

## Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 85.<sup>1</sup> Synthesis of Chain and Ring Compounds containing Molybdenum

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Reactions between  $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  and  $[\text{M}(\text{cod})_2]$  ( $\text{M} = \text{Ni}$  or  $\text{Pt}$ ,  $\text{cod} = \text{cyclo-octa-1,5-diene}$ ) in light petroleum afford the trimetal compounds  $[\text{MMo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ . The latter with 1 equivalent of  $[\text{Pt}(\text{cod})_2]$  in thf (tetrahydrofuran) give the tetranuclear metal compounds  $[\text{MPtMo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{cod})(\eta\text{-C}_5\text{H}_5)_2]$ , while  $[\text{NiMo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  with two equivalents of  $[\text{Pt}(\text{cod})_2]$  yields the pentanuclear metal complex  $[\text{NiPt}_2\text{Mo}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\text{cod})_2(\eta\text{-C}_5\text{H}_5)_2]$ . The  $\text{cod}$  ligands in the latter may be replaced with  $[\text{W}(\equiv\text{CPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  to afford the heptanuclear metal compound  $[\text{NiPt}_2\text{Mo}_2\text{W}_2(\mu\text{-CPh})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ . The reagents  $[\text{PtW}\{\mu\text{-C}(\text{R})\text{CO}\}(\text{CO})(\text{PMe}_3)(\text{cod})(\eta\text{-C}_5\text{H}_5)]$  ( $\text{R} = \text{Ph}$  or  $\text{C}_6\text{H}_4\text{Me-4}$ ) have been used to prepare the trimetal complexes  $[\text{PtM}'\text{M}''(\mu\text{-CR})(\mu\text{-CR}')(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  ( $\text{M}' = \text{M}'' = \text{W}$ ,  $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ,  $\text{R}' = \text{Me}$ ;  $\text{M}' = \text{W}$ ,  $\text{M}'' = \text{Mo}$ ,  $\text{R} = \text{R}' = \text{C}_6\text{H}_4\text{Me-4}$ ;  $\text{M}' = \text{W}$ ,  $\text{M}'' = \text{Mo}$ ,  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{C}_6\text{H}_4\text{Me-4}$ ) and  $[\text{PtMoW}(\mu\text{-CMe})(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$ . The reaction between  $[\text{PtMo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  and an excess of  $[\text{Ni}(\text{cod})_2]$  yields the octanuclear metal complex  $[\text{Ni}_2\text{Pt}_2\text{Mo}_4(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_3(\mu\text{-CO})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_4]$ , formed as a mixture of two isomers. In one isomer a *p*-tolylmethylidene ligand edge-bridges a  $\text{Mo-Ni}$  bond, and in the other a  $\text{Mo-Pt}$  bond. At reflux temperatures in thf the two isomers are converted into the symmetrical species  $[\text{Ni}_2\text{Pt}_2\text{Mo}_4(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_4(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  in which all four alkylidene ligands occupy triply bridging sites. Complicated isomeric mixtures of octanuclear metal clusters, with one edge-bridging and three triply bridging alkylidene ligands, have been obtained from reactions between the complexes  $[\text{PtM}'\text{M}''(\mu\text{-CR})(\mu\text{-CR}')(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  and  $[\text{Ni}(\text{cod})_2]$ . Refluxing these products in thf affords compounds  $[\text{Ni}_2\text{Pt}_2\text{M}'_2\text{W}_2(\mu_3\text{-CR})_2(\mu_3\text{-CR}')_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  ( $\text{M}' = \text{W}$ ,  $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ,  $\text{R}' = \text{Me}$ ;  $\text{M}' = \text{Mo}$ ,  $\text{R} = \text{Ph}$  or  $\text{C}_6\text{H}_4\text{Me-4}$ ,  $\text{R}' = \text{C}_6\text{H}_4\text{Me-4}$ ) in which all four alkylidene groups are triply bridging. However, two isomers exist for each species, and the nature of this isomerism is discussed. Different behaviour was observed on treatment of  $[\text{PtMoW}(\mu\text{-CMe})(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$  with  $[\text{Ni}(\text{cod})_2]$ . The major product was the heptanuclear metal chain cluster  $[\text{NiPt}_2\text{Mo}_2\text{W}_2(\mu\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$ . The new compounds have been characterised by n.m.r. spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}\text{-}\{^1\text{H}\}$ , and  $^{195}\text{Pt}\text{-}\{^1\text{H}\}$  for those species containing platinum).

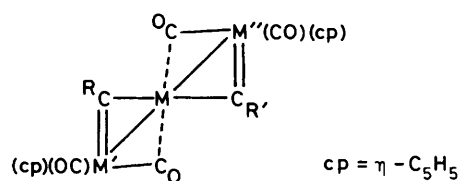
We have recently developed rational procedures for preparing heteropolynuclear metal complexes with structures based on chains of metal atoms, and in which the metal-metal bonds are bridged by alkylidene groups.<sup>2</sup> In the majority of these species  $\text{W-Pt}$  or  $\text{W-Ni}$  bonds form the spine of the molecules, and compounds with up to seven metal atoms in the chain have been characterised. Moreover, as mentioned below, a few complexes in which  $\text{Mo}$  replaces  $\text{W}$  in the chains have also been described.<sup>2b</sup> In attempts to extend the length of the chains beyond seven metal atoms cyclisation reactions were observed, affording metallacycles which we have termed 'star clusters'.<sup>3</sup>

The trimetal compounds  $[\text{PtW}_2(\mu\text{-CR})_2(\text{CO})_4\text{L}_2]$  ( $\text{R} = \text{alkyl}$  or  $\text{aryl}$ ,  $\text{L} = \eta\text{-C}_5\text{H}_5$  or  $\eta\text{-C}_5\text{Me}_5$ ) are the precursors for these syntheses, and these reagents are obtained in high yield by treating solutions containing  $[\text{Pt}(\text{C}_2\text{H}_4)_3]$  with the appropriate alkylidene tungsten complex  $[\text{W}(\equiv\text{CR})(\text{CO})_2\text{L}]$ . The unsaturated nature of the trimetal compounds allows reactions to occur with low-valent metal-ligand fragments. The latter add across what are formally  $\text{W=CR}$  double bonds. Thus treatment of  $[\text{PtW}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (**1a**) with 1 equivalent of an ethylene-saturated toluene solution of  $[\text{Pt}(\text{cod})_2]$  ( $\text{cod} = \text{cyclo-octa-1,5-diene}$ ) affords  $[\text{Pt}_2\text{W}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{cod})(\eta\text{-C}_5\text{H}_5)_2]$  (**2a**). Similarly (**1b**) with  $[\text{Pt}(\text{cod})_2]$  gives (**2b**). Treatment of (**2a**) with a second

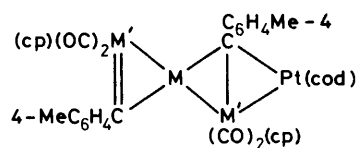
equivalent of  $[\text{Pt}(\text{cod})_2]$  yields the pentanuclear metal complex  $[\text{Pt}_3\text{W}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\text{cod})_2(\eta\text{-C}_5\text{H}_5)_2]$  (**3a**).<sup>2a</sup> In a further reaction, the terminal  $\text{cod}$  ligands in (**3a**) may be displaced by  $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  to give the heptanuclear metal compound  $[\text{Pt}_3\text{W}_4(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (**4a**).<sup>2b</sup>

If  $[\text{Ni}(\text{cod})_2]$  is used in these reactions, instead of  $[\text{Pt}(\text{cod})_2]$ , a different reactivity pattern is observed. Thus with (**1a**), an excess of the nickel reagent gives a mixture of three isomeric metallacycles  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_3(\mu\text{-CO})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_4]$  [**5a** (i) and (ii)] and  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_4(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (**6a**).<sup>2c</sup> These species evidently form *via* intermediates akin to (**2a**) in which the  $\text{Pt}(\text{cod})$  group is replaced by a  $\text{Ni}(\text{cod})$  fragment. Further reaction with (**1a**) produces a heptanuclear metal chain compound which with the  $[\text{Ni}(\text{cod})_2]$  reagent present yields the octanuclear metal complex as an isomeric mixture. Interestingly, the two asymmetric isomers [**5a** (i) and (ii)] are readily converted into the symmetrical structure (**6a**) on refluxing in thf (tetrahydrofuran) solutions.

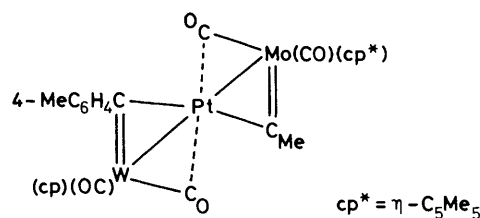
As mentioned above, a few compounds have been described<sup>2b</sup> in which  $\text{Mo}$  replaces  $\text{W}$  in the chains. In this paper we report several other compounds in which  $\text{Mo}$  atoms are present in the spines of the molecules, thus placing the initial observation on a



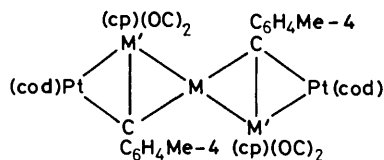
	M	M'	M''	R	R'
(1a)	Pt	W	W	C <sub>6</sub> H <sub>4</sub> Me-4	C <sub>6</sub> H <sub>4</sub> Me-4
(1b)	Ni	W	W	C <sub>6</sub> H <sub>4</sub> Me-4	C <sub>6</sub> H <sub>4</sub> Me-4
(1c)	Pt	Mo	Mo	C <sub>6</sub> H <sub>4</sub> Me-4	C <sub>6</sub> H <sub>4</sub> Me-4
(1d)	Ni	Mo	Mo	C <sub>6</sub> H <sub>4</sub> Me-4	C <sub>6</sub> H <sub>4</sub> Me-4
(1e)	Pt	W	W	C <sub>6</sub> H <sub>4</sub> Me-4	Me
(1f)	Pt	W	Mo	C <sub>6</sub> H <sub>4</sub> Me-4	C <sub>6</sub> H <sub>4</sub> Me-4
(1g)	Pt	W	Mo	Ph	C <sub>6</sub> H <sub>4</sub> Me-4



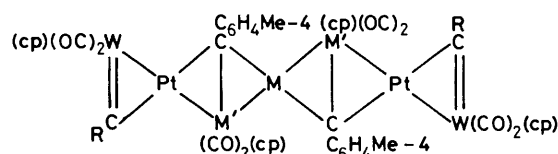
	M	M'
(2a)	Pt	W
(2b)	Ni	W
(2c)	Pt	Mo
(2d)	Ni	Mo



(1h)



	M	M'
(3a)	Pt	W
(3b)	Pt	Mo
(3c)	Ni	Mo



	M	M'	R
(4a)	Pt	W	C <sub>6</sub> H <sub>4</sub> Me-4
(4b)	Pt	Mo	Me
(4c)	Ni	Mo	Ph

firmer basis. We have also established that 'star clusters' can be prepared having Mo atoms in the metallacycle. Moreover, an interesting form of isomerism occurs which is related to different metal atom sequences within the metal cluster framework. In a subsequent paper we shall show that the presence of molybdenum atoms in these systems allows the synthesis of compounds having structures with chains of more than seven metal atoms.

