Stepwise Synthesis of Tungsten–Platinum or –Gold Bonds bridged by Alkylidyne Ligands: *X*-Ray Crystal Structures of $[Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2(cod)_2]$ (cod = cyclo-octa-1,5-diene), $[Pt_2W_3(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)_3]$, and $[AuW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$

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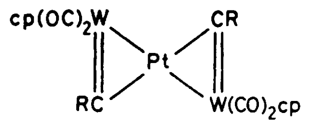
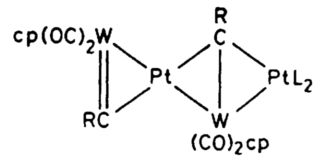
The synthesis of metal complexes with bonds between tungsten and platinum or gold, bridged by tolylidyne ligands, is described; and the molecular structures of the species $[Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2(cod)_2]$ (cod = cyclo-octa-1,5-diene), $[Pt_2W_3(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)_3]$, and $[AuW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ (R = C_6H_4Me-4) have been established by *X*-ray crystallography.

The dominant structural pattern in organo-transition element cluster chemistry is one in which the metal atoms form triangles to which the peripheral ligands are bound.[1] In species with more than three metal atoms the latter generally occupy all or some of the vertices of a triangulated polyhedron.[2] Recently, however, novel raft-like osmium carbonyl cluster structures have been characterised with fused triangles of metal atoms serving as the core.[3] Chain structures held together by metal–metal bonds are generally not found with organometallic species, although such structures are well established in certain metal oxides[4] and in some square-planar complexes of third-row transition elements which allow stacking in one-dimensional chains.[5] Herein we describe a procedure for the stepwise synthesis of a chain of metal atoms containing tungsten bonded to platinum or gold in which alkylidyne carbon atoms play a key role in holding the chain together.

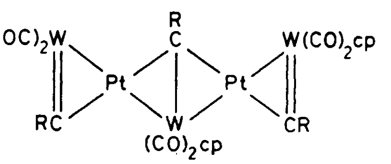
Compound (**1**) has previously been prepared from $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) and $[Pt(C_2H_4)_3]$ in 2:1 molar ratio.[6] When $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-



(1)



(2), L_2 = cod
(5), L = $PMePh_2$



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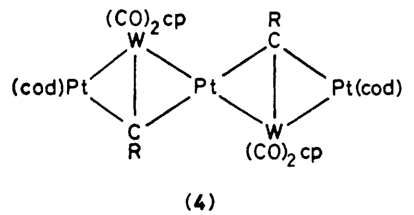

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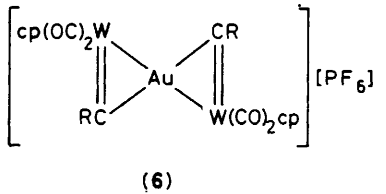

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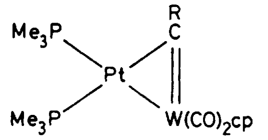

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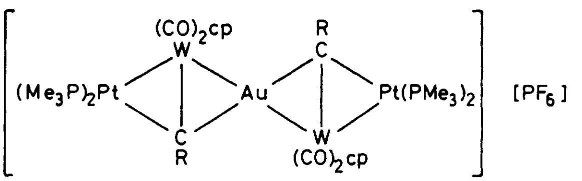

(8)

diene) is used, but with 1 : 1 stoicheiometry, the major product is (2) (60%),† with smaller amounts of (1) (15%) and (3) (5%) being formed. Treatment of (1) with [Pt(cod)$_2$] (1 mol. equiv.) in light petroleum also afforded (2). The latter with more [Pt(cod)$_2$] produces the triplatinum-ditungsten compound (4) (55%). The cod ligand in (2) is readily replaced by $PMePh_2$ to give (5), thereby blocking the platinum metal centre for further chain growth. However, displacement of the cod group in (2) by [W(≡CR)(CO)$_2$(η-C_5H_5)] affords (3) (50%).

The presence of the five metal atom chains in (3) and (4) was firmly established by single-crystal *X*-ray diffraction studies.‡ The molecular structures are shown in Figures 1 and 2, respectively. In both compounds the Pt–Pt separations are too long to represent any significant metal–metal bonding; a similar situation is found in di- and tri-platinum compounds with alkyne ligands transversely bridging the metal–metal

