Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 93.[1] Synthesis of Heteropolynuclear Metal Compounds with Chains of Seven to Eleven Metal Atoms; Crystal Structure of $[Mo_2W_3Pt_6(\mu_3-CMe)_3(\mu_3-CC_6H_4Me-4)_2(CO)_{10}(PMe_2Ph)_4(\eta-C_5H_5)_5]$ †

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Addition of $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) in ethylene-saturated thf (tetrahydrofuran) to the compound $[Mo_2WPt_3(\mu-CMe)(\mu_3-CC_6H_4Me-4)_2(CO)_6(cod)(\eta-C_5H_5)_3]$ in the same solvent affords the heptanuclear metal complex $[Mo_2WPt_4(\mu_3-CMe)(\mu_3-CC_6H_4Me-4)_2(CO)_6(cod)_2(\eta-C_5H_5)_3]$. The cod ligands in the latter species were displaced upon treatment with the reagents $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ (R = C_6H_4Me-4 or Me) to give the nonanuclear metal compounds $[Mo_2W_3Pt_4(\mu-CC_6H_4Me-4)_2(\mu_3-CMe)(\mu_3-CC_6H_4Me-4)_2(CO)_{10}(\eta-C_5H_5)_5]$ and $[Mo_2W_3Pt_4(\mu-CMe)_2(\mu_3-CMe)(\mu_3-CC_6H_4Me-4)_2(CO)_{10}(\eta-C_5H_5)_5]$, respectively. Complexes containing chains of ten or eleven metal atoms have also been prepared. Thus $[Mo_2W_3Pt_4(\mu-CC_6H_4Me-4)_2(\mu_3-CMe)(\mu_3-CC_6H_4Me-4)_2(CO)_{10}(\eta-C_5H_5)_5]$ reacts with an excess of $[Pt(cod)_2]$ to yield a mixture of $[Mo_2W_3Pt_5(\mu-CC_6H_4Me-4)(\mu_3-CMe)(\mu_3-CC_6H_4Me-4)_3(CO)_{10}(cod)(\eta-C_5H_5)_5]$, and $[Mo_2W_3Pt_6(\mu_3-CMe)(\mu_3-CC_6H_4Me-4)_4(CO)_{10}(cod)_2(\eta-C_5H_5)_5]$; and $[Mo_2W_3Pt_6(\mu_3-CMe)_3(\mu_3-CC_6H_4Me-4)_2(CO)_{10}(cod)_2(\eta-C_5H_5)_5]$ is obtained by treating $[Mo_2W_3Pt_4(\mu-CMe)_2(\mu_3-CMe)(\mu_3-CC_6H_4Me-4)_2(CO)_{10}(\eta-C_5H_5)_5]$ with an excess of $[Pt(cod)_2]$. Displacement of the cod ligands from $[Mo_2W_3Pt_6(\mu_3-CMe)_3(\mu_3-CC_6H_4Me-4)_2(CO)_{10}(cod)_2(\eta-C_5H_5)_5]$ by PMe_2Ph yields the complex $[Mo_2W_3Pt_6(\mu_3-CMe)_3(\mu_3-CC_6H_4Me-4)_2(CO)_{10}(PMe_2Ph)_4(\eta-C_5H_5)_5]$, structurally characterised by an *X*-ray diffraction study. The latter established that the spine of the molecule consisted of eleven metal atoms arranged in the sequence PtWPtMoPtMoPtWPtWPt. Each PtMPt (M = Mo or W) triangle (mean distances: Pt–W 2.751, Pt–Mo 2.745, and Pt$\cdots$Pt 3.040 Å) is capped by an alkylidyne fragment (mean distances: μ_3-C–Pt 2.05, μ_3-C–W 2.04, and μ_3-C–Mo 1.98 Å), and the terminal platinum atoms are each ligated by two PMe_2Ph groups.

We have described[2] rational procedures for preparing polynuclear metal complexes in which from three to seven metal atoms are linked to form chain-like structures. In these species the spines of the molecules consist of metal–metal bonds (W–Pt, Mo–Pt, W–Ni, or Mo–Ni) bridged by alkylidyne groups. The syntheses depend for their success on an isolobal mapping of metal–ligand fragments with organic groups,[3] and the generality of the methodology has recently been demonstrated by its extension to W–Rh chain systems.[4]

The chain-cluster compounds containing W, Mo, Pt, or Ni atoms are prepared starting from the trimetal complexes $[M'_2M(\mu-CR)_2(CO)_4L_2]$ (M′ = W or Mo, M = Pt or Ni, R = alkyl or aryl, L = $\eta-C_5H_5$ or $\eta-C_5Me_5$), the latter being obtained by treating the reagents $[M'(\equiv CR)(CO)_2L]$ with $[M(cod)_2]$ (cod = cyclo-octa-1,5-diene). Thus in typical reactions[2a] the species $[M'_2Pt(\mu-CR)_2(CO)_4L_2]$ [M′ = W, R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**1a**); M′ = W, R = Me, L = $\eta-C_5Me_5$ (**1b**); M′ = Mo, R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**1c**)] will add either one Pt(cod) fragment to yield the tetranuclear metal complexes $[M'_2Pt_2(\mu-CR)(\mu_3-CR)(CO)_4(cod)L_2]$ [M′ = W, R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**2a**); M′ = W, R = Me, L = $\eta-C_5Me_5$ (**2b**); M′ = Mo, R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**2c**)] or two Pt(cod) groups to afford the pentanuclear metal clusters $[M'_2Pt_3(\mu_3-CR)_2(CO)_4(cod)_2L_2]$ [M′ = W, R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**3a**); M′ = W, R, = Me, L = $\eta-C_5Me_5$ (**3b**); M′ = Mo, R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**3c**)]. Moreover, the cod ligands in these species are readily displaced by the reagents $[M'(\equiv CR)(CO)_2L]$. Thus (**2a**) with $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ affords $[W_3Pt_2(\mu-CC_6H_4Me-4)_2(\mu_3-CC_6H_4Me-4)(CO)_6(\eta-C_5H_5)_3]$ (**4a**), and (**2b**) with $[W(\equiv CMe)(CO)_2(\eta-C_5Me_5)]$ yields $[W_3Pt_2(\mu-CMe)_2(\mu_3-CMe)(CO)_6(\eta-C_5Me_5)_3]$ (**4b**). Similarly, the compounds (**3**) are precursors for either hexanuclear metal compounds, *e.g.* $[M'_2WPt_3(\mu-CR')(\mu_3-CR)_2(CO)_6(cod)L_3]$ [M′ = W, R′ = R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**5a**); M′ = W, R′ = R = Me, L = $\eta-C_5Me_5$ (**5b**); M′ = Mo, R′ = Me, R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**5c**)], or heptanuclear metal species, *e.g.* $[M'_2W_2Pt_3(\mu-CR')_2(\mu_3-CR)_2(CO)_8L_4]$ [M′ = W, R′ = R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**6a**); M′ = W, R′ = R = Me, L = $\eta-C_5Me_5$ (**6b**); M′ = Mo, R′ = Me, R = C_6H_4Me-4, L = $\eta-C_5H_5$ (**6c**)], depending on whether 1 equivalent or an excess of the appropriate reagent $[M'(\equiv CR)(CO)_2L]$ (R = Me or C_6H_4Me-4) is used.[2b]

In an attempt to extend the length of the metal atom chains, compound (**6a**) was treated with $[Pt(cod)_2]$.[2c] However, this procedure led to the formation of a metallacycle $[W_4Pt_4(\mu-CR)(\mu_3-CR)_3(\mu_3-CO)(CO)_7(\eta-C_5H_5)_4]$ (**7a**; R = C_6H_4Me-4), which on refluxing in thf (tetrahydrofuran) isomerised to the more symmetrical isomer $[W_4Pt_4(\mu_3-CR)_4(CO)_8(\eta-C_5H_5)_4]$ (**7b**). Several other 'star clusters',[5] *e.g.* $[M'_4Ni_2Pt_2(\mu_3-CR)_4(CO)_8(\eta-C_5H_5)_4]$ (M′ = W, R = C_6H_4Me-4 or Ph; M′ = Mo, R = C_6H_4Me-4) and $[M'_2W_2Ni_2Pt_2(\mu_3-CR)_2(\mu_3-CR')_2(CO)_8(\eta-C_5H_5)_4]$ (M′ = W, R = C_6H_4Me-4, R′ = Me; M′ = Mo, R = Ph or C_6H_4Me-4, R′ = C_6H_4Me-4), have been obtained by treating the appropriate trimetal compounds of type (**1**) with $[Ni(cod)_2]$.[2c,d] These syntheses using the trimetal species as precursors probably proceed *via* the intermediacy of molecules

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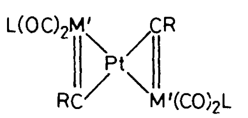
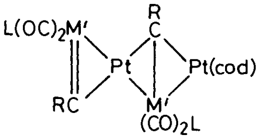
† *Supplementary data available:* see Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.

Non S.I. unit employed: atm = 101325 Pa.

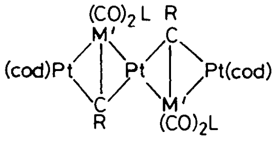
containing chains of seven metal atoms which upon addition of a Ni(cod) fragment cyclise. In this paper we describe how formation of a metallacycle may be avoided, allowing cluster compounds with nine, ten, and eleven metal atoms in the chain to be prepared.[6] The method involves employing as a precursor the heptanuclear metal compound [$\mathrm{Mo_2WPt_4}$(μ_3-CMe)(μ_3-$\mathrm{CC_6H_4}$Me-4)$_2$(CO)$_6$(cod)$_2$(η-$\mathrm{C_5H_5}$)$_3$] (**8**) having terminal Pt(cod) fragments rather than a heptanuclear metal species of type (**6**) with a $\mathrm{W_4Pt_3}$ or $\mathrm{W_2Mo_2Pt_3}$ backbone and terminal C=W groups.