### Results and Discussion

The important precursor  $[PtMo_2(\mu-CC_6H_4Me-4)_2(CO)_4(\eta-C_5H_5)_2]$  (**1c**) was prepared by adding a light petroleum solution of  $[Pt(C_2H_4)_3]$ , generated *in situ* from  $[Pt(cod)_2]$ , to a solution of  $[Mo(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$  dissolved in the same solvent. Compound (**1c**) is isolated in high yield as a red, air stable, crystalline solid, and is characterised by the data given in Tables 1–3. The nickel analogue  $[NiMo_2(\mu-CC_6H_4Me-4)_2(CO)_4(\eta-C_5H_5)_2]$  (**1d**) was similarly prepared using  $[Ni(cod)_2]$  as the source of nickel.

Both (**1c**) and (**1d**) in their i.r. spectra show a band  $[1822$  (**1c**),  $1810$   $cm^{-1}$  (**1d**)] which may be attributed to semi-bridging CO ligands. This is consistent with X-ray diffraction studies carried out earlier<sup>4</sup> on (**1a**) and (**1b**) which showed that one CO group on each tungsten atom strongly semi-bridges the metal-metal

bonds. The  $^{13}C\{-^1H\}$  n.m.r. spectra of the compounds (Table 2) show characteristic resonances for the  $\mu-CC_6H_4Me-4$  nuclei at  $\delta$  323.4 (**1c**) and 333.7 p.p.m. (**1d**), the former signal showing  $^{195}Pt\text{-}^{13}C$  coupling (893 Hz). The  $^{195}Pt\{-^1H\}$  n.m.r. spectrum of (**1c**) shows a resonance at  $\delta$  1741 p.p.m. (Table 3).

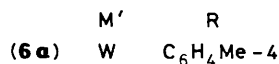
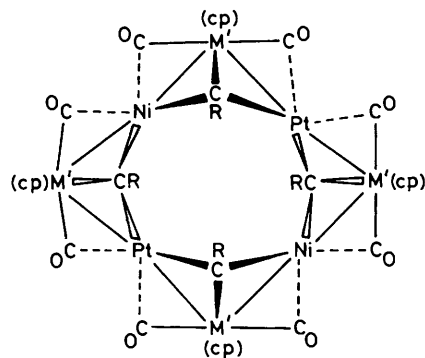
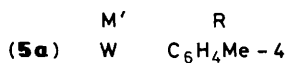
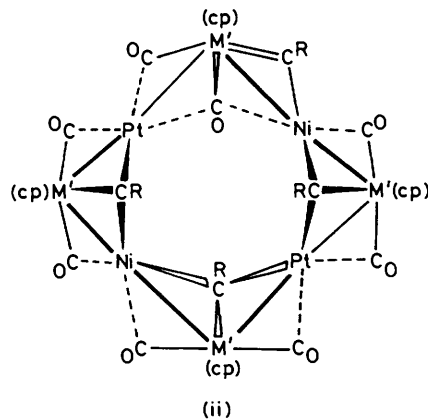
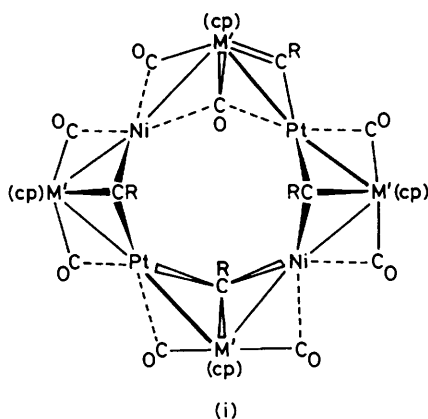
As expected, compounds (**1c**) and (**1d**) in thf react with 1 equivalent of an ethylene-saturated solution of  $[Pt(cod)_2]$  in the same solvent to give the complexes  $[Pt_2Mo_2(\mu-CC_6H_4Me-4)(\mu_3-CC_6H_4Me-4)(CO)_4(cod)(\eta-C_5H_5)_2]$  (**2c**) and  $[NiPtMo_2(\mu-CC_6H_4Me-4)(\mu_3-CC_6H_4Me-4)(CO)_4(cod)(\eta-C_5H_5)_2]$  (**2d**), respectively. Data for (**2c**) and (**2d**) (Tables 1–3) are consistent with the formulations proposed. Thus the presence of semi-bridging CO groups is indicated by i.r. bands at  $1743$   $cm^{-1}$  (**2c**) and  $1744$   $cm^{-1}$  (**2d**). The  $^{195}Pt\{-^1H\}$  n.m.r. data are very diagnostic for these systems. Compound (**2c**) shows resonances at  $\delta$  1392 and 378 p.p.m. The former signal can be assigned to the platinum linked to two molybdenum atoms, and the latter to the Pt(cod) group. These assignments are made on the basis of the data for the trimetal complexes (**1a**)<sup>4</sup> and (**1c**), and those for (**2b**) and (**2d**). Thus in the spectrum of the latter, a complex without a Mo-Pt-Mo group but containing a Pt(cod) fragment, there is one peak at  $\delta$  482 p.p.m.

The presence of an edge-bridging and a triply bridging alkylidyne ligand in the compounds (**2c**) and (**2d**) is clearly evident from their  $^{13}C\{-^1H\}$  n.m.r. spectra (Table 2), with the

**Table 1.** Analytical<sup>a</sup> and physical data for the tri-, tetra-, penta-, and hepta-nuclear metal complexes

Compound	Colour	Yield (%)	$\nu_{\max}(\text{CO})^b/\text{cm}^{-1}$	Analysis (%)	
				C	H
(1c) [PtMo <sub>2</sub> (μ-CC <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> (CO) <sub>4</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	Maroon	74	1 978s, 1 956s, 1 822m,br	42.6 (43.1)	3.0 (2.9)
(1d) [NiMo <sub>2</sub> (μ-CC <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> (CO) <sub>4</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	Maroon	73	1 979s, 1 960s, 1 810m,br	<sup>c</sup> 49.5 (49.4)	3.6 (3.4)
(1e) [PtW <sub>2</sub> (μ-CMe)(μ-CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>4</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	Red	81	1 964s, 1 940s, 1 815m,br	31.7 (30.8)	2.6 (2.1)
(1f) [PtMoW(μ-CC <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> (CO) <sub>4</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	Red	80	1 971s, 1 949s, 1 819m,br	39.3 (39.0)	2.7 (2.6)
(1g) [PtMoW(μ-CPh)(μ-CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>4</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	Red	78	1 973s, 1 951s, 1 820m,br	38.7 (38.3)	2.3 (2.4)
(1h) [PtMoW(μ-CMe)(μ-CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>4</sub> (η-C <sub>5</sub> H <sub>5</sub> )(η-C <sub>5</sub> Me <sub>5</sub> )]	Orange	74	1 964s, 1 937s, 1 823m,br	37.8 (37.9)	3.4 (3.3)
(2c) [Pt <sub>2</sub> Mo <sub>2</sub> (μ-CC <sub>6</sub> H <sub>4</sub> Me-4)(μ <sub>3</sub> -CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>4</sub> (cod)(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	Red	81	1 948s, 1 842s,br, 1 743m,br	40.5 (40.1)	3.3 (3.2)
(2d) [NiPtMo <sub>2</sub> (μ-CC <sub>6</sub> H <sub>4</sub> Me-4)(μ <sub>3</sub> -CC <sub>6</sub> H <sub>4</sub> Me-4)(CO) <sub>4</sub> (cod)(η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	Brown	60	1 946s, 1 838s,br, 1 802 (sh), 1 744m	45.9 (45.5)	3.5 (3.6)
(3c) [NiPt <sub>2</sub> Mo <sub>2</sub> (μ <sub>3</sub> -CC <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> (CO) <sub>4</sub> (cod) <sub>2</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	Orange <sup>d</sup>	38	1 836m, 1 794m, 1 732s	41.3 (42.3)	3.1 (3.7)
(4c) [NiPt <sub>2</sub> Mo <sub>2</sub> W <sub>2</sub> (μ-CPh) <sub>2</sub> (μ <sub>3</sub> -CC <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> (CO) <sub>8</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>4</sub> ]	Brown	58	1 960s, 1 848m,br	36.7 (37.1)	2.5 (2.3)
(10) [NiPt <sub>2</sub> Mo <sub>2</sub> W <sub>2</sub> (μ-CMe) <sub>2</sub> (μ <sub>3</sub> -CC <sub>6</sub> H <sub>4</sub> Me-4) <sub>2</sub> (CO) <sub>8</sub> (η-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (η-C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> ]	Purple	72	1 954s, 1 860s, 1 838s,br	36.2 (36.8)	3.7 (3.2)

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Crystallises containing half a molecule of CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> Colour refers to major isomer.



**Table 2.** Hydrogen-1 and carbon-13 n.m.r. data<sup>a</sup> for the tri-, tetra-, penta-, and hepta-nuclear metal complexes

