Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 62.[1] Synthesis of Penta-, Hexa-, and Hepta-heteronuclear Metal Cluster Compounds involving Tungsten or Molybdenum with Platinum or Nickel: Crystal Structures of the Chain Compounds $[Pt_3W_3(\mu\text{-CMe})(\mu_3\text{-CMe})_2\text{-}(CO)_6(cod)(\eta\text{-}C_5Me_5)_3]\cdot0.5CH_2Cl_2$ and $[Pt_3W_4(\mu\text{-CC}_6H_4Me\text{-}4)_2(\mu_3\text{-CC}_6H_4Me\text{-}4)_2\text{-}(CO)_8(\eta\text{-}C_5H_5)_4]$ *

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Addition of $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene), in tetrahydrofuran (thf) saturated with ethylene, to the compound $[Pt_2W_3(\mu\text{-CMe})_2(\mu_3\text{-CMe})(CO)_6(\eta\text{-}C_5Me_5)_3]$ affords the hexanuclear metal complex $[Pt_3W_3(\mu\text{-CMe})(\mu_3\text{-CMe})_2(CO)_6(cod)(\eta\text{-}C_5Me_5)_3]$. A related compound $[Pt_3Mo_2W\text{-}(\mu\text{-CMe})(\mu_3\text{-CC}_6H_4Me\text{-}4)_2(CO)_6(cod)(\eta\text{-}C_5H_5)_3]$ can be prepared by displacing a cod ligand from $[Pt_3Mo_2(\mu_3\text{-CC}_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]$ with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$. The triplatinumdimolybdenum complex required for this synthesis was obtained from the reaction between excess $[Pt(cod)_2]$ and $[PtMo_2(\mu\text{-CC}_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Several heptanuclear mixed-metal compounds have been prepared. Thus the hexanuclear metal compound $[Pt_3W_3\text{-}(\mu\text{-CMe})(\mu_3\text{-CMe})_2(CO)_6(cod)(\eta\text{-}C_5Me_5)_3]$ reacts with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ to afford $[Pt_3W_4(\mu\text{-CMe})_2(\mu_3\text{-CMe})_2(CO)_8(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_3]$, while the pentanuclear metal compound $[Pt_3W_2(\mu_3\text{-CC}_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]$ with an excess of $[W(\equiv CC_6H_4Me\text{-}4)\text{-}(CO)_2(\eta\text{-}C_5H_5)]$ yields $[Pt_3W_4(\mu\text{-CC}_6H_4Me\text{-}4)_2(\mu_3\text{-CC}_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_4]$. Similarly, $[Pt_3W_4(\mu\text{-CMe})_2(\mu_3\text{-CMe})_2(CO)_8(\eta\text{-}C_5Me_5)_4]$ is obtained from the reaction between $[Pt_3W_3(\mu\text{-CMe})(\mu_3\text{-CMe})_2(CO)_6(cod)(\eta\text{-}C_5Me_5)_3]$ and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$. Complexes containing chains of seven metal atoms incorporating nickel in place of platinum, or molybdenum for a site which could be occupied by tungsten, have also been prepared. These include $[Ni_3W_4\text{-}(\mu\text{-CMe})_2(\mu_3\text{-CMe})_2(CO)_8(\eta\text{-}C_5Me_5)_4]$, $[NiPt_2W_4(\mu\text{-CMe})_2(\mu_3\text{-CMe})_2(CO)_8(\eta\text{-}C_5Me_5)_4]$, $[Pt_3Mo_2W_2(\mu\text{-CMe})_2(\mu_3\text{-CC}_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_4]$, and $[Pt_3Mo_2W_2(\mu\text{-CC}_6H_4Me\text{-}4)_2\text{-}(\mu_3\text{-CC}_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)_2]$. Several of the hexa- and hepta-nuclear metal compounds are formed as mixtures of diastereoisomers which in some cases can be separated, or partially separated, by column chromatography. The isomerism results from different conformations of the metal chains, and is revealed by the n.m.r. data (^{1}H, ^{13}C-$\{^1$H$\}$, and ^{195}Pt-$\{^1$H$\}$), which are reported and discussed. X-Ray diffraction studies were carried out on $[Pt_3W_3(\mu\text{-CMe})(\mu_3\text{-CMe})_2\text{-}(CO)_6(cod)(\eta\text{-}C_5Me_5)_3]$ and $[Pt_3W_4(\mu\text{-CC}_6H_4Me\text{-}4)_2(\mu_3\text{-CC}_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_4]$, the former crystallising with a molecule of CH_2Cl_2 in the unit cell. The X-ray results establish the conformations of particular diastereoisomers of these species, and place the stepwise cluster-building reactions described herein on a firm structural foundation.

Since the discovery that $[Pt(C_2H_4)_3]$ reacts with the tungsten complex $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$) to give the trimetal compound $[PtW_2(\mu\text{-CR})_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (1a)[2] many related species have been characterised, including $[MW_2(\mu\text{-CMe})_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ [M = Ni (1b) or Pt (1c)].[3] In these trimetal complexes, nickel or platinum atoms are ligated by two $C\equiv W$ fragments; the metal atom spines in these molecules are essentially linear. The two metal–metal bonds are each bridged by an alkylidyne group and semi-bridged by a

carbonyl ligand. A distinctive feature of the structures is the presence of the two dimetallacyclopropene rings which form dihedral angles between each other of ca. 80—100°.[2,4]

The unsaturated nature of compounds of type (1) makes them ideal precursors for the preparation of polynuclear metal compounds through addition of metal–ligand fragments to the dimetallacyclopropene rings. Indeed, we have previously reported[3] the rational syntheses of complexes containing chains of four or five metal atoms. Thus treatment of (1a) in toluene with one equivalent of an ethylene-saturated solution of $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) affords $[Pt_2W_2\text{-}(\mu\text{-CC}_6H_4Me\text{-}4)(\mu_3\text{-CC}_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)_2]$ (2a). Moreover, the pentanuclear metal compounds $[Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(cod)_2L_2]$ [R = $C_6H_4Me\text{-}4$, L = $\eta\text{-}C_5H_5$ (3a); R = Me, L = $\eta\text{-}C_5Me_5$ (3b)] may be obtained by treating (1a) and (1c), respectively, with an excess of $[Pt(cod)_2]$. Species with chains of two platinum and three tungsten atoms may be obtained by displacement of the cod ligands in (2a) or (2b) by the appropriate alkylidynetungsten complex. The products of these reactions are the compounds $[Pt_2W_3(\mu\text{-}$

Table 1. Analytical[a] and physical data for the polynuclear metal complexes

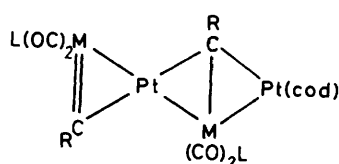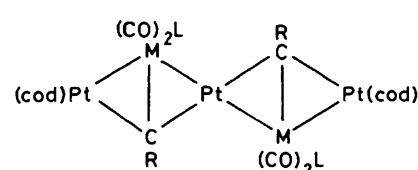| Compound	Colour	Yield (%)	$v_{max.}(CO)$[b]/cm^{-1}	Analysis (%) C	H
(3c) $[Pt_3Mo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]$	Grey[c]	75	1 844m br, 1 734s	[d]36.8 (37.0)	3.4 (3.3)
(6a) $[Pt_3W_3(\mu\text{-}CMe)(\mu_3\text{-}CMe)_2(CO)_6(cod)(\eta\text{-}C_5Me_5)_3]$	Brown	85	1 927m, 1 805s br, 1 717m	31.3 (31.6)	3.5 (3.5)
(6b) $[Pt_3Mo_2W(\mu\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_6(cod)(\eta\text{-}C_5H_5)_3]$	Green	86	1 954m, 1 851s br, 1 759w	33.8 (33.9)	2.9 (2.6)
(7) $[Pt_3W_4(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)_2(CO)_8(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_3]$	Brown	78	1 940s br, 1 811s br	32.4 (34.7)	3.8 (2.9)
(8a) $[Pt_3W_4(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_4]$	Brown	82	1 959s, 1 853m br	31.5 (32.5)	2.3 (2.2)
(8b) $[Pt_3W_4(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)_2(CO)_8(\eta\text{-}C_5Me_5)_4]$	Brown	70	1 932s, 1 812s br	31.9 (30.6)	3.8 (3.3)
(9a) $[Ni_3W_4(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)_2(CO)_8(\eta\text{-}C_5Me_5)_4]$	Brown	80	1 935s, 1 835m br, 1 805m br	36.8 (37.6)	3.5 (4.0)
(9b) $[NiPt_2W_4(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)_2(CO)_8(\eta\text{-}C_5Me_5)_4]$	Brown	64	1 933s, 1 836s br, 1 813s br, 1 768m (sh)	33.8 (32.7)	3.8 (3.5)
(10a) $[Pt_3Mo_2W_2(\mu\text{-}CMe)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_4]$	Green[e]	76	1 959s, 1 844m br	30.5 (30.8)	2.3 (2.1)
(10b) $[Pt_3Mo_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_8\text{-}(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)_2]$	Brown	85	1 949s br, 1 845s br	38.3 (38.5)	3.0 (3.1)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2. [c] Other isomers are green and orange, see text. [d] Contains a molecule of CH_2Cl_2 of crystallisation. [e] Most stable isomer isolated is green, see text.
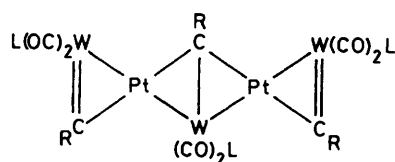

	M	R	L
(1a)	Pt	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(1b)	Ni	Me	$\eta\text{-}C_5Me_5$
(1c)	Pt	Me	$\eta\text{-}C_5Me_5$

	M	R	L
(2a)	W	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(2b)	W	Me	$\eta\text{-}C_5Me_5$
(2c)	Mo	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$

	M	R	L
(3a)	W	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(3b)	W	Me	$\eta\text{-}C_5Me_5$
(3c)	Mo	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$

	R	L
(4a)	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(4b)	Me	$\eta\text{-}C_5Me_5$

	R	L
(5a)	$C_6H_4Me\text{-}4$	$HB(pz)_3$
(5b)	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
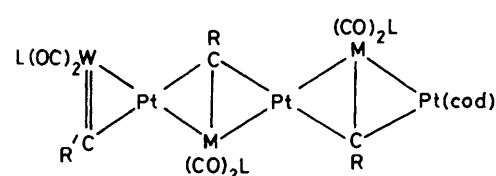
	M	R	R'	L
(6a)	W	Me	Me	$\eta\text{-}C_5Me_5$
(6b)	Mo	$C_6H_4Me\text{-}4$	Me	$\eta\text{-}C_5H_5$
(6c)	W	$C_6H_4Me\text{-}4$	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$

$CR)_2(\mu_3\text{-}CR)(CO)_6L_3]$ [R = $C_6H_4Me\text{-}4$, L = $\eta\text{-}C_5H_5$ (4a); R = Me, L = $\eta\text{-}C_5Me_5$ (4b)].