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† Selected spectroscopic data, i.r. in CH_2Cl_2; n.m.r., ^{13}C-{^1H} and ^{195}Pt-{^1H} in CD_2Cl_2–CH_2Cl_2 and ^{31}P-{^1H} in $CDCl_3$; for ^{195}Pt-{^1H} chemical shifts are to high frequency of Ξ(^{195}Pt) 21.4 MHz: compound (2), dark orange crystals, ν_{CO} (max) at 1 935s, 1 837s(br.), and 1 737s cm^{-1}; ^{13}C-{^1H} n.m.r. δ 310.7 (μ_2-*C*R), 251.8 (μ_3-*C*R), 241.5, 230.0, 228.6, and 221.0 p.p.m. (CO); ^{195}Pt-{^1H}, δ 1 104 [Pt(cod), *J*(PtPt) 1 223 Hz] and 1 367 p.p.m. [PtW_2, *J*(PtPt) 1 223 Hz]. Compound (3), black crystals, ν_{CO} (max) at 1 951s(br.) and 1 845s(br.) cm^{-1}; n.m.r. conformer (3a) (*ca.* 40%), ^{13}C-{^1H}, δ 317.1 [2 × μ_2-C, *J*(PtC) 833, *J*(WC) 151 Hz], 262.7 [1 × μ_3-C, *J*(PtC) 603 Hz], 230.8 [CO, *J*(WC) 171 Hz], 227.3 [CO, *J*(PtC) 44, *J*(WC) 186 Hz], and 224.9 p.p.m. [CO, *J*(WC) 188 Hz]; ^{195}Pt-{^1H}, δ 1 332 p.p.m. [*J*(WPt) 156 and 97 Hz]; conformer (3b) (*ca.* 35%), ^{13}C-{^1H}, δ 307.7 [2 × μ_2-C, *J*(PtC) 916 Hz], 262.7 [1 × μ_3-C, *J*(PtC) 603 Hz], 230.1 [CO, *J*(PtC) 38, *J*(WC) 190 Hz], 221.0 [CO, *J*(WC) 207 Hz], and 219.2 p.p.m. [CO, *J*(WC) 184 Hz]; ^{195}Pt-{^1H}, δ 1 620 p.p.m. [*J*(WPt) 136 Hz]; conformer (3c) (asymmetric, *ca.* 25%), ^{13}C-{^1H}, δ 314.8 [μ_2-C, *J*(PtC) 823 Hz], 308.8 (μ_2-C), 257.3 [μ_3-C, *J*(PtC) 611 Hz], 234.0, 229.8, 220.2, 217.4, and 216.8 p.p.m. (CO); ^{195}Pt-{^1H}, δ 1 377 [*J*(PtPt) 1 523 Hz] and 1 725 p.p.m. [*J*(PtPt) 1 523 Hz]. Compound (4), red brown crystals, ν_{CO} (max) at 1 836s(br.) and 1 729s cm^{-1}; n.m.r., conformer (4a) (*ca.* 65%), ^{13}C-{^1H}, δ 258.3 (μ_3-C), 241.1 and 230.2 p.p.m. (CO); ^{195}Pt-{^1H}, δ 931.3 (PtW_2), and 516.5 p.p.m. [Pt(cod)]; conformer (4b) (*ca.* 35%), ^{13}C-{^1H}, δ 260.3 and 257.3 (μ_3-C), 242.4 p.p.m. (CO). Compound (5), dark orange crystals, ν_{CO} (max) at 1 932s, 1 806m, and 1 765s(br.) cm^{-1}; n.m.r., ^{13}C-{^1H}, δ 311.8 [μ_2-C, *J*(PtC) 904 and 20 Hz], 252.8 [d, μ_3-C, *J*(PC) 51, *J*(PtC) 460 Hz], 240.0, 231.1, 227.5, and 224.0 p.p.m. (CO); ^{31}P-{^1H}, δ 8.5 [d, *J*(PP) 8, *J*(PtP) 3 374 and 16 Hz] and 5.6 p.p.m. [d, *J*(PP) 8, *J*(PtP) 3 687 and 39 Hz]; ^{195}Pt-{^1H}, δ 1 273 [dd, *J*(PPt) 39 and 16, *J*(PtPt) 1 924 Hz] and 0.8 p.p.m. [dd, *J*(PPt) 3 687 and 3 374 Hz]. Compound (6), orange-red crystals, ν_{CO} (max) at 2 024s and 1 969s cm^{-1}; ^{13}C-{^1H} n.m.r., δ 295.8 [μ_2-CR, *J*(WC) 153 Hz] and 211.8 p.p.m. [CO, *J*(WC) 181 Hz]. Compound (8), green crystals, ν_{CO} (max) at 1 925vs and 1 819s(br.) cm^{-1}; n.m.r., mixture of two conformers, ^{13}C-{^1H}, δ 292.6 [d, μ_3-C, *J*(PC) 32 Hz] and 290.9 p.p.m. [d, μ_3-C, *J*(PC) 25 Hz]; ^{31}P-{^1H}, δ −15.3 [d, *J*(PP) 5, *J*(PtP) 4 058 Hz], −25.6 [d, *J*(PP) 5, *J*(PtP) 2 766 Hz], −16.1 [d, *J*(PP) 7, *J*(PtP) 4 037 Hz], and −26.7 p.p.m. [d, *J*(PP) 7, *J*(PtP) 2 764 Hz].