Compound	<sup>1</sup> H(δ) <sup>b</sup>	<sup>13</sup> C(δ) <sup>c</sup>
(1c)	2.26 (s, 6 H, Me-4), 5.60 (s, 10 H, C <sub>5</sub> H <sub>5</sub> ), 6.99, 7.42 [(AB) <sub>2</sub> , 8 H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8]	323.4 [μ-C, J(PtC) 893], 235.9 [CO, J(PtC) 49], 228.1 (CO), 147.8 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> ), J(PtC) 58], 140.6, 131.4, 129.4 (C <sub>6</sub> H <sub>4</sub> ), 93.4 (C <sub>5</sub> H <sub>5</sub> ), 21.9 (Me-4)
(1d)	2.23 (s, 6 H, Me-4), 5.46 (s, 10 H, C <sub>5</sub> H <sub>5</sub> ), 6.96, 7.24 [(AB) <sub>2</sub> , 8 H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8]	333.7 (μ-C), 240.9, 229.7 (CO), 151.2 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 139.3, 129.0, 128.8 (C <sub>6</sub> H <sub>4</sub> ), 93.4 (C <sub>5</sub> H <sub>5</sub> ), 21.9 (Me-4)
(1e)	2.24 (s, 3 H, Me-4), 2.71 (s, 3 H, Me), 5.60 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.66 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 7.01, 7.40 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8]	320.0 [μ-C, J(PtC) 792], 306.9 (μ-C), 225.4, 224.4, 221.9, 221.1 (CO), 151.5 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> ), J(PtC) 47], 139.0, 129.5 (C <sub>6</sub> H <sub>4</sub> ), 91.8, 91.4 (C <sub>5</sub> H <sub>5</sub> ), 44.5 [Me, J(PtC) 44], 21.8 (Me-4)
(1f)	2.22 (s, 3 H, Me-4), 2.26 (s, 3 H, Me-4), 5.57 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.66 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.96—7.43 (m, 8 H, C <sub>6</sub> H <sub>4</sub> )	324.8 [μ-C, J(PtC) 884], 306.6 [μ-C, J(PtC) 829, J(WC) 156], 235.8 [CO, J(PtC) 46], 229.6, 225.2, 220.3 (CO), 151.1 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> ), J(PtC) 46, J(WC) 21], 148.6 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> ), J(PtC) 58], 140.0, 139.4, 130.9, 130.1, 129.5, 129.3 (C <sub>6</sub> H <sub>4</sub> ), 93.2, 91.7 (C <sub>5</sub> H <sub>5</sub> ), 21.8 (2 × Me-4)
(1g)	2.26 (s, 3 H, Me-4), 5.57 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.67 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.98—7.50 (m, 9 H, C <sub>6</sub> H <sub>4</sub> and Ph)	322.0, 303.5 (μ-C), 231.9, 227.6, 221.5, 218.3 (CO), 151.9, 151.7 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> ), Ph], 146.7—126.2 (C <sub>6</sub> H <sub>4</sub> , Ph), 91.3, 89.8 (C <sub>5</sub> H <sub>5</sub> ), 20.5 (Me-4)
(1h)	2.05 (s, 15 H, C <sub>5</sub> Me <sub>5</sub> ), 2.23 (s, 3 H, Me-4), 2.97 (s, 3 H, Me), 5.66 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.98, 7.40 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8]	337.2 [μ-CMe, J(PtC) 826], 304.7 [μ-CC <sub>6</sub> H <sub>4</sub> Me-4, J(PtC) 823], 239.3 [CO, J(PtC) 61], 232.4, 224.0, 222.9 (CO), 151.3 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 138.9, 130.0, 129.4 (C <sub>6</sub> H <sub>4</sub> ), 105.4 (C <sub>5</sub> Me <sub>5</sub> ), 91.6 (C <sub>5</sub> H <sub>5</sub> ), 39.2 [Me, J(PtC) 61], 21.8 (Me-4), 10.8 (C <sub>5</sub> Me <sub>5</sub> )
(2c)	2.27 (s, 6 H, Me-4), 2.40—2.85 (m, 8 H, CH <sub>2</sub> ), 4.00—5.00 (m, 4 H, CH), 5.18 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.50 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.86—7.43 (m, 8 H, C <sub>6</sub> H <sub>4</sub> )	328.7 (μ-C), 267.3 (μ <sub>3</sub> -C), 246.4, 236.6, 235.3, 231.6 (CO), 150.8, 149.8 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 139.1—123.4 (C <sub>6</sub> H <sub>4</sub> ), 111.9, 105.0, 97.3 (CH), 94.2 (C <sub>5</sub> H <sub>5</sub> ), 93.9 (CH), 93.0 (C <sub>5</sub> H <sub>5</sub> ), 31.0, 30.6, 29.7, 29.3 (CH <sub>2</sub> ), 21.8, 21.0 (Me-4)
(2d)	2.12 (s, 3 H, Me-4), 2.27 (s, 3 H, Me-4), 2.10—2.80 (m, 8 H, CH <sub>2</sub> ), 4.00—5.00 (m, 4 H, CH), 4.90 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.37 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.91—7.20 (m, 8 H, C <sub>6</sub> H <sub>4</sub> )	341.6 (μ-C), 281.6 (μ <sub>3</sub> -C), 246.8, 245.8, 238.6, 232.9 (CO), 154.3, 153.2 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 136.7—124.3 (C <sub>6</sub> H <sub>4</sub> ), 110.6, 106.0, 103.4, 93.6 (CH), 93.2, 92.0 (C <sub>5</sub> H <sub>5</sub> ), 29.5 (CH <sub>2</sub> ), 28.9 (2 × CH <sub>2</sub> ), 28.1 (CH <sub>2</sub> ), 20.5, 19.8 (Me-4)
(3c)	<sup>d</sup> 2.18* (s, 3 H, Me-4), 2.22 (s, 6 H, Me-4), 2.34* (s, 3 H, Me-4), 2.35—2.75 (m, 16 H, CH <sub>2</sub> ), 4.40—5.10 (m, 8 H, CH), 5.33 (s, 10 H, C <sub>5</sub> H <sub>5</sub> ), 5.42* (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.46* (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.88—7.11 (m, 16 H, C <sub>6</sub> H <sub>4</sub> )	<sup>e</sup> 149.9 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 129.0—126.5 (C <sub>6</sub> H <sub>4</sub> ), 111.8, 105.9, 105.8, 96.7 (CH), 93.6 (C <sub>5</sub> H <sub>5</sub> ), 31.3, 28.8 (CH <sub>2</sub> ), 28.4 (2 × CH <sub>2</sub> ), 20.8 (Me-4)
(4c)	2.16 (s, 3 H, Me-4), 2.45 (s, 3 H, Me-4), 4.73 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.11 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.15 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.37 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.51—7.82 (m, 18 H, C <sub>6</sub> H <sub>4</sub> and Ph)	315.0, 307.2 (μ-C), 277.3, 273.3 (μ <sub>3</sub> -C), 241.6, 238.0, 228.8, 225.6, 220.9, 219.4, 216.9, 216.0 (CO), 155.4, 153.6, 151.8, 150.6 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> ), Ph], 137.2—125.7 (C <sub>6</sub> H <sub>4</sub> , Ph), 94.8, 94.4, 92.0, 91.2 (C <sub>5</sub> H <sub>5</sub> ), 21.5, 21.3 (Me-4)
(10)	1.89 (s, 15 H, C <sub>5</sub> Me <sub>5</sub> ), 2.00 (s, 15 H, C <sub>5</sub> Me <sub>5</sub> ), 2.06 (s, 3 H, Me-4), 2.14 (s, 3 H, Me-4), 2.30 (s, 3 H, Me), 3.09 (s, 3 H, Me), 5.01 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.26 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 6.68, 6.99 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8], 7.07, 7.81 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8]	<sup>b</sup> 345.9, 344.1 (μ-CMe), 272.5, 272.2 (μ <sub>3</sub> -CC <sub>6</sub> H <sub>4</sub> Me-4), 243.9, 241.5, 235.9, 235.6, 235.4, 234.8, 230.0, 226.1 (CO), 157.0, 156.2 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 134.8—126.7 (C <sub>6</sub> H <sub>4</sub> ), 104.3, 103.9, (C <sub>5</sub> Me <sub>5</sub> ), 92.9, 92.8 (C <sub>5</sub> H <sub>5</sub> ), 41.0, 40.4 (Me), 21.6, 21.1 (Me-4), 10.3 (2 × C <sub>5</sub> Me <sub>5</sub> )

<sup>a</sup> Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature. <sup>b</sup> Measured in  $\epsilon\text{-DCl}_3$ . <sup>c</sup> Hydrogen-1 decoupled chemical shifts are positive to high frequency of SiMe<sub>4</sub>. Measurements in CD<sub>2</sub>Cl<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub> unless otherwise stated. <sup>d</sup> Peaks of minor isomer marked with an asterisk. <sup>e</sup> Quality of spectrum limited by poor solubility, hence all peaks are not listed (see text).

observation of two peaks, one above 300 p.p.m. and one below 300 p.p.m.<sup>2a</sup> The former signal has a chemical shift characteristic for a CR (R = alkyl or aryl) group edge-bridging a metal-metal bond, and that below 300 p.p.m. to a CR group ligating three metal centres.<sup>2a,5</sup>

Previously reported n.m.r. data for (2a) revealed that this species is formed as a mixture of two diastereoisomers. As discussed earlier,<sup>2a</sup> diastereoisomers arise because in the synthesis of the species (2) from the enantiomeric compounds (1) addition of a Pt(cod) fragment can occur to produce two enantiomeric pairs. The individual members of each pair are indistinguishable by n.m.r. spectroscopy, but since the two pairs are diastereoisomers each gives rise to its own characteristic n.m.r. signals, as is found for (2a). Interestingly, examination of the n.m.r. spectra of (2c) and (2d) revealed only peaks for a single isomer. This may indicate the absence of a second isomer, or its relatively poor solubility if present.

To develop this chemistry further, compound (2d) was treated with 1 equivalent of [Pt(cod)<sub>2</sub>] in order to obtain the penta-nuclear metal complex [NiPt<sub>2</sub>Mo<sub>2</sub>(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub>(CO)<sub>4</sub>(cod)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (3c) analogous to (3a) and (3b). Isolation of (3c) via column chromatography revealed that it was formed as a mixture of three isomers, as indicated initially by the appearance of three bands on the column. Compound (3b) is also formed as a mixture of three diastereoisomers, the maximum number possible for this type of product.<sup>2c</sup> Even though the two major isomers of (3c) could be cleanly separated by chromatography, <sup>1</sup>H n.m.r. measurements on the two

**Table 3.** Platinum-195 n.m.r. data<sup>a</sup> for the complexes

Compound	δ <sup>b</sup>	J(WPt)	J(PtPt)
(1c) <sup>c</sup>	1 741		
(1e) <sup>c</sup>	1 680	186	
(1f) <sup>c</sup>	1 697	176	
(1g) <sup>c</sup>	1 706	166	
(1h) <sup>c</sup>	1 709	176	
(2c)	1 392		1 084
	378		1 084
(2d)	482		
(4c)	1 652		
	1 355		
(5b)	1 752		430
	1 595		426
	1 242		430
	1 147		426
(6b)	1 245		
(7) <sup>d</sup>	1 383	69, 165	
	1 289	88, 136	
(8)	1 241		
(9) <sup>d</sup>	1 252	156	
	1 242		
(10)	1 407		
	1 249		
(11)	1 304	158	

<sup>a</sup> Chemical shifts are in p.p.m., coupling constants are in Hz. Measurements are in CD<sub>2</sub>Cl<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub> unless otherwise stated. <sup>b</sup> To high frequency of  $\Xi(^{195}\text{Pt}) = 21.4$  MHz. <sup>c</sup> Measured in CDCl<sub>3</sub>. <sup>d</sup> Peaks for two separable isomers are given (see text).

fractions showed peaks developing for the other. Evidently there is a rapidly established equilibrium between the two isomers in solution.

Reference to molecular models and X-ray diffraction results<sup>2a</sup> allows the three diastereoisomers of the complexes (3) to be classified as 'asymmetric' and 'symmetric,' there being one of the former and two of the latter. The asymmetric isomer does not possess any symmetry elements, whereas the symmetric species possess a two-fold rotation axis through the central metal atom. The <sup>1</sup>H n.m.r. spectrum of the isomeric mixture of (3c) shows that the major isomer, which is orange and elutes most slowly, is a symmetric species, since it shows only one resonance for the η-C<sub>5</sub>H<sub>5</sub> and the Me-4 groups. The other major isomer is asymmetric showing two peaks for the η-C<sub>5</sub>H<sub>5</sub> ligands and two for the Me-4 groups. The two isomers are present in a ratio symmetric:asymmetric of ca. 3:2, based on relative peak intensities in the <sup>1</sup>H n.m.r. spectrum. The third isomer, observed as a green band on the chromatography column, was formed in only trace amounts, and in mixtures of the isomers its <sup>1</sup>H n.m.r. signals were not observed, perhaps being obscured by those of the other species.