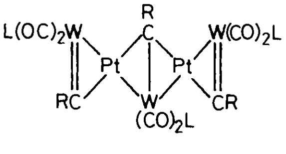
	M'	R	L
(**1a**)	W	C_6H_4Me-4	η-C_5H_5
(**1b**)	W	Me	η-C_5Me_5
(**1c**)	Mo	C_6H_4Me-4	η-C_5H_5



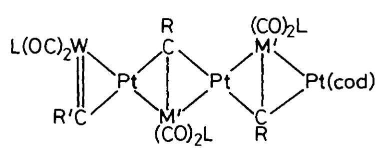
	M'	R	L
(**2a**)	W	C_6H_4Me-4	η-C_5H_5
(**2b**)	W	Me	η-C_5Me_5
(**2c**)	Mo	C_6H_4Me-4	η-C_5H_5



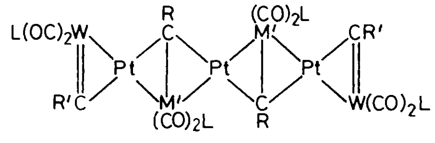
	M'	R	L
(**3a**)	W	C_6H_4Me-4	η-C_5H_5
(**3b**)	W	Me	η-C_5Me_5
(**3c**)	Mo	C_6H_4Me-4	η-C_5H_5



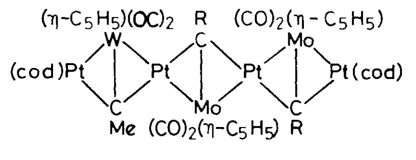
	R	L
(**4a**)	C_6H_4Me-4	η-C_5H_5
(**4b**)	Me	η-C_5Me_5



	M'	R	R'	L
(**5a**)	W	C_6H_4Me-4	C_6H_4Me-4	η-C_5H_5
(**5b**)	W	Me	Me	η-C_5Me_5
(**5c**)	Mo	C_6H_4Me-4	Me	η-C_5H_5



	M'	R	R'	L
(**6a**)	W	C_6H_4Me-4	C_6H_4Me-4	η-C_5H_5
(**6b**)	W	Me	Me	η-C_5Me_5
(**6c**)	Mo	C_6H_4Me-4	Me	η-C_5H_5

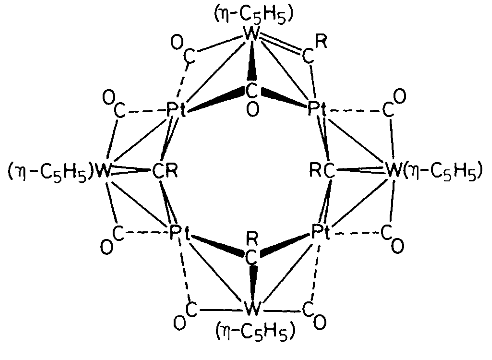


(**8**) R = C_6H_4Me-4

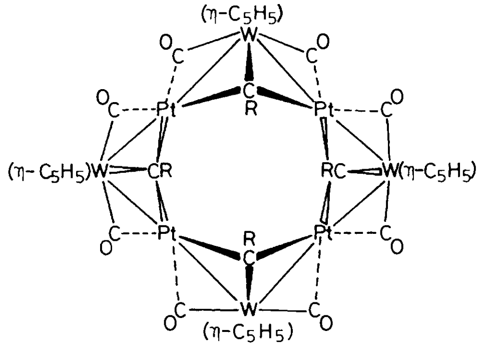
Results and Discussion

Heptanuclear Metal Compounds.—As discussed earlier,[2] the compounds (**2**)—(**6**) can exist in different diastereoisomeric forms, the number of isomers increasing with the length of the metal atom chain. However, not all the possible diastereoisomers are formed in the various syntheses, presumably for steric reasons. For a heptanuclear metal compound of formulation [$\mathrm{M_3Pt_4}$(μ_3-CR)$_3$(CO)$_6$(cod)$_2$$\mathrm{L_3}$] (M = Mo or W, R = alkyl or aryl, L = η-C_5H_5 or η-C_5Me_5) ten diastereoisomers are possible. These are based on three types of metallic skeleton which arise from the different way the three PtMPt triangles which comprise the molecule can be arranged. Representations of these conformers are shown in Figure 1. It should be noted however that these diagrams, are something of a simplification, as the chains incorporate a further degree of 'twist' out of the plane of the page.

Of the three conformers for the metal triangles, only (**C**) represents the orientation suitable for cyclisation to an octanuclear metal ring species. In contrast (**A**) and (**B**) should, in theory, give rise to nine-metal–atom chain complexes if both terminal cod ligands are replaced by alkylidynetungsten fragments. Examination of the molecular structure (Figure 2) established[2b] for the major isomer of the hexanuclear metal complex (**5b**), a species which might function as a precursor to a heptanuclear metal cluster of type (**C**) (Figure 1), reveals that addition of a Pt(cod) group would be sterically disfavoured, as the cod ligands would clash. Consequently, if a seven metal-atom chain compound [$\mathrm{M_3Pt_4}$(μ_3-CR)$_3$(CO)$_6$(cod)$_2$$\mathrm{L_3}$] with two terminal Pt(cod) groups were synthesised it would be expected to adopt configuration (**A**) or (**B**) (Figure 1) and so be a suitable precursor for further chain building reactions. In practice (**5b**) does not react with [Pt(cod)$_2$]. Evidently not only



(**7a**)



(**7b**)

R = C_6H_4Me-4

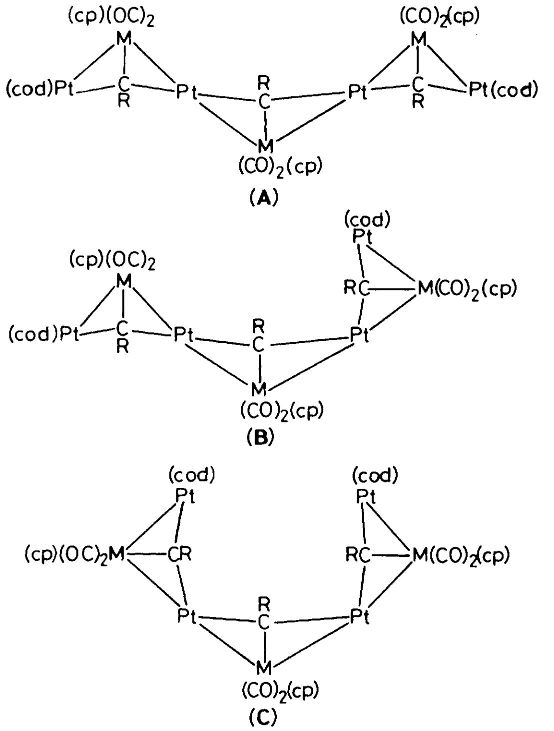


Figure 1. Possible metal skeletons for the compounds $[M_3Pt_4(\mu_3\text{-}CR)_3(CO)_6(cod)_2(\eta\text{-}C_5H_5)_3]$ (M = Mo or W, R = alkyl or aryl, cp = $\eta\text{-}C_5H_5$)

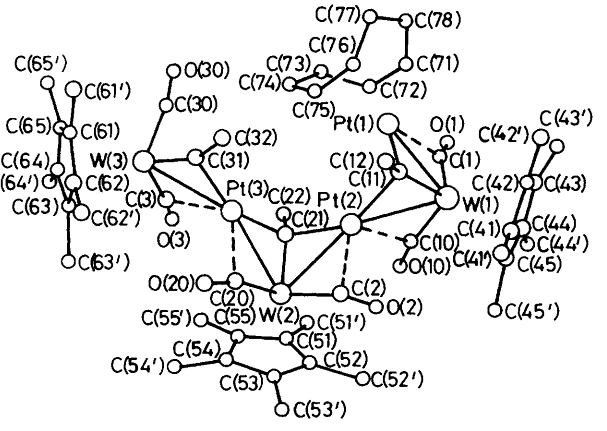


Figure 2. Molecular structure of $[W_3Pt_3(\mu\text{-}CMe)(\mu_3\text{-}CMe)_2(CO)_6(cod)(\eta\text{-}C_5Me_5)_3]$ (**5b**)^{2b}

is it impossible to form a W_3Pt_4 chain conformer of type (**C**), but addition of a Pt(cod) fragment to the 'other side' of the C=W bond is blocked by the bulky $\eta\text{-}C_5Me_5$ group. If the Pt(cod) had added to the 'blocked' side, a chain conformer of type (**B**) would have formed.

In contrast with the inertness of compound (**5b**) towards $[Pt(cod)_2]$, when (**5c**), which is available as a single isomer with a different configuration to the major isomer of (**5b**),^{2b} is treated with 1.5 equivalents of $[Pt(cod)_2]$ the seven-metal-atom complex $[Mo_2WPt_4(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_6(cod)_2(\eta\text{-}C_5H_5)_3]$ (**8**) is formed. Compound (**5c**) is the only hexanuclear metal compound we have prepared so far which shows any reactivity towards $[Pt(cod)_2]$. Complex (**8**) is readily separated from unreacted (**5c**) by column chromatography. It was characterised by the data given in Tables 1—3, and by its fast atom bombardment (f.a.b.) mass spectrum.