In this paper we report complexes containing chains of six or seven metal atoms, thereby further illustrating the designed synthesis of metal cluster species based on metal–ligand fragment addition to compounds of the transition elements which are unsaturated.[5] A preliminary account of some of the results has been given.[6]

Results and Discussion

The platinumdimolybdenum complexes $[PtMo_2(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)_2(CO)_4L_2]$ [L = $HB(pz)_3$ = hydrotris(pyrazol-1-yl)- borate (5a); L = $\eta\text{-}C_5H_5$ (5b)] have recently been prepared.[4,7] The existence of these species leads to the possibility of their use, via the methodology developed previously,[3] in the synthesis of complexes with chains of metal atoms incorporating molybdenum. To test this idea the reaction between (5b) and $[Pt(cod)_2]$ was investigated.

A mixture of (5b) and $[Pt(cod)_2]$ in tetrahydrofuran (thf) saturated with ethylene at ca. 0 °C affords the pure crystalline compound $[Pt_3Mo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]$ (3c), data for which are given in Tables 1—3. Compound (3c) is the molybdenum analogue of the previously prepared[3] platinum–tungsten compound (3a), mentioned above. Examination of the ^1H n.m.r. spectrum of (3c) (Table 2) revealed that it

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the new complexes

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(3c)[d]	[e]2.23 (s, 6 H, Me-4), 2.27 * (s, 3 H, Me-4), 2.33 † (s, 6 H, Me-4), 2.36—3.80 (m, 48 H, CH$_2$), 2.42 * (s, 3 H, Me-4), 4.60—4.90 (m, 24 H, CH), 5.00 * (s, 5 H, C$_5$H$_5$), 5.06 * (s, 5 H, C$_5$H$_5$), 5.15 † (s, 10 H, C$_5$H$_5$), 5.41 (s, 10 H, C$_5$H$_5$), 6.60—7.30 (m, 24 H, C$_6$H$_4$)	264.5 (2 × μ_3-C), 247.6, 235.4 (CO), 149.9 [C^1(C$_6$H$_4$)], 134.6—127.6 (C$_6$H$_4$), 111.8, 105.9, 105.8, 96.7 (CH), 93.6 (C$_5$H$_5$), 31.3 (CH$_2$), 29.7 (2 × CH$_2$), 28.8 (CH$_2$), 20.8 (Me-4).
(6a)[f]	1.96 (s, 15 H, C$_5$Me$_5$), 1.99 * (s, 15 H, C$_5$Me$_5$), 2.00 (s, 15 H, C$_5$Me$_5$), 2.05 * (s, 15 H, C$_5$Me$_5$), 2.06 (s, 15 H, C$_5$Me$_5$), 2.08 * (s, 15 H, C$_5$Me$_5$), 2.00—3.50 (m, 16 H, CH$_2$), 2.65 (s, 6 H, Me), 3.07 [s, 6 H, Me, J(PtH) 8], 3.50 [s, 6 H, Me, J(PtH) 9], 4.20—5.00 (m, 8 H, CH)	328.6 [μ-C, J(PtC) 686], 326.3 * (μ-C), 282.3 [μ_3-C, J(PtC) 514], 262.5 [μ_3-C, J(PtC) 594], 262.3 * (μ_3-C), 248.7, 247.4,* 239.0,* 237.7, 237.4, 235.5,* 235.4 (CO), 235.0 * (2 × CO), 233.6, 228.7, 226.2 * (CO), 108.6,* 108.3, 105.4 * (CH), 103.6, 103.2, 102.6, 102.3 * (C$_5$Me$_5$), 101.7, 101.6,* 97.1, 95.4, 90.9 * (CH), 43.5 [μ-CMe, J(PtC) 20], 37.2, 33.9 (μ-CMe), 31.7,* 31.5, 29.4, 28.4 * (CH$_2$), 10.5,* 10.3, 10.1,* 9.8, 9.6,* 9.4 (C$_5$Me$_5$)
(6b)	[e]1.98 (s, 3 H, Me-4), 2.32 (s, 6 H, Me and Me-4), 2.20—3.00 (m, 8 H, CH$_2$), 4.20—5.00 (m, 4 H, CH), 5.00 (s, 5 H, C$_5$H$_5$), 5.08 (s, 5 H, C$_5$H$_5$), 5.46 (s, 5 H, C$_5$H$_5$), 6.98—7.55 (m, 8 H, C$_6$H$_4$)	[e]328.1 (μ-C), 285.4, 279.5 (μ_3-C), 245.3, 241.7, 238.7, 236.5, 228.8, 220.6 (CO), 153.2, 152.2 [C^1(C$_6$H$_4$)], 136.2—127.9 (C$_6$H$_4$), 109.2, 107.2, 98.1, 97.5 (CH), 95.5, 95.3, 91.3 (C$_5$H$_5$), 46.3 (μ-CMe), 31.0, 30.4, 29.3, 28.1 (CH$_2$), 21.2, 20.9 (Me-4)
(7)[f]	2.00 * (s, 15 H, C$_5$Me$_5$), 2.01 (s, 15 H, C$_5$Me$_5$), 2.04 (s, 15 H, C$_5$Me$_5$), 2.05 (s, 15 H, C$_5$Me$_5$), 2.08 * (s, 15 H, C$_5$Me$_5$), 2.09 * (s, 15 H, C$_5$Me$_5$), 2.28 (s, 3 H, Me), 2.49 * (s, 3 H, Me), 2.67 * (s, 3 H, Me), 2.70 (s, 3 H, Me), 3.11 (s, 6 H, Me), 3.28 * (s, 6 H, Me), 5.51 * (s, 5 H, C$_5$H$_5$), 5.52 (s, 5 H, C$_5$H$_5$)	326.0, 325.8, 324.1 * (μ-C), 274.7, 267.2 (μ_3-C), 237.5, 236.8, 236.4, 235.7, 235.3,* 233.6, 227.5, 226.5, 221.9,* 219.6 (CO), 103.8, 103.7,* 103.4,* 103.1, 102.7 (C$_5$Me$_5$), 91.6,* 91.2 (C$_5$H$_5$), 46.6, 45.0,* 42.0,* 40.6, 38.4,* 38.2,* 36.5, 36.3 (μ-CMe), 10.4, 9.6, 9.4 (C$_5$Me$_5$)
(8a)	1.98 (s, 3 H, Me-4), 2.10 (s, 3 H, Me-4), 2.24 (s, 3 H, Me-4), 2.35 (s, 3 H, Me-4), 4.77 (s, 5 H, C$_5$H$_5$), 5.39 (s, 5 H, C$_5$H$_5$), 5.47 (s, 5 H, C$_5$H$_5$), 5.71 (s, 5 H, C$_5$H$_5$), 6.10—7.95 (m, 16 H, C$_6$H$_4$)	318.9, 311.4 (μ-C), 265.8, 264.2 (μ_3-C), 233.3, 231.5, 231.2 (CO), 228.9 (2 × CO), 225.1, 222.1, 214.8 (CO), 153.9, 153.7, 152.7, 150.6 [C^1(C$_6$H$_4$)], 137.8—126.2 (C$_6$H$_4$), 93.4, 93.3, 91.6, 91.5 (C$_5$H$_5$), 21.7, 21.4, 21.3, 21.2 (Me-4)
(8b)[g]	[e]2.02 * (s, 30 H, C$_5$Me$_5$), 2.03 (s, 15 H, C$_5$Me$_5$), 2.04 (s, 30 H, C$_5$Me$_5$), 2.07 (s, 15 H, C$_5$Me$_5$), 2.08 * (s, 30 H, C$_5$Me$_5$), 2.31 (s, 3 H, Me), 2.54 * (s, 6 H, Me), 2.62 (s, 3 H, Me), 3.08 (s, 3 H, Me), 3.18 (s, 3 H, Me), 3.32 * (s, 6 H, Me)	326.2, 325.0, 323.5 * (μ-C), 284.9,* 273.9, 266.0 (μ_3-C), 238.0, 237.1, 236.3, 236.0,* 235.6,* 235.5, 235.1, 230.6,* 230.3, 228.8,* 228.7, 227.2 (CO), 103.7,* 103.6, 103.5, 103.3,* 103.0, 102.6 (C$_5$Me$_5$), 43.6,* 42.3, 40.8, 38.3,* 36.5, 36.3 (μ-CMe), 10.4, 10.3, 9.6, 9.4 (C$_5$Me$_5$ and C$_5$Me$_5$*)
(9a)	1.98 (s, 15 H, C$_5$Me$_5$), 1.99 (s, 15 H, C$_5$Me$_5$), 2.02 (s, 15 H, C$_5$Me$_5$), 2.05 (s, 15 H, C$_5$Me$_5$), 2.16 (s, 3 H, Me), 2.22 (s, 3 H, Me), 2.51 (s, 3 H, Me), 2.64 (s, 3 H, Me)	[h]336.3, 335.6 (μ-C), 305.9, 297.6 (μ_3-C), 252.3, 251.2, 250.3, 248.5, 243.9, 238.2, 231.7, 229.4 (CO), 103.6 (2 × C$_5$Me$_5$), 103.3, 103.2 (C$_5$Me$_5$), 45.1, 44.4, 43.2, 42.3 (μ-CMe), 10.5 (2 × C$_5$Me$_5$), 10.0, 9.5 (C$_5$Me$_5$)
(9b)	1.99 (s, 15 H, C$_5$Me$_5$), 2.00 (s, 15 H, C$_5$Me$_5$), 2.05 (s, 15 H, C$_5$Me$_5$), 2.08 (s, 15 H, C$_5$Me$_5$), 2.31 (s, 3 H, Me), 2.54 (s, 3 H, Me), 2.78 (s, 3 H, Me), 2.95 (s, 3 H, Me)	[h]326.1, 325.0 (μ-C), 291.4, 285.8 (μ_3-C), 250.7, 246.8, 237.4, 236.3, 235.1, 229.5, 227.5, 225.2 (CO), 103.6, 103.3 (C$_5$Me$_5$), 102.8 (2 × C$_5$Me$_5$), 41.5, 40.3, 40.2, 39.0 (μ-CMe), 10.6, 10.5, 9.7, 9.5 (C$_5$Me$_5$)
(10a)[g]	[e]1.55 (s, 3 H, Me-4), 1.67 * (s, 6 H, Me-4), 2.23 (s, 3 H, Me-4), 2.30 * (s, 6 H, Me), 2.38 (s, 3 H, Me), 2.92 (s, 3 H, Me), 5.09 (s, 5 H, C$_5$H$_5$), 5.14 * (s, 10 H, C$_5$H$_5$), 5.17 (s, 5 H, C$_5$H$_5$), 5.37 (s, 5 H, C$_5$H$_5$), 5.42 * (s, 10 H, C$_5$H$_5$), 5.51 (s, 5 H, C$_5$H$_5$), 6.78, 6.96 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8], 7.00 *, 7.48 * [(AB)$_2$, 8 H, C$_6$H$_4$, J(AB) 8], 7.12, 7.78 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	[e]328.5 * [2 × μ-C, J(PtC) 780, J(WC) 151], 328.1, 327.8, (μ-C), 283.2 * [2 × μ_3-C, J(PtC) 643], 277.7, 277.3 (μ_3-C), 239.3,* 239.1, 238.7, 238.2, 237.7,* 235.2, 226.1,* 225.8, 224.8, 223.8, 222.8,* 222.6 (CO), 153.0,* 152.8, 151.6 [C^1(C$_6$H$_4$)], 136.2—127.8 (C$_6$H$_4$), 95.4,* 95.0, 94.7, 91.1, 91.0,* 90.9 (C$_5$H$_5$), 45.9, 45.8,* 45.1 (μ-CMe), 21.4, 21.3,* 21.1 (Me-4)
(10b)	[e]1.89 (s, 15 H, C$_5$Me$_5$), 2.05 (s, 15 H, C$_5$Me$_5$), 2.09 (s, 3 H, Me-4), 2.24 (s, 3 H, Me-4), 2.31 (s, 3 H, Me-4), 2.36 (s, 3 H, Me-4), 4.89 (s, 5 H, C$_5$H$_5$), 5.02 (s, 5 H, C$_5$H$_5$), 6.72—7.30 (m, 16 H, C$_6$H$_4$)	[e]319.0, 309.2 (μ-C), 283.6 (2 × μ_3-C), 240.7, 239.1, 238.7, 236.4, 235.7, 232.9, 223.5, 220.1 (CO), 153.2, 152.7, 152.3, 152.1 [C^1-(C$_6$H$_4$)], 137.2—127.0 (C$_6$H$_4$), 104.9, 103.8 (C$_5$Me$_5$), 95.8, 94.6 (C$_5$H$_5$), 21.8 (2 × Me-4), 21.4, 21.0 (Me-4), 10.7, 10.3 (C$_5$Me$_5$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures unless otherwise stated. [b] Measured in CD$_2$Cl$_2$ unless otherwise stated. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe$_4$. Measurements in CD$_2$Cl$_2$–CH$_2$Cl$_2$ unless otherwise stated. Signals due to CH groups of cod ligands show ^{195}Pt satellite peaks with J(PtC) 80—150 Hz. [d] Signals marked (*) or (†) in the ^{1}H spectrum correspond to the two minor isomers present; the ^{13}C spectrum is of the major isomer. [e] Measured in CDCl$_3$. [f] Signals marked (*) correspond to a minor isomer. [g] Signals marked (*) correspond to a symmetric isomer. [h] Measured at −40 °C.