Unfortunately full characterisation of (3c) by multinuclear n.m.r. spectroscopy was frustrated by the insolubility of the compound. Thus no peak for the μ-CC<sub>6</sub>H<sub>4</sub>Me-4 nucleus was observed in the <sup>13</sup>C-<sup>1</sup>H n.m.r. spectrum. The remainder of the spectrum (Table 2) is consistent for the major isomer with a symmetric structure. Thus there are four peaks for the CH=CH groups of the cod ligands and one signal for the η-C<sub>5</sub>H<sub>5</sub> groups. The insolubility prevented measurement of the <sup>195</sup>Pt-<sup>1</sup>H n.m.r. spectrum.

As previously described,<sup>2b</sup> it is possible to synthesise complexes with chains of seven metal atoms *via* displacement of the cod ligands in (3a) or (3b) with the appropriate alkylidynetungsten compound, thereby giving the compounds [MM'Pt<sub>2</sub>W<sub>2</sub>(μ-CR)<sub>2</sub>(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub>(CO)<sub>8</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>] [M = Pt, M' = W, R = C<sub>6</sub>H<sub>4</sub>Me-4 (4a); M = Pt, M' = Mo, R = Me (4b)].<sup>2b</sup> When a thf solution of (3c) is treated with an excess of [W(≡CPh)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)], in the presence of ethylene to labilise the cod ligands in the former reagent, the complex [NiPt<sub>2</sub>Mo<sub>2</sub>W<sub>2</sub>(μ-CPh)<sub>2</sub>(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub>(CO)<sub>8</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>] (4c) is formed. Data for this product are listed in Tables 1–3. The <sup>13</sup>C-<sup>1</sup>H n.m.r. spectrum of (4c) (Table 2) showed peaks corresponding to one isomer of the asymmetric type. Thus there are two μ-CPh, two μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4, eight CO, four η-C<sub>5</sub>H<sub>5</sub>, and two Me-4 resonances. The <sup>195</sup>Pt-<sup>1</sup>H n.m.r. spectrum is very diagnostic as it shows two peaks at δ 1 652 and 1 355 p.p.m., which do not couple, as is seen for all other compounds of this type.

Experiments were next designed to afford compounds of type (I) in which the R and R' groups are different, or in which three different transition elements form the M'-M-M'' spine of the molecules. It was anticipated that such species would act as starting points to the synthesis of a variety of new polynuclear metal compounds, including complexes containing four different transition elements. However, it proved difficult to obtain the desired reagents by treating [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>] with mixtures containing equivalent amounts of the alkylidynetungsten and -molybdenum and -tungsten complexes [M(≡CR)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (M = Mo or W, R = alkyl or aryl). These reactions, involving a mixing of three reagents, generally afforded inseparable mixtures of polynuclear metal species. To obtain the desired products a precursor was sought containing a Pt(cod) group ligated by one [M(≡CR)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] molecule. Unfortunately for this purpose the species [MPt(μ-CR)(CO)<sub>2</sub>(cod)(η-C<sub>5</sub>H<sub>5</sub>)], the presumed intermediates in the preparation of (1a), (1c), and related compounds,<sup>2a</sup> have not been isolated. If the dimetal compounds [MPt(μ-CR)(CO)<sub>2</sub>(cod)(η-C<sub>5</sub>H<sub>5</sub>)] had been isolated then the cod ligand could be displaced by a

different transition metal-alkylidyne reagent so as to produce the required trimetal complex. It was anticipated, however, that the previously reported<sup>6</sup> μ-η-ketenyltungsten compounds [PtW{μ-C(R)CO}(CO)(PMe<sub>3</sub>)(cod)(η-C<sub>5</sub>H<sub>5</sub>)] (R = Ph or C<sub>6</sub>H<sub>4</sub>Me-4) might be suitable precursors. Treatment of these complexes with [M(≡CR')(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (M = Mo or W; R' = Me, Ph, or C<sub>6</sub>H<sub>4</sub>Me-4) could lead to displacement of both the cod and the PMe<sub>3</sub> groups to produce trimetal compounds. This expectation proved correct. As described in the Experimental section, the compounds [PtW<sub>2</sub>(μ-CMe)-(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (1e), [PtMoW(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (1f), and [PtMoW(μ-CPh)(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (1g) were prepared in this manner. Moreover, the complex [PtMoW(μ-CMe)(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)(η-C<sub>5</sub>Me<sub>5</sub>)] (1h), a product containing both η-C<sub>5</sub>H<sub>5</sub> and η-C<sub>5</sub>Me<sub>5</sub> groups, was obtained from the reaction between [PtW{μ-C(C<sub>6</sub>H<sub>4</sub>Me-4)CO}(CO)(PMe<sub>3</sub>)(cod)(η-C<sub>5</sub>H<sub>5</sub>)] and [Mo(≡CMe)(CO)<sub>2</sub>(η-C<sub>5</sub>Me<sub>5</sub>)].

The data for these new trimetal compounds (Tables 1–3) are similar to those for (1a) and (1c). They all show a band (ca. 1 800 cm<sup>-1</sup>) in their i.r. spectra corresponding to a semi-bridging CO group. In the <sup>13</sup>C-<sup>1</sup>H n.m.r. spectra diagnostic resonances for the μ-C nuclei are seen. Comparison with the spectra of (1a) and (1c) allows assignment of signals for the μ-CC<sub>6</sub>H<sub>4</sub>Me-4 groups in the range δ 322–327 p.p.m. when bridging a Mo–Pt bond, and in the range δ 304–307 p.p.m. when bridging a W–Pt bond. The <sup>13</sup>C-<sup>1</sup>H n.m.r. spectra of (1e)–(1h) show four resonances for the CO ligands, indicating that site exchange of these groups does not occur at room temperature on the n.m.r. time-scale.

As mentioned in the Introduction, the reaction between (1a) and [Ni(cod)<sub>2</sub>] follows a different course to that involving [Pt(cod)<sub>2</sub>]. With an excess of the nickel compound, (1a) yields the octanuclear metal clusters (5a) and (6a).<sup>2c</sup> It was of interest, therefore, to study reactions of [Ni(cod)<sub>2</sub>] with the trimetal complexes (1c)–(1h).

Treatment of (1c) with an excess of [Ni(cod)<sub>2</sub>] in thf afforded the black crystalline complex [Ni<sub>2</sub>Pt<sub>2</sub>Mo<sub>4</sub>(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>(μ-CO)(CO)<sub>7</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>] (5b), characterised by the data given in Tables 3–5. It was apparent from the n.m.r. measurements that (5b) was formed as a mixture of two isomers, and that these two isomers were produced in approximately equal amounts, based on relative peak intensities in the n.m.r. spectra. The <sup>13</sup>C-<sup>1</sup>H n.m.r. spectrum (Table 5) was particularly informative, showing two resonances (δ 332.3 and 345.0 p.p.m.) for alkylidyne-carbon nuclei spanning two metal centres, and six resonances (δ 306.8, 308.8, 310.2, 317.0, 317.4, and 323.8 p.p.m.) assignable to alkylidyne-carbon nuclei bridging three metal centres. Although these six signals have chemical shifts above rather than below 300 p.p.m., nevertheless, they can be attributed to μ<sub>3</sub>-C rather than μ-C groups because of the Mo atoms present. This leads to more deshielded signals than those found with analogous W compounds. Thus for (5a) the alkylidyne-carbon nuclei resonances in the <sup>13</sup>C-<sup>1</sup>H n.m.r. spectrum are at δ 326.4, 314.0 (μ-C), 297.6, 297.2, 290.8, 288.2, 288.0, and 284.8 p.p.m. (μ<sub>3</sub>-C).<sup>2c</sup>

There were sixteen CO peaks in the <sup>13</sup>C-<sup>1</sup>H n.m.r. spectrum of (5b), eight corresponding to each isomer [5b(i)] and [5b(ii)]. There were also eight η-C<sub>5</sub>H<sub>5</sub> resonances, four for each isomer. In the <sup>195</sup>Pt-<sup>1</sup>H n.m.r. spectrum (Table 3) two pairs of platinum signals were observed, corresponding to the presence of two inequivalent platinum nuclei in each isomer. All the data strongly support the formulations shown for the two isomers, and are similar to those obtained for the isomers of the related tungsten species (5a) for which an X-ray diffraction study has been carried out.<sup>2c</sup>

In thf, under reflux, (5b) isomerises to the symmetric structure (6b) in which all four *p*-tolylmethylidyne ligands bridge three metal centres. The two isomers of (5a) similarly isomerise to (6a)

**Table 4.** Analytical<sup>a</sup> and physical data for the octanuclear metal compounds

Compound	Colour	Yield (%)	$\nu_{\max}(\text{CO})^b/\text{cm}^{-1}$	Analysis (%)	
				C	H
(5b) $[\text{Ni}_2\text{Pt}_2\text{Mo}_4(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_3(\mu\text{-CO})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_4]$	Black	84	1 846s, 1 826 (sh)	40.8 (40.3)	2.9 (2.7)
(6b) $[\text{Ni}_2\text{Pt}_2\text{Mo}_4(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_4(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$	Black	90	1 842s,br	41.1 (40.3)	2.6 (2.7)
(7) $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$	Black	77	1 830s,br	30.6 (29.0)	2.6 (2.0)
(8) $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_4(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$	Black	83	1 841s,br	36.1 (36.7)	2.6 (2.4)
(9) $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$	Black	80	1 843s,br	35.8 (36.0)	2.5 (2.3)
(11) $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$	Brown	14	1 823s,br, 1 797 (sh)	34.8 (35.7)	3.1 (3.1)

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Measured in  $\text{CH}_2\text{Cl}_2$ .

