Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 63.[1] Synthesis of Eight-membered-ring Metallacycles: *X*-Ray Crystal Structures of $[Pt_4W_4(\mu\text{-}CR)(\mu_3\text{-}CR)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]\cdot CH_2Cl_2$, $[Ni_2Pt_2W_4(\mu\text{-}CR)(\mu_3\text{-}CR)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]\cdot CH_2Cl_2$ ($R = C_6H_4Me$-4), and $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ *

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The reaction between $[Pt_3W_4(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_4]$ and $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) in tetrahydrofuran (thf) affords the compound $[Pt_4W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$. The latter may also be obtained from the reaction between the tetranuclear metal cluster $[Pt_2W_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)_2]$ and ethylene under pressure. The structure of $[Pt_4W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ has been established by *X*-ray diffraction. The molecule has a ring of eight metal atoms with the four platinum and four tungsten atoms in alternating positions, such that the tungsten atoms form the four points of a 'star', and the platinum atoms lie in an essentially square arrangement (mean Pt $\cdots$ Pt 2.954, mean Pt–W 2.754 Å). Three of the tolylmethylidyne groups triply bridge Pt_2W triangles, while the fourth edge-bridges a Pt–W bond. Two of the $\mu_3\text{-}CC_6H_4Me$-4 groups lie on one side of the Pt_4W_4 ring, while the third is on the other side. On this side also a CO ligand asymmetrically bridges the Pt_2W triangle which in a symmetrical isomer would have been occupied by a $\mu_3\text{-}CC_6H_4Me$-4 fragment. One CO group bridges the Pt–W bond adjacent to that spanned by the edge-bridging tolylmethylidyne ligand. The remaining six carbonyl groups semi-bridge the other six Pt–W bonds. The reaction between the trimetal compound $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and an excess of $[Ni(cod)_2]$ affords the compound $[Ni_2Pt_2W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$. The latter is formed as a mixture of two isomers by interchange of the platinum and nickel sites. In one isomer a tolylmethylidyne ligand edge-bridges a Ni–W bond, and in the other a Pt–W bond. An *X*-ray diffraction study showed that in the crystal both isomers are present, leading to disorder at the nickel and platinum sites. In the $Ni_2Pt_2W_4$ rings there is a *trans*-Ni $\cdots$ Ni and a *trans*-Pt $\cdots$ Pt arrangement, as expected from the mode of synthesis. Treatment of $[PtW_2(\mu\text{-}CPh)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with an excess of $[Ni(cod)_2]$ yields an octanuclear $Ni_2Pt_2W_4$ metal complex formed as a separable mixture of three isomers: $[Ni_2Pt_2W_4(\mu\text{-}CPh)(\mu_3\text{-}CPh)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ (two isomers) and $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$. An *X*-ray diffraction study on the latter species confirmed the presence of the eight-membered metal ring in which four tungsten atoms are at the points of a 'star' and there is a central Ni $\cdots$ Pt $\cdots$ Ni $\cdots$ Pt fragment. Four CPh ligands triply bridge the NiPtW triangles, two lying above the mean plane through the eight metal atoms, and two below this plane. The structure has a crystallographic two-fold axis through the centre of the ring. A cluster compound $[NiPt_3W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ (two isomers) has been prepared by addition of $[Ni(cod)_2]$ to the seven-metal-atom chain complex $[Pt_3W_4(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_8(\eta\text{-}C_5H_5)_4]$. In thf at reflux temperatures, the species $[Pt_4W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ and $[Ni_2Pt_2W_4(\mu\text{-}CR)(\mu_3\text{-}CR)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ (R = Ph or C_6H_4Me-4) readily isomerise to their respective symmetrical forms with four triply bridging alkylidyne groups. The $^{13}C\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ n.m.r. data for the various compounds are reported, and are discussed in relation to the molecular structures.

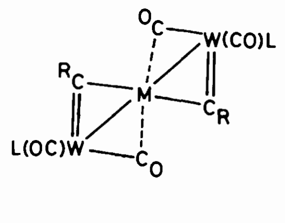
In preceding papers[1,2] we have described methods for synthesising polynuclear metal complexes containing up to seven metal atoms in a chain. In these compounds Pt–W, Pt–Mo, or Ni–W bonds are held together by bridging alkylidyne groups. The syntheses depend on a stepwise combination of the reagents $[M(cod)_2]$ (M = Ni or Pt, cod = cyclo-octa-1,5-diene) with molecules containing reactive C=W(Mo) or C≡W(Mo) sites.

The methodology employed is based on the isolobal model,[3] leading in specific instances to carbon–metal double or triple bonds displaying ligating properties towards metal centres similar to those of alkenes or alkynes.[4,5] Thus the compounds $[W(\equiv CR)(CO)_2L]$ (R = Me, Ph, or C_6H_4Me-4; L = $\eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$) will displace the cod ligands from $[Pt(cod)_2]$ to give trimetal complexes $[PtW_2(\mu\text{-}CR)_2(CO)_4L_2]$ of which **(1a)**,