The presence of three triply bridging alkylidyne ligands in (**8**) is confirmed by the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table 2) which contains peaks at δ 267.1, 263.8, and 259.8 p.p.m., shifts which are characteristic for alkylidyne groups ligating three metal centres.[2] Signals for six carbonyl groups and two inequivalent cod ligands were also observed in this spectrum. In the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum (Table 3) signals corresponding to four inequivalent platinum environments were observed. The resonances at δ 1 234 and 946 p.p.m. may be assigned to those platinum atoms linked to two other metal atoms, whereas the signals at δ 401 and 311 p.p.m. are in the region associated with platinum atoms ligated by cod groups. These assignments are made on the basis of the data for the tri- and tetra-nuclear metal compounds (**1**) and (**2**) reported previously.^{2a} One interesting feature of the spectrum of (**8**) is the observation of a four bond platinum–platinum coupling, which is of a longer range than has been previously observed for these chain-type systems. Another point of interest is that all of the spectral data confirm that (**8**) is formed as a single isomer.

The f.a.b. mass spectrum is also in agreement with the proposed structure. It shows an envelope of peaks at *m*/*z* 1 861, corresponding to the molecular ion minus one cod ligand, and showing the expected isomer distribution. The major peak in the spectrum is at 1 585 corresponding to $[M - 2cod - 6CO]^+$.

Unfortunately the spectroscopic data for (**8**) do not define the diastereomeric form, and an *X*-ray diffraction study was not possible. However, the conformer illustrated [Figure 3(a)] is based on *X*-ray diffraction results carried out on an eleven-atom metal chain compound to be discussed below, and for which (**8**) is a precursor. As the different isomeric forms of these compounds may interconvert in solution there is a possibility that (**8**) may adopt a slightly different conformation. However, the conformer illustrated is as expected, being an example of configuration (A) in Figure 1, and as such is well set up to form longer chain compounds. It was this possibility that was next investigated.

Nonanuclear Metal Complexes.—Treatment of (**8**) in thf with an excess of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, in the presence of ethylene to labilise the cod ligands in the former, produced after appropriate work up the metal cluster species $[Mo_2W_3Pt_4(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(\eta\text{-}C_5H_5)_5]$ (**9a**) in excellent yield. Data characterising this product are listed in Tables 1—3.

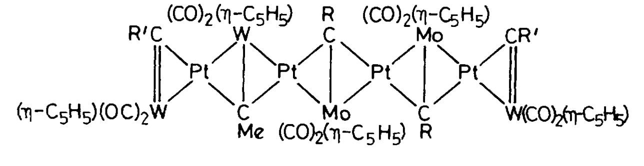
Interestingly, the n.m.r. data for (**9a**) showed that this compound exists in two isomeric forms, produced in approximately equal amounts based on peak intensities. This is in contrast with (**8**) which as mentioned above exists as a single isomer. Thus the $^{13}C\text{-}\{^1H\}$ spectrum of (**9a**) shows resonances at δ 305.0, 308.5, 308.7, and 318.5 p.p.m., all of which lie in the region associated with tolylmethylidyne ligands edge-bridging a metal–metal bond.[2] The six signals in the range δ 269.3—281.9 p.p.m. were similarly assigned to alkylidyne ligands bridging three metal atoms; three peaks for each isomer. Other diagnostically useful resonances for the isomeric mixture were those observed for the twenty carbonyl ligands, and for ten cyclopentadienyl rings.

In the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum the presence of two isomers was again revealed, as eight signals were observed, for four inequivalent platinum atoms in each conformer. As expected, there were no signals in this spectrum in the chemical shift range associated with terminal 'Pt(cod)' groups. By examination of the Pt···Pt coupling constants it is possible to assign the signals for each isomer (Table 3). Another feature of interest is that the platinum atoms at the ends of the chain, *i.e.* those that show only one Pt···Pt coupling constant, appear in a group at higher chemical shift (δ 1 235—1 663 p.p.m.) than those

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

	Compound	Colour	Yield (%)	$\nu_{max.}(CO)^{b}/cm^{-1}$	Analysis (%) C	Analysis (%) H
(8)	$[Mo_2WPt_4(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_6(cod)_2(\eta\text{-}C_5H_5)_3]$	Brown	62	1 848s, 1 812(sh), 1 736s	33.4 (33.5)	3.3 (2.8)
(9a)	$[Mo_2W_3Pt_4(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(\eta\text{-}C_5H_5)_5]$	Brown	87	1 956s, 1 862s br	32.6 (32.2)	2.4 (2.2)
(9b)	$[Mo_2W_3Pt_4(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(\eta\text{-}C_5H_5)_5]$	Brown	92	1 957s, 1 855s	28.8 (28.3)	2.3 (2.0)
(10)	$[Mo_2W_3Pt_5(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(CO)_{10}(cod)(\eta\text{-}C_5H_5)_5]$	Brown	30	1 951m, 1 862s br, 1 818m (sh), 1 744w (sh)	32.8 (32.2)	4.2 (2.5)
(11a)	$[Mo_2W_3Pt_6(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_4(CO)_{10}(cod)_2(\eta\text{-}C_5H_5)_5]$	Brown	43	1 865s br, 1 784s, 1 744(sh)	33.4 (32.1)	3.4 (2.5)
(11b)	$[Mo_2W_3Pt_6(\mu_3\text{-}CMe)_3(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(cod)_2(\eta\text{-}C_5H_5)_5]$	Brown	80	1 851s br, 1 771s, 1 740(sh)	30.0 (29.0)	2.8 (2.4)
(11c)	$[Mo_2W_3Pt_6(\mu_3\text{-}CMe)_3(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(PMe_2Ph)_4(\eta\text{-}C_5H_5)_5]$	Brown	90	1 870m br, 1 750s	32.2 (31.8)	2.8 (2.7)

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



	R	R'
(9a)	C_6H_4Me-4	C_6H_4Me-4
(9b)	C_6H_4Me-4	Me

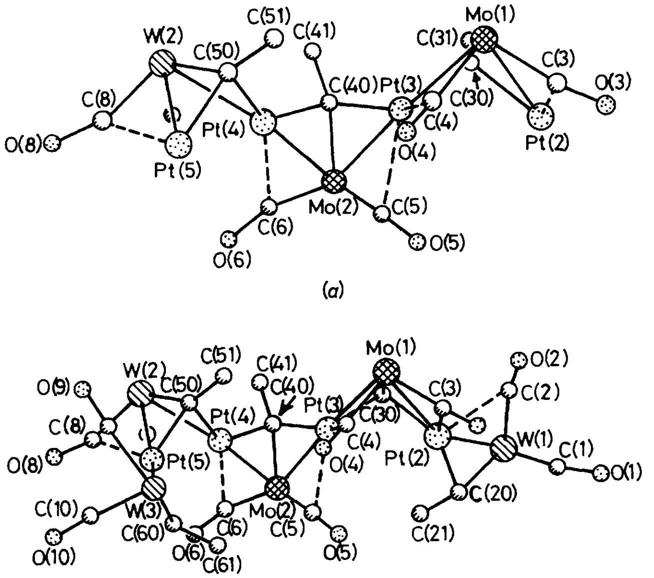


Figure 3. (*a*) Probable molecular structure of the heptanuclear metal complex $[Mo_2WPt_4(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_6(cod)_2(\eta\text{-}C_5H_5)_3]$ (**8**), with the aryl, cod, and $\eta\text{-}C_5H_5$ groups omitted for clarity. (*b*) Probable molecular structure of the nonanuclear metal complex $[Mo_2W_3Pt_4(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(\eta\text{-}C_5H_5)_5]$ (**9b**) with the aryl and cyclopentadienyl ligands omitted for clarity

platinum atoms in the 'centre' or 'middle' of the chain. The resonances for this second group of platinum atoms occur in the range δ 872—1 059 p.p.m.

Further evidence for the proposed formulation for (**9a**) came from the f.a.b. mass spectrum. An envelope of peaks for the molecular ion was observed centred at *m*/*z* 2 568, and as is usual in these systems the strongest peak in the spectrum at 2 288 corresponds to the molecular ion minus ten carbonyl ligands. As for compound (**8**), the data presented above define the composition of (**9a**) but do not elucidate its isomeric configuration. Unfortunately attempts to grow single crystals of (**9a**) suitable for an *X*-ray diffraction study were frustrated by the partial decomposition of the cluster in solution even at −30 °C to give octanuclear metal–ring type compounds.

Treatment of compound (**8**) with $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ proceeded in a similar manner, and the nonanuclear metal species $[Mo_2W_3Pt_4(\mu\text{-}CMe)_2(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(\eta\text{-}C_5H_5)_5]$ (**9b**) was isolated as brown crystals, after chromatography on alumina. As for (**9a**), decomposition in solution frustrated attempts to grow single crystals for an *X*-ray diffraction study. The compound was, however, fully characterised by its n.m.r. spectra (Tables 2 and 3) and its f.a.b. mass spectrum. The latter displayed peaks for the molecular ion centred at *m*/*z* 2 416, and signals corresponding to the sequential loss of ten CO ligands. The most intense peak (*m*/*z* 2 136) in the spectrum corresponded to that for the molecular ion minus ten CO groups.

In contrast with (**9a**), the compound (**9b**) was isolated in a single isomeric form. Consequently the ^1H n.m.r. spectrum of (**9b**) shows signals for five methyl groups, and five cyclopentadienyl ligands, as well as aromatic protons for two tolyl rings. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum confirmed the presence of the five alkylidyne units and their bonding modes. Thus the existence of two alkylidyne groups bridging two pairs of metal atoms was confirmed by the observation of signals at δ 329.4 and 328.9 p.p.m. The three alkylidyne ligands bridging three metal atoms gave rise to resonances at δ 275.9, 274.8, and 273.7 p.p.m.

Again the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum (Table 3) was very diagnostic. That (**9b**) contains four inequivalent platinum atoms was confirmed by the observation of peaks at δ 1 284, 1 181, 1 073, and 855 p.p.m.; again none of these resonances lies in the region associated with 'Pt(cod)' groups. Unfortunately the poor solubility of (**9b**) limited the quality of this spectrum, and so coupling constants could not be measured.