**Table 5.** Hydrogen-1 and carbon-13 n.m.r. data<sup>a</sup> for the octanuclear metal compounds

Compound	$^1\text{H}(\delta)^b$	$^{13}\text{C}(\delta)^c$
(5b)	2.11, 2.16, 2.19, 2.22 (s × 4, 3 H, Me-4), 2.29, 2.37 (s × 2, 6 H, Me-4), 4.54, 4.79, 4.97, 5.00, 5.07, 5.27, 5.30, 5.60 (s × 5, $\text{C}_5\text{H}_5$ ), 6.18—7.91 (m, 32 H, $\text{C}_6\text{H}_4$ )	345.0, 332.3 ( $\mu\text{-C}$ ), 323.8, 317.4, 317.0, 310.2, 308.8, 306.8 ( $\mu_3\text{-C}$ ), 265.3, 252.6, 252.2, 251.2, 250.1, 246.6, 246.0, 241.5, 240.9, 240.8, 240.0, 239.5, 238.8, 235.7, 235.1, 234.9 (CO), 158.7, 158.6, 158.1, 157.4, 157.1, 156.4, 156.3, 154.4 [ $\text{C}^1(\text{C}_6\text{H}_4)$ ], 137.9—125.1 ( $\text{C}_6\text{H}_4$ ), 97.3, 97.2, 97.1, 97.0, 96.9, 96.4, 96.2, 95.9 ( $\text{C}_5\text{H}_5$ ), 28.4 (4 × Me-4), 21.8 (4 × Me-4)
(6b)	2.19 (s, 12 H, Me-4), 4.97 (s, 20 H, $\text{C}_5\text{H}_5$ ), 6.55, 7.17 [(AB) <sub>2</sub> , 16 H, $\text{C}_6\text{H}_4$ , J(AB) 7]	320.7 ( $\mu_3\text{-C}$ ), 251.4, 239.8 (CO), 157.4 [ $\text{C}^1(\text{C}_6\text{H}_4)$ ], 136.7—126.5 ( $\text{C}_6\text{H}_4$ ), 97.3 ( $\text{C}_5\text{H}_5$ ), 21.9 (Me-4)
(7) <sup>d</sup>	(i) 2.12, 2.32 (s × 2, 6 H, Me, Me-4), 5.19, 5.27 (s × 2, 10 H, $\text{C}_5\text{H}_5$ ), 7.00—7.88 (m, 8 H, $\text{C}_6\text{H}_4$ ) (ii) 2.07 (s, 6 H, Me-4), 3.62 (s, 6 H, Me), 5.11, 5.38 (s × 2, 10 H, $\text{C}_5\text{H}_5$ ), 6.48, 7.01 [(AB) <sub>2</sub> , 8 H, $\text{C}_6\text{H}_4$ , J(AB) 8]	306.7, 293.1 ( $\mu_3\text{-C}$ ), 248.8, 243.2, 237.3, 229.2 (CO), 158.8 [ $\text{C}^1(\text{C}_6\text{H}_4)$ ], 137.1—127.6 ( $\text{C}_6\text{H}_4$ ), 95.1, 93.6 ( $\text{C}_5\text{H}_5$ ), 51.8 (Me), 21.5 (Me-4)
(8)	2.17, 2.19 (s × 2, 6 H, Me-4), 4.96, 5.06 (s × 2, 10 H, $\text{C}_5\text{H}_5$ ), 6.58—7.20 (m, 16 H, $\text{C}_6\text{H}_4$ )	<sup>b,e</sup> 157.3, 157.0 [ $\text{C}^1(\text{C}_6\text{H}_4)$ ], 136.0—126.5 ( $\text{C}_6\text{H}_4$ ), 96.9, 95.2 ( $\text{C}_5\text{H}_5$ ), 21.8, 18.2 (Me-4)
(9)	<sup>f</sup> (i) 2.15 (s, 6 H, Me-4), 4.99, 5.07 (s × 2, 10 H, $\text{C}_5\text{H}_5$ ), 6.85—7.80 (m, 18 H, $\text{C}_6\text{H}_4$ , Ph) (ii) 2.19 (s, 6 H, Me-4), 4.96, 5.06 (s × 2, 10 H, $\text{C}_5\text{H}_5$ ), 6.58—7.36 (m, 18 H, $\text{C}_6\text{H}_4$ , Ph)	<sup>b</sup> 318.0, 300.0 ( $\mu_3\text{-C}$ ), 249.9, 244.8, 239.9, 239.7 (CO), 158.2, 155.6 [ $\text{C}^1(\text{C}_6\text{H}_4$ and Ph)], 135.3—124.7 ( $\text{C}_6\text{H}_4$ and Ph), 96.4, 92.3 ( $\text{C}_5\text{H}_5$ ), 21.4 (Me-4) <sup>c</sup> 127.0—124.6 ( $\text{C}_6\text{H}_4$ and Ph), 96.1, 94.5 ( $\text{C}_5\text{H}_5$ ), 20.8 (Me-4)
(11)	1.87 (s, 30 H, $\text{C}_5\text{Me}_5$ ), 2.09 (s, 6 H, Me-4), 3.59 (s, 6 H, Me), 5.05 (s, 10 H, $\text{C}_5\text{H}_5$ ), 7.18, 7.34 [(AB) <sub>2</sub> , 8 H, $\text{C}_6\text{H}_4$ , J(AB) 7]	314.9, 289.7 ( $\mu_3\text{-C}$ ), 243.1, 242.7, 229.1, 226.9 (CO), 153.6 [ $\text{C}^1(\text{C}_6\text{H}_4)$ ], 135.2—126.2 ( $\text{C}_6\text{H}_4$ ), 104.7 ( $\text{C}_5\text{Me}_5$ ), 94.1 ( $\text{C}_5\text{H}_5$ ), 43.5 (Me), 21.7 (Me-4), 9.4 ( $\text{C}_5\text{Me}_5$ )

<sup>a</sup> Chemical shifts ( $\delta$ ) in p.p.m., coupling constants in Hz. <sup>b</sup> Measured in  $\text{CDCl}_3$ . <sup>c</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe<sub>4</sub>. Measurements in  $\text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$  at room temperature unless otherwise stated. <sup>d</sup> First set of data refers to the first isomer from the chromatography column. The second refers to the second compound from the column. <sup>e</sup> Quality of spectrum limited by very poor solubility, hence all peaks not listed. <sup>f</sup> First set of data refers to the *cis* isomer.

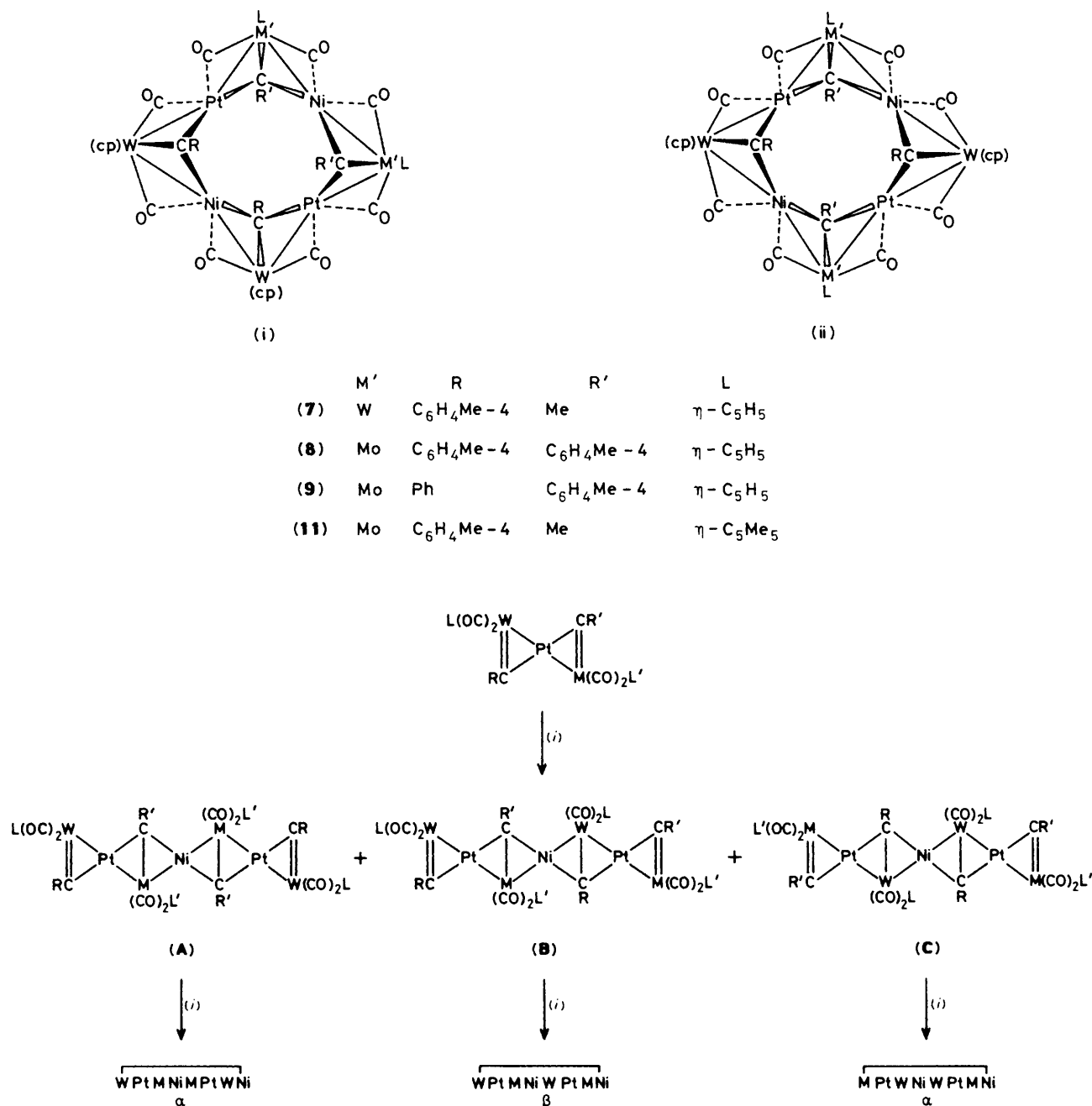
when refluxed in thf solution. The data for (6b) are in complete accord with the structure shown. In the  $^{13}\text{C}\text{-}\{^1\text{H}\}$  n.m.r. spectrum the four symmetrically disposed triply bridging alkyldiene groups give rise to a single resonance at  $\delta$  320.7 p.p.m. and the  $^{195}\text{Pt}\text{-}\{^1\text{H}\}$  n.m.r. spectrum also shows a single peak at  $\delta$  1 245 p.p.m. The corresponding  $^{13}\text{C}\text{-}\{^1\text{H}\}$  and  $^{195}\text{Pt}\text{-}\{^1\text{H}\}$  n.m.r. data for (6a) are 305.7 p.p.m. and 1 236 p.p.m., respectively.<sup>2c</sup>

The reaction between (1e) and  $[\text{Ni}(\text{cod})_2]$  was next investigated with the objective of obtaining an octanuclear metallacycle with two different alkyldiene ligands. When after 2 h the crude reaction mixture was chromatographed, two fractions were observed on the column. The first yielded a product which n.m.r. studies revealed corresponded to a single 'symmetric' isomer of an eight-metal ring cluster, *i.e.* a species  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (7) in which the four alkyldiene groups triply bridge metal triangles, two on one side of the eight-membered ring and two on the other, as in the compounds (6).<sup>2c</sup> This is in contrast with

'unsymmetric' structures such as those of (5) in which one of the alkyldiene ligands edge-bridges a metal-metal bond, while the other three occupy triply bridging sites. The second fraction obtained from the reaction between (1e) and  $[\text{Ni}(\text{cod})_2]$  proved to be much more complicated, displaying in its  $^1\text{H}$  n.m.r. spectrum twenty resonances for  $\eta\text{-C}_5\text{H}_5$  groups, ten signals for Me groups, and ten peaks for Me-4 substituents.

