, 1953s, and 1915s cm^{-1} (toluene). NMR (CD_2Cl_2): ^{1}H, δ −4.55 ppm (d of t, 1 H, WH, J(PH) 5, 54, J(WH) 28 Hz); ^{31}P-$\{^1H\}$, δ 170.1 (d, 2 × FeW(μ-PPh_2), J(PP) 24, J(WP) 230 Hz), and 195.7 ppm (t, Fe_2(μ-PPh_2), J(PP) 24 Hz); ^{13}C-$\{^1H\}$, δ 219.6 (d of d, 2 × FeCO, J(PC) 8, 10 Hz), 217.0 (d of t, μ_3-C, J(PC) 40, 12 Hz), and 215.4 ppm (t, 2 × FeCO, J(PC) 17 Hz).

8 For Compound VI, ν_{max}(CO) at 2021s, 1999s, 1978s, and 1962 m cm^{-1} (CH_2Cl_2). NMR (CD_2Cl_2): ^{31}P-$\{^1H\}$, δ 202.0 (d, 2 × FeW(μ-PPh_2), J(PP) 20, J(WP) 356 Hz), and 208.8 ppm (t, Fe_2(μ-PPh_2), J(PP) 20 Hz); ^{13}C-$\{^1H\}$, δ 312.2 (d, μ_3-C, J(PC) 28 Hz), 212.7 (d, 2 × FeCO, J(PC) 8 Hz), and 209.5 ppm (t, 2 × FeCO, J(PC) 20 Hz).

9 For Compound IX, ν_{max}(CO) at 2039m, 2014s, 1984s, 1977m, 1958w, and 1880wbr cm^{-1} (cyclohexane). NMR (CD_2Cl_2): ^{1}H, δ −13.92 ppm (d, 1 H, μ-H, J(PH) 25, J(WH) 44 Hz); ^{31}P-$\{^1H\}$, δ 239.0 ppm (br,s, μ-PPh_2); ^{13}C-$\{^1H\}$ (−70° C), δ 246.0 (d, μ_3-CMe, J(PC) 25 Hz), 223.2 (s, WCO, J(WC) 160 Hz), 212.6 (s, WCO, J(WC) 131 Hz), and 206.7, 205.4, 203.8 ppm (3 × s, CoCO).

10 Crystal data for IX: $C_{25}H_{19}Co_2O_6PW$, M = 748.1, monoclinic, space group $P2_1/c$, a 13.694(5), b 27.188(9), c 14.779(5) Å, β 110.97(2)°, U 5 138(3) Å^3, $Z = 8$, D_X 1.93 g cm^{-3}, $F(000) = 2880$, μ-(Mo-K_α) 59.4 cm^{-1}. Current $R = 0.035$ ($R_W = 0.039$) for 5770 absorption corrected intensities (22° C, θ—2θ scans, $2\theta \leqslant 50°$, $I \geqslant 2.5\sigma(I)$, Nicolet P3m diffractometer, Mo-K_α X-radiation ($\bar{\lambda}$ 0.71069 Å)). The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this communication.

11 For compound X, ν_{max}(CO) at 2081s, 2053sbr, and 2026m cm^{-1} (CH_2Cl_2). NMR (CD_2Cl_2): ^{1}H, δ −16.6 ppm (d, 2 H, 2 × μ-H, J(PH) 20, J(WH) 46 Hz); ^{31}P-$\{^1H\}$, δ 264.0 ppm (s,br, μ-PPh_2).

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