Figure 3(*b*) shows the most likely configuration for (**9b**). Again the postulated structure is based on an *X*-ray diffraction study on a compound discussed below to which

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

Compound	$^1H(\delta)$[b]	$^{13}C(\delta)$[c]
(**8**)	2.18 (s, 3 H, Me-4), 2.20 (s, 3 H, Me-4), 2.30—2.80 (m, 16 H, CH_2), 3.70 (s, 3 H, Me), 4.60—5.30 (m, 8 H, CH), 4.84, 5.41, 5.46 (s × 3, 15 H, C_5H_5), 6.54, 6.68 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 6.82, 7.40 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	267.1, 263.8, 259.8 (μ_3-C), 247.6, 244.2, 240.7, 236.9, 235.3, 227.1 (CO), 151.7, 149.5 [$C^1(C_6H_4)$], 136.2—127.3 (C_6H_4), 112.2, 112.1, 105.6, 105.5, 103.8, 98.1, 96.6, 94.4 (CH), 94.0, 93.5, 91.9 (C_5H_5), 39.3 (μ-C*Me*), 31.2, 31.1, 31.0, 29.7, 29.6, 29.5, 29.1, 28.7 (CH_2), 21.1, 20.7 (Me-4)
(**9a**)[d]	2.21 (s, 6 H, Me-4), 2.26 (s, 6 H, Me-4), 2.31 (s, 6 H, Me-4), 2.37 (s, 6 H, Me-4), 3.14, 3.55 (s × 2, 6 H, Me), 4.61, 4.76, 5.06, 5.08, 5.37, 5.43, 5.45, 5.47, 5.52, 5.63 (s × 10, 50 H, C_5H_5), 6.84—7.51 (m, 32 H, C_6H_4)	318.5, 308.7, 308.5, 305.0 (μ-C), 281.9, 277.8, 276.4, 275.7, 269.4, 269.3 (μ_3-C), 240.1, 240.0, 238.3, 237.4, 236.8, 235.8, 235.6, 235.5, 231.7, 231.2, 230.2, 228.4, 227.1, 226.3, 224.9, 220.9, 220.5, 220.3, 219.5, 218.6 (CO), 155.2, 153.6, 153.5, 153.0, 152.6, 152.2, 152.0, 151.9 [$C^1(C_6H_4)$], 138.7—126.6 (C_6H_4), 95.6, 95.3, 94.7, 94.6, 93.4, 93.0, 92.2 (C_5H_5), 91.8 (2 × C_5H_5), 91.7 (C_5H_5), 32.0, 26.0 (μ-C*Me*), 21.9, 21.8 (Me-4), 21.7, 21.5, 21.3 (2 × Me-4)
(**9b**)	1.75, 2.32, 2.35, 2.95, 3.34 (s × 5, 15 H, Me and Me-4), 4.80, 5.12, 5.33, 5.45, 5.60 (s × 5, 50 H, C_5H_5), 6.77—7.70 (m, 8 H, C_6H_4)	329.4, 328.9 (μ-C), 275.9, 274.8, 273.7 (μ_3-C), 239.3, 238.9, 238.4, 237.0, 230.7, 230.4, 226.2, 225.8, 223.9, 219.4 (CO), 153.6, 152.0 [$C^1(C_6H_4)$] 136.6—127.8 (C_6H_4), 95.6, 94.7, 92.5, 91.6, 91.5 (C_5H_5), 32.0, 26.0, 22.8 (μ-C*Me*), 21.2, 14.3 (Me-4)
(**10**)	2.23, 2.29, 2.34, 2.42 (s × 4, 12 H, Me-4), 2.50—2.90 (m, 8 H, CH_2), 3.50 (s, 3 H, Me), 4.40—5.10 (m, 4 H, CH), 4.62 (s, 5 H, C_5H_5), 5.18 (s, 10 H, C_5H_5), 5.29, 5.51 (s × 2, 10 H, C_5H_5), 6.80—7.70 (m, 16 H, C_6H_4)	308.4 (μ-C), 277.8, 275.7, 268.6, 263.1 (μ_3-C), 241.8, 240.7, 239.9, 238.5, 235.4, 235.0, 228.1, 225.4, 225.3, 220.9 (CO), 153.8, 153.6, 152.6, 152.1 [$C^1(C_6H_4)$], 138.9—125.7 (C_6H_4), 111.0, 104.2, 102.3, 98.0 (CH), 95.6, 95.0, 93.6, 93.5, 92.0 (C_5H_5), 32.3 (μ-C*Me*), 32.0, 30.2, 29.3, 28.4 (CH_2), 22.8, 21.8, 21.5, 21.4 (Me-4)
(**11a**)[d]	2.10—2.50 (m, 24 H, Me-4), 2.50—2.90 (m, 32 H, CH_2), 3.59, 3.60 (s × 2, 6 H, Me), 4.40—5.25 (m, 16 H, CH), 4.63, 4.67, 4.71, 4.76, 5.02, 5.03, 5.32, 5.37, 5.44, 5.58 (s × 10, 50 H, C_5H_5), 6.50—7.60 (m, 32 H, C_6H_4)	275.2, 271.5, 269.8, 267.7, 265.5, 265.4, 264.3 (μ_3-C), 262.3 (2 × μ_3-C), 257.6 (μ_3-C), 244.8, 243.5, 243.2, 243.1, 240.2, 240.1, 239.9, 238.4, 237.8, 236.1, 236.0, 234.8, 234.0, 231.1, 225.9, 225.6, 225.4, 225.1, 224.6, 222.3 (CO), 155.4—126.5 (C_6H_4), 111.0, 110.6, 105.5, 105.0, 102.4, 101.3, 100.8, 100.4, 99.2, 98.9, 98.7, 98.6, 98.2, 96.5, 95.8, 95.6 (CH), 95.1, 94.4, 94.3, 94.1, 93.9 (C_5H_5), 93.5, 92.7 (2 × C_5H_5), 92.6 (C_5H_5), 43.1, 42.2 (μ-C*Me*), 32.0—28.0 (CH_2), 21.5—20.5 (Me-4)
(**11b**)	2.13, 2.16 (s × 2, 6 H, Me-4), 2.20—2.80 (m, 16 H, CH_2), 3.37, 3.40, 3.66 (s × 3, 9 H, Me), 4.60—5.20 (m, 8 H, CH), 4.71, 4.79, 5.41 (s × 3, 15 H, C_5H_5), 5.45 (s, 10 H, C_5H_5), 6.69, 6.73 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 7.21, 7.29 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	267.1, 266.2, 265.4, 262.6, 259.2 (μ_3-C), 245.7, 244.6, 242.2, 240.2, 236.5, 235.0, 233.7 (CO), 227.9 (2 × CO), 226.4 (CO), 151.5, 151.2 [$C^1(C_6H_4)$], 138.3—128.3 (C_6H_4), 112.5, 112.3, 105.1, 104.2, 99.4, 98.5, 96.4, 95.4 (CH), 94.2 (2 × C_5H_5), 92.2 (C_5H_5), 91.8 (2 × C_5H_5), 42.8, 41.7 (Me), 31.4 (2 × CH_2), 31.1, 30.8, 29.6, 29.3, 29.0, 28.6 (CH_2), 21.0 (2 × Me-4)
(**11c**)	[e] 1.40—2.00 (m, 24 H, PMe), 2.10, 2.12 (s × 2, 6 H, Me-4), 2.34, 3.37, 3.39 (s × 3, 9 H, Me), 4.61, 4.66 (s × 2, 10 H, C_5H_5), 5.44 (s, 10 H, C_5H_5), 5.47 (s, 5 H, C_5H_5), 6.50—7.70 (m, 28 H, Ph and C_6H_4)	266.8 [d, μ_3-C, J(PC) 55], 266.1, 263.2 (μ_3-C), 261.3 [d, μ_3-C, J(PC) 52], 259.0 (μ_3-C) 247.8, 244.7 (CO), 241.8 [d, CO, J(PC) 9], 239.2 [d, CO, J(PC) 9], 238.0, 237.4, 234.5, 229.6, 223.4, 221.0 (CO), 151.3—126.6 (Ph and C_6H_4), 93.0, 92.8, 91.2, 91.0, 90.9 (C_5H_5), 44.1, 42.9, 40.9 (C*Me*), 20.2, 20.1 (Me-4), 18.8—10.8 (PMe)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperature. [b] Measured in $CDCl_3$ 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. Signals due to CH groups of cod ligands show ^{195}Pt satellite peaks with J(PtC) 80–150 Hz. [d] Spectrum shows two isomers present in approximately equal amounts. [e] Measured in CD_2Cl_2.

(**9b**) is a precursor. The configuration shown, as would be expected, incorporates the metal core of (**8**), with the cod ligands of the latter being replaced by $MeC{\equiv}W(CO)_2(\eta\text{-}C_5H_5)$ fragments.

Ten- and Eleven-metal-atom Complexes.—The reactions described so far have shown how the problem of chain cyclisation may be overcome, and how complexes containing up to nine metal atoms may be synthesised. Since the new compounds (**9**) contain $C{\equiv}W$ bonds terminating the chains, it was of interest to establish whether reaction would occur with $[Pt(cod)_2]$ thereby further extending the series. The preparation of longer chains was a likely outcome, although one intriguing possibility was the occurrence of further cyclisation reactions. In the latter context, Hoffmann and co-workers[7] have predicted the existence of a cyclic compound $[Pt_6(\mu\text{-}RC_2R)_6]$ (R = alkyl or aryl). Such a species would be isolobally mapped with a metallacycle of the type $[M_6Pt_6(\mu_3\text{-}CR)_6(CO)_{12}(\eta\text{-}C_5H_5)_6]$ (M = Mo or W, R = alkyl or aryl).