To understand why such a complicated mixture of isomeric species is produced it is necessary to consider how the reaction proceeds. It is assumed that the initial step is the linking of two molecules of the trinuclear metal complex by a single nickel atom to give a seven-metal-atom chain cluster, as illustrated for a generalised system in the accompanying Scheme. Support for this assumption comes from the observation that treatment of  $[\text{PtW}_2(\mu\text{-CMe})_2(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2]$  with 1 equivalent of  $[\text{Ni}(\text{cod})_2]$  affords the heptanuclear metal cluster  $[\text{NiPt}_2\text{W}_4(\mu\text{-CMe})_2(\mu_3\text{-CMe})_2(\text{CO})_8(\eta\text{-C}_5\text{Me}_5)_4]$ .<sup>2b</sup>

The number of isomeric octanuclear metal species produced in the reactions, derived from the heptanuclear metal com-



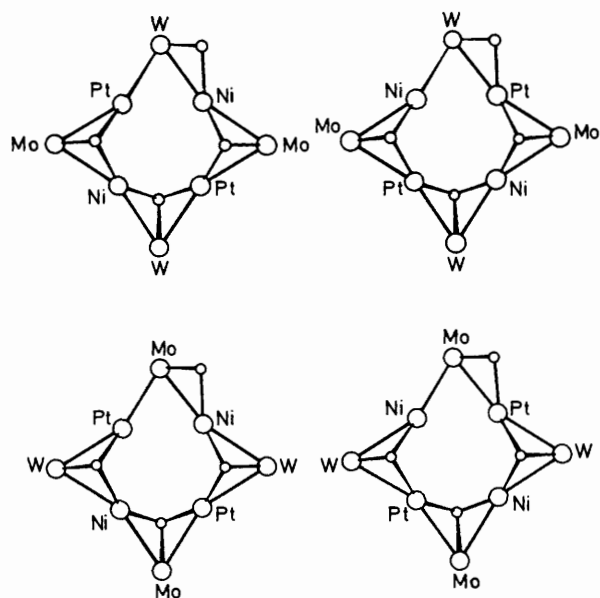
**Scheme.** M = Mo or W, R or R' = alkyl or aryl, L or L' = η-C<sub>5</sub>H<sub>5</sub> or η-C<sub>5</sub>Me<sub>5</sub>. (i) [Ni(cod)<sub>2</sub>]

plexes, depends not only on the number of different transition elements involved but whether the substituents R or R' on the alkylidene carbon atoms are the same or different. Thus for the heptanuclear metal precursors, three isomers (A), (B), and (C) (see Scheme) can form if M = W and R ≠ R', or if M = Mo. Statistically, formation of (B) will be twice as likely as that of (A) or (C), leading theoretically to a 1:2:1 isomer ratio. The next stage in the process will be ring formation, following addition of a second nickel atom. As depicted in the Scheme, this leads to two different core structures (α or β) if the groups R and R' are different, or if M = Mo rather than W. Since (B) is present in twice the amount of (A) or (C), other factors being the same, equal quantities of α and β will be formed.

By analogy with the formation of (5a) and (5b), it would be

expected that the initially formed metallacycles would be 'unsymmetric' in the sense that one alkylidene group would edge-bridge a metal-metal bond, whereas the other three would occupy triply bridging sites. For a generalised system, such as that depicted in the Scheme, for each of the frameworks α or β four isomers are thus possible, since the edge-bridging alkylidene group can span W-Pt, W-Ni, M-Pt, or M-Ni bonds. However, if the mixture is thermally isomerised so that all four alkylidene groups are in triply bridging sites the number of isomers is reduced from eight to two.

In the reaction between (1e) and [Ni(cod)<sub>2</sub>] the second eluate from the chromatography column contains a mixture of unsymmetric isomers of the eight-metal-atom ring cluster. Moreover, <sup>1</sup>H n.m.r. spectroscopy indicates the presence of

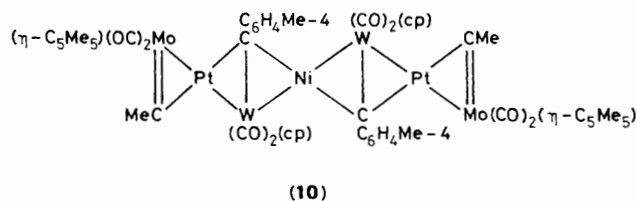


**Figure.** The metal atom core structures and arrangements of the bridging alkyldiene-carbon atom in the four 'asymmetric' isomers of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu\text{-CR})(\mu_3\text{-CR})_3(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  having the metal atom sequence  $\text{MoPtWNiMoPtWNi}$ . The alternative metal atom sequence  $\text{MoNiWPTWNiMoPt}$  also gives rise to four asymmetric isomers depending on whether the  $\mu\text{-CR}$  group bridges a  $\text{W-Ni}$ ,  $\text{W-Pt}$ ,  $\text{Mo-Ni}$ , or  $\text{Mo-Pt}$  bond

five of the possible eight isomers, the other three presumably having converted into the thermodynamically more stable symmetric structure  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (7). The two isomers of the latter arise as a result of the two possible dispositions of the  $\mu_3\text{-CMe}$  and  $\mu_3\text{-CC}_6\text{H}_4\text{Me-4}$  groups. Interestingly, if the reaction between (1e) and  $[\text{Ni}(\text{cod})_2]$  is carried out over longer periods of time, the second band from the column contains only one unsymmetric isomer, together with a second symmetric isomer of (7) in ca. 2:1 ratio, based on relative peaks heights in the  $^1\text{H}$  n.m.r. spectra. If the first isomer mixture (that produced after a 2 h reaction time) is refluxed in thf a small amount of the first symmetric isomer of (7) and a larger amount of the second (ca. 1:3) are formed. However, if the reaction mixture obtained after several hours is refluxed only the second symmetric isomer is produced. This implies that the isomerisation to the 'first' symmetric isomer is much quicker than to the 'second.'

The two symmetric isomers of (7) have been fully characterised by their n.m.r. data (Tables 3 and 5). The  $^{13}\text{C}\text{-}\{^1\text{H}\}$  n.m.r. spectrum of each isomer shows two  $\mu_3\text{-CR}$  ( $\text{R} = \text{Me}$  or  $\text{C}_6\text{H}_4\text{Me-4}$ ) resonances. Diagnostically the  $^{195}\text{Pt}\text{-}\{^1\text{H}\}$  n.m.r. spectra of both species show only a single resonance, because the platinum atoms are equivalent. However, these resonances show two sets of  $^{183}\text{W}$  satellite peaks in accord with the presence of  $\text{W}(\text{CMe})$  and  $\text{W}(\text{CC}_6\text{H}_4\text{Me-4})$  groups. Unfortunately the n.m.r. data do not allow a distinction between [7(i)] and [7(ii)].

When (1f) was treated with  $[\text{Ni}(\text{cod})_2]$  the situation was somewhat different, although the initial reaction again produced a mixture of species. The  $^1\text{H}$  n.m.r. spectrum showed the presence of one symmetric isomer, and four unsymmetric isomers (Figure). Refluxing the mixture in thf yielded only one symmetric isomer of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_4(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (8). For a reason as yet not understood only one metal framework is produced and all possible isomers for this framework (one symmetric and four unsymmetric) are formed.



Inspection of the Scheme shows that the core of the molecule could have the metal atom sequence  $\overline{\text{WPtMoNiMoPtWNi}}$  ( $\alpha$  form) or  $\overline{\text{WPtMoNiWPTWNi}}$  ( $\beta$  form). For a symmetrical isomer these correspond to [8(i)] or [8(ii)], respectively. In the latter the two Mo and the two W atoms occupy transoid positions in the star cluster, whereas in the former these pairs of atoms are cisoid. One explanation for the observed behaviour might be that one of the  $\text{M}=\text{C}$  or  $\text{M}'=\text{C}$  groups in (1f) is considerably more reactive than the other. In the heptanuclear metal chain precursor (see Scheme) this would favour formation of isomer (A) or isomer (C) rather than (B), and thus the metal sequence  $\alpha$  would occur in the symmetric isomer of the octanuclear metal species, viz. [8(i)]. This complex was very insoluble and complete  $^{13}\text{C}\text{-}\{^1\text{H}\}$  n.m.r. data were not obtained.

Different behaviour was again observed when compound (1g) was treated with an excess of  $[\text{Ni}(\text{cod})_2]$ . Chromatography of the reaction mixture gave in this case three separable eluates. The first fraction showed in the  $^1\text{H}$  n.m.r. spectrum only four resonances for  $\eta\text{-C}_5\text{H}_5$  groups and these were in two pairs. This suggests that this fraction contains a mixture of the two possible symmetric isomers of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  [9(i) and 9(ii)]. The other two eluates both showed eight  $\eta\text{-C}_5\text{H}_5$  resonances in their  $^1\text{H}$  n.m.r. spectra. These eluates thus contain four of the possible unsymmetric isomers for this system. On refluxing these fractions in thf for several hours each group of unsymmetric isomers, containing the edge-bridging alkyldiene ligands, affords a single but different symmetric isomer of (9). This implies that the two groups of unsymmetric isomers, separated by chromatography, have different metal atom sequences.

The data for the symmetric isomers of (9) are given in Tables 3–5. As before, the n.m.r. results by themselves do not define the isomer [9(i) or 9(ii)] to which they correspond. However, in this case a full analysis of the system was possible via an independent synthesis of [9(i)], which has the cisoid arrangement of the  $\text{Mo}_2$  and  $\text{W}_2$  atom pairs. Compound (4c) is one of the possible intermediates in the reaction between (1g) and  $[\text{Ni}(\text{cod})_2]$ , as can be inferred by reference to the Scheme. Hence if (4c) is treated with  $[\text{Ni}(\text{cod})_2]$  and the mixture thermally isomerised it should form [9(i)]. In practice this occurred, and the product obtained was identical with that produced by refluxing the first mixture of unsymmetric isomers obtained from the chromatography column in the reaction of (1g) with  $[\text{Ni}(\text{cod})_2]$ . Hence in Table 5 data for [9(i)], having the metal atom sequence  $\overline{\text{MoNiMoPtWNiWPT}}$ , are listed first.

