Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 47.[1] Synthesis of Tri-, Tetra-, and Penta-heteronuclear Metal Cluster Compounds involving Tungsten with Platinum or Nickel: Crystal Structures of the Compounds $[\mathrm{Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2}]$ and $[\mathrm{Pt_2W_3(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)_3}]$ ($\mathrm{R = C_6H_4Me\text{-}4}$, cod = cyclo-octa-1,5-diene) *

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Tris(ethylene)platinum, prepared *in situ* from $[\mathrm{Pt(cod)_2}]$ (cod = cyclo-octa-1,5-diene), reacts with the compounds $[\mathrm{W(\equiv CR)(CO)_2L}]$ to give the complexes $[\mathrm{PtW_2(\mu\text{-}CR)_2(CO)_4L_2}]$ (R = Me or Ph, $\mathrm{L = \eta\text{-}C_5H_5}$; R = Me, Ph, or $\mathrm{C_6H_4Me\text{-}4}$, $\mathrm{L = \eta\text{-}C_5Me_5}$). The analogous nickel compounds $[\mathrm{NiW_2(\mu\text{-}CR)_2(CO)_4L_2}]$ have also been prepared using $[\mathrm{Ni(cod)_2}]$. Treatment of the trinuclear metal species $[\mathrm{MW_2(\mu\text{-}CR)_2(CO)_4L_2}]$ with one equivalent of $[\mathrm{Pt(cod)_2}]$ affords the tetranuclear metal compounds $[\mathrm{MPtW_2(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(cod)L_2}]$ (M = Ni or Pt, $\mathrm{R = C_6H_4Me\text{-}4}$, $\mathrm{L = \eta\text{-}C_5H_5}$ or $\mathrm{\eta\text{-}C_5Me_5}$; M = Pt, R = Me, $\mathrm{L = \eta\text{-}C_5Me_5}$), while with two equivalents of $[\mathrm{Pt(cod)_2}]$ the pentanuclear metal complexes $[\mathrm{Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(cod)_2L_2}]$ ($\mathrm{R = C_6H_4Me\text{-}4}$, $\mathrm{L = \eta\text{-}C_5H_5}$; R = Me, $\mathrm{L = \eta\text{-}C_5Me_5}$) are obtained. These tetra- and penta-nuclear metal compounds were generally isolated as isomeric mixtures, as revealed by n.m.r. measurements (^{1}H, ^{13}C-{^{1}H}, and ^{195}Pt-{^{1}H}). An *X*-ray diffraction study structurally characterised a symmetrical isomer of $[\mathrm{Pt_3W_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2}]$, a molecule having a crystallographic two-fold rotation axis. The structure comprises two 'butterfly' μ_3-$\mathrm{CPt_2W}$ fragments sharing a wing-tip platinum vertex, with isosceles metal triangles [Pt–W 2.751(1) and 2.748(1), Pt $\cdots$ Pt 3.089(1) Å] capped by the $\mathrm{CC_6H_4Me\text{-}4}$ groups. The terminal Pt atoms each carry a cod ligand, and the four CO groups semi-bridge Pt–W bonds. The pentanuclear metal compounds $[\mathrm{Pt_2W_3(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_6L_3}]$ ($\mathrm{R = C_6H_4Me\text{-}4}$, $\mathrm{L = \eta\text{-}C_5H_5}$; R = Me or $\mathrm{C_6H_4Me\text{-}4}$, $\mathrm{L = \eta\text{-}C_5Me_5}$), $[\mathrm{Pt_2W_3(\mu\text{-}CMe)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2}]$, and $[\mathrm{Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2}]$ have also been prepared by treating the appropriate tetranuclear metal compound $[\mathrm{Pt_2W_2(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(cod)L_2}]$ with an alkylidynetungsten complex so as to displace the cod ligand. Again isomeric mixtures were produced, and identified by n.m.r. spectroscopy. An *X*-ray diffraction study established the molecular structure of one of the three isomers of $[\mathrm{Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3}]$. The molecule has an essentially planar five-metal atom framework, with two edge-bridging and one triply bridging tolylmethylidyne groups. Four of the six CO ligands semi-bridge W–Pt bonds [W–C–O 163—168(2) Å] and each tungsten carries an $\mathrm{\eta\text{-}C_5H_5}$ group, with each terminal W atom having one linearly bound CO. The Pt $\cdots$ Pt separation [2.949(2) Å] implies little direct metal–metal bonding between these atoms. Bond lengths to the central μ_3-$\mathrm{CC_6H_4Me\text{-}4}$ ligand are μ_3-C–Pt 2.02(3) and 2.09(2), μ_3-C–W 1.99(3) Å, while those to the edge-bridging $\mathrm{CC_6H_4Me\text{-}4}$ groups are μ-C–W 1.96(2) (mean) and μ-C–Pt 2.03(2) Å (mean).

The tungsten complex $[\mathrm{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)}]$ ($\mathrm{R = C_6H_4Me\text{-}4}$) reacts with $[\mathrm{Pt(C_2H_4)_3}]$ and with $[\mathrm{Ni(cod)_2}]$ (cod = cyclo-octa-1,5-diene) to give the trinuclear metal compounds $[\mathrm{MW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2}]$ [M = Pt (**1a**) or Ni (**1b**)]. The structures of these species have been established by *X*-ray diffraction.[2] In both complexes the two metal–metal bonds of the W–M–W spine are edge-bridged by a tolylmethylidyne group and semi-bridged by a carbonyl ligand. In this paper we describe the trinuclear metal complexes (**1c**)—(**1f**) and (**1i**)—(**1l**), analogues of (**1a**) or (**1b**) but with μ-CMe or μ-CPh groups in place of μ-$\mathrm{CC_6H_4Me\text{-}4}$, and with $\mathrm{\eta\text{-}C_5H_5}$ or $\mathrm{\eta\text{-}C_5Me_5}$ ligands on the tungsten atoms. The compounds (**1g**), (**1h**), and (**1m**) represent structural analogues of compounds (**1a**) and (**1b**) but with an $\mathrm{\eta\text{-}C_5Me_5}$ ligand on the tungsten atoms. We then describe how compounds of type (**1**) may be used to prepare other complexes containing four or five metal atoms.

In the context of the isolobal model[3] the platinumditungsten compound (**1a**) is related to the compound $[\mathrm{Pt(RC_2R)_2}]$ ($\mathrm{R = C_6H_4Me\text{-}4}$),[4] since CR and $\mathrm{W(CO)_2(\eta\text{-}C_5H_5)}$ fragments have similar frontier orbitals and the same number of valence electrons. An interesting feature of the family of compounds [Pt(alkyne)$_2$] is their ability to add further platinum(0) groups to form di- or tri-platinum species with bridging alkyne ligands, *e.g.* $[\mathrm{Pt_2(\mu\text{-}PhC_2Ph)(\eta\text{-}PhC_2Ph)(PPh_3)_2}]$ or [Pt$_3$-

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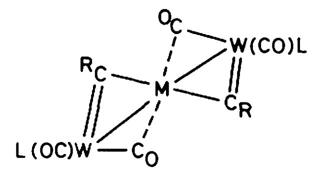
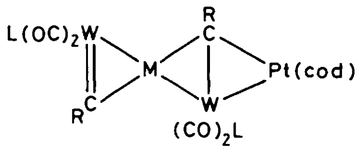
* 2,2,4,4-Tetracarbonyl-1,5-bis(η-cyclo-octa-1′,5′-diene)-2,4-bis(η-cyclopentadienyl)-1,2,3;3,4,5-bis(μ_3-*p*-tolylmethylidyne)-1,3,5-triplatinum-2,4-ditungsten and 1,1,3,3,5,5-hexacarbonyl-1,3,5-tris(η-cyclopentadienyl)-1,2;4,5-bis(μ-*p*-tolylmethylidyne)-2,3,4-μ_3-*p*-tolylmethylidyne-2,4-diplatinum-1,3,5-tritungsten (both 4*Pt–W*).

Supplementary data available (No. SUP 56586, 9 pp.): thermal parameters, hydrogen atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Daltons Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

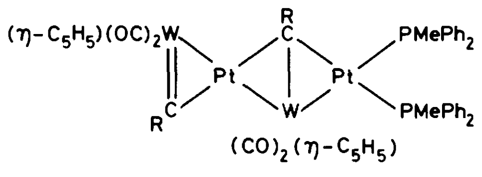
Non-S.I. unit employed: atm = 101 325 Pa.



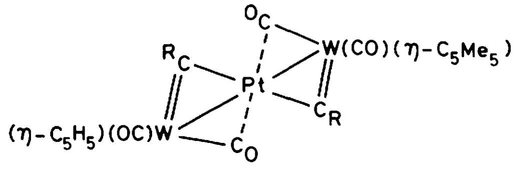
	M	R	L
(**1a**)	Pt	C_6H_4Me-4	η-C_5H_5
(**1b**)	Ni	C_6H_4Me-4	η-C_5H_5
(**1c**)	Pt	Me	η-C_5H_5
(**1d**)	Pt	Ph	η-C_5H_5
(**1e**)	Pt	Me	η-C_5Me_5
(**1f**)	Pt	Ph	η-C_5Me_5
(**1g**)	Pt	C_6H_4Me-4	η-C_5Me_5
(**1i**)	Ni	Me	η-C_5H_5
(**1j**)	Ni	Ph	η-C_5H_5
(**1k**)	Ni	Me	η-C_5Me_5
(**1l**)	Ni	Ph	η-C_5Me_5
(**1m**)	Ni	C_6H_4Me-4	η-C_5Me_5



	M	R	L
(**2a**)	Pt	C_6H_4Me-4	η-C_5H_5
(**2b**)	Pt	Me	η-C_5Me_5
(**2c**)	Pt	C_6H_4Me-4	η-C_5Me_5
(**2e**)	Ni	C_6H_4Me-4	η-C_5H_5
(**2f**)	Ni	C_6H_4Me-4	η-C_5Me_5



(**2d**) R = C_6H_4Me-4



(**1h**) R = C_6H_4Me-4

(μ-$PhC_2Ph)_2(PEt_3)_4$]. In these reactions, one or both of the terminally bound alkyne groups in the precursors [Pt(alkyne)$_2$] become bridging. These results suggested the interesting possibility that the compounds (**1**) might co-ordinate with suitable metal–ligand fragments *via* their C=W bonds. Depending on the bonding requirements of the added metal–ligand groups, the resulting products might have open or chain-like metal-containing structures, or alternatively have closed structures in which alkylidyne ligands cap a metal atom triangle. Metal-chain structures with transversely bridging μ-RC≡W(CO)$_2$-(η-C_5H_5) groups are likely to arise if mononuclear nickel or platinum fragments are added, since in their organo complexes these elements prefer a valence shell with 16 electrons and a co-ordination mode where they are ligated by four, three, or two ligands. Hence one can envisage, for example, adding a Pt(cod) fragment, or other ML_2 (d^{10}) carbene-like groups, to one or both of the C=W centres in the compounds (**1**), and subsequently displacing the cod ligand with C≡W so as to increase the length of the metal atom chain. It was with these ideas in mind that the studies reported herein were undertaken. Some of the results have been the subject of a preliminary communication.[5]

Results and Discussion

Trinuclear Metal Compounds.—The compounds [PtW_2(μ-$CR)_2(CO)_4L_2$] (**1c**)—(**1g**) (R = Me or Ph, L = η-C_5H_5; R = Me, Ph, or C_6H_4Me-4, L = η-C_5Me_5) were prepared by adding light petroleum or tetrahydrofuran (thf) solutions of [$Pt(C_2H_4)_3$], generated *in situ* from [$Pt(cod)_2$], to solutions of the appropriate alkylidynetungsten complex [W(≡CR)(CO)$_2$L] dissolved in the same solvent. The compound [PtW_2(μ-CC_6H_4Me-4)$_2(CO)_4$(η-C_5H_5)(η-C_5Me_5)] (**1h**) was obtained by adding [$Pt(C_2H_4)_3$] to a mixture of [W(≡CC_6H_4Me-4)-$(CO)_2$(η-C_5H_5)] and [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5Me_5)]. The platinumditungsten complexes were characterised by the data given in Tables 1—3. The various species are soluble in thf, CH_2Cl_2, or toluene and partially soluble in light petroleum from which they may be crystallised. The tolylmethylidyne and phenylmethylidyne derivatives are more robust than the methylmethylidyne compounds, and all are stable in solution for short periods of time. They may be routinely stored under nitrogen in the solid state, preferably in a refrigerator.