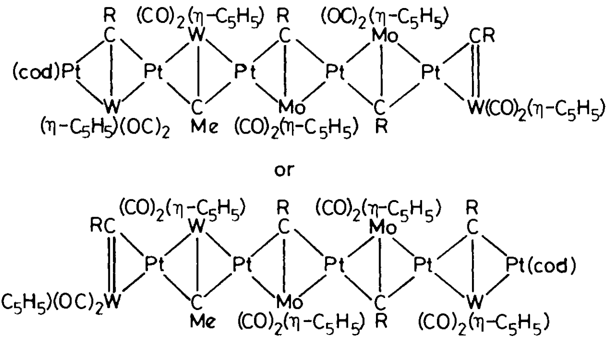
Addition of 2 equivalents of $[Pt(cod)_2]$, dissolved in ethylene-saturated thf, to a solution of (**9a**) in the same solvent gave a mixture of products. Careful column chromatography on alumina allowed partial separation of the two compounds $[Mo_2W_3Pt_5(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(CO)_{10}(cod)(\eta\text{-}C_5H_5)_5]$ (**10**) and $[Mo_2W_3Pt_6(\mu_3\text{-}CMe)(\mu_3\text{-}CC_6H_4Me\text{-}4)_4(CO)_{10}(cod)_2(\eta\text{-}C_5H_5)_5]$ (**11a**), with the latter eluting from the column more slowly. The ratio of (**10**) to (**11a**) produced in the reaction was approximately 5:8, though separation was difficult, and the two fractions were generally slightly contaminated with each other. Data for (**10**) and (**11a**) are given in Tables 1—3 and are in accord with the proposed structures.

The ten metal-atom complex (**10**) is formed as a single isomer, and so its ^{13}C-{^{1}H} n.m.r. spectrum shows characteristic signals for one alkylidyne carbon nucleus spanning a dimetal centre, and four alkylidyne groups triply bridging metal triangles. Other diagnostically useful resonances include those for ten carbonyl ligands and for a single cod moiety. The ^{195}Pt-{^{1}H}

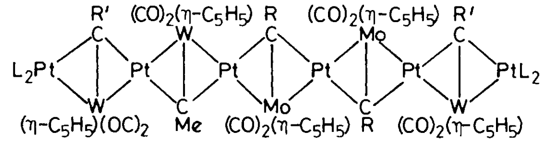
Table 3. Platinum-195 n.m.r. data[a] for the new complexes

Compound	δ^b	J(PtPt)
(8)	1 234	439, 332
	946	1 211, 332, 78
	401	439, 78
	311	1 211
(9a)	1 663	1 252
	1 493*	1 431
	1 482	1 177
	1 235*	1 147
	1 059	1 573, 1 177
	1 042*	1 431, 1 431
	923*	1 431, 1 147
	872	1 573, 1 252
(9b)	1 284	
	1 181	
	1 073	
	855	
(10)	1 507	1 209
	1 057	1 209, 1 005
	955	1 250, 1 005
	651	1 250, 1 055
	355	1 055
(11a)	1 505	
	1 424*	606, 410
	1 084*	1 200, 410
	1 078	
	1 029	
	937	
	786*	1 064, 606
	594*	1 272, 1 200
	587	
	333	
	329*	1 272
	321*	1 064
(11b)	1 500	351, 351
	1 105	1 318, 351
	959	1 123, 351
	762	1 377, 1 318
	339	1 377
	319	1 318
(11c)[c]	1 507	195, 190
	1 113	1 201, 190
	877	1 787
	679	1 953, 1 201
	−35	
	−86	

[a] Chemical shifts are in p.p.m., coupling constants are in Hz. Measurements in CD_2Cl_2–CH_2Cl_2 at room temperature. [b] To high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz. Values marked with an asterisk refer to a second isomer (see text). [c] Signals at δ −35 and −86 p.p.m are d of d with J(PPt) 3 870, 3 755, 3 188, and 3 150 Hz.



(10) R = C_6H_4Me-4



	R	R′	L_2
(11a)	C_6H_4Me-4	C_6H_4Me-4	cod
(11b)	C_6H_4Me-4	Me	cod
(11c)	C_6H_4Me-4	Me	PMe_2Ph x 2

n.m.r. spectrum shows signals for five inequivalent platinum atoms, the resonances falling into three groups. As with **(9a)**, the platinum atom which lies at the other end of the chain from the 'Pt(cod)' group, *i.e.* that which has close contact with only one other platinum atom, resonates at the lowest field (δ 1 507 p.p.m.). The peaks at δ 1 057, 955, and 651 p.p.m. all show two sets of platinum satellites (Table 3), and so correspond to the central platinum atoms of the chain, *i.e.* those with other platinum nuclei on either side of them. Finally the signal at δ 355 p.p.m. lies in the chemical shift range associated with a terminal Pt(cod) group.[2]

The n.m.r. data do not elucidate the ordering of the metal atom spine in this molecule, and the two alternatives are shown. Addition of a Pt(cod) fragment may occur at either of the two W=C double bonds in **(9a)**. As the latter is unsymmetrical these two possible additions can give rise to one or other of the two isomers of **(10)** illustrated.

In the f.a.b. mass spectrum a signal occurs at *m*/*z* 2 871 for the molecular ion. As with the other compounds in this series, peaks for successive loss of the cod ligand and then carbonyl groups were observed, the major peak at *m*/*z* 2 483 corresponding to loss of the cod ligand and all ten carbonyl groups.

In contrast with **(10)**, compound **(11a)** is formed as a mixture of two diastereoisomers, present in approximately equal amounts, as inferred from the peak heights in the n.m.r. spectra. The presence of the two isomers is immediately apparent from the ^{13}C-$\{^1H\}$ n.m.r. spectrum (Table 2) which reveals resonances corresponding to ten triply bridging μ_3-CC_6H_4Me-4 nuclei. Further diagnostically useful signals in this spectrum include those for twenty carbonyl ligands (ten for each isomer), four cod ligands (two inequivalent cod groups exist in each isomer), and ten cyclopentadienyl groups.

Interestingly, the ^{195}Pt-$\{^1H\}$ n.m.r. spectrum of **(11a)** (Table 3) shows what appears to be the presence of small amounts of two other isomers, in addition to the two major ones. The appearance of more isomers in the ^{195}Pt-$\{^1H\}$ n.m.r. spectrum than in the ^1H or ^{13}C-$\{^1H\}$ spectra has been noted previously,[2b] but the reason for this remains unknown. Any distinction between the different types of platinum atom present in the molecule in terms of their ^{195}Pt chemical shifts is very arbitrary in this case, since no clear groupings of chemical shifts of the signals are observed. A f.a.b. mass spectrum of **(11a)** showed an envelope of peaks at *m*/*z* 3 174 for the molecular ion, peaks for loss of two cod ligands and ten carbonyl groups, the major peak being observed at 2 678 for $[M - 2\,\text{cod} - 10\,\text{CO}]^+$.

As the above synthesis gave relatively low yields of both **(10)** and **(11a)** attempts were made to obtain high-yield routes to both compounds. In an effort to produce **(10)** as the only product from the reaction, compound **(9a)** was treated with 1 equivalent of $[Pt(cod)_2]$. After stirring for 4 h the reaction mixture contained **(10)** but significant amounts of unreacted **(9a)** remained. Separation of these two compounds by column chromatography was not possible. Using as much as 3 equiv-

Table 4. Selected internuclear separations (Å) and angles (°) for [$Mo_2W_3Pt_6(\mu_3\text{-}CMe)_3(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(PMe_2Ph)_4(\eta\text{-}C_5H_5)_5$] (**11c**), with estimated standard deviations in parentheses