was formed as a mixture of three isomers. Indeed, upon column chromatography of the crude reaction mixture the three isomers appear sequentially as grey, green, and orange bands. It was possible to separate the grey band from the other two; however, the orange and green species could only be partially separated. Moreover, when a ^{1}H n.m.r. spectrum of the grey isomer is measured, resonances due to the other isomers soon appear, indicating a fast equilibration between the three species in solution. At equilibrium, relative peak heights in the ^{1}H n.m.r. spectrum indicate that the orange, grey, and green isomers are present in *ca.* 8:3:1 ratio. In the ^{13}C-{^{1}H} and ^{195}Pt-{^{1}H} n.m.r. spectra only peaks due to the orange isomer are generally observed, although freshly prepared solutions initially display some peaks attributable to the grey form. This is because

complex (3c) is relatively insoluble, and the time required for accumulation of the spectral data exceeds that required for establishment of the equilibrium in which the orange isomer predominates.

Compound (3c) may also be obtained by treating the tetra-nuclear metal complex [Pt$_2$Mo$_2$(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$-Me-4)(CO)$_4$(cod)(η-C$_5$H$_5$)$_2$] (2c)[7] with 1.2 equivalents of [Pt(cod)$_2$], thereby illustrating the stepwise synthesis of a five-metal-atom chain complex from a four-metal-atom chain species. In this alternative preparation of (3c), the three isomers are also formed.

In earlier work[3] with (3a) and (3b), it was observed from n.m.r. data that the former existed in solution as an inseparable mixture of two isomers, and the latter as a single isomer.

M≡≡≡C—R Pt (M') (A) Pt(cod)

M≡≡≡C—R Pt (M') (cod)Pt (B)

α (i) (i) β (i) β (i) α

(cod)Pt M≡C—R Pt (M') Pt(cod) (C)

(cod)Pt M≡C—R Pt (M') Pt(cod) (D)

(cod)Pt M≡C—R Pt (M') (cod)Pt (E)
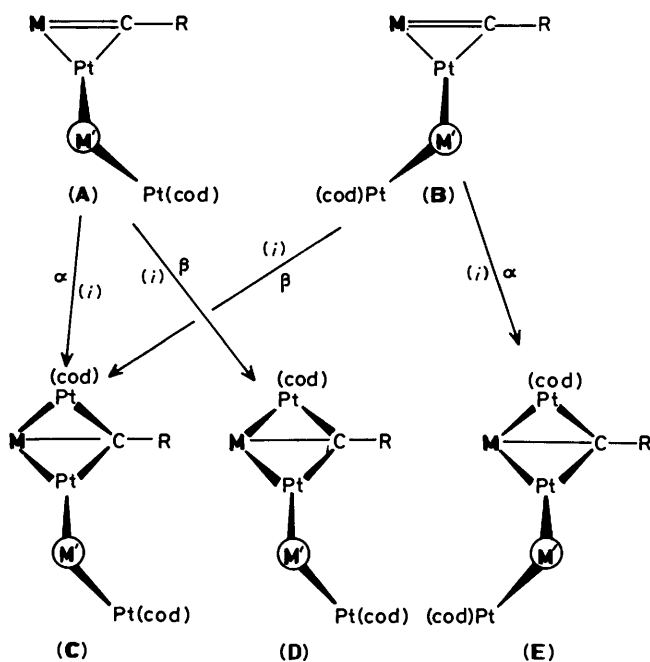
Scheme. M = M(CO)$_2$(η-C$_5$H$_5$) group with M = Mo or W; M′ = M(CR)(CO)$_2$(η-C$_5$H$_5$) with the M=C group vertical to the M$_2$C plane in (A) and (B); R = C$_6$H$_4$Me-4; α and β refer to the direction of attack of a Pt(cod) fragment (i) on a Pt$_2$M$_2$ species such as (2a) or (2c). Conformers (D) and (E) have two-fold molecular symmetry (see ref. 3)

Moreover, a third isomer of (3a) was observed but could not be characterised due to its insolubility. The observation of three isomers of (3c), and their partial separation and re-equilibration, is particularly interesting. Based on considerations discussed previously,[3] three is the maximum number of isomers expected for a five-metal-atom chain species of the Pt$_3$M$_2$ (M = Mo or W) type. This may be deduced as follows. Addition of a Pt(cod) fragment to the trimetal complex (5b) would afford two stereo-isomers of the tetranuclear product (2c), these being (A) and (B) of the Scheme. Since trinuclear compounds such as (1) or (5b) exist as a mixture of two enantiomers, both (A) and (B) have an enantiomeric partner [(A′) and (B′)] but these partners are not distinguishable by n.m.r. spectroscopy. In the metal-chain lengthening process, addition of a Pt(cod) fragment to the compounds (2) affords the Pt$_3$M$_2$ (M = W or Mo) species (3). Examining only the stereoisomers (A) and (B) of the Scheme, and appreciating that an analogous process would occur with the enantiomers (A′) and (B′) (not shown), it can be seen that the transformation from a Pt$_2$M$_2$ species to Pt$_3$M$_2$ cluster via addition of a Pt(cod) group produces three diastereoisomeric (unique) metal complexes (C), (D), and (E). In the Scheme, α corresponds to addition of a Pt(cod) moiety above the plane defined by the atoms MPtC, and β corresponds to addition of the Pt(cod) fragment below the plane MPtC. These two processes would lead to formation of the three isomers (C), (D), and (E) in the ratio 2:1:1. As mentioned above, three isomers of (3c) are observed in the ^{1}H n.m.r. spectrum (Table 2). However, the proportions of these isomers differ from that predicted by the Scheme, presumably due to steric reasons.

Consideration of molecular models reveals that isomer (C) does not possess any symmetry elements, and is therefore classed as 'asymmetric'. Such an isomer would exhibit three resonances in its ^{195}Pt-{^{1}H} n.m.r. spectrum for the three inequivalent platinum sites, and two μ$_3$-C signals in the ^{13}C-{^{1}H} spectrum corresponding to the two non-equivalent alkylidyne carbon nuclei. The ^{195}Pt-{^{1}H} and ^{13}C-{^{1}H} n.m.r.

