Synthesis of μ_3-Alkylidynetrimetal Complexes: *X*-Ray Crystal Structures of $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ and $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_2\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$

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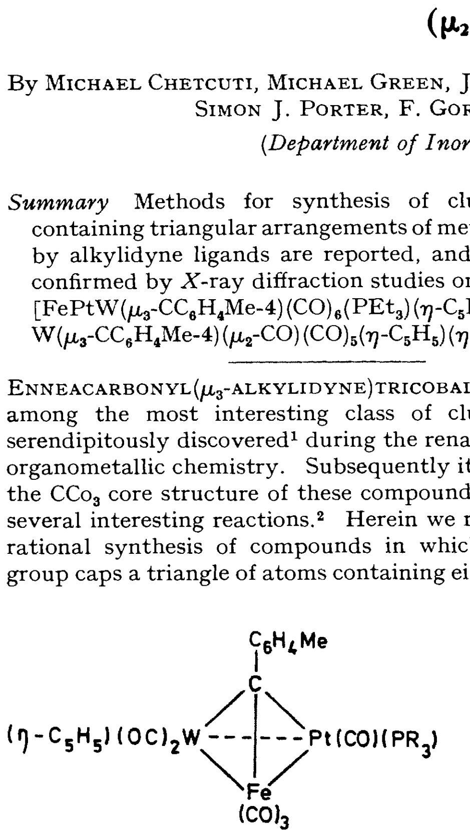
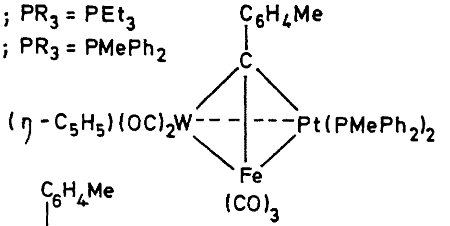
Summary Methods for synthesis of cluster complexes containing triangular arrangements of metal atoms capped by alkylidyne ligands are reported, and such structures confirmed by *X*-ray diffraction studies on the compounds $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ and $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_2\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$.

ENNEACARBONYL(μ_3-ALKYLIDYNE)TRICOBALT complexes are among the most interesting class of cluster compound serendipitously discovered[1] during the renaissance period of organometallic chemistry. Subsequently it was shown that the CCo_3 core structure of these compounds is preserved in several interesting reactions.[2] Herein we report a stepwise rational synthesis of compounds in which an alkylidyne group caps a triangle of atoms containing either two or three different transition metals. The method, having a wide applicability across the transition metal series, involves reaction of a mononuclear metal–alkylidyne complex either with two different low-valent metal compounds in sequence, or with a reactive dimetal species.

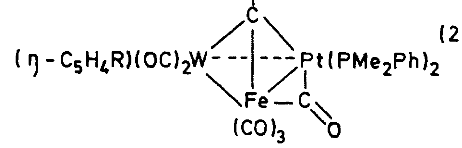


(1)

a; $PR_3 = PEt_3$
b; $PR_3 = PMePh_2$

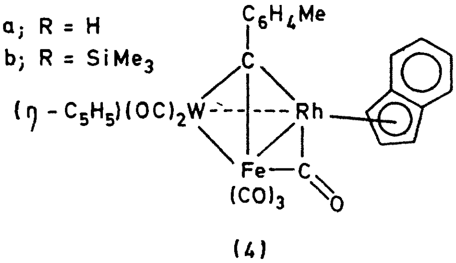


(2)



(3)

a; R = H
b; R = $SiMe_3$



(4)

A pentane solution of $[Pt(C_2H_4)_3]$,[3] treated with 2 equiv. of PEt_3, reacted with $[W(CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$[4] to give the dimetal compound[5] $[PtW(\mu_2\text{-}CC_6H_4Me\text{-}4)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$. Reaction of the latter in tetrahydrofuran (thf) with $[Fe_2(CO)_9]$ at room temperature afforded $[Fe(CO)_4(PEt_3)]$ and a black crystalline complex (**1a**) {m.p. 124—127 °C decomp.; ν_{CO} (methylcyclohexane) 2 035m, 2 013s, 1 985s, 1 954s, 1 933s, and 1 877m cm^{-1}; ^{13}C (^1H decoupled) n.m.r. spectrum ($CDCl_3$–CD_2Cl_2), μ_3-C resonance at 323 p.p.m. [d, *J*(PC) 9, *J*(PtC) 404, *J*(WC) 110 Hz]} in 40% yield.