Finally, the reaction between (1h) and  $[\text{Ni}(\text{cod})_2]$  was studied. Chromatography of the crude reaction mixture produced three eluates. The major product was present in the eluate which was removed last from the column, and was dark purple in colour. The i.r. spectrum of the compound in the CO region was different from that of an octanuclear metallacyclic cluster, but was very similar to that of the heptanuclear metal species (4a). The purple major product was fully characterised (Tables 2 and 3) as  $[\text{NiPt}_2\text{Mo}_2\text{W}_2(\mu\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$  (10). The  $^{13}\text{C}\text{-}\{^1\text{H}\}$  n.m.r. spectrum showed resonances for two  $\mu\text{-C}$  nuclei at  $\delta$  344.1 and 345.9 p.p.m., and two signals for  $\mu_3\text{-C}$  nuclei at  $\delta$  272.2 and 272.5 p.p.m. These data are consistent with an 'asymmetric' seven-



metal-atom chain. The formation of (10) shows that the reaction between (1h) and  $[\text{Ni}(\text{cod})_2]$  can cease before addition of another nickel atom gives a metallacycle. As discussed above (Scheme), three isomeric forms are possible for a heptanuclear metal chain compound. The relatively deshielded resonances for the  $\mu\text{-C}$  nuclei in the  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectrum of (10) are consistent with the structure shown, with the ethylidyne groups edge-bridging Mo-Pt bonds [type (C) of the Scheme]. If the chain terminated with  $\text{W}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{Pt}$  fragments, the  $\mu\text{-C}$  nuclei would have been expected to resonate in the range  $\delta$  310–315 p.p.m., as observed for all other such compounds.<sup>2c</sup>

The formation of (10), as opposed to other possibilities, is consistent with the presence of the  $\eta\text{-C}_5\text{Me}_5$  ligand. The steric bulk and electron-donating properties of this group might reduce the reactivity of the dimetallacyclopropene unit containing Mo in (1h), compared with that containing W. The  $^{195}\text{Pt}\{-^1\text{H}\}$  n.m.r. data (Table 3) for (10) are in agreement with the structure, since there are two resonances for non-equivalent platinum atoms occupying sites too far apart to observe  $^{195}\text{Pt}\text{-}^{195}\text{Pt}$  coupling.

It is not surprising that compound (10) does not readily add another Ni atom and cyclise to a ring structure, since the metallacycle would have a structure in which two  $\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)$  fragments would be cisoid to one another in the 'star' cluster, thereby creating steric problems. It is noteworthy that  $[\text{NiPt}_2\text{W}_4(\mu\text{-CMe})_2(\mu_3\text{-CMe})_2(\text{CO})_8(\eta\text{-C}_5\text{Me}_5)_4]$  does not react with  $[\text{Ni}(\text{cod})_2]$ .<sup>7</sup>

The other products from the reaction between (1h) and  $[\text{Ni}(\text{cod})_2]$  were next examined. These were contained in the first and second eluates removed from the chromatography column. The first compound to elute corresponded to ca. 20% of the product mixture. It was identified by the data given in Tables 3–5 as the symmetric ring cluster  $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$  (11), possessing the metal atom sequence  $\text{WPtMoNiWPtMoNi}$ . This complex would arise by addition of Ni to a heptanuclear chain cluster structurally similar to (B) in the Scheme (with  $\text{M} = \text{Mo}$ ,  $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ,  $\text{R}' = \text{Me}$ ,  $\text{L} = \eta\text{-C}_5\text{H}_5$ , and  $\text{L}' = \eta\text{-C}_5\text{Me}_5$ ). The isomer of type (B) would be produced in smaller quantity than (10), due to the lower reactivity of the Mo-containing dimetallacyclopropene ring in (1h), discussed above.

The second eluate from the column, ca. 5% of the product mixture, appeared to contain a second symmetric octanuclear metal ring cluster, and an isomer in which an alkylidyne fragment edge-bridges a metal-metal bond. Refluxing this mixture in thf isomerised the asymmetric species into the accompanying symmetric species. Unfortunately, due to the very low yield, it was not possible to obtain  $^{13}\text{C}\{-^1\text{H}\}$  and  $^{195}\text{Pt}\{-^1\text{H}\}$  n.m.r. data on the latter, but this species is very probably the symmetric isomer of (11) with the metal atom sequence  $\text{WPtMoNiMoPtWNi}$ . It could derive from addition of a nickel atom to a heptanuclear metal species of type (A) (Scheme), which would be produced in smaller quantities than a species of type (B), due to the aforementioned lower reactivity of the Mo-containing dimetallacyclopropene ring in (1h).

To confirm these structural assignments, compound (10) was treated with a large excess of  $[\text{Ni}(\text{cod})_2]$ . Chromatography of the reaction mixture afforded mostly unreacted (10), but eluting first was a trace (ca. 5%) of the symmetric isomer of (11) mentioned above. Since the isomer of (11) with the metal atom sequence  $\text{WPtMoNiMoPtWNi}$  can be obtained directly from (10), and the same isomer would form from a heptanuclear species of type (A) as discussed above, the nature of the various products from the reaction involving (1h) and  $[\text{Ni}(\text{cod})_2]$  is established.

The results described in this paper demonstrate that metal atom chain structures containing molybdenum are readily

obtained, as are eight-membered ring metallacycles containing molybdenum with core structures of the type  $(\mu_3\text{-C})_4\text{Ni}_2\text{Pt}_2\text{Mo}_4$  and  $(\mu_3\text{-C})_4\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2$ . Several of the products became accessible as a result of the synthesis of the new trimetal species (1e)–(1h). These contain either two different alkylidyne groups (1e), or an  $\eta\text{-C}_5\text{H}_5$  and an  $\eta\text{-C}_5\text{Me}_5$  ring (1h), or three different transition elements (1f)–(1h).

## Experimental

The techniques employed and the instrumentation used have been described previously.<sup>2b</sup> Light petroleum refers to that fraction of b.p. 40–60 °C. Alumina used for chromatography columns was BDH aluminium oxide (Brockman, Activity II). The compound  $[\text{Ni}(\text{cod})_2]$  was purchased from Strem Chemicals Inc., and  $[\text{Pt}(\text{cod})_2]$  was prepared as described elsewhere.<sup>8</sup> The complexes  $[\text{M}(\equiv\text{CR})(\text{CO})_2\text{L}]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{R} = \text{Me}$ ,  $\text{Ph}$ , or  $\text{C}_6\text{H}_4\text{Me-4}$ ;  $\text{L} = \eta\text{-C}_5\text{H}_5$  or  $\eta\text{-C}_5\text{Me}_5$ )<sup>9</sup> and  $[\text{WPt}\{\mu\text{-C}(\text{R})\text{CO}\}(\text{CO})(\text{PMe}_3)(\text{cod})(\eta\text{-C}_5\text{H}_5)]$  ( $\text{R} = \text{Ph}$  or  $\text{C}_6\text{H}_4\text{Me-4}$ )<sup>6</sup> were obtained as previously described. Analytical and other data for the new compounds are given in Tables 1 and 4.

*Synthesis of the Trinuclear Metal Compounds.*—(i) The compound  $[\text{Pt}(\text{cod})_2]$  (0.32 g, 0.78 mmol) in cold (0 °C) ethylene-saturated light petroleum (30 cm<sup>3</sup>) was slowly added to a cold light petroleum (50 cm<sup>3</sup>) solution of  $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (0.50 g, 1.56 mmol). The mixture was warmed to room temperature (1 h) with stirring and then the solvent removed *in vacuo*. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$ –light petroleum (20 cm<sup>3</sup>, 1:1) and chromatographed, eluting with the same solvent mixture. The first eluate contained a trace of unreacted  $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  and this was followed by the major product  $[\text{PtMo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (1e) (0.48 g) isolated as maroon crystals.

(ii) The compounds  $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (0.50 g, 1.56 mmol) and  $[\text{Ni}(\text{cod})_2]$  (0.21 g, 0.76 mmol) were mixed and thf (20 cm<sup>3</sup>) was added. The contents of the Schlenk tube were magnetically stirred (1 h) at room temperature. Solvent was removed *in vacuo*, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ –light petroleum (20 cm<sup>3</sup>, 1:1), and chromatographed. Elution with the same solvent mixture gave initially an eluate containing a trace of  $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ . The second, dark red, elute was collected, and the solvent removed *in vacuo*. The residue was crystallised from  $\text{CH}_2\text{Cl}_2$ –light petroleum (10 cm<sup>3</sup>, 1:5) to give maroon crystals of  $[\text{NiMo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (1d) (0.39 g).

(iii) To a solution of  $[\text{PtW}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{CO}\}(\text{CO})(\text{PMe}_3)(\text{cod})(\eta\text{-C}_5\text{H}_5)]$  (0.20 g, 0.25 mmol) in thf (20 cm<sup>3</sup>) was added  $[\text{W}(\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (0.09 g, 0.27 mmol), and the reaction mixture was stirred for 1 h. Solvent was removed *in vacuo*, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ –light petroleum (10 cm<sup>3</sup>, 1:1) and chromatographed. A dark red eluate was collected, and after solvent was removed *in vacuo* crystallisation of the residue from  $\text{CH}_2\text{Cl}_2$ –light petroleum (7 cm<sup>3</sup>, 1:5) gave red crystals of  $[\text{PtW}_2(\mu\text{-CMe})(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (1e) (0.19 g).

(iv) Red crystals of  $[\text{PtMoW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (1f) (0.17 g) were obtained from  $[\text{PtW}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{CO}\}(\text{CO})(\text{PMe}_3)(\text{cod})(\eta\text{-C}_5\text{H}_5)]$  (0.20 g, 0.25 mmol) and  $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (0.08 g, 0.25 mmol) in thf (20 cm<sup>3</sup>) using the same procedure as that for (1e).

(v) Similarly,  $[\text{PtW}\{\mu\text{-C}(\text{Ph})\text{CO}\}(\text{CO})(\text{PMe}_3)(\text{cod})(\eta\text{-C}_5\text{H}_5)]$  (0.20 g, 0.25 mmol) in thf (20 cm<sup>3</sup>) with  $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (0.08 g, 0.25 mmol) in the same solvent (20 cm<sup>3</sup>) gave red crystals of  $[\text{PtMoW}(\mu\text{-CPh})(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (1g) (0.18 g) after chromatography and crystallisation.

(vi) The compound  $[\text{PtW}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{CO}\}(\text{CO})\text{-}(\text{PMe}_3)(\text{cod})(\eta\text{-C}_5\text{H}_5)]$  (0.20 g, 0.25 mmol) was dissolved in thf (25 cm<sup>3</sup>) and  $[\text{Mo}(\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$  (0.08 g, 0.25 mmol) was added. The mixture was stirred for 1 h. Solvent was removed *in vacuo*, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ -light petroleum (10 cm<sup>3</sup>, 1:1) and chromatographed. The dark red eluate was collected, and after solvent was removed *in vacuo*, crystallisation of the residue from  $\text{CH}_2\text{Cl}_2$ -light petroleum (7 cm<sup>3</sup>, 1:5) gave dark orange crystals of  $[\text{PtMoW}(\mu\text{-CMe})\text{-}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$  (**1h**) (0.17 g).