Table 3. Platinum-195 n.m.r. data[a] for the new complexes

Compound	δ[b]	J(PtPt)
(3c)[c]	903	460
	396	460
(6a)	1 417	960
	984	1 083, 960
	308	1 083
	1 286*	962
	295*	
(6b)[c]	1 195	1 397
	747	1 397, 1 377
	358	1 377
(7)	1 411	1 250
	1 245	
	1 170	1 250
(8a)	1 497	1 452
	1 209	1 510
	1 079	1 452, 1 510
	1 488*	1 452
	1 466*	1 552
	996*	1 452, 1 552
(8b)	[d]1 418	1 797
	[e]1 253	1 201
	[f]1 161	1 797, 1 201
	1 361*	1 836
(9b)	[g]1 532	
	[h]1 389	
(10a)[c]	1 303	1 960
	1 104	1 715
	1 051	1 960, 1 715
	1 240*	1 806
	888*	1 806
(10b)[c]	1 534	1 494
	1 098	1 494, 1 050
	1 085	1 050

[a] Chemical shifts are in p.p.m., coupling constants are in Hz. Measurements are in CD$_2$Cl$_2$–CH$_2$Cl$_2$ unless otherwise stated. [b] δ Values are to high frequency of Ξ(^{195}Pt) = 21.4 MHz. Values marked (*) refer to a minor or symmetric isomer (see text). In some spectra not all the peaks for a particular isomer are observed. [c] Measured in CDCl$_3$. [d] J(WPt) 195 Hz. [e] J(WPt) 175 Hz. [f] J(WPt) 137 Hz. [g] J(WPt) 176 Hz. [h] J(WPt) 166 and 126 Hz.

spectra of (3b) show these patterns.[3] Isomers (D) and (E) both possess two-fold rotation axes through the central platinum atom, and these two isomers are therefore classed as 'symmetric'. It may be mentioned in passing that conformation (E) corresponds to the diastereoisomer identified in an X-ray diffraction study of (3a).[3] For the symmetrical isomers of the Pt$_3$M$_2$ compounds both terminal platinum sites are equivalent, thus leading to the observation of two ^{195}Pt resonances for the three platinum atoms. Similarly, both μ$_3$-C sites of each isomer are equivalent in the ^{13}C-{^{1}H} n.m.r. spectra. Thus examination of the ^{195}Pt-{^{1}H} (Table 3) and ^{13}C-{^{1}H} (Table 2) n.m.r. data for (3c) reveal that a 'symmetric' orange-coloured isomer predominates in solution.

Reactions leading to the synthesis of compounds with chains of six metal atoms were next investigated. Addition of one equivalent of [Pt(cod)$_2$] to (4b) in thf gave brown crystals of [Pt$_3$W$_3$(μ-CMe)(μ$_3$-CMe)$_2$(CO)$_6$(cod)(η-C$_5$Me$_5$)$_3$] (6a). The compound was characterised by the data given in Tables 1—3. The ^{1}H, ^{13}C-{^{1}H}, and ^{195}Pt-{^{1}H} n.m.r. spectra showed signals corresponding to the presence of two isomers. However, the ^{13}C-{^{1}H} data did not show all the expected peaks due to the minor isomer, due either to coincidence of resonances or weak signals, or both. Although both isomers could be seen as distinct bands on the chromatography column they could not be physically

The ^{195}Pt-{^{1}H} and ^{13}C-{^{1}H} n.m.r.

Table 4. Selected internuclear distances (Å) and angles (°) for the complex $[Pt_3W_3(\mu\text{-CMe})(\mu_3\text{-CMe})_2(CO)_6(cod)(\eta\text{-}C_5Me_5)_3]\cdot0.5CH_2Cl_2$ (6a)

Pt(1)···Pt(2)	3.109(2)	Pt(2)···Pt(3)	3.201(2)	Pt(1)-W(1)	2.729(2)	Pt(2)-W(1)	2.747(2)
Pt(2)-W(2)	2.738(2)	Pt(3)-W(2)	2.716(2)	Pt(3)-W(3)	2.718(2)	W(1)-C(11)	1.99(1)
Pt(1)-C(11)	2.04(2)	Pt(2)-C(11)	2.12(2)	W(2)-C(21)	1.99(2)	Pt(2)-C(21)	2.07(2)
Pt(1)-C(21)	2.08(1)	W(3)-C(31)	1.84(2)	Pt(3)-C(31)	2.05(2)	W(1)-C(1)	1.95(2)
Pt(1)-C(1)	2.25(2)	W(1)-C(10)	1.94(2)	Pt(2)-C(10)	2.35(1)	W(2)-C(2)	1.96(2)
Pt(2)-C(2)	2.26(2)	W(2)-C(20)	1.98(2)	Pt(3)-C(20)	2.28(2)	W(3)-C(30)	1.97(3)
W(3)-C(3)	1.95(2)	Pt(3)-C(3)	2.40(2)	Pt(1)-C(71)	2.25(2)	Pt(1)-C(72)	2.25(2)
Pt(1)-C(75)	2.29(2)	Pt(1)-C(76)	2.25(2)	W(1)-C(cp)*	2.34	W(2)-C(cp)*	2.35
W(3)-C(cp)*	2.33						
Pt(1)-Pt(2)-Pt(3)	103.1(1)	Pt(1)-W(1)-Pt(2)	69.2(1)	W(1)-Pt(2)-W(2)	148.5(1)	Pt(2)-W(2)-Pt(3)	71.9(1)
W(2)-Pt(3)-W(3)	148.4(1)	W(1)-C(11)-C(12)	144(1)	Pt(1)-C(11)-C(12)	122(1)	Pt(2)-C(11)-C(12)	112(1)
W(2)-C(21)-C(22)	146(1)	Pt(2)-C(21)-C(22)	115(1)	Pt(3)-C(21)-C(22)	117(1)	W(3)-C(31)-C(32)	153(1)
Pt(3)-C(31)-C(32)	118(1)	W(1)-C(1)-O(1)	157(1)	W(1)-C(10)-O(10)	167(1)	W(2)-C(2)-O(2)	162(2)
W(2)-C(20)-O(20)	165(2)	W(3)-C(3)-O(3)	168(1)	W(3)-C(30)-O(30)	171(2)	C(1)-W(1)-C(10)	86.7(8)
C(1)-W(1)-C(11)	102.3(7)	C(10)-W(1)-C(11)	106.9(6)	C(2)-W(2)-C(20)	89.3(6)	C(2)-W(2)-C(21)	103.2(7)
C(20)-W(2)-C(21)	104.7(8)	C(3)-W(3)-C(30)	93.1(8)	C(3)-W(3)-C(31)	107.2(7)	C(30)-W(3)-C(31)	90.9(8)

* Mean distance to the pentamethylcyclopentadienyl ring-carbon atoms.

separated by this technique. Nevertheless, an X-ray diffraction study described below showed only one isomer to be present in the crystal.

The hexanuclear metal-chain compound $[Pt_3Mo_2W(\mu\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_6(cod)(\eta\text{-}C_5H_5)_3]$ (6b) was prepared by adding $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ to (3c). Data for (6b) are given in Tables 1—3, and interestingly only one isomer was observed. Attempts to prepare $[Pt_3W_3(\mu\text{-}CC_6H_4Me\text{-}4)\text{-}(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_6(cod)(\eta\text{-}C_5H_5)_3]$ (6c) from (3a) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, or from (4a) and $[Pt(cod)_2]$, were unsuccessful. Mixtures of products were obtained which could not be unambiguously characterised.

It was considered important to establish the molecular structure of one of the six-metal-atom chain complexes by a single-crystal X-ray diffraction study. Suitable crystals of (6a) were available, and the results are summarised in Table 4; the molecular structure is shown in Figure 1.

The six metal atoms in the chain are almost coplanar with the greatest out-of-plane deviation (0.18 Å) being shown by Pt(1), carrying the cod ligand. The metal–metal bonds are bridged by three ethylidyne ligands, and semi-bridged by carbonyl groups. Two ethylidyne fragments [C(11)C(12) and C(21)C(22)] adopt triply bridging modes on opposite sides of the Pt_3W_3 chain, while one ethylidyne group [C(31)C(32)] edge bridges the Pt(3)–W(3) bond. The dimensions of the Pt(3)C(31)W(3) ring [C(31)-Pt(3) 2.05(2), C(31)-W(3) 1.84(2), Pt(3)-W(3) 2.718(2) Å] are very similar to those of the dimetallacyclopropene rings in (1a) (mean distances: μ-C–Pt 2.02, μ-C–W 1.91, Pt–W 2.713 Å).[2]

The μ_3-CPt$_2$W fragment was first established by X-ray crystallography in the trimetal compound $[Pt_2W(\mu_3\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ [Pt–W 2.785(3), Pt···Pt 2.989(3), and μ_3-C–Pt (or W) 2.05(4) Å].[8] The dimensions of the μ_3-CPt$_2$W groups in (6a) [mean distances: Pt–W 2.732, Pt···Pt 3.155, μ_3-C–Pt 2.08, μ_3-C–W 1.99 Å], however, are best compared with those in (3a) [mean distances: Pt–W 2.751, Pt···Pt 3.089, μ_3-C–Pt 2.07, μ_3-C–W 2.02 Å].[3] In the three compounds $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2\text{-}(\eta\text{-}C_5H_5)]$, (3a), and (6a) the Pt···Pt separations imply little or no direct metal–metal bonding, and may largely reflect the stereochemical requirements of the bridging alkylidyne ligands. The Pt–W separations in (6a) are in the range 2.716(2)—2.747(2) Å, these values conforming closely to those found previously in species with such bonds bridged by alkylidene or alkylidyne groups.[8,9]
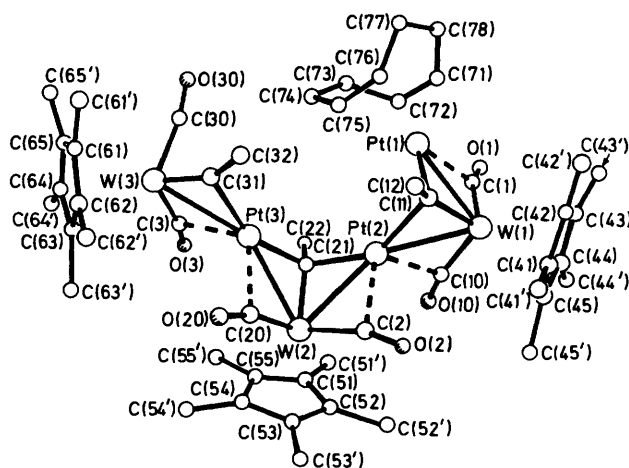
Figure 1. The molecular structure of $[Pt_3W_3(\mu\text{-}CMe)(\mu_3\text{-}CMe)_2(CO)_6\text{-}(cod)(\eta\text{-}C_5Me_5)_3]$ (6a) showing the atom labelling scheme

Each tungsten atom carries an $\eta\text{-}C_5Me_5$ group, and W(3) is also bound by a terminal CO ligand [W(3)–C(30)–O(30) 171(2)°]. The remaining carbonyl groups form W–C–O angles in the range 157—168°, with Pt···CO interactions of 2.25—2.40 Å. The terminal platinum atom Pt(1) is ligated by the cod ligand, with the plane defined by the contact carbon atoms C(71)C(72)C(75)C(76) lying at 83° to that of the plane Pt(1)C(11)W(1). The co-ordination geometries at Pt(2) and Pt(3) are such that the dihedral angles between the planes Pt(2)C(11)W(1) and Pt(2)C(21)W(2), and Pt(3)C(21)W(2) and Pt(3)C(31)W(3) are 88 and 80°, respectively.