The nickel compounds [NiW_2(μ-$CR)_2(CO)_4L_2$] (**1i**)—(**1m**) (R = Me or Ph, L = η-C_5H_5; R = Me, Ph, or C_6H_4Me-4, L = η-C_5Me_5) were similarly prepared using [$Ni(cod)_2$] as the source of the nickel, and data for these complexes are given in Tables 1 and 2. The nickelditungsten species are less stable both thermally and to air than their platinum-containing analogues.

In the i.r. spectra of the compounds (**1a**) and (**1b**)[2] and (**1c**)—(**1m**) (Table 1) there is a band in the carbonyl stretching region in the range 1 820—1 785 cm^{-1} which may be attributed to semi-bridging or possibly in some cases bridging CO groups. As mentioned above, *X*-ray diffraction studies on (**1a**) and (**1b**)

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

Compound	Colour	Yield (%)	$\nu_{max.}(CO)$[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
(**1c**) $[PtW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5H_5)_2]$	Orange	88	1 963s, 1 937s, 1 817m br	25.5 (25.2)	2.0 (1.9)
(**1d**) $[PtW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$	Maroon	71	1 970s, 1 946s, 1 820m br	34.2 (34.2)	2.2 (2.0)
(**1e**) $[PtW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$	Orange	65	1 946s, 1 921s, 1 793m br	33.1 (33.6)	3.4 (3.6)
(**1f**) $[PtW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$	Maroon	94	1 950s, 1 929s, 1 795m br	41.0 (40.6)	3.7 (3.6)
(**1g**) $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$	Crimson	92	1 948s, 1 927s, 1 794m br	41.7 (41.7)	3.8 (3.8)
(**1h**) $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$	Crimson	42	1 958s, 1 935s, 1 806m br	38.7 (38.9)	3.2 (3.2)
(**1i**) $[NiW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5H_5)_2]$	Crimson	71	1 963s, 1 938s, 1 804m br	30.1 (29.9)	2.2 (2.2)
(**1j**) $[NiW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$	Black	75	1 970s, 1 949s, 1 805m br	39.5 (39.7)	2.4 (2.4)
(**1k**) $[NiW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$	Crimson	84	1 948s, 1 922s, 1 785m br	38.8 (39.0)	4.0 (4.2)
(**1l**) $[NiW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$	Maroon	78	1 954s, 1 933s, 1 790m br	46.2 (46.2)	4.1 (4.1)
(**1m**) $[NiW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$	Maroon	94	1 952s, 1 931s, 1 790m br	47.2 (47.3)	4.4 (4.4)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2.

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

Compound	^1H (δ)[b]	^{13}C (δ)[c]
(**1c**)	2.63 [s, 6 H, Me, J(PtH) 13], 5.65 (s, 10 H, C_5H_5)	318.9 [μ-C, J(PtC) 791, J(WC) 159], 223.6, 221.8, (CO), 91.4 (C_5H_5), 44.2 [Me, J(PtC) 60, J(WC) 22]
(**1d**)	5.73 (s, 10 H, C_5H_5), 7.15—7.54 (m, 10 H, Ph)	307.0 (μ-C), 225.3, 220.5 (CO), 153.2 [C^1(Ph)], 129.3, 128.3, 128.1 (Ph), 91.5 (C_5H_5)
(**1e**)	2.13 (s, 30 H, C_5Me_5), 2.46 [s, 6 H, Me, J(PtH) 16]	316.2 [μ-C, J(PtC) 758, J(WC) 162], 230.1 [CO, J(WC) 176, J(PtC) 27], 228.1 [CO, J(WC) 180, J(PtC) 35], 103.7 (C_5Me$_5$), 39.7 [Me, J(PtC) 51, J(WC) 22], 10.8 (C_5*Me*$_5$)
(**1f**)	2.05 (s, 30 H, C_5Me_5), 7.21—7.35 (m, 10 H, Ph)	[d]305.8 [μ-C, J(PtC) 792, J(WC) 164], 231.0, 229.0 (CO), 152.4 [C^1(Ph), J(PtC) 22], 129.3, 128.5, 127.6 (Ph), 104.5 (C_5Me$_5$), 10.8 (C_5*Me*$_5$)
(**1g**)	[e]2.06 (s, 30 H, C_5Me_5), 2.21 (s, 6 H, Me-4), 6.97, 7.27 [$(AB)_2$, 8 H, C_6H_4, J(AB) 8]	306.5 [μ-C, J(PtC) 786, J(WC) 162], 230.4 [CO, J(WC) 182, J(PtC) 37], 229.3 [CO, J(WC) 182, J(PtC) 37], 150.7 [$C^1(C_6H_4)$, J(PtC) 31], 137.8, 129.5, 129.2, 128.9 (C_6H_4), 104.4 (C_5Me$_5$), 21.8 (Me-4), 10.7 (C_5*Me*$_5$)
(**1h**)	[e]2.08 (s, 15 H, C_5Me_5), 2.22 (s, 6 H, Me-4), 5.60 (s, 5 H, C_5H_5), 6.96, 7.28 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 6.98, 7.42 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	[d]308.3 [μ-C, J(PtC) 798, J(WC) 159], 305.0 [μ-C, J(PtC) 826, J(WC) 159], 232.1, 226.6, 225.6, 223.9 (CO), 150.2 [$C^1(C_6H_4)$, J(PtC) 46], 149.6 [$C^1(C_6H_4)$, J(PtC) 37], 139.3, 138.6, 130.9, 129.5, 129.3 (C_6H_4), 104.6 (C_5Me$_5$), 91.7 (C_5H_5), 21.9 (Me-4), 11.0 (C_5*Me*$_5$)
(**1i**)[f]	2.35 (s, 6 H, Me), 5.57 (s, 10 H, C_5H_5)	
(**1j**)	5.54 (s, 10 H, C_5H_5), 7.10—7.33 (m, 10 H, Ph)	[d]315.2 [μ-C, J(WC) 172], 232.4 [CO, J(WC) 180], 223.6 [CO, J(WC) 190], 157.1 [C^1(Ph), J(WC) 27], 128.2, 127.8, 127.5 (Ph), 92.1 (C_5H_5)
(**1k**)	2.10 (s, 30 H, C_5Me_5), 2.14 (s, 6 H, Me)	[d]326.1 [μ-C, J(WC) 174], 237.3 [CO, J(WC) 184], 230.9 [CO, J(WC) 186], 103.6 (C_5Me$_5$), 41.6 [Me, J(WC) 24], 10.8 (C_5*Me*$_5$)
(**1l**)	1.96 (s, 30 H, C_5Me_5), 7.10—7.39 (m, 10 H, Ph)	[d]313.4 [μ-C, J(WC) 174], 236.0 [CO, J(WC) 184], 232.1 [CO, J(WC) 186], 157.3 [C^1(Ph), J(WC) 27], 128.1, 126.6, 125.7 (Ph), 104.4 (C_5Me$_5$), 10.8 (C_5*Me*$_5$)
(**1m**)	[e]1.98 (s, 30 H, C_5Me_5), 2.18 (s, 6 H, Me-4), 6.96, 7.14 [$(AB)_2$, 8 H, C_6H_4, J(AB) 8]	314.2 [μ-C, J(WC) 171], 235.5 [CO, J(WC) 184], 232.4 [CO, J(WC) 186], 155.0 [$C^1(C_6H_4)$, J(WC) 28], 136.8, 128.8, 126.1 (C_6H_4), 104.4 (C_5Me$_5$), 21.9 (Me-4), 10.7 (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_2Cl_2 unless otherwise stated. [c] Hydrogen-1 decoupled to high frequency of $SiMe_4$, measured in CD_2Cl_2–CH_2Cl_2. [d] Measured at −40 °C. [e] Measured in $CDCl_3$. [f] Compound decomposes in solution, $^{13}C\text{-}\{^1H\}$ spectrum not measured.

revealed that one CO group on each tungsten atom strongly semi-bridges the metal–metal bonds. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of all the compounds (Table 2) show a characteristic resonance for the μ-*C*R group in the range 326—305 p.p.m. The spectrum of compound (**1h**), which represents the only unsymmetrical trinuclear metal compound, shows two such peaks at δ 308.3 and 305.0 p.p.m. Except for complex (**1d**), for which the spectrum was not of sufficient quality, all the alkylidyne-carbon signals of the platinum-containing compounds show ^{195}Pt satellite peaks [J(PtC) *ca.* 760—830 Hz]. The $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectra of (**1c**)—(**1h**) (Table 3) show a singlet peak with ^{183}W satellites. The ^{183}W–^{195}Pt couplings are significantly larger for the μ-CMe species (**1c**) and (**1e**).

Tetranuclear Metal Compounds.—Having prepared the compounds (**1**) it was then possible to investigate whether or not a Pt(cod) fragment could be added to one or both of the two C=W bonds present in these species. Treatment of (**1a**) in toluene with one equivalent of an ethylene-saturated solution of $[Pt(cod)_2]$ afforded the orange crystalline compound $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)_2]$ (**2a**). The related compounds $[Pt_2W_2(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(cod)L_2]$ [R = Me, L = η-C_5Me_5 (**2b**); R = C_6H_4Me-4, L = η-C_5Me_5 (**2c**)] and $[NiPtW_2(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(cod)L_2]$ [R = C_6H_4Me-4, L = η-C_5H_5 (**2e**); R = C_6H_4Me-4, L = η-C_5Me_5 (**2f**)] were similarly prepared from (**1e**) and (**1g**), and from (**1b**) and (**1m**), respectively, using thf as solvent. The ethylene present

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

Compound	δ[b]	J(WPt)	J(PtPt)
(1c)	1 723	196	
(1d)	1 670	176	
(1e)	1 728	191	
(1f)	1 740	166	
(1g)	1 717	166	
(1h)	1 685	176	
(2a)[c]	1 367	186, 112	1 221
	354	118	1 223
	*1 103	186, 108	1 236
	*409		1 236
(2b)[c]	*1 437	166	1 240
	*320		1 230
	1 287	205, 127	1 221
	377		1 221
(2c)[c]	1 152	166	1 221
	380	127	1 221
	*1 417	156	1 143
	*325		1 143
(2d)[d]	1 273[e]		1 924
	1[e]		1 924
(2e)	457		
(2f)[c]	439	142	
	*481	136	
(3a)[c]	932		
	516		
	*916		
	*360		
(3b)	865	175, 118	1 289, 1 230
	475		1 230
	296		1 299
(4a)[f]	**(A)** 1 620	136	
	(A′) 1 332	156, 97	
	(B) *1 725		1 523
	*1 377	137	1 523
(4b)[f]	**(A)** 1 424	190, 117	
	(B) *1 772	205, 146	1 187
	*1 343	166, 142	1 187
(4c)[f]	**(A)** 1 668	166	
	(A′) 1 400		
	(B) *1 860	186, 146	1 299
	*1 338	146	1 299
(5a)[f]	**(A)** *1 419		
	*1 415		
	(B) 1 865	197, 137	1 318
	1 330	157	1 309
(5b)[f]	**(A)** 1 710		1 132
	1 621		1 132
	(A′) 1 425	176, 98	1 938
	1 362		1 938
	(B) 1 849	146	1 445
	1 327	156	1 445
	(B′) 1 826		1 338
	1 405		1 338

[a] Chemical shifts are in p.p.m., coupling constants are in Hz. Measurements are in CD_2Cl_2–CH_2Cl_2. [b] δ Values are to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz. [c] Peaks asterisked in spectra of **(2a)**—**(2c)**, **(2f)**, and **(3a)** refer to the minor isomer (see text). [d] Phosphorus-31 n.m.r.: δ [relative to 85% H_3PO_4 (external), measured in $CDCl_3$], 8.5 [d, J(PP) 8, J(PtP) 3 374, 16] and 5.6 p.p.m. [d, J(PP) 8, J(PtP) 3 687, 39 Hz]. [e] d of d signals, J(PPt) 39 and 16. [f] Letters **(A)** and **(A′)** refer to data for symmetric isomers, **(B)** and **(B′)** to data for asymmetric isomers (see text). Asterisk refers to data for minor isomer. In **(4a)**—**(5b)** absolute stereochemistry is not implied by the letters **A**, **A′**, **B**, and **B′**.