‡ 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.

Crystal data for (3): $C_{45}H_{36}O_6Pt_2W_3$, M = 1 614.5, monoclinic, space group $P2_1/c$ (No. 14), a = 17.271(13) b = 12.066(7), c = 22.041(9) Å, β = 111.99(6)°, U = 4 315(5) Å^3, Z = 4, D_c = 2.44 g cm^{-3}, $F(000)$ = 2 928, μ(Mo-K_α) = 149 cm^{-1}. Current R 0.055 (R' 0.052) for 4 316 absorption corrected intensities (293 K, 2.9 $\leqslant 2\theta \leqslant$ 50°) measured on a Nicolet *P*3*m* diffractometer [$I \geqslant 2.5\sigma(I)$]; Mo-K_α *X*-radiation, graphite monochromator ($\bar{\lambda}$ = 0.710 69 Å); blocked-cascade least squares refinement.

Crystal data for (4): $C_{46}H_{48}O_4Pt_3W_2 \cdot CH_2Cl_2$, M = 1 617, monoclinic, space group $P2/n$ (non-standard setting No. 13), a = 11.502(9), b = 12.181(2), c = 16.828(3) Å, β = 93.80(4)°, U = 2 352(2) Å^3, Z = 2, D_m = 2.22 g cm^{-3}, D_c = 2.23 g cm^{-3} (298 K), $F(000)$ = 1 490, μ(Mo-K_α) = 140.5 cm^{-1}. Final R 0.034 (R' 0.035) for 2 658 independent absorption corrected data [200 K, $2\theta \leqslant$ 50°, $I \geqslant 2\sigma(I)$].

Crystal data for (6): $C_{30}H_{24}AuF_6O_4PW_2$, M = 1 158, orthorhombic, space group *Pnna* (No. 52), a = 10.024(11), b = 22.247(12), c = 13.905(5) Å, U = 3 101(4) Å^3, Z = 4, D_c = 2.42 g cm^{-3}, $F(000)$ = 2 128, μ(Mo-K_α) = 123.9 cm^{-1}. Final R 0.050 (R' 0.046) for 1 654 independent absorption corrected data [200 K, $2\theta \leqslant$ 50°, $I \geqslant 2\sigma(I)$].

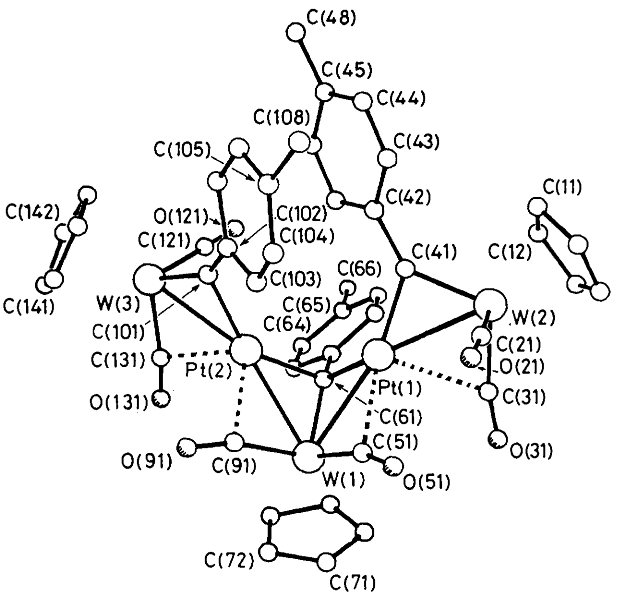

Figure 1. Molecular structure of $[Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (3). Dimensions: Pt(1)–W(1) 2.773(2), Pt(1)–W(2) 2.718(2), Pt(2)–W(1) 2.723(2), Pt(2)–W(3) 2.713(2), Pt(1) · · · · Pt(2) 2.949(2), W(1)–C(61) 1.99(3), W(2)–C(41) 1.97(3), W(3)–C(101) 1.94(3), Pt(1)–C(41) 2.03(2), Pt(1)–C(61) 2.03(3), Pt(2)–C(61) 2.09(3), Pt(2)–C(101) 2.03(3) Å; ∠W(1)–C(51)–O(51) 163(2), W(2)–C(31)–O(31) 168(2), W(3)–C(131)–O(131) 169(3), W(1)–Pt(2)–W(3) 154.5(1), W(1)–Pt(1)–W(2) 149.0(1), Pt(1)–W(1)–Pt(2) 64.9(1)°.