The isomer of (6a) characterised crystallographically is one of eight possible diastereoisomers based on different directions of attack of a Pt(cod) fragment on (4b). This may be deduced via extensions of the considerations discussed above for the formation of species with five metal atoms (Scheme). However, such an analysis does not predict which isomers might be sterically unfavourable, very possibly resulting in fewer than eight species being formed. Lack of symmetry of these isomers classifies them as 'asymmetric' in the context of the earlier discussion.

Following the characterisation of the species (6a) and (6b), attention was next given to the preparation of polynuclear metal

compounds with chains of seven metal atoms. One obvious approach to such complexes would be *via* displacement of the cod ligand in (6a) or (6b) with an alkylidyne–tungsten or –molybdenum compound. To test this approach, a thf solution of (6a) was treated with [W(≡CMe)(CO)₂(η-C₅H₅)] in the presence of ethylene in order to labilise[10] the cod ligand in (6a). This reaction afforded the complex [Pt₃W₄(μ-CMe)₂(μ₃-CMe)₂(CO)₈(η-C₅H₅)(η-C₅Me₅)₃] (7), formed as a partially separable mixture of two isomers. Based on relative intensities of the peaks in the ¹H n.m.r. spectrum (Table 2) the isomers, which are light and dark brown in colour, are present in *ca.* 1:4 ratio. In the ¹³C-{¹H} n.m.r. spectrum all the peaks due to the major isomer may be seen, but for the minor isomer this is not so; presumably due to weak signals or overlapping peaks. Only resonances due to the major isomer are listed for the ¹⁹⁵Pt-{¹H} spectrum (Table 3) due to the complicated pattern of peaks observed. Isomers of (7) may arise either because the precursor (6a) was an isomeric mixture or because the MeC≡W(CO)₂(η-C₅H₅) fragment adopts different orientations during displacement of the cod ligand from (6a).

(7) L = η-C₅Me₅

	R	L
(8a)	C₆H₄Me-4	η-C₅H₅
(8b)	Me	η-C₅Me₅
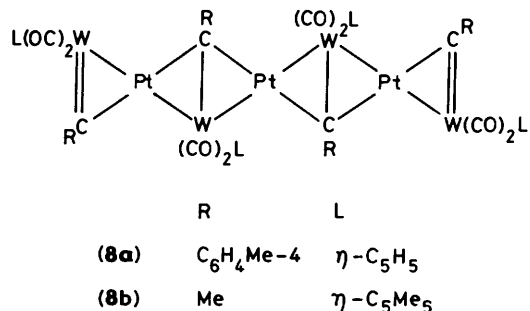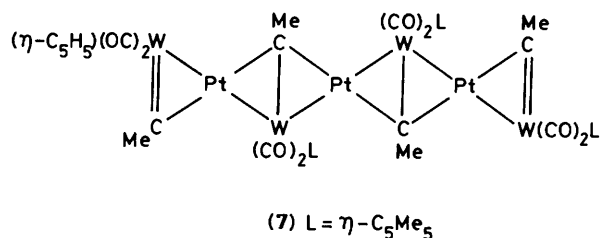
An alternative strategy for preparing compounds with chains of seven metal atoms would be to treat a five-metal-atom chain compound having terminal Pt(cod) groups with excess of an alkylidyne–tungsten or –molybdenum complex. This method was used to prepare [Pt₃W₄(μ-CC₆H₄Me-4)₂(μ₃-CC₆H₄-Me-4)₂(CO)₈(η-C₅H₅)₄] (8a). The reaction between (3a) and an excess of [W(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)] in thf, in the presence of ethylene, gave compound (8a), characterised by the data given in Tables 1—3. In the ¹H and ¹³C-{¹H} n.m.r. spectra of (8a) peaks due to only one isomer are observed. However, the ¹⁹⁵Pt n.m.r. spectrum (Table 3) shows the presence of two isomers with a total of six observed resonances, corresponding to the presence of two asymmetric species. The signals at δ 1 079 and 996 p.p.m. correspond to the central Pt atom of each isomer since two different ¹⁹⁵Pt–¹⁹⁵Pt couplings on each of the resonances are observed. It is difficult to account for the absence of signals for a second isomer in the ¹H or ¹³C-{¹H} n.m.r. spectra.

It is probable that (6c) is an intermediate in the synthesis of (8a) from (3a) and excess [W(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)]. However, as mentioned above, attempts to obtain (6c) by employing the reagents in *ca.* 1:1 ratio afforded only a complex inseparable mixture.

Displacement of the cod group in (6a) with [W(≡CMe)-(CO)₂(η-C₅Me₅)] afforded the heptanuclear metal compound [Pt₃W₄(μ-CMe)₂(μ₃-CMe)₂(CO)₈(η-C₅Me₅)₄] (8b). Data for this complex are summarised in Tables 1—3, and it was apparent from the n.m.r. spectra that two isomers comprising a symmetric and an asymmetric species are produced in approximately equal amounts. In one experiment the less soluble 'symmetric' isomer was separated successfully by fractional crystallisation, and exhibited a relatively simple ¹H n.m.r. spectrum with two μ-CMe and two η-C₅Me₅ resonances. Similarly, the ¹³C-{¹H} n.m.r. spectrum showed one μ-CMe, one μ₃-CMe, four CO, two C₅Me₅, two C₅*Me₅*, and two μ-C*Me* resonances. Evidently this particular isomer has considerable symmetry.

An analysis of the number of isomers possible for the seven-metal-atom chain compounds is possible, based on the earlier discussion relating to the Scheme. Ten diastereoisomers are predicted, four of which may be classed as 'symmetric' and six as 'asymmetric'. The symmetric isomers have a two-fold rotation axis about the central platinum atom, thus simplifying the observed n.m.r. spectra. Thus, only half the number of peaks are

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Table 5. Selected internuclear distances (Å) and angles (°) for the complex [Pt₃W₄(μ-CC₆H₄Me-4)₂(μ₃-CC₆H₄Me-4)₂(CO)₈(η-C₅H₅)₄] (8a)

Pt(1)···Pt(2)	2.994(3)	Pt(2)···Pt(3)	2.963(3)	Pt(1)–W(1)	2.740(3)	Pt(1)–W(2)	2.719(3)
Pt(2)–W(2)	2.769(3)	Pt(2)–W(3)	2.725(3)	Pt(3)–W(3)	2.730(3)	Pt(3)–W(4)	2.705(3)
W(2)–C(21)	2.01(4)	Pt(1)–C(21)	2.10(4)	Pt(2)–C(21)	2.12(4)	W(3)–C(31)	1.99(3)
Pt(2)–C(31)	2.09(3)	Pt(3)–C(31)	2.06(4)	W(1)–C(11)	1.93(4)	Pt(1)–C(11)	2.00(4)
W(4)–C(41)	2.00(5)	Pt(3)–C(41)	2.02(5)	W(1)–C(1)	1.92(5)	Pt(1)–C(1)	2.33(4)
W(1)–C(10)	1.91(6)	W(2)–C(20)	2.10(4)	Pt(1)–C(20)	2.36(5)	W(2)–C(2)	1.90(5)
Pt(2)–C(2)	2.26(5)	W(3)–C(3)	1.98(5)	Pt(2)–C(3)	2.42(5)	W(3)–C(30)	1.90(4)
Pt(3)–C(30)	2.21(4)	W(4)–C(4)	1.90(6)	W(4)–C(40)	2.00(5)	Pt(3)···C(40)	2.82
W(1)–C(cp) *	2.36	W(2)–C(cp) *	2.34	W(3)–C(cp) *	2.40	W(4)–C(cp) *	2.36

| Pt(1)–Pt(2)–Pt(3)	127.0(1)	W(1)–Pt(1)–W(2)	161.2(1)	Pt(1)–W(2)–Pt(2)	66.1(1)	W(2)–Pt(2)–W(3)	148.2(1)
Pt(2)–W(3)–Pt(3)	65.8(1)	W(3)–Pt(3)–W(4)	161.6(1)	W(2)–C(21)–C(22)	148(3)	Pt(1)–C(21)–C(22)	121(3)
Pt(2)–C(21)–C(22)	114(2)	W(3)–C(31)–C(32)	141(2)	Pt(2)–C(31)–C(32)	121(2)	Pt(3)–C(31)–C(32)	121(2)
W(1)–C(11)–C(12)	150(3)	Pt(1)–C(11)–C(12)	121(3)	W(4)–C(41)–C(42)	150(3)	Pt(3)–C(41)–C(42)	125(3)
W(1)–C(1)–O(1)	167(4)	W(1)–C(10)–O(10)	173(5)	W(2)–C(2)–O(2)	160(4)	W(2)–C(20)–O(20)	161(4)
W(3)–C(3)–O(3)	167(3)	W(3)–C(30)–O(30)	162(3)	W(4)–C(4)–O(4)	165(5)	W(4)–C(40)–O(40)	173(4)
C(1)–W(1)–C(10)	87(2)	C(1)–W(1)–C(11)	103(2)	C(10)–W(1)–C(11)	87(2)	C(2)–W(2)–C(20)	92(2)
C(2)–W(2)–C(21)	103(2)	C(20)–W(2)–C(21)	107(2)	C(3)–W(3)–C(30)	88(2)	C(3)–W(3)–C(31)	108(2)
C(30)–W(3)–C(31)	101(2)	C(4)–W(4)–C(40)	88(2)	C(4)–W(4)–C(41)	81(2)	C(40)–W(4)–C(41)	97(2)

* Mean distance to the cyclopentadienyl ring-carbon atoms.
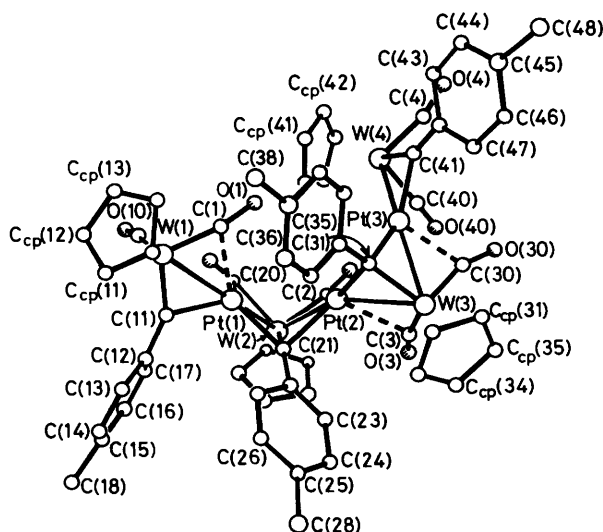
Figure 2. The molecular structure of $[Pt_3W_4(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_4]$ **(8a)** showing the atom labelling scheme


seen in the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the symmetric isomers compared with the asymmetric species. In most cases the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectra are of insufficient quality to assign peaks for the symmetric isomers, or these signals may be obscured by resonances of an asymmetric isomer. However, two ^{195}Pt resonances are predicted for a symmetric isomer of a Pt_3W_4 compound and three resonances for an asymmetric isomer. It seems a characteristic of the syntheses described herein, however, that fewer isomers than that anticipated from the theoretically possible number are produced.