Table 4. Analytical[a] and physical data for the tetra- and penta-nuclear metal complexes

Compound	Colour	Yield (%)	$\nu_{max.}(CO)$[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
(2a) $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)_2]$	Orange	80	1 935s, 1 837s br, 1 737m br	35.1 (34.7)	2.9 (2.7)
(2b) $[Pt_2W_2(\mu\text{-}CMe)(\mu_3\text{-}CMe)(CO)_4(cod)(\eta\text{-}C_5Me_5)_2]$	Brown	82	1 916m br, 1 796s br, 1 715m br	33.5 (33.2)	3.8 (3.7)
(2c) $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5Me_5)_2]$	Brown	78	1 923s br, 1 806s br, 1 715m br	40.0 (39.6)	3.9 (3.9)
(2d) $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)_2]$	Orange	90	1 932s, 1 866m, 1 765s br	42.2 (41.8)	3.3 (3.1)
(2e) $[NiPtW_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)_2]$	Brown	61	1 931m, 1 833s br, 1 734m br	38.5 (38.7)	3.1 (3.1)
(2f) $[NiPtW_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5Me_5)_2]$	Brown	57	1 917m, 1 809s br, 1 715m br	43.2 (43.7)	4.3 (4.3)
(3a) $[Pt_3W_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]$	Brown	85	1 836s br, 1 729s br	33.3 (33.5)	3.1 (2.9)
(3b) $[Pt_3W_2(\mu_3\text{-}CMe)_2(CO)_4(cod)_2(\eta\text{-}C_5Me_5)_2]$	Brown	35	1 809s, 1 775s, 1 712s	33.1 (32.9)	3.6 (3.7)
(4a) $[Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$	Black	95	1 951s br, 1 845s br	33.4 (33.5)	2.5 (2.2)
(4b) $[Pt_2W_3(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5Me_5)_3]$	Brown	90	1 936s, 1 847m br, 1 807m br	31.4 (31.6)	3.5 (3.4)
(4c) $[Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5Me_5)_3]$	Brown	98	1 936s, 1 823m br, 1 794m br	39.6 (39.5)	3.6 (3.7)
(5a) $[Pt_2W_3(\mu\text{-}CMe)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$	Brown	90	1 941s, 1 859m br, 1 817m br	31.9 (32.2)	2.8 (3.0)
(5b) $[Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$	Brown	94	1 939s, 1 830m br	38.8 (37.6)	3.5 (3.2)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2.

Table 5. Hydrogen-1 and carbon-13 n.m.r. data[a] for the tetra-and penta-nuclear metal complexes

Compd.	^{1}H (δ)[b]	^{13}C (δ)[c]
(2a)	2.22 (s, 6 H, Me-4), 2.25 (s, 6 H, Me-4), 2.00—2.80 (m, 16 H, CH_2), 4.00—5.60 (m, 8 H, CH), 5.24 (s, 5 H, C_5H_5), 5.35* (s, 5 H, C_5H_5), 5.52* (s, 5 H, C_5H_5), 5.60 (s, 5 H, C_5H_5), 6.82—7.46 (m, 16 H, C_6H_4)	314.5* [μ-C, *J*(PtC) 764], 310.6 [μ-C, *J*(PtC) 922], 260.7* [μ_3-C, *J*(PtC) 612, 576], 251.7 [μ_3-C, *J*(PtC) 660, 580], 242.4* [*J*(PtC) 245], 241.6 [*J*(PtC) 248], 234.4,* 233.1,* 230.2 [*J*(PtC) 32], 228.7 [*J*(PtC) 39], 221.5,* 220.9 [CO, *J*(PtC) 22], 153.1,* 152.7,* 151.7, 151.4 [$C^1(C_6H_4)$], 138.5—127.4 (C_6H_4), 111.3, 104.0, 102.8, 95.8 (CH), 92.3, 91.5 (C_5H_5), 32.5, 31.5, 30.5, 29.9, 29.5, 27.6 (CH_2), 21.7, 20.9 (Me-4)
(2b)	2.02* (s, 15 H, C_5Me_5), 2.03 (s, 15 H, C_5Me_5), 2.05* (s, 15 H, C_5Me_5), 2.06 (s, 15 H, C_5Me_5), 2.07—2.70 (m, 16 H, CH_2), 2.26 [s, 3 H, μ-CMe, *J*(PtH) 7], 2.46* (s, 3 H, μ-CMe), 3.07* [s, 3 H, μ_3-CMe, *J*(PtH) 8], 3.34 [s, 3 H, μ_3-CMe, *J*(PtH) 8], 4.40—5.20 (m, 8 H, CH)	[d] 320.3 [μ-C, *J*(PtC) 689], 316.4* [μ-C, *J*(PtC) 852], 260.7 [μ_3-C, *J*(PtC) 586, 504], 252.5* [μ_3-C, *J*(PtC) 576], 249.2 [*J*(PtC) 264], 249.1 [*J*(PtC) 254], 238.4, 238.2, 236.8, 234.9, 229.3, 227.3 (CO), 108.8, 107.6 (CH), 103.4, 103.1, 101.8, 101.7 (C_5Me_5), 101.2, 98.3, 97.3 (2 C), 97.0, 95.0 (CH), 40.6 [μ- or μ_3-CMe, *J*(PtC) 17], 39.4 (μ- or μ_3-CMe), 31.8, 31.3, 30.7 (2 C), 30.4, 30.2, 28.7, 28.3 (CH_2), 10.6, 10.5, 10.3, 9.9 (C_5Me_5)
(2c)	1.94 (s, 15 H, C_5Me_5), 1.95 (s, 30 H, C_5Me_5), 1.96* (s, 15 H, C_5Me_5), 2.26 (s, 6 H, Me-4), 2.35 (s, 6 H, Me-4), 2.05—2.80 (m, 16 H, CH_2), 3.80—5.00 (m, 8 H, CH), 6.85—7.32 (m, 16 H, C_6H_4)	315.6 [μ-C, *J*(PtC) 740], 312.0* (μ-C), 262.9 [μ_3-C, *J*(PtC) 556], 254.3* (μ_3-C), 249.0 [*J*(PtC) 270], 240.7, 238.0*, 237.9, 226.4, 226.0* (CO), 152.1,* 151.5, 149.9 [$C^1(C_6H_4)$], 137.5—126.7 (C_6H_4), 108.4,* 107.3, 104.8 (CH), 104.4, 103.6,* 103.1, 103.0 (C_5Me_5), 100.2,* 98.1, 97.4,* 97.0 (CH), 33.5, 33.2,* 32.3,* 31.9, 27.4,* 26.9 (3 C, CH_2), 21.8, 21.0 (Me-4), 10.5,*, 10.2, 10.1,* 9.9 (C_5Me_5)
(2d)	[e] 1.08 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 24], 1.68 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 34], 2.11 (s, 3 H, Me-4), 2.21 (s, 3 H, Me-4), 4.53 (s, 5 H, C_5H_5), 5.61 (s, 5 H, C_5H_5), 6.80—7.80 (m, 28 H, Ph and C_6H_4)	311.8 [μ-C, *J*(PtC) 904, 20], 252.8 [d, μ_3-C, *J*(PC) 51, *J*(PtC) 460], 240.0, 231.1, 227.5, 224.0 (CO), 157.2 [$C^1(C_6H_4)$, *J*(PtC) 54], 156.3 [$C^1(C_6H_4)$], 142.0—122.7 (C_6H_4 and Ph), 92.5, 91.4 (C_5H_5), 21.6, 20.9 (Me-4), 16.3 [d, MeP, *J*(PC) 31, *J*(PtC) 28], 10.5 [d, MeP, *J*(PC) 30, *J*(PtC) 36]
(2e)	2.15 (s, 3 H, Me-4), 2.32 (s, 3 H, Me-4), 2.10—2.80 (m, 8 H, CH_2), 4.00—5.00 (m, 4 H, CH), 5.01 (s, 5 H, C_5H_5), 5.50 (s, 5 H, C_5H_5), 6.94—7.24 (m, 8 H, C_6H_4)	323.2 (μ-C), 266.6 [μ_3-C, *J*(PtC) 610], 242.2 [*J*(PtC) 226], 241.0, 235.8, 223.1 (CO), 158.9, 155.2 [$C^1(C_6H_4)$], 136.9—123.8 (C_6H_4), 111.4, 105.3, 103.5, 93.6 (CH), 92.7, 91.8 (C_5H_5), 30.4, 29.4 (CH_2), 21.8, 21.0 (Me-4)
(2f)	1.76* (s, 30 H, C_5Me_5), 1.93 (s, 15 H, C_5Me_5), 1.94 (s, 15 H, C_5Me_5), 2.18 (s, 3 H, Me-4), 2.22* (s, 3 H, Me-4), 2.28 (s, 3 H, Me-4), 2.36* (s, 3 H, Me-4), 2.05—2.80 (m, 16 H, CH_2), 4.00—5.00 (m, 8 H, CH), 6.93—7.45 (m, 16 H, C_6H_4)	[d] 324.8 (μ-C), 321.7* (μ-C), 267.2* (μ_3-C), 252.8 (μ_3-C), 252.1, 250.5, 247.4, 226.8 (CO), 155.1 [$C^1(C_6H_4)$], 152.8 [$C^1(C_6H_4)$, *J*(PtC) 37], 137.4—125.4 (C_6H_4), 108.8, 107.9,* 105.5 (CH), 104.3, 103.6 (C_5Me_5), 103.2 (CH), 103.1, 103.0 (C_5Me_5), 100.6,* 95.6, 94.5* (CH), 34.0,* 33.2, 32.3, 32.0,* 28.2, 27.1, 26.3* (CH_2), 22.0, 21.1 (Me-4), 10.4, 10.3 (C_5Me_5)
(3a)	[e] 2.23* (s, 6 H, Me-4), 2.33 (s, 6 H, Me-4), 2.10—2.70 (m, 16 H, CH_2), 4.40—5.10 (m, 8 H, CH), 5.22 (s, 10 H, C_5H_5), 5.47* (s, 10 H, C_5H_5), 6.67,* 6.80* [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8], 6.93, 7.03 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8]	[d,e] 257.5 [2 μ_3-C, *J*(PtC) 590], 248.3* (2 μ_3-C), 243.8,* 243.0, 229.3 (CO), 152.9, 149.7* [$C^1(C_6H_4)$], 134.0—127.0 (C_6H_4), 110.9,* 110.2, 104.6,* 104.1,* 102.1, 94.9* (CH), 93.0, 91.5 (C_5H_5), 86.9 (CH), 33.1 (2 C), 31.5,* 29.5,* 28.9,* 27.2,* 26.9, 26.1 (CH_2), 21.1, 20.8* (Me-4)
(3b)	1.93 (s, 15 H, C_5Me_5), 1.99 (s, 15 H, C_5Me_5), 2.00—3.28 (m, 8 H, CH_2), 3.07 [s, 3 H, Me, *J*(PtH) 7], 3.27 (s, 3 H, Me), 4.30—5.20 (m, 4 H, CH)	[d] 253.9 [μ_3-C, *J*(PtC) 562], 252.3 [μ_3-C, *J*(PtC) 620], 251.4 [*J*(PtC) 304], 246.4 [*J*(PtC) 166], 240.9, 240.0 (CO), 107.9, 106.8, 103.3 (CH), 101.8, 100.9 (C_5Me_5), 100.1, 98.0 (2 C), 96.5, 90.5 (CH), 34.7, 33.6 (CH_2), 33.2 (Me), 32.8, 31.3, 29.1, 27.9, 26.6, 26.4 (CH_2), 10.3, 9.9 (C_5Me_5)
(4a)	2.14 (s, 6 H, Me-4), 2.26 (s, 6 H, Me-4), 2.31 (s, 6 H, Me-4), 2.20—2.32* (m, 9 H, Me-4), 5.19* (s, 5 H, C_5H_5), 5.30 (s, 10 H, C_5H_5), 5.38 (s, 20 H, C_5H_5), 5.48* (s, 5 H, C_5H_5), 5.59* (s, 5 H, C_5H_5), 6.50—7.70 (m, 36 H, C_6H_4)	317.1 [2 μ-C, *J*(PtC) 833, *J*(WC) 151], 314.8* [μ-C, *J*(PtC) 823], 308.8* (μ-C), 307.7 [2 μ-C, *J*(PtC) 916], 262.7 [μ_3-C, *J*(PtC) 603], 257.3 [μ_3-C, *J*(PtC) 611], 256.7* (μ_3-C), 230.7, 230.1, 227.3, 224.9, 221.0, 219.2 (CO), 153.1—127.4 (C_6H_4), 92.9, 92.6, 92.2, 91.4, 90.9 (C_5H_5), 21.7, 21.4 (Me-4)
(4b)	2.07 (s, 15 H, C_5Me_5), 2.09 (s, 45 H, C_5Me_5), 2.11 (s, 30 H, C_5Me_5), 2.38* (s, 3 H, μ-CMe), 2.50* (s, 3 H, μ-CMe), 2.67 (s, 6 H, μ-CMe), 3.03 (s, 3 H, μ_3-CMe), 3.09* (s, 3 H, μ_3-CMe)	[d] 325.3* (μ-C), 325.0 [2 μ-C, *J*(PtC) 718], 317.6* [μ-C, *J*(PtC) 845], 270.7* (μ_3-C), 268.7 [μ_3-C, *J*(PtC) 530, *J*(WC) 194], 238.1 [*J*(WC) 174], 236.9,* 231.7,* 231.5, 230.6,* 228.3, 224.4 [*J*(WC) 176], 220.0* (CO), 103.6, 103.1, 102.5,* 102.4 (C_5Me_5), 41.4,* 41.2, 39.0, 34.7 (μ-CMe), 11.0, 10.5, 9.7, 9.4* (C_5Me_5)
(4c)	1.82* (s, 30 H, C_5Me_5), 1.84 (s, 60 H, C_5Me_5), 1.92* (s, 15 H, C_5Me_5), 1.97 (s, 30 H, C_5Me_5), 2.16 (s, 9 H, Me-4), 2.29 (s, 18 H, Me-4), 6.35—7.66 (m, 36 H, C_6H_4)	[d] 318.7* (μ-C), 316.3 [2 μ-C, *J*(PtC) 796], 307.1* (μ-C), 265.5* (μ_3-C), 263.4 [μ_3-C, *J*(PtC) 580], 237.8, 236.8 (2 CO), 224.2, 222.7, 219.5 (CO), 152.9—123.9 (C_6H_4), 104.2, 103.3, 103.1,* 102.9* (C_5Me_5), 21.8, 21.6 (Me-4), 10.8,* 10.3, 9.3* (C_5Me_5)
(5a)	1.85 (s, 15 H, C_5Me_5), 2.01* (s, 15 H, C_5Me_5), 2.09* (s, 15 H, C_5Me_5), 2.10 (s, 15 H, C_5Me_5), 2.24* (s, 3 H, Me-4), 2.28 (s, 3 H, Me-4), 2.80 (s, 3 H, μ-CMe), 3.00 (s, 3 H, μ-CMe), 3.25* (s, 3 H, μ-CMe), 5.54* (s, 5 H, C_5H_5), 5.56 (s, 5 H, C_5H_5), 7.04—7.33 (m, 8 H, C_6H_4)	[d] 326.3* (μ-C), 325.5 [μ-C, *J*(PtC) 740, *J*(WC) 159], 313.9* (μ-C), 308.4 [μ-C, *J*(PtC) 932], 275.3* (μ_3-C), 272.1 [μ_3-C, *J*(PtC) 588, 520, *J*(WC) 130], 237.5 [*J*(WC) 172], 237.3 [*J*(WC) 172], 229.6, 228.5, 220.1, 217.2 (CO), 154.6 [$C^1(C_6H_4)$, *J*(WC) 20], 152.7* [$C^1(C_6H_4)$], 138.9—124.1 (C_6H_4), 103.7, 103.4,* 103.0,* 102.6 (C_5Me_5), 92.5,* 91.4 (C_5H_5), 41.6, 35.1 (μ-CMe), 21.8 (Me-4), 10.5, 9.4,* 9.2 (C_5Me_5)
(5b)	1.84 (s, 15 H, C_5Me_5), 1.97 (s, 15 H, C_5Me_5), 2.13 (s, 3 H, Me-4), 2.15 (s, 3 H, Me-4), 2.31 (s, 3 H, Me-4), 5.36 (s, 5 H, C_5H_5), 6.12—7.69 (m, 12 H, C_6H_4)	328.7, 317.9, 317.5 (μ-C), 270.7, 264.9 (μ_3-C), 236.8 (CO), 151.0—128.3 (C_6H_4), 104.3, 103.8, 103.4, 103.1 (C_5Me_5), 92.3, 91.4, 90.9 (C_5H_5), 21.8, 21.6 (Me-4), 10.8, 10.6, 10.4, 9.3 (C_5Me_5)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, and measurements at room temperature unless otherwise stated. Peaks marked with an asterisk correspond to the minor isomer. [b] Measured in CD_2Cl_2 unless otherwise stated. [c] Hydrogen-1 decoupled chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2 at room temperature unless otherwise stated. Signals due to CH groups of cod ligands show ^{195}Pt satellite peaks with *J*(PtC) 80—150 Hz. [d] Measured at −40 °C. [e] Measured in $CDCl_3$.