Pt(2)–W(1)	2.737(4)	Pt(1)–W(1)	2.779(4)	Pt(5)–C(50)	2.13(4)	W(3)–C(60)	2.01(5)
Pt(3)–Mo(1)	2.724(6)	Pt(2)–Mo(1)	2.750(6)	Pt(5)–C(60)	2.07(5)	Pt(6)–C(60)	2.05(4)
Pt(4)–Mo(2)	2.775(6)	Pt(3)–Mo(2)	2.729(6)	W(1)–C(1)	1.90(5)	Pt(1)–C(1)	2.32(4)
Pt(5)–W(2)	2.759(4)	Pt(4)–W(2)	2.720(4)	W(1)–C(2)	2.09(7)	Pt(2)–C(2)	2.57(6)
Pt(6)–W(3)	2.779(4)	Pt(5)–W(3)	2.732(5)	Mo(1)–C(3)	1.88(5)	Pt(2)–C(3)	2.18(6)
Pt(1) ··· Pt(2)	2.965(5)	Pt(2) ··· Pt(3)	3.171(5)	Mo(1)–C(4)	1.97(5)	Pt(3)–C(4)	2.26(6)
Pt(3) ··· Pt(4)	3.160(5)	Pt(4) ··· Pt(5)	3.000(5)	Mo(2)–C(5)	2.00(6)	Pt(3)–C(5)	2.48(5)
Pt(5) ··· Pt(6)	2.902(5)	Pt(1)–P(1)	2.32(2)	Mo(2)–C(6)	1.91(6)	Pt(4)–C(6)	2.16(6)
Pt(1)–P(2)	2.27(2)	Pt(6)–P(3)	2.28(2)	W(2)–C(7)	2.07(8)	Pt(4)–C(7)	2.55(7)
Pt(6)–P(4)	2.33(2)	W(1)–C(20)	2.12(4)	W(2)–C(8)	2.00(5)	Pt(5)–C(8)	2.18(5)
Pt(1)–C(20)	1.92(5)	Pt(2)–C(20)	2.10(4)	W(3)–C(9)	1.98(5)	Pt(5)–C(9)	2.65(5)
Mo(1)–C(30)	1.97(6)	Pt(2)–C(30)	2.07(6)	W(3)–C(10)	1.84(7)	Pt(6)–C(10)	2.42(8)
Pt(3)–C(30)	1.99(5)	Mo(2)–C(40)	1.98(4)	W(1)–C(cp)*	2.33	Mo(1)–C(cp)*	2.34
Pt(3)–C(40)	2.00(4)	Pt(4)–C(40)	2.13(4)	Mo(2)–C(cp)*	2.34	W(2)–C(cp)*	2.31
W(2)–C(50)	1.98(5)	Pt(4)–C(50)	2.13(4)	W(3)–C(cp)*	2.38		
Pt(1)–Pt(2)–Pt(3)	135.0(1)	Pt(1)–C(20)–C(21)	138(4)	Pt(5)–C(60)–C(61)	117(3)	P(1)–Pt(1)–C(2)	164(1)
Pt(3)–Pt(4)–Pt(5)	131.3(1)	Mo(1)–C(30)–C(31)	142(4)	W(1)–C(1)–O(1)	148(4)	P(1)–Pt(1)–C(1)	81(1)
Pt(1)–W(1)–Pt(2)	65.0(1)	Pt(3)–C(30)–C(31)	119(4)	Mo(1)–C(3)–O(3)	161(4)	P(3)–Pt(6)–C(60)	100(1)
Pt(2)–Mo(1)–Pt(3)	70.8(1)	Pt(3)–C(40)–C(41)	123(3)	Mo(2)–C(5)–O(5)	169(4)	C(1)–W(1)–C(2)	86(2)
Pt(3)–Mo(2)–Pt(4)	70.0(1)	W(2)–C(50)–C(51)	143(3)	W(2)–C(7)–O(7)	175(5)	C(5)–Mo(2)–C(6)	86(2)
Pt(4)–W(2)–Pt(5)	66.4(1)	Pt(5)–C(50)–C(51)	120(4)	W(3)–C(9)–O(9)	174(5)	C(9)–W(3)–C(10)	82(3)
Pt(5)–W(3)–Pt(6)	63.5(1)	W(1)–C(20)–C(21)	130(4)	P(1)–Pt(1)–P(2)	94.7(6)	P(3)–Pt(6)–P(4)	96.3(6)
Pt(2)–Pt(3)–Pt(4)	169.8(1)	Pt(2)–C(20)–C(21)	109(3)	Pt(6)–C(60)–C(61)	133(4)	P(2)–Pt(1)–C(20)	98(1)
Pt(4)–Pt(5)–Pt(6)	134.9(1)	Pt(2)–C(30)–C(31)	112(3)	W(1)–C(2)–O(2)	167(5)	P(2)–Pt(1)–C(1)	158(1)
W(1)–Pt(2)–Mo(1)	148.2(1)	Mo(2)–C(40)–C(41)	144(4)	Mo(1)–C(4)–O(4)	162(5)	P(4)–Pt(6)–C(60)	159(1)
Mo(1)–Pt(3)–Mo(2)	175.2(2)	Pt(4)–C(40)–C(41)	106(2)	Mo(2)–C(6)–O(6)	156(5)	C(3)–Mo(1)–C(4)	88(2)
Mo(2)–Pt(4)–W(2)	149.9(2)	Pt(4)–C(50)–C(51)	116(3)	W(2)–C(8)–O(8)	154(5)	C(7)–W(2)–C(8)	87(2)
W(2)–Pt(5)–W(3)	150.3(1)	W(3)–C(60)–C(61)	132(4)	W(3)–C(10)–O(10)	160(6)		

* Mean distance to the cyclopentadienyl ring-carbon atoms.

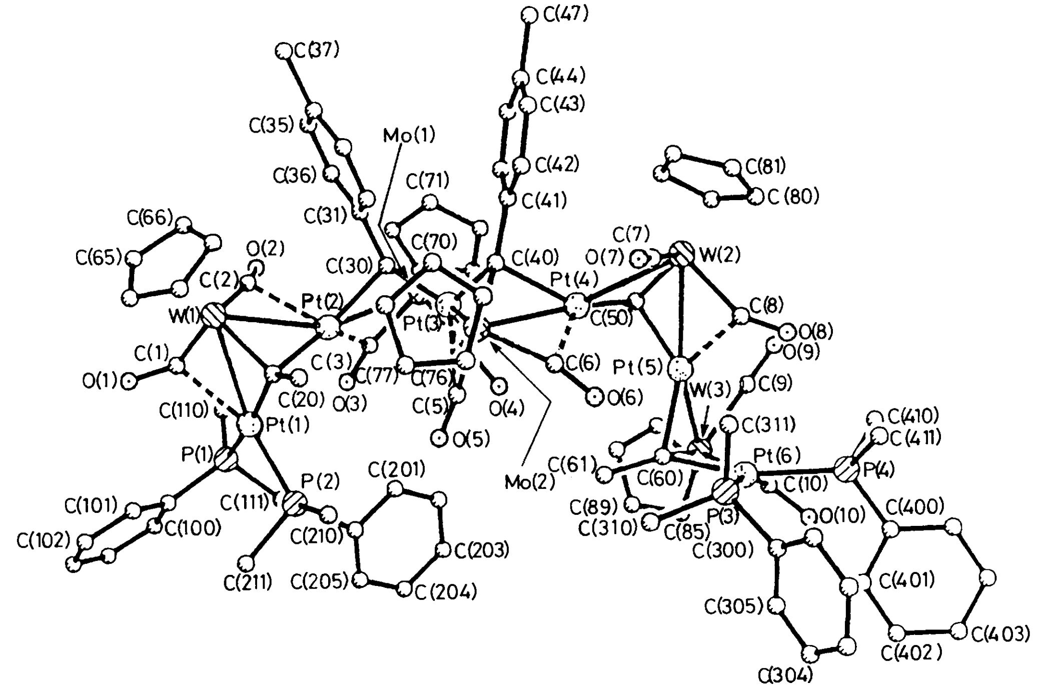


Figure 4. The molecular structure of [$Mo_2W_3Pt_6(\mu_3\text{-}CMe)_3(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(PMe_2Ph)_4(\eta\text{-}C_5H_5)_5$] (**11c**) showing the crystallographic numbering system

alents of [$Pt(cod)_2$] in the reaction with (**9a**) did not affect the product distribution greatly.

In a related synthesis, a thf solution of (**9b**) was treated with 2.5 equivalents of [$Pt(cod)_2$] in ethylene-saturated thf. This reaction afforded in high yield (*ca.* 80%) the eleven-metal-atom complex [$Mo_2W_3Pt_6(\mu_3\text{-}CMe)_3(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(cod)_2(\eta\text{-}C_5H_5)_5$] (**11b**) as the only product. No decanuclear metal species analogous to (**10**) was observed. The data for (**11b**) are listed in Tables 1—3. In contrast with (**11a**), compound (**11b**) is formed as a single diastereoisomer.

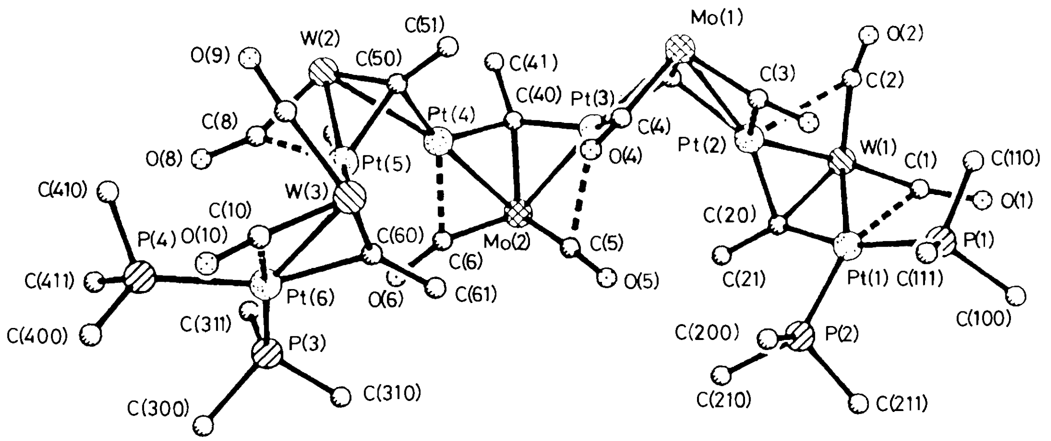


Figure 5. A simplified view of compound (**11c**) to illustrate the $Mo_2W_3Pt_6$ chain structure, with the η-C_5H_5, C_6H_4Me-4, and substituents on the P atoms omitted for clarity

Unfortunately, crystals of (**11b**) suitable for an *X*-ray diffraction study could not be grown. To circumvent this difficulty the compound was derivatised to afford a product which did form suitable single crystals. Treatment of (**11b**) with an excess of PMe_2Ph in CH_2Cl_2 yielded essentially quantitatively the complex $[Mo_2W_3Pt_6(\mu_3\text{-}CMe)_3(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{10}(PMe_2Ph)_4(\eta\text{-}C_5H_5)_5]$ (**11c**) in which the cod ligands of (**11b**) are replaced by PMe_2Ph groups. The spectroscopic data for (**11c**) are consistent with the proposed formulation and are also very similar to those of (**11b**), suggesting similar conformations. In the n.m.r. spectra some differences arise because of the presence of the PMe_2Ph ligands in (**11c**). Thus in the ^{13}C-$\{^1H\}$ n.m.r. spectrum, two of the signals assigned to triply bridging alkylidyne-carbon atoms appear as doublets, due to phosphorus coupling. The values of the coupling constants [*J*(PC) 55, 52 Hz] are similar to those found in other species with an alkylidyne ligand *trans* to a phosphine group, for example $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [*J*(PC) 59][8] and $[WPt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ [*J*(PC) 42].[9] Signals for two of the carbonyl groups in (**11c**) also appear as doublets. The ^{195}Pt-$\{^1H\}$ and ^{31}P-$\{^1H\}$ n.m.r. spectra are also in agreement with the proposed formulation. As expected, the former shows two resonances, which appear as doublets of doublets, as well as four singlets; the two different types of signal having very different chemical shifts. The singlets resonate in the expected range for 'chain' platinum atoms, whereas the other two signals (δ −35 and −86 p.p.m.) occur in that part of the spectrum associated with $Pt(PR_3)_2$ groups when ligated by an alkylidyne metal fragment (*cf.* the ^{195}Pt-$\{^1H\}$ n.m.r. spectrum of $[W_2Pt_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)_2]$ which shows a peak at δ 1 p.p.m.).[2a] Signals for four inequivalent phosphine ligands are observed in the ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**11c**).