An alternative synthesis of **(8b)** involves treating the compound **(3b)** with an excess of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$. However, **(3b)**[3] is more difficult to prepare than **(6a)**. Compound **(8b)** also occasionally appears as a by-product in the synthesis of **(1c)** from $[Pt(cod)_2]$ and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$, suggesting that under the right conditions these platinum and tungsten reagents might copolymerise.

It was considered important to establish the molecular structure of a Pt_3W_4 compound by X-ray diffraction, and suitable crystals of **(8a)** were available for this purpose. The results of this study are summarised in Table 5 and the molecular structure of the isomer identified in this manner is shown in Figure 2.

As anticipated by the method of synthesis of **(8a)** from **(3a)**, the spine of the former consists of a Pt_3W_4 chain with the two terminal Pt–W bonds [Pt(1)–W(1) and Pt(3)–W(4)] each bridged by a tolylmethylidyne ligand. The central $Pt(1)W(2)Pt(2)W(3)Pt(3)$ fragment, with which the two triply bridging tolylmethylidyne groups are bound, is of different stereochemistry to the Pt_3W_2 fragment identified in the X-ray diffraction study of **(3a)**.[3] The various metal–metal and alkylidynecarbon–metal distances are similar to those found in **(3a)**, **(4a)**, and **(6a)** and call for no comment. Apart from the carbonyl groups C(10)O(10) and C(4)O(4) attached to W(1) and W(4), respectively, all the carbonyl ligands semi-bridge the Pt–W bonds. However, Pt(3) shows only a slight interaction [ca. 2.82 Å] with C(40) [W(4)–C(40)–O(40) 173(4)°]. The dihedral angles between adjacent $\overline{Pt(\mu\text{-}C)W}$ planes at Pt(1), Pt(2), and Pt(3) are 83, 87, and 88°, respectively.

The central $Pt(1)W(2)Pt(2)W(3)Pt(3)$ core of **(8a)** is 'asymmetric', corresponding to configuration **(C)** of the Scheme. As mentioned above, **(8a)** is formed as essentially one isomer, and
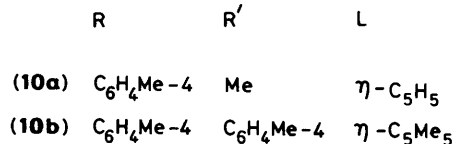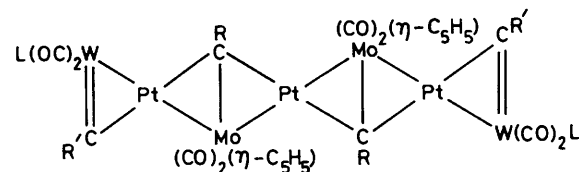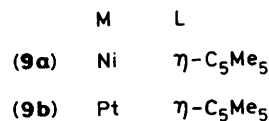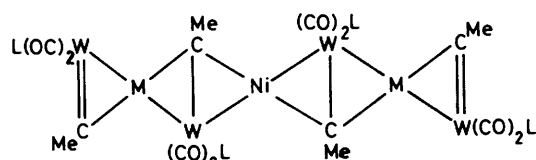
in high yield (Table 1). Moreover, the 'asymmetry' of **(8a)** is confirmed in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table 2) which displays two $\mu\text{-}C$, two $\mu_3\text{-}C$, seven CO (one signal corresponding in intensity to two carbonyl ligands), four $C^1(C_6H_4)$, four C_5H_5, and four Me-4 resonances. Since **(3a)**, the precursor of **(8a)**, exists as a mixture of three diastereoisomers, it follows that during the course of the synthesis of **(8a)** the symmetrical isomers **(D)** and **(E)** of the Scheme have rearranged to a core structure of type **(C)**. It may be that under the reaction conditions, with ethylene present to labilise the cod ligands, a terminal $Pt(C_2H_4)_n$ $(n = 1$ or $2)$ group could change its orientation with respect to the $\mu\text{-}C\text{-}W$ fragment to which it is attached prior to ethylene displacement by $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in a chain-growth process. Sterically it may not be possible to add two $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ molecules to the symmetrical metal atom frameworks **(D)** and **(E)**. It was noted earlier that the pentanuclear Pt_3Mo_2 species **(3c)** exists with a facile equilibrium between three isomers, and this may imply a greater flexibility in the conformations of molybdenum-containing chains.

The existence of trimetal compounds such as **(1b)** raises the interesting possibility of constructing complexes with chains of metal atoms incorporating nickel. To investigate this possibility two equivalents of **(1b)** were treated with one equivalent of $[Ni(cod)_2]$. In this manner the brown crystalline compound $[Ni_3W_4(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)_2(CO)_8(\eta\text{-}C_5Me_5)_4]$ **(9a)** was obtained, data for which are given in Tables 1 and 2. Examination of the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. data reveals the presence in solution of one isomer. The latter is an 'asymmetric' species. Thus the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table 2) shows two $\mu\text{-}C$, two $\mu_3\text{-}C$, and eight CO resonances, measured at $-40\ ^\circ C$.

Compound **(9a)** was initially observed in the synthesis of **(1b)**, when an excess of $[Ni(cod)_2]$ was present. Reaction of excess $[Ni(cod)_2]$ with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ affords **(9a)** in good yield but by this method it is contaminated with traces of **(1b)** from which it is not possible to separate completely by chromatography. Analogous reactions with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ yield no Ni_3W_4 complex.

Compound [NiPt$_2$W$_4$(μ-CMe)$_2$(μ_3-CMe)$_2$(CO)$_8$(η-C$_5$Me$_5$)$_4$] (9b), also containing a chain of seven metal atoms but incorporating nickel and platinum together with tungsten, was prepared by treating (1c) with 0.5 equivalents (or slight excess) of [Ni(cod)$_2$]. Compound (9b) was characterised in the usual manner (Tables 1—3). Samples of (9b) used for n.m.r. measurements are contaminated with traces of (1c), suggesting instability of the former in solution. Treatment of (9b) with [Pt(cod)$_2$] affords primarily unreacted starting material and trace amounts of a 'star cluster'[11] with a NiPt$_3$W$_4$ core. Addition of a Pt(PMe$_3$)$_2$ fragment to (9b) in order to produce an eight-metal-atom chain complex was also unsuccessful.

The compound [Pt$_3$Mo$_2$W$_2$(μ-CMe)$_2$(μ_3-CC$_6$H$_4$Me-4)$_2$-(CO)$_8$(η-C$_5$H$_5$)$_4$] (10a) in which both molybdenum and tungsten atoms are incorporated in the metal spine is produced in good yield from the reaction between (3c) and an excess of [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)]. Complex (10a) is formed as a chromatographically separable mixture of two isomers (green and brown, ca. 2:1). Examination of ^{1}H and ^{13}C-$\{^1$H$\}$ n.m.r. data (Table 2) revealed that the green isomer was of the 'symmetric' type and the brown 'asymmetric'. In accord with the previous discussion, the ^{13}C-$\{^1$H$\}$ n.m.r. spectrum of the symmetrical green isomer shows (Table 2) one μ-C, one μ_3-C, four CO, two C$_5$H$_5$, one μ-CMe, and one Me-4 resonances, while for the brown species twice as many signals for each of these groups is observed. The brown isomer slowly converts to the green isomer in solution, hence the ^{13}C-$\{^1$H$\}$ n.m.r. spectrum of the former always shows signals due to the latter. The reverse process seems less favoured. If in the synthesis of (10a) the reaction is allowed to proceed for less than ca. 8 h, significant amounts of compound (6b) are observed, indicating the stepwise nature of the process converting (3c) into (10a).

The reaction between (3c) and [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$Me$_5$)] affords the complex [Pt$_3$Mo$_2$W$_2$(μ-CC$_6$H$_4$Me-4)$_2$-(μ_3-CC$_6$H$_4$Me-4)$_2$(CO)$_8$(η-C$_5$H$_5$)$_2$(η-C$_5$Me$_5$)$_2$] (10b), produced as a single isomer. Using reaction times of less than ca. 3 h produces mixtures of products.

The results described in this paper, taken with those reported earlier,[3] demonstrate the stepwise synthesis of new types of heteronuclear metal cluster compounds containing up to seven metal atoms in a chain. Several of these species are formed as mixtures of diastereoisomers due to the different possible conformations of the metal chains. In the latter it is possible to vary the transition element between platinum or nickel, and between tungsten and molybdenum, demonstrating the versatility of this approach. In the succeeding paper[12] we shall demonstrate how the seven-metal-atom chain species may, via addition of a platinum or nickel atom, be converted into eight-metal-atom ring structures.