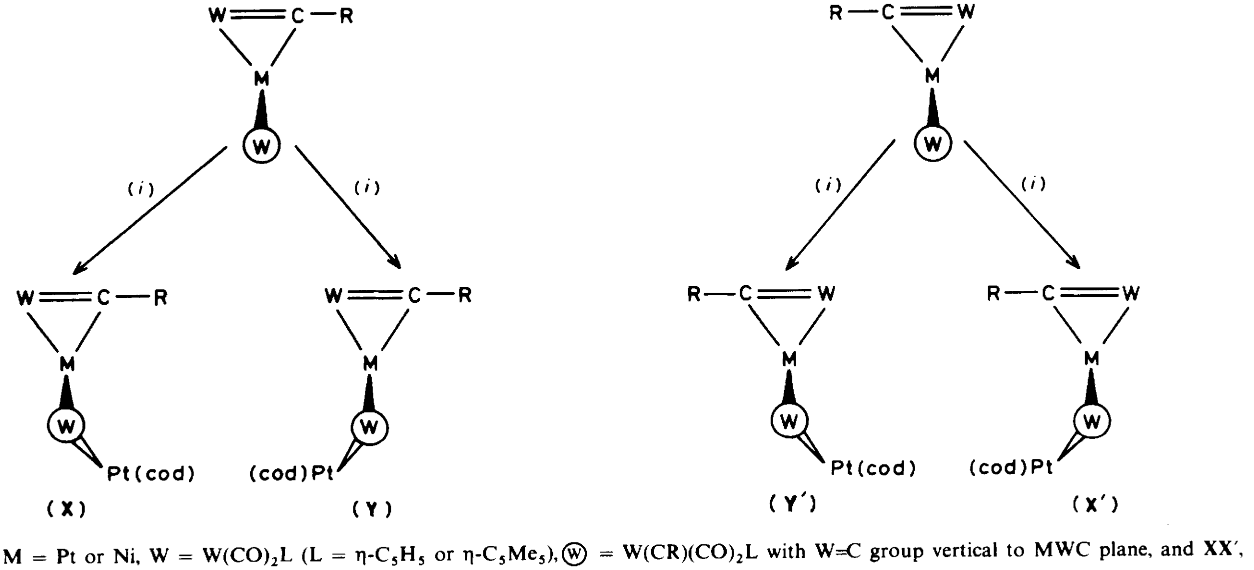
labilises the cod ligands on the platinum, and probably the reactive species are the 'mixed' olefin complexes $[Pt(C_2H_4)_n(cod)]$ (n = 1 or 2).[6] The cod ligand in the product (**2a**) is readiiy displaced by an excess of $PMePh_2$ in CH_2Cl_2 to give $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)_2]$ (**2d**). Substitution of cod ligands by different phosphines is also possible, as is the possibility of adding different $Pt(PR_3)_2$ fragments to the trinuclear metal compounds.

Data for the new compounds (**2**) are summarised in Tables 3—5. They are stable in air for reasonable periods, but are best stored under nitrogen in a refrigerator. In their i.r. spectra measured in CH_2Cl_2 (Table 4), they all show a band in the range 1 765—1 715 cm^{-1}, suggesting the presence of strongly semi-bridging CO ligands. The n.m.r. data [$^{195}Pt\text{-}\{^1H\}$ (Table 3), and ^1H and $^{13}C\text{-}\{^1H\}$ (Table 5)] support the structures proposed for these tetranuclear metal compounds. However, for each species, except (**2d**) and (**2e**), two isomers are present in solution. Assignments, of resonances in Tables 3 and 5 have been made on the basis of relative peak intensities, with peaks due to the minor isomer being marked with an asterisk. The isomeric proportions for each complex are *ca.* 2:1 for (**2a**), 1.2:1 for (**2b**), 3:1 for (**2c**), and 2:1 for (**2f**). The $^{195}Pt\text{-}\{^1H\}$ data are the more informative since in the ^1H and $^{13}C\text{-}\{^1H\}$ spectra signals due to the minor isomer are in some instances obscured by, or are coincident with, signals for the major isomer, thus making assignments difficult.

For the diplatinum compounds (**2a**)—(**2c**) the $^{195}Pt\text{-}\{^1H\}$ spectra (Table 3) would be expected to show two resonances for each isomer; one for the Pt(cod) group and one for the platinum linking the two tungsten atoms. In agreement, the spectrum of (**2a**) has two sets of signals at δ 1 367 and 354 p.p.m., and at δ 1 103 and 409 p.p.m., respectively. For each pair, the resonance with the largest chemical shift is assigned to the platinum linked to two tungstens, and the smaller shift to the Pt(cod) group. These assignments are made on the basis of the data for (**2e**) and (**2f**) and those for the trinuclear metal compounds (**1c**)—(**1h**). Thus in the spectrum of (**2f**), a complex without a W–Pt–W group, there are two peaks at 481 and 439 p.p.m., corresponding to Pt(cod) groups in different environments in the two isomers of this species. Similarly, for (**2e**) one isomer is observed with the ^{195}Pt resonance at 457 p.p.m., corresponding to the Pt(cod) group. These chemical shifts are similar to one of the signals seen for each isomer of (**2a**)—(**2c**). Moreover, the other resonance observed for each isomer of (**2a**)—(**2c**) (*ca.* 1 100—1 400 p.p.m.) is more comparable with the single peak observed in the spectra of (**1c**)—(**1h**) (*ca.* 1 670—1 740 p.p.m.) which contain W–Pt–W groups with edge-bridging alkylidyne ligands. Interestingly, compounds (**2d**) and (**2e**) had spectra indicating the presence of only one isomer in solution. This should not be taken to mean that only one isomer exists for these species, since the observation may merely reflect the experimental procedures employed in the syntheses, or the variable solubility of the different isomers present.

The presence of an edge-bridging and a triply bridging alkylidyne group in the compounds (**2**) is clearly evident from their $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (Table 5). For each of the compounds for which two isomers are present, *viz.* (**2a**)—(**2c**) and (**2f**), the spectra show a pattern of four resonances in the range 325—252 p.p.m. In each spectrum two of the peaks appear above 300 p.p.m. and two below 300 p.p.m. Those above 300 p.p.m. may be assigned to *C*R groups which are edge-bridging a metal–metal bond,[7] and those below 300 p.p.m. to *C*R groups bridging three metal centres.[8] For compound (**2a**) the resonances for the alkylidyne carbon nuclei are seen at δ 314.5, 310.6, 260.7, and 251.7 p.p.m. Those signals at δ 310.6 and 251.7 p.p.m. are assigned to the major isomer on the basis of their greater peak intensities. It it noteworthy that the resonance for the triply bridging alkylidyne carbon nucleus for each isomer shows two distinct $^{195}Pt\text{–}^{13}C$ couplings [δ 260.7 p.p.m., *J*(PtC) 612 and 576 Hz, and δ 251.7 p.p.m., *J*(PtC) 660 and 580 Hz], in accord with structures having a $\mu_3\text{-}CPt_2W$ system with two platinum nuclei in different environments. Resonances for the edge-bridging μ-C nuclei occur at δ 314.5 p.p.m. (minor isomer) and 310.6 p.p.m. (major isomer) with *J*(PtC) values of 764 and 922 Hz, respectively. These couplings are significantly larger than those for the μ_3-C nuclei. The formation of (**2e**) as a single isomer is confirmed by the appearance of only two alkylidyne carbon resonances at δ 323.2 (μ-C) and 266.6 (μ_3-C) p.p.m. with only the latter showing $^{195}Pt\text{–}^{13}C$ coupling (610 Hz). In agreement, the $^{195}Pt\text{-}\{^1H\}$ spectrum of (**2e**) (Table 3) shows a single peak at δ 457 p.p.m. In contrast the other nickel-containing tetranuclear metal complex (**2f**) has two resonances (δ 439 and 481 p.p.m.) in its $^{195}Pt\text{-}\{^1H\}$ spectrum, with four alkylidyne carbon signals (δ 324.8, 321.7, 267.2, and 252.8 p.p.m.) in the $^{13}C\text{-}\{^1H\}$ spectrum, confirming the presence of two isomers. The detection of only one isomer of (**2e**) may be due to the insolubility of a second conformer.