Crystal data: $C_{25}H_{27}FeO_6PPtW$, *M* 889·3, orthorhombic, space group $Pna2_1$, *a* = 16·010(7), *b* = 8·954(8), *c* = 18·450(9) Å, *U* = 2 659(3) Å^3, *Z* = 4, D_m = 2·10, D_c = 2·22 g cm^{-3}, *F*(000) = 1 672, μ(Mo-K_α) 97·8 cm^{-1}. Current *R* 0·0505, (R′ 0·0500) for 2 703 reflections [220 K, $2\theta \leqslant 55°$, $I \geqslant 2{\cdot}5\sigma(I)$, Syntex $P2_1$ diffractometer, Mo-K_α (λ 0·710 69 Å).†

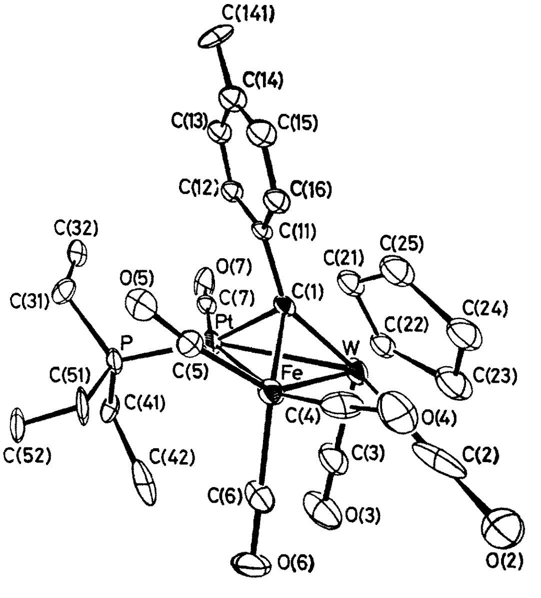


FIGURE 1. Molecular structure of (**1a**), $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$. Pt–W, 2·775(1); Pt–Fe, 2·542(3); W–Fe, 2·784(3); Pt–C(1), 2·23(2); W–C(1), 2·00(2); Fe–C(1), 1·90(2) Å; Pt–C(1)–C(11), 117·3(13); Fe–C(1)–C(11), 127·8(14); W–C(1)–C(11), 138·8(14)°.

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† 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.

The molecular structure (Figure 1) contains the μ_3-CFePtW core with the alkylidyne ligand asymmetrically bridging the metal triangle [Fe–C(1) 1·90(2), Pt–C(1) 2·23(2), W–C(1) 2·00(2) Å]. The platinum atom has lost a phosphine ligand and carries a terminal CO ligand, thus accounting for the formation of $[Fe(CO)_4(PEt_3)]$ in the reaction which gave (**1a**). Synthesis[5] of $[PtW(\mu_2\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$ followed by treatment with $[Fe_2(CO)_9]$ gave (**1b**) (45% yield), and a small amount of (**2**), the structure of the latter was determined by *X*-ray diffraction.[6] The ^{13}C (^1H decoupled) n.m.r. spectrum of (**1b**) established the presence of the μ_3-alkylidyne-carbon atom [327 p.p.m., d, *J*(PC) 7, *J*(PtC) 410, *J*(WC) 125 Hz] and the CO ligands on tungsten (δ 220 and 219 p.p.m.), iron [216, *J*(PtC) 29], and platinum [187, d, *J*(PC) 7, *J*(PtC) 1 614 Hz].