Experimental

Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere. Solvents were rigorously dried before use, and light petroleum refers to that fraction of b.p. 40—60 °C. The i.r. spectra were measured with Nicolet MX-10 and MX-5 spectrophotometers and n.m.r. spectra with JEOL JNM GX 400, GX 270, and FX 90Q spectrometers. Alumina used in chromatography was B.D.H. aluminium oxide (Brockman activity II). Chromatography columns were generally ca. 20 cm in length and 3.5 cm in internal diameter. The compound [Ni(cod)$_2$] was purchased from Strem Chemicals Inc., and [Pt(cod)$_2$] was prepared as described elsewhere.[13] The complexes [W($\equiv$CR)(CO)$_2$L] (R = Me or C$_6$H$_4$Me-4; L = η-C$_5$H$_5$ or η-C$_5$Me$_5$) were obtained as previously described,[14,15] as were compounds (1b), (1c), (3a),

Table 6. Crystal data and experimental parameters *

Compound	(6a)	(8a)
Formula	C$_{50}$H$_{66}$O$_6$Pt$_3$W$_3$·0.5CH$_2$Cl$_2$	C$_{60}$H$_{48}$O$_8$Pt$_3$W$_4$
M	1 942.4	2 217.7
Crystal system	Triclinic	Triclinic
Crystal habit	Rhombs	Rhombs
Colour	Burgundy	Black
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.935(6)	10.210(4)
b/Å	13.242(7)	15.946(11)
c/Å	18.193(9)	18.967(14)
α/°	80.53(4)	89.87(6)
β/°	81.22(4)	97.60(5)
γ/°	67.39(4)	106.63(5)
U/Å^3	2 605(2)	2 931(3)
Z	2	2
D$_c$/g cm^{-3}	2.48	2.51
F(000)	1 782	2 003
T/K	293	293
μ(Mo-K$_\alpha$)/cm^{-1}	149.46	152.46
Crystal size (mm)	0.20 × 0.15 × 0.15	0.40 × 0.30 × 0.30
2θ$_{min.,max.}$/°	0,50	3,50
Data recorded	9 392	10 774
Data unique	9 215	9 904
Data used	5 573	5 094
n in I ⩾ nσ(I)	2.5	4.0
Absorption correction	Empirical	Numerical
Developed zone faces		⟨100⟩ ⟨010⟩ ⟨001⟩
No. of parameters refined	626	264
g in weighting scheme	0.0003	0.0015
w^{-1} = [σ^2(F) + g|F|^2]		
R (R')	0.044 (0.039)	0.075 (0.078)

* All data were collected on a Nicolet P3m automated diffractometer, operating in θ–2θ scan mode, using Mo-K$_\alpha$ X-radiation (graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å). Refinement was by blocked-cascade least-squares methods.

and (4b).[3] Analytical and other data for the new complexes are given in Table 1.

Synthesis of the Complex [Pt$_3$Mo$_2$(μ_3-CC$_6$H$_4$Me-4)$_2$(CO)$_4$-(cod)$_2$(η-C$_5$H$_5$)$_2$].—A cold (0 °C) ethylene-saturated thf (20 cm^3) solution of [Pt(cod)$_2$] (0.25 g, 0.61 mmol) was treated with (5b) (0.20 g, 0.24 mmol) in the same solvent (10 cm^3). After stirring for 3 h, solvent was removed *in vacuo*, and the residue dissolved in CH$_2$Cl$_2$ (10 cm^3) and chromatographed. Elution with CH$_2$Cl$_2$ afforded first a grey band, followed by green and orange bands corresponding to isomers of the product. The three eluates were combined and solvent was removed *in vacuo*. The residue was recrystallised from CH$_2$Cl$_2$–light petroleum (10 cm^3, 1:3) to yield purple *crystals* of [Pt$_3$Mo$_2$(μ_3-CC$_6$H$_4$-Me-4)$_2$(CO)$_4$(cod)$_2$(η-C$_5$H$_5$)$_2$] (3c) (0.26 g).

Synthesis of Hexanuclear Metal Compounds.—(i) A sample of [Pt(cod)$_2$] (0.05 g, 0.13 mmol) was dissolved in cold (0 °C) ethylene-saturated thf (10 cm^3) and added slowly to an ethylene-saturated thf (20 cm^3) solution of (4b) (0.20 g, 0.13 mmol). The resulting solution was stirred for 3 h. Solvent was removed *in vacuo*, and the residue dissolved in CH$_2$Cl$_2$ (ca. 5 cm^3) and chromatographed, thereby affording two poorly resolved reddish brown and orange-brown bands. Elution with CH$_2$Cl$_2$ and removal of solvent *in vacuo* gave brown *crystals* of [Pt$_3$W$_3$-(μ-CMe)(μ_3-CMe)$_2$(CO)$_6$(cod)(η-C$_5$Me$_5$)$_3$] (6a) (0.20 g).

(ii) Compound (3c) (0.10 g, 0.07 mmol) in thf (25 cm^3) was added to [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] (0.025 g, 0.07 mmol) and

Table 7. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) with estimated standard deviations in parentheses for (6a)

Atom	x	y	z	Atom	x	y	z
Pt(1)	5 087(1)	2 688(1)	2 013(1)	C(41)	2 887(16)	2 853(15)	39(9)
Pt(2)	3 852(1)	973(1)	2 149(1)	C(42)	3 350(15)	3 666(14)	24(10)
Pt(3)	5 590(1)	−1 102(1)	3 143(1)	C(43)	2 496(17)	4 533(14)	395(9)
W(1)	3 131(1)	2 977(1)	1 284(1)	C(44)	1 488(18)	4 232(17)	666(10)
W(2)	3 399(1)	−886(1)	2 745(1)	C(45)	1 762(18)	3 153(16)	448(11)
W(3)	7 539(1)	−2 300(1)	3 925(1)	C(41')	3 426(26)	1 817(15)	−368(12)
C(11)	4 766(14)	1 784(12)	1 324(9)	C(42')	4 535(20)	3 667(20)	−408(12)
C(12)	5 795(14)	978(12)	861(10)	C(43')	2 565(22)	5 629(15)	425(12)
C(21)	3 861(14)	133(12)	3 216(8)	C(44')	342(19)	4 927(18)	1 066(11)
C(22)	3 559(16)	832(13)	3 840(9)	C(45')	875(22)	2 558(21)	569(14)
C(31)	7 451(14)	−1 703(12)	2 941(9)	C(51)	1 464(15)	−528(13)	3 429(10)
C(32)	8 007(16)	−1 551(15)	2 152(10)	C(52)	1 404(17)	−725(15)	2 699(11)
C(1)	3 201(15)	3 970(15)	1 945(10)	C(53)	2 174(17)	−1 821(13)	2 593(10)
O(1)	2 855(12)	4 767(10)	2 264(7)	C(54)	2 705(17)	−2 325(13)	3 273(10)
C(10)	2 058(15)	2 556(13)	2 079(11)	C(55)	2 254(15)	−1 492(13)	3 777(9)
O(10)	1 235(11)	2 485(9)	2 505(7)	C(51')	731(19)	498(16)	3 803(12)
C(2)	3 391(16)	−282(13)	1 686(9)	C(52')	519(17)	83(17)	2 165(12)
O(2)	3 253(14)	−134(10)	1 040(7)	C(53')	2 308(23)	−2 388(17)	1 924(11)
C(20)	4 960(15)	−2 090(15)	2 499(10)	C(54')	3 529(21)	−3 501(14)	3 446(13)
O(20)	5 729(11)	−2 892(9)	2 280(8)	C(55')	2 517(21)	−1 730(19)	4 590(10)
C(3)	5 906(15)	−1 709(13)	4 436(10)	C(61)	9 395(17)	−3 771(17)	3 817(13)
O(3)	5 028(11)	−1 480(11)	4 850(7)	C(62)	8 519(20)	−4 111(14)	3 698(11)
C(30)	7 998(19)	−1 123(16)	4 163(11)	C(63)	7 728(19)	−4 092(15)	4 360(12)
O(30)	8 414(13)	−537(10)	4 342(8)	C(64)	8 178(22)	−3 765(14)	4 914(10)
C(71)	5 547(17)	4 075(13)	2 274(10)	C(65)	9 166(20)	−3 538(15)	4 569(14)
C(72)	5 245(18)	3 561(14)	2 932(10)	C(61')	10 417(23)	−3 666(26)	3 243(19)
C(73)	6 138(21)	2 769(18)	3 467(11)	C(62')	8 442(34)	−4 544(22)	2 975(15)
C(74)	6 687(21)	1 624(16)	3 337(12)	C(63')	6 690(22)	−4 495(18)	4 412(21)
C(75)	6 779(15)	1 417(14)	2 527(12)	C(64')	7 576(31)	−3 704(18)	5 658(12)
C(76)	7 142(14)	1 940(13)	1 881(11)	C(65')	9 931(33)	−3 240(19)	5 022(24)
C(77)	7 681(19)	2 811(19)	1 873(15)	Cl	799(13)	8 888(10)	24(7)
C(78)	6 792(19)	3 930(18)	1 929(13)	C	−917(36)	9 968(32)	226(22)

the mixture syringed into a Fischer-Porter vessel. The mixture was pressurised with C_2H_4 (3 atm) and stirred for 6 h. Solvent was then removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 cm^3) and chromatographed. Elution with CH_2Cl_2 afforded a green eluate. Solvent was removed *in vacuo*, and the residue recrystallised from CH_2Cl_2–light petroleum (10 cm^3, 1:8) to give green-brown *crystals* of [$Pt_3Mo_2W(\mu$-CMe)(μ_3-CC$_6$H$_4$-Me-4)$_2$(CO)$_6$(cod)(η-C$_5$H$_5$)$_3$] (6b) (0.10 g).

Synthesis of Heptanuclear Metal Compounds.—(*i*) A thf (15 cm^3) solution of (6a) (0.15 g, 0.08 mmol) was syringed into a Fischer-Porter vessel containing [$W(\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] (0.05 g, 0.15 mmol) in the same solvent (5 cm^3), and the reactants pressurised with C_2H_4 (3 atm) for 2 h. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (*ca.* 6 cm^3) and chromatographed. Elution with CH_2Cl_2 removed unreacted [$W(\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] (0.02 g), followed by two poorly resolved light and dark brown eluates. Collection of these two fractions, removal of solvent *in vacuo* and crystallis-ation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1:5) afforded brown *crystals* of [$Pt_3W_4(\mu$-CMe)$_2(\mu_3$-CMe)$_2$(CO)$_8$-(η-C$_5$H$_5$)(η-C$_5$Me$_5$)$_3$] (7) (0.13 g).

(*ii*) In a similar preparation, compound (3a) (0.20 g, 0.12 mmol) in thf (10 cm^3) with [$W(\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.15 g, 0.37 mmol) in the same solvent (10 cm^3) under ethylene (3 atm) gave, after column chromatography with CH_2Cl_2 as eluant, unreacted [$W(\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.05 g), and with thf–CH_2Cl_2 (1:9) as eluant [$Pt_3W_4(\mu$-CC$_6$H$_4$Me-4)$_2$-(μ_3-CC$_6$H$_4$Me-4)$_2$(CO)$_8$(η-C$_5$H$_5$)$_4$] (8a) (0.22 g). The latter was obtained as brown *crystals* from CH_2Cl_2–light petroleum (1:10).