The formation of isomers in the synthesis of compounds

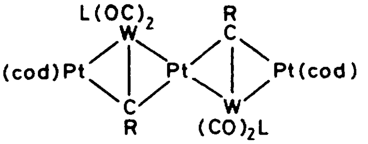


Scheme. M = Pt or Ni, W = $W(CO)_2L$ (L = η-C_5H_5 or η-C_5Me_5), Ⓦ = $W(CR)(CO)_2L$ with W≡C group vertical to MWC plane, and XX′, YY′ are enantiomeric pairs. (*i*) + Pt(cod)

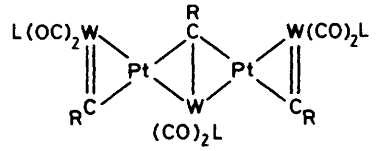
Table 6. Selected interatomic distances (Å) and angles (°) for the compound $[Pt_3W_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]\cdot CH_2Cl_2$ (**3a**)

Pt(1)–W(1)	2.751(1)	Pt(1)–C	2.078(10)	Pt(1) ··· C(2)	2.34(1)	Pt(2) ··· C(1)	2.27(1)
Pt(1) ··· Pt(2)	3.089(1)	Pt(2)–C	2.072(11)	W(1)–C(2)	1.99(1)	C–C(01)	1.49(2)
Pt(2)–W(1)	2.748(1)	W(1)–C	2.022(11)	W(1)–C(1)	1.97(1)	C(1)–O(1)	1.18(1)
Pt(2)–C(21)	2.25(1)	Pt(2)–C(22)	2.25(1)	Pt(2)–C(25)	2.24(1)	C(2)–O(2)	1.16(2)
Pt(2)–C(26)	2.25(1)	W(1)–C(cp)[a]	2.36(1)				
Pt(2)–W(1)–Pt(1)	68.4(1)	W(1)–Pt(1)–W(1′)[b]	176.0(1)	Pt(1)–C–W(1)	84.3(4)	Pt(2)–C–W(1)	84.3(4)
Pt(2)–C–Pt(1)	96.2(5)	Pt(2)–C–C(01)	122.1(7)	Pt(1)–C–C(01)	117.5(7)	W(1)–C–C(01)	140.4(8)
W(1)–C(1)–O(1)	158.2(10)	W(1)–C(2)–O(2)	166.4(10)	Pt(2)–C(1)–W(1)	80.4(4)	Pt(1)–C(2)–W(1)	78.5(5)

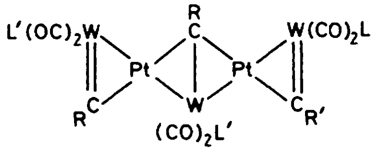
[a] Mean distance to cyclopentadienyl carbons. [b] Primes are used to denote atoms related by the crystallographic two-fold axis.



	R	L
(**3a**)	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$
(**3b**)	Me	$\eta\text{-}C_5Me_5$



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



	R	R′	L	L′
(**5a**)	Me	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$	$\eta\text{-}C_5Me_5$
(**5b**)	$C_6H_4Me\text{-}4$	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$	$\eta\text{-}C_5Me_5$

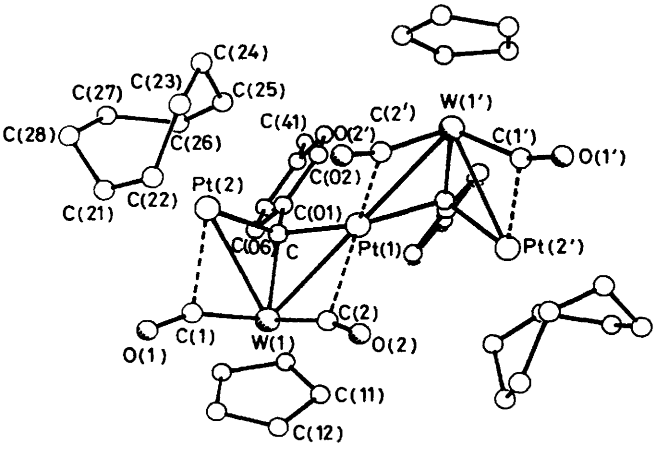


Figure 1. The molecular structure of $[Pt_3W_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]\cdot CH_2Cl_2$ (**3a**) showing the crystallographic numbering

(**2a**)—(**2c**) and (**2f**) is understandable in terms of the direction of addition of Pt(cod) fragments to the precursors (**1a**), (**1e**), (**1g**), and (**1m**), respectively (Scheme). The trinuclear metal compounds are enantiomeric, and addition of a Pt(cod) fragment can occur in four ways to afford the enantiomeric pairs **X**, **X′** and **Y**, **Y′**. The individual members of each pair (enantiomers) are not distinguishable by n.m.r. spectroscopy, but since the two pairs are stereoisomers each would give rise to its own characteristic n.m.r. signals, as is observed.

Pentanuclear Metal Complexes.—Having prepared the compounds (**2a**)—(**2c**), (**2e**), and (**2f**) by adding one equivalent of $[Pt(cod)_2]$ to the appropriate trinuclear metal complex it was of interest to establish whether the trinuclear metal compounds would add Pt(cod) groups to both C=W centres on treatment with an excess of $[Pt(cod)_2]$ so as to produce compounds containing Pt_3W_2 chains. This expectation has been realised in reactions between an excess of $[Pt(cod)_2]$ and (**1a**) and (**1e**) in ethylene-saturated thf, thereby affording the stable pentanuclear metal complexes $[Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(cod)_2L_2]$ [$R = C_6H_4Me\text{-}4$, $L = \eta\text{-}C_5H_5$ (**3a**); R = Me, $L = \eta\text{-}C_5Me_5$ (**3b**)], data for which are given in Tables 3—5.

Suitable crystals of (**3a**) were available for an *X*-ray diffraction study and the results are summarised in Table 6 and the molecular structure is shown in Figure 1. The five-metal atom framework is symmetrical since it lies astride a two-fold rotation axis, and crystallising in a centrosymmetric space group two enantiomers are simultaneously observed. The structure can be regarded as comprising two 'butterfly' μ_3-CPt_2W fragments sharing a wing-tip vertex Pt(1). The sides of the isosceles metal triangles [Pt(1)–W(1) 2.751(1), Pt(2)–W(1) 2.748(1), and Pt(1)$\cdots$Pt(2) 3.089(1) Å] are essentially symmetrically bridged by the CC_6H_4Me-4 groups [C–Pt(1) 2.078(10), C–Pt(2) 2.072(11), and C–W(1) 2.022(11) Å]. These dimensions may be compared with those in $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ [Pt–W 2.758(3), Pt$\cdots$Pt 2.989(3), μ-C–Pt 2.06(4), and μ-C–W 2.04(4) Å],[9] a molecule which also has a 'butterfly' μ_3-CPt_2W core.

The terminal Pt atoms each carry a cod ligand in the tub form with mean Pt–C separations of 2.25(1) Å, and angle of 'bite' 84°.[6] The CO ligands semi-bridge the Pt–W bonds [W–C(1)–O(1) 158.2(10), W(1)–C(2)–O(2) 166.4(10)°], with Pt–C(O) distances of *ca.* 2.3 Å. The two metal triangles [Pt(2)W(1)Pt(1) and Pt(2′)W(1′)Pt(1)] are inclined at 15° to one another, whereas the dihedral angle between the two symmetry-related μ-CPtW triangles is 92°. The tolyl groups are parallel within 15°, and lie perpendicular to the metal triangles to which they are attached *via* μ_3-C, but are inclined (30°) to the Pt(1)$\cdots$Pt(2) [Pt(1)$\cdots$Pt(2′)] vector. The semi-bridging CO ligands are on the same side of the metal atom plane, and are approximately equidistant from it (1.2 and 1.5 Å), while the CC_6H_4Me-4 ligands are on the opposite side (−1.2 Å).

From the n.m.r. data for (**3a**) and (**3b**) (Tables 3 and 5) it is evident that the former was prepared as a mixture of two isomers (*ca.* 2:1), and the latter as a single isomer. The particular crystal of (**3a**) studied by *X*-ray diffraction corresponds to an isomer of this complex with a symmetrical structure (two-fold axis of symmetry) and the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum should, therefore, show two resonances for this isomer. However, the observed spectrum (Table 3) shows two pairs of resonances at δ 932 and 516, and at 916 and 360 p.p.m., and this corresponds to the presence in solution of two symmetrical isomers. Due to the poor quality of the spectrum and low solubility of the complex, $^{195}Pt\text{–}^{195}Pt$ coupling was not resolved. The resonances at δ 516 and 360 p.p.m. are assigned to the Pt(cod) groups in each diastereoisomer, and the signals at 932 and 916 p.p.m. to the central platinum atoms of each species. In accord with the symmetrical structures of the two isomers, the $^{13}C\text{-}\{^1H\}$ data (Table 5) reveal one μ_3-C resonance for each conformer, each of the two μ_3-C groups being equivalent.

In contrast to (**3a**), the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum of (**3b**) shows three resonances at δ 865, 475, and 296 p.p.m. The signal at 865 p.p.m. may be ascribed to the central platinum and the last two to Pt(cod) groups in different chemical environments. In agreement, the resonance at δ 865 p.p.m. shows two distinct $^{195}Pt\text{–}^{195}Pt$ couplings (1 289 and 1 230 Hz) and two $^{183}W\text{–}^{195}Pt$ couplings (175 and 118 Hz). In the $^{13}C\text{-}\{^1H\}$ spectrum the two μ_3-C signals would each be expected to show two $^{195}Pt\text{–}^{13}C$ couplings, however, only one coupling was resolved for each resonance (562 and 620 Hz, see Table 5). Evidently the terminal Pt(cod) groups in (**3b**) are not rotating since eight resonances for the CH_2 groups of the two Pt(cod) fragments are observed, and seven signals (two coincident peaks) are seen for the CH groups. In some of the chain compounds having Pt(cod) groups, the cod ligand carbon nuclei (CH or CH_2) may be equivalent in the isomers giving coincidence for some peaks, or the Pt(cod) moieties may rotate thus averaging signals.

The presence of Pt(cod) groups in complex (**3b**) in different environments with respect to the central μ-C_2W_2Pt core leads us to classify the single isomer observed as 'asymmetric.' Examination of models and considerations similar to those discussed earlier for the tetranuclear metal compounds reveal that addition of a Pt(cod) fragment to (**X**) and (**Y**) (Scheme), so as to produce a Pt_3W_2 chain, can occur to produce three diastereoisomers (each having an enantiomeric partner). Two of the diastereoisomers are symmetric, leading to two ^{195}Pt resonances (end platinums equivalent), and one is asymmetric, leading to three ^{195}Pt n.m.r. resonances. During chromatography of (**3a**) another isomer was observed, but it proved too insoluble to characterise by n.m.r. spectroscopy.

Compounds (**3a**) and (**3b**) were prepared by adding Pt(cod) fragments to both C≡W groups in (**1a**) and (**1e**). They may also be prepared by adding one equivalent of 'Pt(cod)' to (**2a**) and (**2b**).