**Synthesis of the Tetranuclear Metal Compounds.**—(i) A cold (0 °C) ethylene-saturated thf (20 cm<sup>3</sup>) solution of  $[\text{Pt}(\text{cod})_2]$  (0.12 g, 0.29 mmol) was added slowly to a thf (10 cm<sup>3</sup>) solution of  $[\text{PtMo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (0.20 g, 0.29 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 was dissolved in  $\text{CH}_2\text{Cl}_2$  (5 cm<sup>3</sup>) and chromatographed. Elution with the same solvent afforded a dark red eluate. Removal of solvent and crystallisation from  $\text{CH}_2\text{Cl}_2$ -light petroleum (10 cm<sup>3</sup>, 1:5) gave dark red crystals of  $[\text{Pt}_2\text{Mo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4\text{-}(\text{cod})(\eta\text{-C}_5\text{H}_5)_2]$  (**2c**) (0.21 g).

(ii) Using an analogous procedure, brown crystals of  $[\text{NiPtMo}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{cod})(\eta\text{-C}_5\text{H}_5)_2]$  (**2d**) (0.21 g) were prepared from  $[\text{Pt}(\text{cod})_2]$  (0.12 g, 0.29 mmol) and (**1d**) (0.20 g, 0.29 mmol). The dark brown product was eluted from the column using neat  $\text{CH}_2\text{Cl}_2$ .

**Synthesis of the Complex  $[\text{NiPt}_2\text{Mo}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2\text{-}(\text{CO})_4(\text{cod})_2(\eta\text{-C}_5\text{H}_5)_2]$ .**—Compound (**2d**) (0.20 g, 0.20 mmol) in cold ethylene-saturated thf (20 cm<sup>3</sup>) was slowly added to an ethylene-saturated thf (20 cm<sup>3</sup>, at 0 °C) solution of  $[\text{Pd}(\text{cod})_2]$  (0.09 g, 0.22 mmol). After warming to room temperature, and stirring for 3 h, solvent was removed *in vacuo*. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 cm<sup>3</sup>), and chromatographed. Elution with the same solvent gave three bands on the column, grey, green, and orange. Collection of these bands and removal of solvent *in vacuo* afforded brown microcrystals of  $[\text{NiPt}_2\text{Mo}_2\text{-}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\text{cod})_2(\eta\text{-C}_5\text{H}_5)_2]$  (**3c**) (0.10 g).

**Synthesis of the Complex  $[\text{NiPt}_2\text{Mo}_2\text{W}_2(\mu\text{-CPh})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ .**—A thf (25 cm<sup>3</sup>) solution of compound (**3c**) (0.15 g, 0.11 mmol) was syringed into a Fischer-Porter vessel containing  $[\text{W}(\equiv\text{CPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (0.07 g, 0.18 mmol). The reactants were pressurised with  $\text{C}_2\text{H}_4$  (2 atm, ca.  $2 \times 10^5$  Pa) for 2 h. Solvent was removed *in vacuo*, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (5 cm<sup>3</sup>) and chromatographed. Elution with the same solvent removed unreacted  $[\text{W}(\equiv\text{CPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ , followed by a slow-moving brown band. Collection of this fraction, removal of solvent *in vacuo*, and crystallisation of the residue from  $\text{CH}_2\text{Cl}_2$ -light petroleum (10 cm<sup>3</sup>, 1:8) afforded brown crystals of  $[\text{NiPt}_2\text{Mo}_2\text{W}_2\text{-}(\mu\text{-CPh})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (**4c**) (0.12 g).

**Synthesis of the Octanuclear Metal Compounds.**—(i) The compound  $[\text{Ni}(\text{cod})_2]$  (0.26 g, 0.95 mmol) was added to a solution of (**1c**) (0.20 g, 0.24 mmol) in thf (20 cm<sup>3</sup>), and the mixture was stirred for 2 h under nitrogen. Solvent was removed *in vacuo*, the residue dissolved in  $\text{CH}_2\text{Cl}_2$  (5 cm<sup>3</sup>) and chromatographed. Removal of solvent *in vacuo* from the green-brown eluate, and crystallisation from  $\text{CH}_2\text{Cl}_2$ -light petroleum (10 cm<sup>3</sup>, 1:5), yielded black crystals of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_4(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_3(\mu\text{-CO})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_4]$  (**5b**) (0.18 g).

(ii) The species (**5b**) (0.20 g, 0.11 mmol) was refluxed in thf (20 cm<sup>3</sup>) for 4 h. Solvent was removed *in vacuo*, and crystallisation of the residue from  $\text{CH}_2\text{Cl}_2$ -light petroleum (10 cm<sup>3</sup>, 1:5)

gave black crystals of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_4(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_4(\text{CO})_8\text{-}(\eta\text{-C}_5\text{H}_5)_4]$  (**6b**) (0.18 g).

(iii) The compound  $[\text{Ni}(\text{cod})_2]$  (0.15 g, 0.54 mmol) was added to a thf solution (25 cm<sup>3</sup>) of (**1e**) (0.20 g, 0.21 mmol), and the mixture was stirred for 3 h at room temperature. Solvent was removed *in vacuo*, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ -light petroleum (10 cm<sup>3</sup>, 2:1) and chromatographed. Eluting with the same solvent mixture gave initially a grey band followed by a green band. Removal of solvent *in vacuo*, and crystallisation of the separate fractions from  $\text{CH}_2\text{Cl}_2$ -light petroleum (1:5), gave grey microcrystals of  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (**7**, *cis* or *trans*) (0.08 g), and green-brown microcrystals of a mixture of the unsymmetrical isomers of  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu\text{-CMe})(\mu_3\text{-CMe})\text{-}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\mu\text{-CO})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_4]$  and  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_4]$ .

The latter mixture was dissolved in thf (20 cm<sup>3</sup>) and refluxed for 2 h. Solvent was removed *in vacuo*, and the residue dissolved in  $\text{CH}_2\text{Cl}_2$ -light petroleum (10 cm<sup>3</sup>, 1:1). Chromatography, eluting with the same solvent mixture, gave a grey band followed by a green-brown eluate. Removal of solvent *in vacuo* from the eluates, and crystallisation of the fractions as before, yielded grey microcrystals of  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (**7**, *cis* or *trans*) (0.02 g) and green microcrystals of  $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2\text{-}(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (**7**, *cis* or *trans*) (0.06 g).

(iv) A solution of the complex (**1f**) (0.20 g, 0.22 mmol) in thf (30 cm<sup>3</sup>) was added to  $[\text{Ni}(\text{cod})_2]$  (0.14 g, 0.50 mmol), and the mixture was stirred for 2 h. Removal of solvent *in vacuo*, dissolving the residue in  $\text{CH}_2\text{Cl}_2$  (15 cm<sup>3</sup>), followed by chromatography, and removal of solvent from the eluate, gave a black oil. This was dissolved in thf (30 cm<sup>3</sup>) and the solution refluxed for 3 h. Removal of solvent *in vacuo*, and crystallisation of the residue from  $\text{CH}_2\text{Cl}_2$ -light petroleum (15 cm<sup>3</sup>, 1:1), gave black microcrystals of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_4\text{-}(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (**8**) (0.18 g).

(v) To a solution of complex (**1g**) (0.20 g, 0.22 mmol) in thf (30 cm<sup>3</sup>) was added  $[\text{Ni}(\text{cod})_2]$  (0.14 g, 0.50 mmol), and the mixture was stirred for 2 h. After this time, solvent was removed *in vacuo* and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ -light petroleum (15 cm<sup>3</sup>, 1:1). Chromatography, eluting with the same solvent mixture, gave three separable bands, green, brown, and grey. The three eluates were collected individually. The last two were each dissolved in thf (20 cm<sup>3</sup>), after solvent had been removed *in vacuo*. Recrystallisation of the first eluate from  $\text{CH}_2\text{Cl}_2$ -light petroleum (8 cm<sup>3</sup>, 1:5) gave the two 'symmetric' isomers of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8\text{-}(\eta\text{-C}_5\text{H}_5)_4]$  (**9**) (0.04 g). The thf solutions from the last two eluates were refluxed for 2 h, solvent was removed *in vacuo*, and the residues were recrystallised from  $\text{CH}_2\text{Cl}_2$ -light petroleum (9 cm<sup>3</sup>, 1:5). The brown eluate gave one symmetric isomer of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$  (**9**) (0.05 g) as black microcrystals, the other eluate gave the other possible 'symmetric' isomer (0.08 g) of (**9**) as black microcrystals.

(vi) The compound  $[\text{Ni}(\text{cod})_2]$  (0.21 g, 0.80 mmol) was added to a thf solution (20 cm<sup>3</sup>) of (**1h**) (0.20 g, 0.22 mmol) and the mixture was stirred for 2 h. Solvent was removed *in vacuo* and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ -light petroleum (10 cm<sup>3</sup>, 1:1), and chromatographed. Elution with the same solvent mixture gave three bands on the column: green, grey, and purple. Removal of solvent *in vacuo*, and crystallisation of the separate fractions from  $\text{CH}_2\text{Cl}_2$ -light petroleum (1:5) gave green microcrystals of  $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu_3\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$  (**11**) (0.03 g), brown microcrystals of the other isomer of this 'symmetric' ring compound (0.01 g) and purple microcrystals of  $[\text{NiPt}_2\text{Mo}_2\text{W}_2\text{-}$

$(\mu\text{-CMe})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_5\text{Me}_5)_2]$  (**10**)  
(0.15 g).

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### References

- 1 Part 84. D. D. Devore, J. A. K. Howard, J. C. Jeffery, M. U. Pilotti, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1989, 303.
- 2 (a) G. P. Elliott, J. A. K. Howard, T. Mise, I. Moore, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 2091; (b) S. J. Davies, G. P. Elliott, J. A. K. Howard, C. M. Nunn, and F. G. A. Stone, *ibid.*, 1987, 2177; (c) G. P. Elliott, J. A. K. Howard, T. Mise, C. M. Nunn, and F. G. A. Stone, *ibid.*, p. 2189.

- 3 G. P. Elliott, J. A. K. Howard, T. Mise, C. M. Nunn, and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 190.
- 4 T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1981, 763.
- 5 J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodwood, *J. Chem. Soc., Dalton Trans.*, 1983, 2075; J. A. Abad, E. Delgado, M. E. Garcia, M. J. Grosse-Ophoff, I. J. Hart, J. C. Jeffery, M. S. Simmons, and F. G. A. Stone, *ibid.*, 1987, 41.
- 6 J. C. Jeffery, C. Sambale, M. F. Schmidt, and F. G. A. Stone, *Organometallics*, 1982, **1**, 1597.
- 7 G. P. Elliot, Ph.D. Thesis, Bristol University, 1987.
- 8 J. L. Spencer, *Inorg. Synth.*, 1979, **19**, 213.
- 9 E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397; W. Uedelhoven, K. Eberl, and F. R. Kreissl, *ibid.*, 1979, **112**, 3376.

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