Treatment of $[PtW(\mu_2\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$, obtained from $[W(CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(C_2H_4)(PMe_2Ph)_2]$, with $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$ gives (70% yield) purple crystals of (**3a**) [m.p. 95 °C (decomp.), ν_{CO} (hexane) 2 017m, 1 995s, 1 953m, 1 927s, 1 913s, 1 879m, and 1 763m cm^{-1}]. The ^{13}C, ^{31}P, and ^{195}Pt n.m.r. spectra revealed both dynamic behaviour, and the chiral nature[7] of the cluster. At room temperature the ^{13}C n.m.r. spectrum showed a resonance for the μ_3-C atom [295 p.p.m., t, *J*(PC) 11, *J*(PtC) 472, *J*(WC) 111 Hz], two resonances for the tungsten bonded CO ligands, but only one signal for the iron-bound CO groups. However, at −100 °C (CD_2Cl_2, ^{13}CO enrichment), CO ligand signals were at δ 242 [WCO, *J*(WC) 184, *J*(PtC) 22], 233 [WCO, *J*(WC) 210, *J*(PtC) 19], 225 [d, μ-CO, *J*(PC) 5, *J*(PtC) 39], and 221 and 216 (FeCO, br, rel. int. 1 : 2) p.p.m. Moreover, the chirality of the cluster was indicated by four carbon-13 CH_3P resonances [doublets, *J*(PC) 27—32 Hz] at 18, 16, 10·5, and 7·0 p.p.m. Whereas the ^{31}P (^1H decoupled, to low frequency of ext. H_3PO_4) n.m.r. spectrum at room temperature had one resonance {δ −5·6 p.p.m. [br, *J*(PtP) 3 347 Hz]}, at −90 °C there were two signals at δ −13·5 [d, *J*(PP) 46, *J*(PtP) 3 618] and 0·6 p.p.m. [d, *J*(PP) 46, *J*(PtP) 2 993, *J*(WP) 32 Hz]. In accord with the ^{31}P spectrum, the ^{195}Pt n.m.r. spectrum was a triplet at room temperature {δ [in p.p.m. to high frequency of Ξ (^{195}Pt) = 21·4 MHz] −390·7 [*J*(PtP) 3 339]} and a doublet of doublets at −95 °C {δ −477·3 [*J*(PtP) 3 646 and 2 991 Hz]}. Compound (**3b**) was similarly prepared from $[W(CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_4SiMe_3)]$.

Reaction of $[W(CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with indenyl(dicarbonyl)rhodium affords $[RhW(\mu_2\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ which on treatment with $[Fe_2(CO)_9]$ in thf (room temperature) gives purple crystals (60%) of (**4**) {ν_{CO}(hexane), 2 033m, 1 987s, 1 953m, 1 935m, 1 901w, and 1 825w cm^{-1}, ^{13}C n.m.r. ($CDCl_3$, room temperature), 287 [μ-CC_6H_4Me-4, d, J(RhC) 34] and 213 p.p.m. (CO)}. The spectroscopic properties‡ of (**4**) merited a single crystal *X*-ray diffraction study.

Crystal data: $C_{28}H_{19}FeO_6RhW$, *M* 793·7, monoclinic, space group $P2_1/c$, $a = 9{\cdot}018(2)$, $b = 15{\cdot}572(4)$, $c = 18{\cdot}503(6)$ Å, $\beta = 103{\cdot}69(2)°$, $U = 2524(1)$ Å^3, $Z = 4$, $D_m = 2{\cdot}05$, $D_c = 2{\cdot}09$ g cm^{-3}, $F(000) = 1520$, μ(Mo-K_α) 58·9 cm^{-1}. Current *R* 0·032 (*R'* 0·034) for 4 445 reflections [298 K, $2\theta \leqslant 55°$, $I \geqslant 2{\cdot}5\sigma(I)$, Mo-$K_\alpha$ ($\bar{\lambda}$ 0·710 69 Å)].

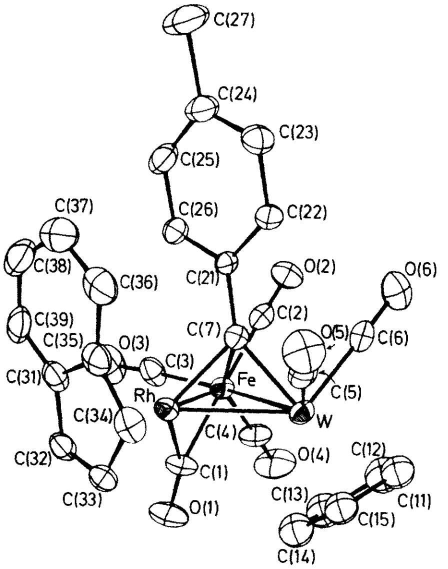
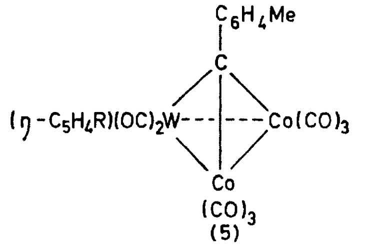
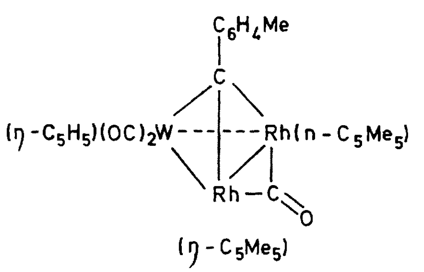