An alternative method for stepwise synthesis of a five-metal atom chain might be to displace the cod ligand in compounds of type (**2**) with an alkylidynetungsten complex $[W(\equiv CR)(CO)_2L]$ (R = C_6H_4Me-4 or Me, L = η-C_5H_5 or η-C_5Me_5). To investigate this possibility compounds (**2a**), (**2b**), and (**2c**) were treated with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$, and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$, respectively, in the presence of ethylene, and with CH_2Cl_2 or thf as solvent. These reactions afforded the diplatinumtritungsten complexes $[Pt_2W_3(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_6L_3]$ [R = C_6H_4Me-4, L = η-C_5H_5 (**4a**); R = Me, L = η-C_5Me_5 (**4b**); R = C_6H_4-Me-4, L = η-C_5Me_5 (**4c**)]. Similarly, reactions between (**2b**) or (**2c**) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ gave the pentanuclear metal compounds $[Pt_2W_3(\mu\text{-}CMe)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ (**5a**) and $[Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ (**5b**), respectively. Data for the compounds (**4**) and (**5**) are given in

Table 7. Selected interatomic distances (Å) and angles (°) for the compound $[Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (**4a**)

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)$\cdots$Pt(2)	2.949(2)	W(1)–C(61)	1.99(3)	Pt(1)–C(61)	2.02(3)	Pt(2)–C(61)	2.09(2)
C(61)–C(62)	1.52(4)	Pt(1)–C(41)	2.02(2)	W(2)–C(41)	1.98(2)	C(41)–C(42)	1.44(3)
W(3)–C(101)	1.94(3)	Pt(2)–C(101)	2.03(2)	C(101)–C(102)	1.45(4)	W(2)–C(21)	1.96(3)
C(21)–O(21)	1.19(4)	W(2)–C(31)	2.00(2)	Pt(1)$\cdots$C(31)	2.51(2)	C(31)–O(31)	1.14(3)
W(1)–C(51)	1.99(3)	Pt(1)$\cdots$C(51)	2.34(3)	C(51)–O(51)	1.21(4)	W(1)–C(91)	1.97(2)
Pt(2)$\cdots$C(91)	2.28(3)	C(91)–O(91)	1.21(3)	W(3)–C(121)	2.00(3)	C(121)–O(121)	1.15(3)
W(3)–C(131)	1.98(3)	Pt(2)$\cdots$C(131)	2.40(4)	C(131)–O(131)	1.18(4)	C(cp)–W(1)	2.34(3)*
C(cp)–W(2)	2.33(3)*	C(cp)–W(3)	2.33(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)	W(1)–C(51)–O(51)	163(2)
W(1)–C(91)–O(91)	166(2)	W(2)–C(21)–O(21)	175(2)	W(2)–C(31)–O(31)	168(2)	W(3)–C(121)–O(121)	180(3)
W(3)–C(131)–O(131)	168(3)	Pt(1)–W(2)–C(41)	47.8(6)	Pt(2)–W(3)–C(101)	48.2(6)	W(2)–C(41)–Pt(1)	85.7(8)
W(3)–C(101)–Pt(2)	86(1)	C(41)–Pt(1)–W(1)	163(1)	C(101)–Pt(2)–W(1)	153(1)	W(3)–Pt(2)–C(61)	140(1)
C(61)–Pt(1)–W(2)	147(1)	Pt(1)–W(2)–C(31)	62(1)	Pt(2)–W(3)–C(131)	59(1)	W(3)–Pt(2)–C(101)	46(1)
W(2)–Pt(1)–C(41)	47(1)	Pt(2)–W(1)–C(91)	55(1)	Pt(1)–W(1)–C(51)	56(1)	W(3)–C(101)–C(102)	149(2)
Pt(2)–C(101)–C(102)	124(2)	W(2)–C(41)–C(42)	141(1)	Pt(1)–C(41)–C(42)	130(2)	Pt(1)–C(61)–C(62)	122(1)
Pt(2)–C(61)–C(62)	115(1)	W(1)–C(61)–C(62)	143(2)				

* Mean distance to cyclopentadienyl carbons.

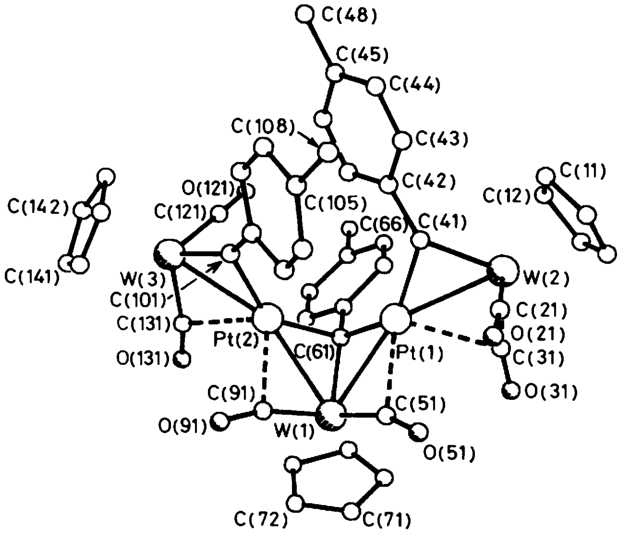


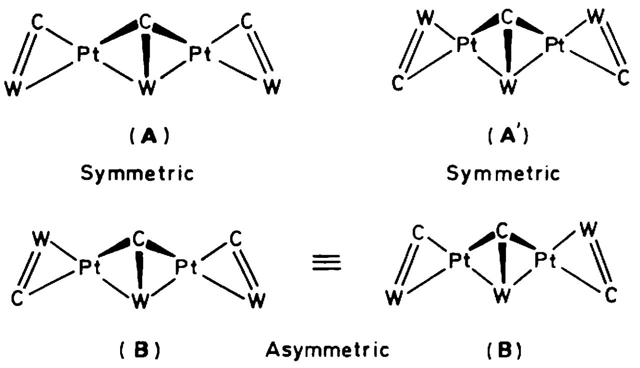
Figure 2. The molecular structure of [$Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3$] (**4a**) showing the crystallographic numbering

Tables 3—5. All these complexes were formed as isomeric mixtures, as deduced from the n.m.r. spectra discussed below.

In the synthesis of (**4a**) crystals were obtained suitable for *X*-ray diffraction. The results are summarised in Table 7 and a view of the isomer of (**4a**) characterised in this manner is shown in Figure 2. The molecule has an essentially planar five-metal atom chain [maximum deviation Pt(1) 0.7 Å], and there are two edge-bridging and one triply bridging tolymethylidyne groups. Four of the six CO ligands semi-bridge W–Pt bonds with their W–C–O angles in the range 163—168(2)°, and with Pt ··· C(O) contact distances of 2.3—2.5 Å. The W–Pt–W angles 154.5(1) and 149.0(1)° are significantly different. The W(1)–Pt(1) [2.773(2) Å] and W(1)–Pt(2) [2.723(2) Å] separations are longer than W(2)–Pt(1) [2.718(2) Å] and W(3)–Pt(2) [2.713(2) Å]. The Pt ··· Pt distance [2.949(2) Å] implies little or no direct metal–metal bonding, and may be compared with those found in the bridged-alkyne complexes [$Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4$] [2.904(1) Å][4] and [$Pt_2(\mu\text{-}PhC_2SiMe_3)(cod)_2$] [2.914(0) Å].[10] In the latter, the platinum–platinum distances are thought to be determined by the steric and orbital requirements of the bridging alkynes, and similar requirements of the central C(61)–W(1) group in (**4a**) probably determine the Pt–Pt distance in this complex also.

At Pt(1), the dihedral angle between the planes Pt(1)C(41)-W(2) and Pt(1)C(61)W(1) is 60°. The corresponding angle at Pt(2) is 86.3°. Treating the central Pt(1)C(61)W(1)Pt(2) core as a butterfly unit, hinged at C(61)–W(1), the dihedral angle is relatively acute at 92°. The triply bridging C(61) atom is fairly symmetrically related to the three metal atoms [C(61)–Pt(1) 2.02(3), C(61)–Pt(2) 2.09(2), and C(61)–W(1) 1.99(3) Å]. The two terminal Pt–W linkages are asymmetrically bridged by the atoms C(41) and C(101), respectively, as expected for unsaturation in the C(41)–W(2) [1.98(2) Å] and C(101)–W(3) [1.94(3) Å] bonds.[11] These distances are within the range found for such separations in complexes with similar three-membered ring systems.[7] The tolyl rings [C(42)—C(47) and C(102)—C(107)] are almost parallel (9° deviation), and are twisted by 32 and 43° out of the plane of their associated dimetallacyclopropene rings. The tolyl ring C(62)—C(68) is approximately perpendicular to the Pt(1)Pt(2)W(1) triangle.

As mentioned above, the n.m.r. spectra of the compounds (**4**) and (**5**) (Tables 3 and 5) showed they were formed as isomeric mixtures. These molecules are defined by a central μ_3-CPt$_2$W core. Addition of a C≡W fragment to the platinum atoms can be done in three ways giving rise to three diastereoisomers, two being symmetric and one asymmetric, with respect to the central core. The *X*-ray results correspond to symmetric isomer (**A**). The ^{195}Pt-{^{1}H} n.m.r. spectrum of (**4a**) (Table 3) revealed a predominant mixture of two symmetric isomers (platinum sites equivalent) and a small amount of an asymmetric isomer (platinum sites non-equivalent). Correspondingly, in the ^{13}C-{^{1}H} n.m.r. spectrum a symmetric isomer would be expected to display one μ-*C*R resonance for the two equivalent edge-bridging groups and one μ_3-*C*R resonance for the triply bridging carbon nucleus. In contrast an asymmetric isomer would be expected to show two inequivalent μ-*C*R resonances and one μ_3-*C*R signal. The pattern observed in the spectrum of complex (**4a**) (Table 5) is in agreement with this supposition. There are peaks for the two symmetric isomers at δ 317.1 (μ-C) and 262.7 p.p.m. (μ_3-C), and at δ 307.7 (μ-C) and 257.3 p.p.m. (μ_3-C), with signals for the minor asymmetric isomer appearing at 314.8, 308.8 (μ-C) and 256.7 p.p.m. (μ_3-C). Similar considerations apply to the n.m.r. data for the other compounds (**4**).



For the compounds (**5**) the spectra are even more complex as an asymmetry is built into the molecules by introduction of carbyne groups with different substitutents. The ^{195}Pt-{^{1}H} n.m.r. spectra are the more informative, as the presence of isomers coupled with poor solubility means that assignments of the ^{1}H and ^{13}C-{^{1}H} spectra are virtually impossible, and such data for these compounds are at best a listing of observed signals. Asymmetric isomers are observed in the ^{195}Pt-{^{1}H} n.m.r. spectra of both (**5a**) and (**5b**) with two resonances seen for each isomer in the ranges 1 865—1 826 and 1 405—1 327 p.p.m., as expected. From previous considerations for compounds (**4a**)—(**4c**), the symmetric isomers of (**5a**) and (**5b**) might be expected to show only one ^{195}Pt resonance per isomer. However, two are observed at 1 419 and 1 415 p.p.m. for (**5a**), while four are seen at 1 710 and 1 621, and at 1 425 and 1 362 p.p.m., with resolved ^{195}Pt–^{195}Pt coupling, for the two 'symmetric' isomers of (**5b**). Thus although the metal atom frameworks are in the possible 'symmetrical' arrangements, sufficient asymmetry is engendered by the end C=W groups to make the platinum atoms non-equivalent. These isomers are described as 'symmetric' in Table 3.

The objective of the work described in this paper was to demonstrate how metal atom clusters containing a chain of metal atoms may be systematically prepared using the ligating properties of C≡W groups. In succeeding papers we shall report species with longer chains or rings of metal atoms.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere unless otherwise stated. All solvents were rigorously dried before use. 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 JNM FX 90Q and FX 200 spectrometers. Alumina used in chromatography was B.D.H. aluminium oxide (Brockman activity II). Chromatography columns were *ca.* 20 cm in length and 3.5 cm internal diameter unless otherwise stated. Ethylene used was BOC reagent grade. The compound $[Ni(cod)_2]$ was purchased from Strem Chemicals Inc. and $[Pt(cod)_2]$ was prepared as described elsewhere.[12] The complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me, Ph, or $C_6H_4Me\text{-}4$) and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5Me_5)]$ (R = Me, Ph, or $C_6H_4Me\text{-}4$) were prepared by published routes[13] or adaptation of published routes.[14] Analytical and other data for new complexes are given in Tables 1 and 4.