The molecular structure of (**11c**), established by *X*-ray diffraction, is shown in Figure 4. A more simplified view with the cyclopentadienyl and aromatic groups omitted is presented in Figure 5. Selected interatomic parameters are listed in Table 4. The molecule consists of five μ_3-$CMPt_2$ (M = Mo or W) groups linked together, four of the platinum atoms sharing vertices.

Of the six platinum atoms present, all except Pt(1) and Pt(6) are approximately tetrahedrally co-ordinated by alkylidyne-metal fragments, a feature common to all compounds of this type. However, Pt(1) and Pt(6) have essentially square planar co-ordination geometries, being ligated by one alkylidyne tungsten fragment, and two PMe_2Ph groups. In a similar way the platinum atoms in the trinuclear metal species $[WPt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ also have square planar geometries.[9] These differences in co-ordination geometry have been rationalised for the isolobal systems $[Pt(RC_2R)_2]$, in which the platinum atom is in a tetrahedral environment with respect to the alkyne groups, and $[Pt(RC_2R)(PR'_3)_2]$ which exhibits a square planar geometry for the platinum with respect to the ligated atoms.[10]

The dimensions of the μ_3-$CMPt_2$ (M = Mo or W) fragments in (**11c**) (mean distances: Pt–W 2.751, Pt–Mo 2.745, Pt···Pt 3.040, μ_3-C–Pt 2.05, μ_3-C–W 2.04, and μ_3-C–Mo 1.98 Å) are best compared with those of the hexanuclear metal species (**5b**)[2b] (mean distances Pt–W 2.732, Pt···Pt 3.155, μ_3-C–Pt 2.08, μ_3-C–W 1.99 Å). Obviously there is little variation between these two sets of figures, indicating a fairly fixed geometry for this particular structural unit. The Pt···Pt separations in both species imply little or no direct metal–metal bonding.

All of the carbonyl ligands except, C(7)O(7) and C(9)O(9), semi-bridge W–Pt bonds [the M–C–O angles vary from 148(4) to 169(4)°]. Surprisingly, C(7)–O(7) and C(9)–O(9) appear to be essentially terminally bound to W(2) and W(3) respectively. This is in contrast with the structures determined for all the other 'chain-type' compounds. The *X*-ray diffraction study of (**11c**) places the results described in this paper on a firm structural basis.

Conclusions

The successful synthesis of compounds (**8**)—(**11**) has illustrated how the problem of 'chain cyclisation' may be overcome, and has, in theory, opened the way to the preparation of metal chain clusters of any desired length. However practical difficulties, such as the separation of product mixtures or further cyclisation reactions, may limit the range of syntheses available. An interesting 'target' molecule is the twelve-metal atom ring compound $[Mo_2W_4Pt_6(\mu_3\text{-}CMe)_4(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_{12}(\eta\text{-}C_5H_5)_6]$ which should be accessible *via* the species (**11b**).

Experimental

The techniques employed and the instrumentation used have been described previously.[2] Light petroleum refers to that fraction of b.p. 40—60 °C. Alumina used for chromatography columns (*ca.* 30 × 3 cm^3) was BDH aluminium oxide (Brockman, Activity II). The compounds $[Pt(cod)_2]$[11] and $[M'(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M′ = Mo or W; R = Me or

C_6H_4Me-4)[12] were obtained as previously described. Analytical and other data for the new complexes are given in Table 1.

Synthesis of the Complex [$Mo_2WPt_4(\mu_3$-CMe)(μ_3-CC_6H_4-Me-4)$_2$(CO)$_6$(cod)$_2$(η-C_5H_5)$_3$].—A cold (0 °C) ethylene-saturated thf (20 cm^3) solution of [Pt(cod)$_2$] (0.05 g, 0.12 mmol) was treated with compound (**5c**) (0.15 g, 0.09 mmol) in the same solvent (25 cm^3). After stirring for 4 h, solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2–light petroleum (15 cm^3, 4:1) and chromatographed. Elution with the same solvent mixture afforded first a green band containing unreacted (**5c**), followed by a brown band. Collection of the latter fraction, removal of solvent *in vacuo*, and crysallisation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1:5) afforded brown *microcrystals* of [$Mo_2WPt_4(\mu_3$-CMe)(μ_3-CC_6H_4Me-4)$_2$(CO)$_6$(cod)$_2$(η-C_5H_5)$_3$] (**8**) (0.11 g).

Synthesis of Nonanuclear Metal Compounds.—(*i*) A thf (15 cm^3) solution of compound (**8**) (0.15 g, 0.08 mmol) was syringed into a Fischer–Porter vessel containing [W($\equiv CC_6H_4Me$-4)(CO)$_2$(η-C_5H_5)] (0.13 g, 0.32 mmol) in the same solvent (20 cm^3), and the reaction vessel was pressurised with C_2H_4 (2 atm) for 3 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (15 cm^3, 3:1) and chromatographed. Elution with the same solvent mixture removed unreacted [W($\equiv CC_6H_4Me$-4)(CO)$_2$(η-C_5H_5)], followed by a dark brown eluate. Collection of the second fraction, removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1:5) afforded brown *microcrystals* of [$Mo_2W_3Pt_4(\mu$-CC_6H_4Me-4)$_2$(μ_3-CMe)(μ_3-CC_6H_4Me-4)$_2$(CO)$_{10}$(η-C_5H_5)$_5$] (**9a**) (0.17 g).

(*ii*) In a similar preparation, compound (**8**) (0.15 g, 0.08 mmol) in thf (15 cm^3) was added to a thf solution (10 cm^3) of [W($\equiv$CMe)(CO)$_2$(η-C_5H_5)] (0.10 g, 0.30 mmol) in a Fischer–Porter vessel. This mixture was stirred under ethylene pressure (2 atm) for 3 h before solvent was removed *in vacuo*. The resultant residue was dissolved in CH_2Cl_2 (10 cm^3) and chromatographed, eluting with the same solvent. A first, yellow fraction from the column contained unreacted [W($\equiv$CMe)(CO)$_2$(η-C_5H_5)] and was discarded. The second dark brown eluate from the column was collected, solvent was removed *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1:5) afforded chocolate brown *microcrystals* of [$Mo_2W_3Pt_4(\mu$-CMe)$_2$(μ_3-CMe)(μ_3-CC_6H_4Me-4)$_2$(CO)$_{10}$(η-C_5H_5)$_5$] (**9b**) (0.17 g).

Synthesis of the Ten- and Eleven-Metal-atom Compounds.—(*i*) A sample of [Pt(cod)$_2$] (0.07 g 0.17 mmol) was dissolved in cold (0 °C) ethylene-saturated thf (10 cm^3) and added slowly to a thf (20 cm^3) solution of compound (**9a**) (0.15 g, 0.06 mmol). The resulting solution was stirred for 4 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (10 cm^3) and chromatographed, thereby affording two poorly resolved dark brown bands. Collection of these two eluates, removal of solvent *in vacuo*, and crystallisation of the residues from CH_2Cl_2–light petroleum (10 cm^3, 1:5) afforded brown *crystals* of [$Mo_2W_3Pt_5(\mu$-CC_6H_4Me-4)(μ_3-CMe)(μ_3-CC_6H_4Me-4)$_3$(CO)$_{10}$(cod)(η-C_5H_5)$_5$] (**10**) (0.05 g) from the first fraction, and brown *crystals* of [$Mo_2W_3Pt_6(\mu_3$-CMe)(μ_3-CC_6H_4Me-4)$_4$(CO)$_{10}$(cod)$_2$(η-C_5H_5)$_5$] (**11a**) (0.08 g) from the second fraction.

(*ii*) Compound (**9b**) (0.15 g, 0.06 mmol) in thf (20 cm^3) was slowly added to an ethylene-saturated thf (20 cm^3 at 0 °C) solution of [Pt(cod)$_2$] (0.06 g, 0.17 mmol). After warming to room temperature and stirring for 3 h, solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (10 cm^3) and chromatographed. Elution with the same solvent afforded a slow-moving brown band, which was collected. Removal of solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1:5) afforded brown *crystals* of [$Mo_2W_3Pt_6(\mu_3$-CMe)$_3$(μ_3-CC_6H_4Me-4)$_2$(CO)$_{10}$(cod)$_2$(η-C_5H_5)$_5$] (**11b**) (0.15 g).