FIGURE 2 Molecular structure of (**4**), $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_2\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$. Rh–W, 2·760(1), Rh–Fe, 2·583(1), W–Fe, 2·772(1), Rh–C(7), 2·035(6), W–C(7), 2·093(6), Fe–C(7), 2·029(6), Rh–C(1), 1·928(7), Fe–C(1), 2·022(7) Å; Rh–C(1)–Fe, 81·6(2), Rh–C(7)–C(21), 120·3(5), Fe–C(7)–C(21), 127·8(4), W–C(7)–C(21), 140·6(4)°.

The triangle formed by the three metal atoms (Figure 2) is bridged asymmetrically across the Fe–Rh bond by a carbonyl ligand [Fe–C(1) 2·022(7), Rh–C(1) 1·928(7) Å], and is capped by the alkylidyne group [Fe–C(7) 2·029, Rh–C(7) 2·035(6), and W–C(7) 2·093(6) Å].†



(**5**)
a, R = H
b, R = SiMe$_3$



(**6**)

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‡ The i.r. band at 1 825 cm^{-1} was suggestive of a bridging or semi-bridging CO, and the molecule undergoes CO ligand site exchange in solution. Moreover, the ^{13}C n.m.r. spectrum showed nine resonances for the carbon atoms of the indenyl group, in accord with the rhodium atom being a chiral centre.

The compound $[W(CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ reacts with $[Co_2(CO)_8]$ or $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$[8] to give, respectively, in high yield (*ca.* 70—90%) complexes (**5a**)[9] and (**6**) {purple crystals, m.p. 248 °C decomp., ν_{CO}(hexane) 1 961s, 1 905s, 1 733m cm^{-1}; ^{13}C n.m.r. ($CDCl_3$), 271 [μ-CC$_6$H$_4$Me-4, t, *J*(RhC) 34 Hz], 244 [μ-CO, t, *J*(RhC) 44 Hz], and 218 p.p.m. [WCO, *J*(WC) 161 Hz]. Compound (**5b**) was obtained from $[W(CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_4SiMe_3)]$ and $[Co_2(CO)_8]$. The ^{13}C n.m.r. spectrum of (**5a**) shows only one resonance for the CO ligands at −100 °C, whereas the spectrum of (**5b**) at −70 °C shows two distinct resonances at 209 [WCO, *J*(WC) 166 Hz] and 202 p.p.m. (CoCO).

Since the $W(CO)_2(\eta\text{-}C_5H_5)$ fragment is isolobal with RC≡, addition of the mononuclear carbyne complex across the Co_2 and Rh_2 dimetal centres of $[Co_2(CO)_8]$ and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ to give (**5**) and (**6**) is formally analogous to the reaction of acetylenes with these and related molecules, affording tetrahedrane-type structures with a dicarbadimetalla-core.[10]

Complexes (**1**) and (**2**) have 48 cluster valence electrons, in contrast with the compounds (**3**)—(**6**) and $[Co_3(\mu\text{-}CR)(CO)_9]$, all of which have 50 cluster valence electrons leading to 6 skeletal bond pairs.[11] Introduction of platinum or rhodium atoms into four-atom core structures often leads to 'butterfly' rather than tetrahedral configurations[12] and it is therefore interesting that the 50 electron species (**3**), (**4**), and (**6**) adopt the *closo*-structure. However, the energy difference between the tetrahedral and butterfly structures may be sufficiently small to allow the intermediacy of the latter in the dynamic behaviour of (**3a**) and (**4**).

We thank the S.R.C. for support and the Commonwealth Scholarship Commission for a scholarship (M.J.C.).

(*Received*, 15*th July* 1980; *Com.* 769.)

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[12] The 60-electron clusters $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ and $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$ (Hacac = acetylacetone) adopt butterfly configurations for the metal atom cores (L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, in the press) rather than tetrahedral structures such as are found in, for example, $[Os_3Ni(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ (*ibid.*) or $[Ir_4(CO)_{12}]$ (M. R. Churchill and J. P. Hutchinson, *Inorg. Chem.*, 1978, **17**, 3528).