Synthesis of Trinuclear Metal Compounds.—For the platinum compounds, the general procedure involves initial dissolution of the required amount of $[Pt(cod)_2]$ in cold (0 °C) ethylene-saturated solvent, usually light petroleum (*ca.* 30—40 cm^3) or thf (*ca.* 10 cm^3). The $[Pt(cod)_2]$ dissolves slowly (*ca.* 0.1 g every 2 min), with stirring (magnetic follower), and with C_2H_4 continuously bubbling through the solution. The $[Pt(C_2H_4)_3]$ thus prepared *in situ* is transferred slowly (*ca.* 10 min) into a usually cold (0 °C) and stirred solution [light petroleum (*ca.* 50—150 cm^3) or thf (*ca.* 20 cm^3)] containing the alkylidynetungsten compound. The transfer is accomplished *via* a canula [flexible stainless-steel tubing, 50 cm × 1 mm (internal diameter)] employing ethylene pressure to effect movement of the solution. The resulting mixture may then be cooled to induce crystallisation of the product, or stirred for a period under nitrogen, followed by removal of the solvent *in vacuo*. The residue is then dissolved in a mixture of CH_2Cl_2–light petroleum and chromatographed to obtain the desired complex.

For the nickel-containing compounds, solid $[Ni(cod)_2]$ is added to the appropriate alkylidynetungsten compound dissolved in toluene. Alternatively, the solid reactants are mixed and thf added, with stirring of the mixture. Chromatography was necessary for purification of all the nickel-containing complexes.

(*i*) The compound $[Pt(cod)_2]$ (0.31 g, 0.75 mmol) in cold ethylene-saturated light petroleum (30 cm^3) was slowly added to a cold light petroleum (50 cm^3) solution of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.50 g, 1.5 mmol). The mixture was warmed to room temperature (1 h) with stirring, and then recooled to 0 °C. Solvent was removed with a syringe, and the residue washed with light petroleum (3 × 10 cm^3) and vacuum dried to give orange *crystals* of $[PtW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **(1c)** (0.57 g).

(*ii*) Similarly, $[Pt(cod)_2]$ (0.35 g, 0.86 mmol) in ethylene-saturated light petroleum (40 cm^3) with $[W(\equiv CPh)(CO)_2(\eta\text{-}C_5H_5)]$ (0.68 g, 1.7 mmol) in the same solvent (150 cm^3) gave purple-red *crystals* of $[PtW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **(1d)** (0.60 g).

(*iii*) The compound $[Pt(cod)_2]$ (0.25 g, 0.61 mmol) in cold ethylene-saturated thf (20 cm^3) was added to $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.50 g, 1.25 mmol) in the same solvent (15 cm^3) at room temperature. The resulting red solution was stirred for 2.5 h, and then solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (1:1) and chromatographed, eluting with the same solvent mixture. The first eluate contained a trace of unreacted $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$, and this was followed by the major product $[PtW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ **(1e)** (0.40 g) isolated as orange *crystals*. A final eluate fraction contained $[Pt_2W_3(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5Me_5)_3]$ **(4b)** (0.14 g), isolated as brown *crystals*.

(*iv*) The compound $[Pt(cod)_2]$ (0.23 g, 0.56 mmol) in cold ethylene-saturated light petroleum (30 cm^3) was added to $[W(\equiv CPh)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.46 g, 1.0 mmol) in the same solvent (100 cm^3 at 0 °C). The purple solution was stirred (1 h) at room temperature, then concentrated to *ca.* 10 cm^3 and chilled to −20 °C overnight. Removal of solvent, and drying *in vacuo*, afforded maroon *crystals* of $[PtW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ **(1f)** (0.53 g).

(*v*) Using the same procedure as for **(1f)**, crimson *crystals* of the complex $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ **(1g)** (0.56 g) were obtained from $[Pt(cod)_2]$ (0.23 g, 0.56 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.50 g, 1.1 mmol).

(*vi*) A mixture of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.48 g, 1.0 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.50 mmol) was dissolved in cold ethylene-saturated light petroleum (100 cm^3), and treated with a solution of $[Pt(C_2H_4)_3]$ {from $[Pt(cod)_2]$ (0.23 g, 0.56 mmol)} in cold light petroleum (30 cm^3). The mixture was warmed to room temperature, and purple crystals of **(1a)** (0.10 g) removed by filtration through a glass frit. The filtrate was collected, the solvent removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (1:2) and chromatographed. Gradient elution with CH_2Cl_2–light petroleum increasing the CH_2Cl_2 concentration from 1:2 to 2:1 afforded in sequence after removal of solvent, red $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.20 g), red **(1g)** (0.19 g), and red $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ **(1h)** (0.23 g). The latter was purified by recrystallisation from CH_2Cl_2–light petroleum (1:5) to give crimson *crystals*.

(*vii*) The compounds $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.30 g, 0.90 mmol) and $[Ni(cod)_2]$ (0.12 g, 0.44 mmol) were mixed together and thf (10 cm^3) added. The mixture was stirred (1 h) at room temperature, solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (3:1) and chromatographed. Elution with the same solvent mixture gave initially an eluate containing $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.03 g). The second eluate (orange-brown) was collected and the solvent was removed *in vacuo*. The residue was recrystallised from CH_2Cl_2–light petroleum (1:5) to give crimson *crystals* of $[NiW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **(1i)** (0.23 g).

(*viii*) Crimson-black *crystals* of $[NiW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **(1j)** (0.32 g) were prepared following a similar procedure to that described for **(1i)**, by using $[Ni(cod)_2]$ (0.14 g, 0.50 mmol) and $[W(\equiv CPh)(CO)_2(\eta\text{-}C_5H_5)]$ (0.40 g, 1.0 mmol). The eluant used for chromatography was CH_2Cl_2–light petroleum (2:1).

(*ix*) Crimson *crystals* of $[NiW_2(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ **(1k)** (0.18 g) were similarly prepared from $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.30 g, 0.75 mmol) and $[Ni(cod)_2]$ (0.07 g, 0.25 mmol) in thf (10 cm^3). Unreacted $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ was eluted from the chromatography column with CH_2Cl_2–light petroleum (1:3). An orange band was then eluted with CH_2Cl_2–light petroleum (1:1). Removal of solvent *in vacuo* afforded crimson *crystals* of **(1k)**.

(*x*) The compound $[Ni(cod)_2]$ (0.14 g, 0.50 mmol) was added to a toluene (30 cm^3) solution containing $[W(\equiv CPh)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.46 g, 1.0 mmol). After stirring for 1 h at room temperature, solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (1:1) and chromatographed. Eluting with the same solvent mixture gave a red-brown eluate. Removal of solvent *in vacuo*, and recrystallisation from CH_2Cl_2–light petroleum (1:5), afforded maroon *crystals* of $[NiW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ **(1l)** (0.38 g).

(*xi*) Maroon *crystals* of $[NiW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ **(1m)** (0.48 g) were obtained, as in the synthesis of **(1l)**, from $[Ni(cod)_2]$ (0.14 g, 0.50 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.48 g, 1.0 mmol) in toluene (30 cm^3).

Synthesis of the Tetranuclear Metal Complexes.—(*i*) The compound $[Pt(cod)_2]$ (0.12 g, 0.30 mmol) in cold ethylene-saturated toluene (5 cm^3) was slowly added to a toluene solution (40 cm^3, at 0 °C) of (**1a**) (0.30 g, 0.30 mmol). The resulting dark mixture was warmed to room temperature and stirred (3 h). Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 and chromatographed. Initially the column was eluted with CH_2Cl_2–light petroleum (2:1) to remove trace amounts of (**1a**). Subsequent elution was with neat CH_2Cl_2, and then thf–CH_2Cl_2 (1:50) to remove an orange band. Removal of solvent *in vacuo* and recrystallisation of the residue from CH_2Cl_2–light petroleum (1:5) afforded orange *crystals* of complex $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)_2]$ (**2a**) (0.31 g).

(*ii*) A sample of $[Pt(cod)_2]$ (0.12 g, 0.30 mmol) in cold ethylene-saturated thf (15 cm^3) was slowly added to (**1e**) (0.30 g, 0.30 mmol) in the same solvent (15 cm^3, 0 °C). After warming to room temperature, and stirring for 3 h, solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 and chromatographed (10-cm column). Elution with CH_2Cl_2–light petroleum (1:1) afforded a trace of (**1e**) as a red band. Further elution using thf–CH_2Cl_2 (1:25) gave an orange eluate. Removal of solvent and recrystallisation from CH_2Cl_2–light petroleum (1:5) afforded brown *crystals* of $[Pt_2W_2(\mu\text{-}CMe)(\mu_3\text{-}CMe)(CO)_4(cod)(\eta\text{-}C_5Me_5)_2]$ (**2b**) (0.32 g).

(*iii*) Dark brown *crystals* of $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5Me_5)_2]$ (**2c**) (0.23 g) were obtained from $[Pt(cod)_2]$ (0.09 g, 0.22 mmol) and (**1g**) (0.23 g, 0.20 mmol) in thf using the same procedure as that for (**2b**). The product was eluted from the chromatography column using neat CH_2Cl_2.

(*iv*) Compound (**2a**) (0.66 g, 0.50 mmol) in CH_2Cl_2 (15 cm^3) was treated with an excess of $PMePh_2$ in light petroleum. After stirring for 30 min, solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (1:1) and chromatographed. Gradient elution, increasing to neat CH_2Cl_2, afforded a brown eluate. Removal of solvent and crystallisation of the residue from light petroleum gave orange *crystals* of $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)_2]$ (**2d**) (0.72 g).

(*v*) A cold ethylene-saturated thf (20 cm^3) solution of $[Pt(cod)_2]$ (0.12 g, 0.29 mmol) was added slowly to a thf (30 cm^3) solution of (**1b**) (0.20 g, 0.23 mmol) also at 0 °C. The resulting brown solution was warmed to room temperature and stirred for 2 h. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (3:1) and chromatographed. Gradient elution, increasing to neat CH_2Cl_2, afforded a trace of (**1b**) followed by a brown eluate. Removal of solvent and crystallisation from light petroleum gave brown *crystals* of $[NiPtW_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)_2]$ (**2e**) (0.16 g).

(*vi*) Similarly, $[Pt(cod)_2]$ (0.09 g, 0.22 mmol) in thf (20 cm^3) with (**1m**) (0.20 g, 0.20 mmol) in the same solvent (30 cm^3) gave brown *crystals* of $[NiPtW_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5Me_5)_2]$ (**2f**) (0.15 g) after chromatography.

Synthesis of the Pentanuclear Metal Complexes.—(*i*) Compound (**1a**) (0.30 g, 0.29 mmol) in cold ethylene-saturated thf (10 cm^3) was slowly added to an ethylene-saturated thf (20 cm^3 at 0 °C) solution of $[Pt(cod)_2]$ (0.36 g, 0.88 mmol). After warming to room temperature and stirring for 3 h, solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 and chromatographed. Gradient elution, increasing to thf–CH_2Cl_2 (1:20), afforded three poorly resolved bands red, pale yellow, and bright yellow in colour. The middle eluate is often contaminated with traces of (**2a**). Collection of the first two bands and removal of solvent *in vacuo* afforded brown *microcrystals* of $[Pt_3W_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]$ (**3a**) (0.40 g).

(*ii*) A cold ethylene-saturated thf (20 cm^3) solution of $[Pt(cod)_2]$ (0.25 g, 0.61 mmol) was treated with (**1e**) (0.20 g, 0.20 mmol) dissolved in the same solvent (10 cm^3 at 0 °C). After warming to room temperature and stirring (3 h), solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (3:1) and chromatographed. Gradient elution, increasing to neat CH_2Cl_2, afforded two poorly resolved fractions. The first orange-red eluate afforded brown crystals of (**2b**) (0.10 g). The second darker eluate yielded brown *crystals* of $[Pt_3W_2(\mu_3\text{-}CMe)_2(CO)_4(cod)_2(\eta\text{-}C_5Me_5)_2]$ (**3b**) (0.10 g), crystallised from light petroleum. This compound may be contaminated with (**2b**) and may require rechromatographing and recrystallisation from CH_2Cl_2–light petroleum (1:5).