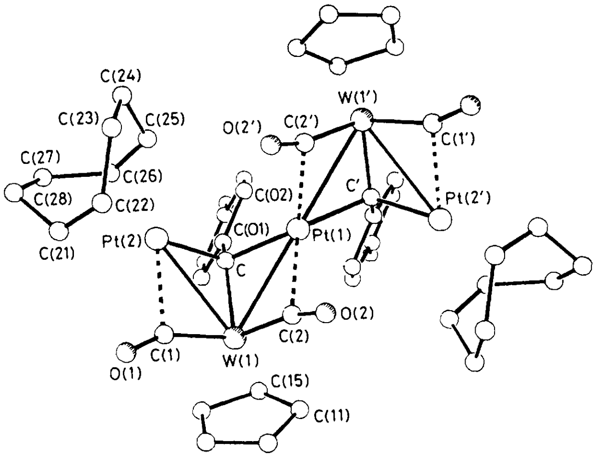

Figure 2. Molecular structure of $[Pt_3W_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2(cod)_2]$ (4). Dimensions: Pt(1)–W(1) 2.751(1), Pt(2)–W(1) 2.748(1), Pt(1) · · · · Pt(2) 3.089(1), Pt(1)–C 2.078(10), Pt(2)–C 2.072(11), W(1)–C 2.023(11) Å; ∠W(1)–C(1)–O(1) 158.2(10), W(1)–C(2)–O(2) 166.4(10), Pt(1)–W(1)–Pt(2) 68.4(1), W(1)–Pt(1)–W(1') 176.0(1)°.

vectors.[7,8] The Pt–W bonds are semi-bridged by CO groups in (3) and (4). Whereas in (3) two of the CR ligands are doubly bridging and one is triply bridging, in (4) the two CR ligands are triply bridging. In (3) the geometry about Pt(1) and Pt(2) is not identical, with Pt(1) more severely distorted from tetrahedral co-ordination. Thus, the angle between the planes Pt(1)•W(2)•C(41) and Pt(1)•W(1)•C(61) is 60.0°, whereas the corresponding angle at Pt(2) is 86.3°. In solution, (3) and (4), with their twisted metal atom chain structures, exist as mixtures of conformers, as evidenced by the additional peaks seen in the n.m.r. spectra.† The two $Pt_2(\mu_3\text{-}CR)$ fragments in (4) share a common vertex Pt(1), and the molecule lies astride a two-fold rotation axis. The symmetry related $PtW(\mu_3\text{-}C)$ triangles have a dihedral angle of 92°.

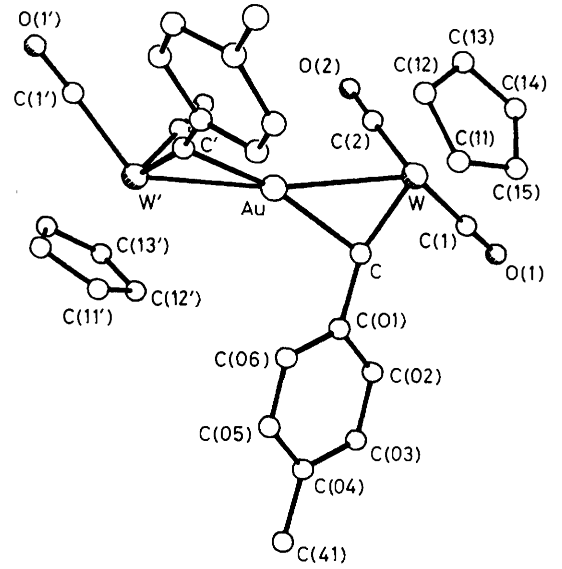

Figure 3. Molecular structure of the cation of the salt $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ (6). Dimensions: Au–W 2.752(1), Au–C 2.119(17), W–C 1.832(16) Å; ∠W–Au–W' 162.8(1), W–C(1)–O(1) 177.5(17), W–C(2)–O(2) 178.2(13)°.

The Pt^0 (d^{10}) atoms in the structures may be replaced by Au^I (d^{10}). Thus the salt (6)† may be prepared by addition of $[AuCl\{\overline{S(CH_2)_3CH_2}\}]^9$ to a mixture of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $TlPF_6$ in thf (tetrahydrofuran). Similarly, $[AuCl\{\overline{S(CH_2)_3CH_2}\}]$ and a mixture of (7)[10] and $TlPF_6$ in thf yielded the pentanuclear metal compound (8). The structure of (6) was established by X-ray diffraction,‡ and the cation is shown in Figure 3. The metal atom chain is significantly non-linear [162.8(1)°] as found in (1) [165.5(0)°]. However, in contrast with the latter, none of the CO ligands in (6) is semi-bridging. Moreover, the angle between the two $AuW(\mu\text{-}C)$ planes is 61° compared with a value of 97° for the $PtW(\mu\text{-}C)$ planes in (1).[6]

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