(*iii*) Compound (**11b**) (0.15 g, 0.05 mmol) in CH_2Cl_2 (15 cm^3) was treated with an excess of PMe_2Ph (0.30 mmol). After stirring for 30 min, solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed. Elution wih the same solvent afforded a brown eluate. Removal of solvent and crystallisation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1:5) gave brown *crystals* of [$Mo_2W_3Pt_6(\mu_3$-CMe)$_3$(μ_3-CC_6H_4Me-4)$_2$(CO)$_{10}$(PMe_2Ph)$_4$(η-C_5H_5)$_5$] (**11c**) (0.15 g). ^{31}P-{^1H} N.m.r. (in CD_2Cl_2): δ −4.75 [d, *J*(PP) 5, *J*(PtP) 3 755], −5.12 [d, *J*(PP) 7, *J*(PtP) 3 870], −7.45 [d, *J*(PP) 5, *J*(PtP) 3 188], and −8.25 p.p.m. [d, *J*(PP) 5, *J*(PtP) 3 150 Hz]. Chemical shifts are to high frequency relative to 85% H_3PO_4 (external).

Crystal Structure Determination.—Compound (**11c**) was crystallised from CH_2Cl_2 and an elongated prism (*ca.* 0.2 × 0.3 × 0.7 mm) was sealed into a Lindemann glass capillary under nitrogen, with CH_2Cl_2 to prevent solvent loss from the lattice. Over a short time, collapse of the crystals occurs unless CH_2Cl_2 vapour is present. Diffracted intensities were collected (ω—2θ scans) at ambient temperatures on a Nicolet P3/mv automated four-circle diffractomter in the range $3 \leqslant 2\theta \leqslant 50°$ and these showed a small, 5—10% decay over the experimental period of 3 weeks. From 20 016 recorded intensities, 18 493 were unique but only 6 160 with $F \geqslant 6\sigma(F)$ were used in the last stages of refinement, after correction for Lorentz and polarisation effects and for those of *X*-ray absorption. An empirical absorption correction was applied to all data using 289 measured ψ scans.

Crystal data. $C_{89}H_{92}Mo_2O_{10}P_4Pt_6W_3$, M = 3 359.6, monoclinic, a = 42.37(2), b = 12.262(8), c = 40.71(4) Å, β = 98.57(7)°, U = 20 920(30) Å^3, Z = 8, D_c = 2.13 g cm^{-3}, $F(100)$ 12 320, space group $C2/c$ (no. 15), Mo-K_α *X*-radiation (graphite monochromator, λ = 0.710 73 Å), μ(Mo-K_α) 117.7 cm^{-1}.

The structure was solved by direct methods,[13] with subsequent difference density syntheses. Full anisotropic refinement of atomic displacement parameters was restricted to the eleven metal and four phosphorus atoms. All carbon atoms of five- and six-membered rings were constrained to regular pentagons and hexagons respectively, and refined isotropically. Hydrogen atoms were included at calculated positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for those belonging to methyl groups, and fixed isotropic thermal parameters (*ca.* 1.2 $U_{\text{equiv.}}$ of the parent carbon atom) for the remainder.

Refinement by blocked-cascade least squares led to R = 0.091 (R' = 0.092), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0035|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed some large ripples near the metal atom skeleton (*ca.* ±3.0 e Å^{-3}) but no chemical significance was attached to the largest of these (+5 e Å^{-3}) which was only 1.2 Å from Pt(4). Residual electron density in the lattice cavities was assumed to represent the included CH_2Cl_2 (see above), but this could not be modelled satisfactorily and, therefore was not included in the final structure-factor calculations, molecular formula, or calculated density. Intensity data quality and resolution were not outstandingly high, as a result of sample quality, crystal mounting difficulties, and the two long cell axes. All atomic scattering factors and corrections for anomalous dispersion were taken from ref. 14. The atomic co-ordinates for (**11c**) are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Table 5. Atomic co-ordinates (× 10^4) for compound (**11c**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	4 742(1)	4 081(2)	9 155(1)	C(65)	5 179(7)	2 490(34)	10 218(11)
Pt(2)	4 307(1)	2 290(2)	9 284(1)	C(66)	4 906	1 810	10 208
Pt(3)	3 556(1)	2 018(2)	9 224(1)	C(67)	4 637	2 489	10 221
Pt(4)	2 803(1)	2 105(2)	9 077(1)	C(68)	4 743	3 589	10 239
Pt(5)	2 352(1)	2 234(2)	8 436(1)	C(69)	5 078	3 590	10 237
Pt(6)	1 989(1)	3 967(2)	8 070(1)	C(70)	4 228(8)	−945(36)	9 005(11)
W(1)	4 833(1)	2 826(2)	9 730(1)	C(71)	3 935	−1 134	9 125
W(2)	2 272(1)	839(2)	8 949(1)	C(72)	3 683	−1 017	8 854
W(3)	2 388(1)	2 584(2)	7 780(1)	C(73)	3 821	−756	8 567
Mo(1)	3 948(1)	691(4)	8 931(1)	C(74)	4 158	−711	8 660
Mo(2)	3 191(1)	3 493(3)	9 499(1)	C(75)	2 965(7)	4 068(35)	9 938(12)
P(1)	5 094(3)	3 894(13)	8 775(4)	C(76)	3 059	5 009	9 773
P(2)	4 450(4)	5 417(13)	8 866(5)	C(77)	3 397	5 035	9 815
P(3)	1 952(3)	5 245(14)	8 470(5)	C(78)	3 513	4 110	10 006
P(4)	1 442(4)	3 721(15)	7 916(5)	C(79)	3 247	3 513	10 082
C(1)	5 166(11)	3 275(39)	9 496(13)	C(80)	1 925(9)	−606(40)	8 840(12)
O(1)	5 469(10)	3 503(37)	9 503(12)	C(81)	1 964	−361	9 184
C(2)	4 844(14)	1 345(55)	9 475(17)	C(82)	2 286	−577	9 320
O(2)	4 907(9)	608(35)	9 363(11)	C(83)	2 446	−956	9 059
C(3)	4 280(11)	1 531(40)	8 798(14)	C(84)	2 223	−974	8 763
O(3)	4 477(8)	1 905(30)	8 627(10)	C(85)	2 619(10)	2 914(38)	7 294(11)
C(4)	3 639(12)	1 747(45)	8 694(15)	C(86)	2 572	1 770	7 312
O(4)	3 477(9)	2 188(33)	8 490(11)	C(87)	2 771	1 375	7 599
C(5)	3 412(11)	3 961(42)	9 123(14)	C(88)	2 940	2 275	7 758
O(5)	3 563(7)	4 397(27)	8 923(9)	C(89)	2 846	3 226	7 570
C(6)	2 803(14)	3 808(49)	9 212(17)	C(101)	5 471(11)	5 549(45)	9 036(12)
O(6)	2 568(9)	4 352(31)	9 098(10)	C(102)	5 729	6 267	9 067
C(7)	2 291(15)	1 957(58)	9 333(20)	C(103)	5 942	6 238	8 836
O(7)	2 278(10)	2 550(37)	9 540(12)	C(104)	5 896	5 490	8 575
C(8)	1 949(11)	1 819(40)	8 687(14)	C(105)	5 638	4 772	8 545
O(8)	1 691(9)	2 139(33)	8 602(11)	C(100)	5 426	4 801	8 775
C(9)	2 129(11)	1 293(43)	7 862(14)	C(110)	5 243(18)	2 626(62)	8 761(22)
O(9)	1 988(10)	471(39)	7 889(13)	C(111)	4 924(18)	3 877(70)	8 303(20)
C(10)	2 004(16)	3 039(55)	7 548(19)	C(201)	4 050(19)	4 313(68)	8 463(18)
O(10)	1 797(10)	3 312(37)	7 304(12)	C(202)	3 892	3 927	8 160
C(20)	4 465(9)	3 817(35)	9 478(12)	C(203)	3 923	4 475	7 866
C(21)	4 203(11)	4 363(41)	9 605(14)	C(204)	4 112	5 408	7 875
C(30)	3 958(12)	1 220(46)	9 390(15)	C(205)	4 270	5 794	8 178
C(32)	3 846(6)	1 307(23)	9 984(8)	C(200)	4 240	5 246	8 471
C(33)	3 893	938	10 312	C(210)	4 104(13)	6 134(52)	9 022(17)
C(34)	4 111	102	10 408	C(211)	4 707(16)	6 527(57)	8 805(19)
C(35)	4 282	−365	10 176	C(301)	1 404(11)	6 587(36)	8 543(11)
C(36)	4 235	4	9 848	C(302)	1 203	7 472	8 450
C(31)	4 017	840	9 752	C(303)	1 245	8 098	8 174
C(37)	4 154(20)	−251(75)	10 797(23)	C(304)	1 488	7 840	7 990
C(40)	3 187(8)	1 881(30)	9 475(11)	C(305)	1 689	6 955	8 083
C(42)	2 941(7)	960(21)	9 913(9)	C(300)	1 647	6 329	8 359
C(43)	2 895	50	10 106	C(310)	2 279(14)	6 095(54)	8 633(18)
C(44)	3 022	−957	10 035	C(311)	1 856(13)	4 741(48)	8 859(15)
C(45)	3 195	−1 055	9 771	C(401)	1 395(12)	5 312(66)	7 454(20)
C(46)	3 241	−146	9 578	C(402)	1 211	5 990	7 225
C(41)	3 114	862	9 649	C(403)	886	5 782	7 133
C(47)	2 957(13)	−1 938(47)	10 233(16)	C(404)	745	4 894	7 270
C(50)	2 618(9)	1 051(35)	8 679(12)	C(405)	929	4 217	7 498
C(51)	2 857(11)	469(40)	8 520(14)	C(400)	1 254	4 426	7 590
C(60)	2 466(10)	3 591(39)	8 173(13)	C(410)	1 342(16)	2 385(57)	7 794(20)
C(61)	2 744(9)	4 212(36)	8 319(12)	C(411)	1 195(15)	3 921(57)	8 263(18)

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