(*iii*) A CH_2Cl_2 (10 cm^3) solution of (**2a**) (0.10 g, 0.08 mmol) was syringed into a Fischer–Porter vessel containing $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.06 g, 0.15 mmol) in the same solvent (10 cm^3). The vessel was pressurised with C_2H_4 (2 atm) for 30 min. Solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (1:1) and chromatographed. Gradient elution, increasing to neat CH_2Cl_2, removed unreacted $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.03 g), followed by a dark brown eluate. Removal of solvent and crystallisation from light petroleum gave black *crystals* of $[Pt_2W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (**4a**) (0.12 g).

(*iv*) A solution of compound (**2b**) (0.10 g, 0.08 mmol) in CH_2Cl_2 (10 cm^3) was syringed into a Fischer–Porter vessel containing $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.06 g, 0.15 mmol) in the same solvent (10 cm^3). The vessel was pressurised with C_2H_4 (2 atm) for 30 min. Solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2–light petroleum (2:1) and chromatographed (10-cm column). The first eluate contained unreacted $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5Me_5)]$ (0.03 g). The second eluate was orange-red. Removal of solvent and crystallisation from light petroleum gave brown *crystals* of $[Pt_2W_3(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5Me_5)_3]$ (**4b**) (0.11 g).

(*v*) Compound (**2c**) (0.29 g, 0.20 mmol) in cold ethylene-

Table 8. Crystal data and experimental parameters*

Compound	(**3a**)	(**4a**)
	$C_{46}H_{48}O_4Pt_3W_2\cdot CH_2Cl_2$	$C_{45}H_{36}O_6Pt_2W_3$
M	1 702.8	1 614.5
Crystal system	Monoclinic	Monoclinic
Crystal habit	Plates	Prisms
Colour	Red	Black
Space group	$P2/n$ (non-standard setting, no. 13)	$P2_1/c$ (no. 14)
a/Å	11.502(9)	17.271(13)
b/Å	12.181(2)	12.066(7)
c/Å	16.828(3)	22.041(9)
β/°	93.80(4)	111.99(6)
U/Å^3	2 352(2)	4 260(5)
Z	2	4
D_c/g cm^{-3}	2.41	2.53
F(000)	1 525	2 927
T/K	220	293
μ(Mo-K_α)/cm^{-1}	140.5	149.1
Crystal size/mm	0.05 × 0.16 × 0.30	0.19 × 0.20 × 0.15
2θ/° (min., max.)	3, 45	3, 53
Data recorded	3 112	10 135
Data unique	3 063	7 234
Data used	2 658	4 316
n in $I \geqslant n\sigma(I)$	2.0	2.5
Absorption correction method	Numerical (faces)	Empirical (Ψ scans)
g in weighting scheme $w^{-1} = [\sigma^2(F) + g\|F\|^2]$	0.000 48	0.000 93
$R(R')$	0.034 (0.035)	0.054 (0.050)

* Nicolet $P3m$ automated diffractometer, operating in an ω—2θ scan mode, with Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å. Refinement was by blocked-cascade least squares.

saturated thf (50 cm^3) was treated portionwise with [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$Me$_5$)] (0.15 g, 0.30 mmol) with C$_2$H$_4$ bubbling through the mixture and stirring (45 min). After warming to room temperature and further stirring (4 h), solvent was removed *in vacuo*, and the brown residue dissolved in CH$_2$Cl$_2$–light petroleum (1:1) and chromatographed. Slow elution recovered initially unreacted [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$Me$_5$)] (0.05 g), and this was followed by a slow-moving dark brown band. Removal of solvent and crystallisation of the residue from light petroleum afforded dark brown *crystals* of [Pt$_2$W$_3$(μ-CC$_6$H$_4$Me-4)$_2$(μ$_3$-CC$_6$H$_4$Me-4)(CO)$_6$(η-C$_5$Me$_5$)$_3$] (**4c**) (0.36 g).

(*vi*) Compounds (**2b**) (0.10 g, 0.08 mmol) and [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.06 g, 0.15 mmol) each dissolved in CH$_2$Cl$_2$ (10 cm^3) were placed in a Fischer–Porter vessel and pressurised with C$_2$H$_4$ (2 atm). After 30 min, solvent was removed *in vacuo* and the residue dissolved in CH$_2$Cl$_2$–light petroleum (1:1) and chromatographed. Gradient elution, increasing to neat CH$_2$Cl$_2$, afforded initially unreacted [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.03 g) followed by a red eluate. Removal of solvent *in vacuo* and crystallisation of the residue from CH$_2$Cl$_2$–light petroleum afforded brown *crystals* of [Pt$_2$W$_3$(μ-CMe)(μ-CC$_6$H$_4$Me-4)(μ$_3$-CMe)(CO)$_6$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)$_2$] (**5a**) (0.11 g).

(*vii*) Compound (**2c**) (0.49 g, 0.34 mmol) in cold ethylene-saturated thf (50 cm^3) was treated portionwise with [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.15 g, 0.37 mmol) with ethylene bubbling through the mixture (0 °C for 1 h). After warming to room temperature and stirring for a further 3 h, solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$–light petroleum (1:1) and chromatographed. Slow elution with the same solvent mixture afforded a trace of orange [W(≡CC$_6$H$_4$-

Table 9. Atomic positional parameters (fractional co-ordinates; × 10^4) with estimated standard deviations in parentheses, for complex (**3a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	2 500	1 409(1)	2 500	C(13)	6 476(11)	1 451(12)	3 981(7)
Pt(2)	2 582(1)	1 723(1)	4 325(1)	C(14)	6 027(10)	382(11)	4 061(7)
W(1)	4 521(1)	1 489(1)	3 469(1)	C(15)	5 736(11)	−27(11)	3 273(7)
C(1)	4 314(10)	2 617(10)	4 286(7)	C(22)	1 915(11)	3 309(10)	4 814(7)
O(1)	4 545(7)	3 376(7)	4 702(5)	C(21)	2 379(11)	2 692(11)	5 445(7)
C(2)	4 046(10)	2 652(12)	2 687(7)	C(23)	614(11)	3 410(11)	4 594(8)
O(2)	3 981(9)	3 421(8)	2 279(5)	C(24)	−51(10)	2 302(12)	4 526(8)
C	3 075(10)	553(10)	3 519(6)	C(25)	677(10)	1 337(10)	4 337(7)
C(01)	2 723(10)	−623(10)	3 576(6)	C(26)	1 274(11)	685(10)	4 924(7)
C(02)	1 663(10)	−1 000(11)	3 211(6)	C(27)	1 316(10)	932(12)	5 803(6)
C(03)	1 376(10)	−2 126(10)	3 224(6)	C(28)	1 633(12)	2 114(11)	6 027(6)
C(04)	2 129(12)	−2 879(10)	3 600(7)	Cl(1) *	5 937(4)	5 945(4)	2 939(2)
C(05)	3 170(12)	−2 503(10)	3 961(7)	Cl(2) *	7 503(4)	4 430(4)	3 815(3)
C(06)	3 454(11)	−1 379(10)	3 969(6)	Cs *	6 062(15)	4 937(14)	3 685(9)
C(41)	1 842(15)	−4 069(12)	3 599(9)	Hsa *	5 846	5 251	4 177
C(11)	6 017(9)	800(12)	2 732(7)	Hsb *	5 546	4 340	3 538
C(12)	6 495(10)	1 715(12)	3 172(7)				

* Solvent atoms.

Table 10. Atomic positional parameters (fractional co-ordinates: × 10^4), with estimated standard deviations in parentheses, for complex (**4a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	1 215(1)	979(1)	1 683(1)	C(65)	3 190(21)	451(21)	176(12)
Pt(2)	2 870(1)	1 957(1)	2 408(1)	C(66)	3 594(23)	−51(28)	−267(15)
W(2)	69(1)	−681(1)	1 382(1)	C(67)	2 597(17)	−126(23)	290(12)
W(3)	4 492(1)	1 579(1)	3 172(1)	C(68)	2 236(17)	254(19)	700(11)
W(1)	1 567(1)	3 210(1)	1 625(1)	C(71)	776(15)	4 784(17)	1 180(11)
C(11)	56(19)	−2 608(22)	1 420(14)	C(72)	1 583(16)	5 122(20)	1 454(12)
C(12)	167(18)	−2 306(20)	845(12)	C(73)	2 063(19)	4 613(21)	1 110(13)
C(13)	−559(17)	−1 760(20)	452(13)	C(74)	1 490(17)	3 938(20)	622(13)
C(14)	−1 092(17)	−1 737(19)	753(12)	C(75)	713(19)	4 057(22)	655(13)
C(15)	−743(19)	−2 240(22)	1 347(14)	C(91)	2 205(18)	3 507(19)	2 559(13)
C(21)	−363(15)	−56(19)	2 012(12)	O(91)	2 507(13)	3 910(15)	3 099(9)
O(21)	−576(14)	372(14)	2 412(11)	C(101)	3 459(14)	1 030(17)	3 218(11)
C(31)	−233(15)	707(19)	854(10)	C(102)	3 033(16)	457(19)	3 578(13)
O(31)	−537(12)	1 401(12)	488(9)	C(103)	2 276(19)	790(23)	3 596(14)
C(41)	1 248(16)	−604(15)	1 988(11)	C(104)	1 921(18)	264(21)	3 983(13)
C(42)	1 951(15)	−1 315(17)	2 322(11)	C(105)	2 240(16)	−709(19)	4 306(13)
C(43)	1 831(16)	−2 161(16)	2 745(10)	C(106)	2 990(17)	−1 083(20)	4 298(13)
C(44)	2 452(21)	−2 891(18)	3 023(13)	C(107)	3 397(16)	−497(24)	3 950(13)
C(45)	3 237(16)	−2 859(19)	2 931(13)	C(108)	1 787(24)	−1 449(23)	4 660(16)
C(46)	3 332(15)	−1 985(21)	2 545(12)	C(121)	4 446(15)	558(19)	2 444(12)
C(47)	2 704(14)	−1 231(18)	2 255(11)	O(121)	4 421(11)	−33(15)	2 026(9)
C(48)	3 949(19)	−3 644(24)	3 257(16)	C(131)	4 174(21)	2 811(22)	2 531(14)
C(51)	634(18)	2 645(19)	1 857(14)	O(131)	4 139(12)	3 545(16)	2 171(10)
O(51)	13(12)	2 591(14)	1 984(10)	C(141)	5 723(20)	2 522(26)	3 832(14)
C(61)	2 062(15)	1 825(16)	1 431(13)	C(142)	5 956(25)	1 502(28)	3 727(17)
C(62)	2 457(14)	1 337(17)	979(9)	C(143)	5 613(23)	670(31)	3 948(17)
C(63)	3 072(12)	1 930(19)	847(11)	C(144)	5 166(22)	1 255(27)	4 271(16)
C(64)	3 440(17)	1 470(24)	429(14)	C(145)	5 193(23)	2 324(30)	4 202(16)

Me-4)(CO)$_2$(η-C$_5$H$_5$)], followed by a dark brown eluate. Removal of the solvent gave brown *crystals* of [Pt$_2$W$_3$(μ-CC$_6$H$_4$Me-4)$_2$(μ_3-CC$_6$H$_4$Me-4)(CO)$_6$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)$_2$] **(5b)** (0.55 g).

Crystal Structure Determinations.—The crystal and other experimental data for compounds **(3a)** and **(4a)** are summarised in Table 8. The lattice of **(3a)** contained a disordered molecule of CH_2Cl_2. All data were corrected for Lorentz, polarisation and *X*-ray absorption effects. The structures were solved by Patterson and Fourier methods by which all non-hydrogen atoms were located and refined with anisotropic thermal parameters. Hydrogen atoms were incorporated at calculated positions (C–H 0.96 Å, riding model) except for those on the cod ligands of **(3a)** bonded to Pt(2). These were incorporated at their positions found from the electron-density maps. Maximum residual density in the electron-difference density maps at convergence showed local maxima of *ca.* 2 e Å^{-3} near the metal atoms only. Scattering factors were from ref. 15, and all computations were carried out with the SHELXTL system of programs[16] using an Eclipse (Data General) computer. Atom co-ordinates for **(3a)** and **(4a)** are given in Tables 9 and 10 respectively.

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