(*iii*) The Fischer-Porter vessel was charged with compound

(6a) (0.20 g, 0.10 mmol) in thf (15 cm^3), [$W(\equiv$CMe)(CO)$_2$(η-C$_5$Me$_5$)] (0.09 g, 0.20 mmol) in thf (5 cm^3), and C_2H_4 (3 atm). After 2 h, with stirring, solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 1:1) and chromatographed. Eluting with the same solvent mixture gave initially unreacted [$W(\equiv$CMe)(CO)$_2$(η-C$_5$Me$_5$)] (0.05 g) followed by a red-brown band. Removal of solvent *in vacuo*, and crystallisation from CH_2Cl_2–light petroleum (*ca.* 20 cm^3, 1:5), afforded brown *crystals* of [$Pt_3W_4(\mu$-CMe)$_2(\mu_3$-CMe)$_2$(CO)$_8$-(η-C$_5$Me$_5$)$_4$] (8b) (0.16 g).

(*iv*) A thf (10 cm^3) solution of (1b) (0.11 g, 0.13 mmol) was treated with [Ni(cod)$_2$] (0.02 g, 0.07 mmol). After stirring for 1.5 h at room temperature, solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2–light petroleum (5 cm^3, 3:1) and chromatographed. Eluting with the same solvent mixture removed a brown band. Removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 1:10) afforded brown *crystals* of [Ni$_3$W$_4(\mu$-CMe)$_2$-(μ_3-CMe)$_2$(CO)$_8$(η-C$_5$Me$_5$)$_4$] (9a) (0.09 g).

(*v*) The compound [Ni(cod)$_2$] (0.03 g, 0.11 mmol) was added to a thf (15 cm^3) solution of (1c) (0.20 g, 0.20 mmol). After stirring for 2 h at room temperature, solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 2:1) and chromatographed. Elution with the same solvent mixture removed a brown band. Removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 1:10) gave brown *crystals* of [NiPt$_2$W$_4$-(μ-CMe)$_2(\mu_3$-CMe)$_2$(CO)$_8$(η-C$_5$Me$_5$)$_4$] (9b) (0.13 g).

(*vi*) Compound (3c) (0.10 g, 0.07 mmol) was dissolved in thf (20 cm^3) and syringed into a Fischer-Porter vessel containing [$W(\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] (0.20 g, 0.60 mmol). The vessel was pressurised with C_2H_4 (3 atm) and the mixture stirred at

Table 8. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) with estimated standard deviations in parentheses for (8a)

Atom	x	y	z	Atom	x	y	z
W(1)	2 094(2)	4 173(1)	3 833(1)	C$_{cp}$(23)	3 613	2 966	273
W(2)	3 557(2)	2 881(1)	1 534(1)	C$_{cp}$(24)	3 920	3 820	587
W(3)	−1 309(2)	499(1)	1 240(1)	C$_{cp}$(25)	5 155	3 971	1 073
W(4)	2 098(2)	−559(1)	3 208(1)	C(31)	−666(32)	1 024(22)	2 217(17)
Pt(1)	2 390(2)	3 445(1)	2 578(1)	C(33)*	−1 408(30)	953(15)	3 416(14)
Pt(2)	1 071(2)	1 731(1)	1 777(1)	C(34)	−2 055	1 261	3 920
Pt(3)	141(2)	−18(1)	2 388(1)	C(35)	−2 438	2 028	3 808
C(11)	2 622(34)	4 658(23)	2 944(18)	C(36)	−2 176	2 487	3 190
C(13)*	2 288(25)	6 022(20)	2 402(16)	C(37)	−1 529	2 180	2 686
C(14)	2 752	6 765	2 011	C(32)	−1 146	1 413	2 779
C(15)	3 971	6 901	1 713	C(38)	−3 019(43)	2 379(29)	4 401(22)
C(16)	4 724	6 295	1 805	C(3)	273(47)	830(32)	692(25)
C(17)	4 259	5 553	2 197	O(3)	1 020(39)	906(26)	281(21)
C(12)	3 041	5 416	2 495	C(30)	−1 010(38)	−618(25)	1 355(20)
C(18)	4 406(54)	7 816(35)	1 354(28)	O(30)	−1 017(35)	−1 369(24)	1 246(19)
C(1)	1 960(42)	2 954(28)	3 706(22)	C$_{cp}$(31)*	−3 707(40)	4(21)	1 011(22)
O(1)	1 751(30)	2 171(20)	3 742(16)	C$_{cp}$(32)	−3 400	899	1 255
C(10)	4 009(62)	4 358(41)	4 151(33)	C$_{cp}$(33)	−2 726	1 413	694
O(10)	5 165(39)	4 510(27)	4 279(21)	C$_{cp}$(34)	−2 616	835	151
C$_{cp}$(11)*	918(31)	5 152(18)	4 139(15)	C$_{cp}$(35)	−3 222	−36	347
C$_{cp}$(12)	1 983	5 173	4 707	C(41)	51(46)	−883(30)	3 175(24)
C$_{cp}$(13)	1 678	4 340	5 017	C(43)*	−1 092(23)	−1 677(18)	4 131(12)
C$_{cp}$(14)	424	3 804	4 640	C(44)	−2 287	−2 156	4 393
C$_{cp}$(15)	−46	4 305	4 097	C(45)	−3 567	−2 316	3 971
C(21)	1 684(28)	3 063(26)	1 503(20)	C(46)	−3 651	−1 996	3 287
C(23)*	223(26)	3 093(15)	405(12)	C(47)	−2 455	−1 516	3 024
C(24)	−710	3 442	−13	C(42)	−1 176	−1 357	3 446
C(25)	−1 250	4 046	288	C(48)	−4 964(66)	−2 886(44)	4 178(37)
C(26)	−857	4 301	1 006	C(4)	1 772(57)	−1 757(40)	3 421(31)
C(27)	75	3 952	1 424	O(4)	1 551(44)	−2 434(32)	3 696(24)
C(22)	615	3 348	1 123	C(40)	2 110(46)	−898(31)	2 196(25)
C(28)	−2 213(48)	4 480(34)	−133(26)	O(40)	2 264(37)	−1 076(25)	1 628(21)
C(2)	3 197(45)	1 653(31)	1 628(24)	C$_{cp}$(41)*	3 031(33)	563(22)	4 077(17)
O(2)	3 407(32)	930(22)	1 720(17)	C$_{cp}$(42)	3 595	−139	4 258
C(20)	4 510(45)	3 124(30)	2 593(24)	C$_{cp}$(43)	4 419	−223	3 730
O(20)	5 280(34)	3 320(23)	3 037(18)	C$_{cp}$(44)	4 363	427	3 223
C$_{cp}$(21)*	5 612(29)	3 210(24)	1 059(17)	C$_{cp}$(45)	3 505	913	3 437
C$_{cp}$(22)	4 658	2 589	565				

* Atom of a rigid group; remaining atoms of the group have identical standard deviations.

room temperature for 9 h. Removal of solvent *in vacuo* afforded a brown oil, which was dissolved in CH_2Cl_2–light petroleum (10 cm³, 4:1) and chromatographed. Elution with the same solvent mixture gave a fast moving green band and a slower moving brown band. Collection of the green eluate, removal of solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2–light petroleum (*ca.* 10 cm³, 1:10) gave dark green *crystals* of a symmetric isomer of $[Pt_3Mo_2W_2(\mu\text{-CMe})_2(\mu_3\text{-CC}_6H_4Me\text{-4})_2\text{-}(CO)_8(\eta\text{-C}_5H_5)_4]$ (**10a**) (0.07 g). Similarly, the brown eluate afforded brown *crystals* of an asymmetric isomer of (**10a**) (0.03 g).

(*vii*) In a similar procedure to that employed to obtain (**10a**), a mixture of $[W(\equiv CC_6H_4Me\text{-4})(CO)_2(\eta\text{-C}_5Me_5)]$ (0.20 g, 0.42 mmol) and (**3c**) (0.10 g, 0.07 mmol) in thf (20 cm³) under ethylene (3 atm) for 3 h afforded a red-brown residue after removal of solvent. The solid residue was dissolved in CH_2Cl_2 (5 cm³) and the solution was chromatographed using the same solvent. A red eluate contained unreacted $[W(\equiv CC_6H_4Me\text{-4})\text{-}(CO)_2(\eta\text{-C}_5Me_5)]$. This was followed by a brown eluate from which, after removal of solvent *in vacuo* and recrystallisation from CH_2Cl_2–light petroleum (*ca.* 10 cm³, 1:10), brown *crystals* of $[Pt_3Mo_2W_2(\mu\text{-CC}_6H_4Me\text{-4})_2(\mu_3\text{-CC}_6H_4Me\text{-4})_2\text{-}(CO)_8(\eta\text{-C}_5H_5)_2(\eta\text{-C}_5Me_5)_2]$ (**10b**) (0.13 g) were obtained.

Crystal Structure Determinations.—The crystal and other experimental data for compounds (**6a**) and (**8a**) are summarised in Table 6. The unit cell of (**6a**) contained one molecule of CH_2Cl_2 (disordered). All data were corrected for Lorentz, polarisation, and *X*-ray absorption effects. The structures were solved, and all non-hydrogen atoms located, by Patterson and Fourier methods. For (**6a**) the non-hydrogen atoms were refined anisotropically except the carbon atom of the disordered CH_2Cl_2 molecule, while for (**8a**) only the metal atoms were so treated. For both complexes the tolyl, methyl, and cyclopentadienyl groups were refined with rigid group geometries. Hydrogen atoms were incorporated at calculated positions (C–H 0.96 Å, with tied isotropic thermal parameters 1.2 times U_{eq} for the attached carbon atom). The cod ligand hydrogen atoms in (**6a**) were incorporated with a riding mode. Maximum residual density in the electron-density difference maps at convergence showed local maxima of *ca.* 1.37 e Å⁻³ near the metal atoms only for (**6a**) and *ca.* 5.0 e Å⁻³ for (**8a**). Scattering factors were from ref. 16, and all computations were carried out with the SHELXTL system of programs [17] using an Eclipse (Data General) computer. Atomic co-ordinates for (**6a**) and (**8a**) are given in Tables 7 and 8, respectively.

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