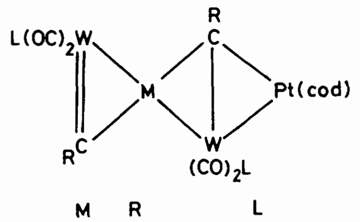
* 2,3-μ-Carbonyl-2,4,4,6,6,8,8-heptacarbonyl-2,4,6,8-tetrakis(η-cyclopentadienyl)-1,2-μ-(*p*-tolylmethylidyne)-3,4,5;5,6,7;1,7,8-tris(μ_3-*p*-tolylmethylidyne)-*cyclo*-1,3,5,7-tetraplatinum-2,4,6,8-tetratungsten-(8 *Pt–W*) -dichloromethane (1/1) and -3,7-dinickel-1,5-diplatinum-2,4,6,8-tetratungsten(4 *Ni–W*)(4 *Pt–W*)-dichloromethane (1/1), and 2,2,4,4,6, 6,8,8-octacarbonyl-2,4,6,8-tetrakis(η-cyclopentadienyl)-1,2,3;-3,4,5;5,6,7;1,7,8-tetra(μ_3-phenylmethylidyne)-*cyclo*-1,5-dinickel-3,7-diplatinum-2,4,6,8-tetratungsten(4 *Ni–W*)(4 *Pt–W*), respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

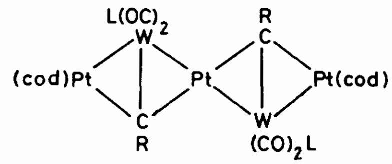
Non-S.I. unit employed: atm = 101 325 Pa.



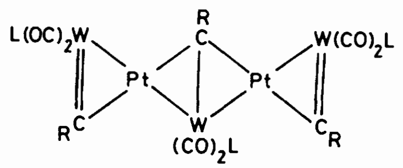
	M	R	L
(1a)	Pt	C_6H_4Me-4	η-C_5H_5
(1b)	Ni	C_6H_4Me-4	η-C_5H_5
(1c)	Pt	Ph	η-C_5H_5
(1d)	Ni	Ph	η-C_5H_5
(1e)	Pt	Me	η-C_5Me_5
(1f)	Ni	Me	η-C_5Me_5



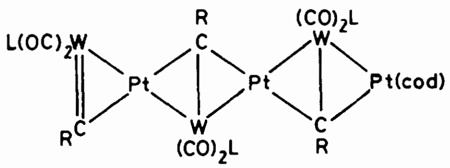
	M	R	L
(2a)	Pt	C_6H_4Me-4	η-C_5H_5
(2b)	Ni	C_6H_4Me-4	η-C_5H_5



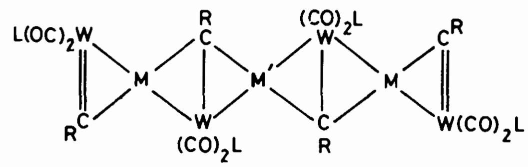
	R	L
(3a)	C_6H_4Me-4	η-C_5H_5
(3b)	Me	η-C_5Me_5



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



	R	L
(5a)	C_6H_4Me-4	η-C_5H_5
(5b)	Me	η-C_5Me_5



	M	M′	R	L
(6a)	Pt	Pt	C_6H_4Me-4	η-C_5H_5
(6b)	Pt	Pt	Me	η-C_5Me_5
(6c)	Ni	Ni	Me	η-C_5Me_5
(6d)	Pt	Ni	Me	η-C_5Me_5

(**1c**), and (**1e**) are examples. Similarly, the nickel compounds [NiW_2(μ-CR)$_2$(CO)$_4$L$_2$] [R = C_6H_4Me-4, L = η-C_5H_5 (**1b**); R = Ph, L = η-C_5H_5 (**1d**); R = Me, L = η-C_5Me_5 (**1f**)] have also been prepared from reactions between the complexes [W(≡CR)(CO)$_2$L] and [Ni(cod)$_2$].[2] These trimetal compounds contain reactive C=W groups to which Pt(cod) fragments, isolobal with carbene, may be attached. Depending on whether one or two Pt(cod) groups are added the products are tetra- or penta-nuclear metal complexes, *e.g.* [$MPtW_2$(μ-CR)(μ$_3$-CR)(CO)$_4$(cod)(η-C_5H_5)$_2$] [R = C_6H_4Me-4; M = Pt (**2a**) or Ni (**2b**)] or [Pt_3W_2(μ$_3$-CR)$_2$(CO)$_4$(cod)$_2$L$_2$] [R = C_6H_4Me-4, L = η-C_5H_5 (**3a**); R = Me, L = η-C_5Me_5 (**3b**)]. Moreover, the cod ligand in (**2a**) may be displaced by [W(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)] to yield the diplatinumtritungsten compound [Pt_2W_3(μ-CC_6H_4Me-4)$_2$(μ$_3$-CC_6H_4Me-4)(CO)$_6$(η-C_5H_5)$_3$] (**4a**). The related compound [Pt_2W_3(μ-CMe)$_2$(μ$_3$-CMe)(CO)$_6$(η-C_5Me_5)$_3$] (**4b**) can be prepared by a similar method. Species of types (**3**) and (**4**)[2] may be used as precursors to complexes having a chain of six or seven metal atoms. Examples of compounds in these two categories include [Pt_3W_3(μ-CR)(μ$_3$-CR)$_2$(CO)$_6$(cod)L$_3$] [R = C_6H_4Me-4, L = η-C_5H_5 (**5a**); R = Me, L = η-C_5Me_5 (**5b**)] and [$M_2M'W_4$(μ-CR)$_2$(μ$_3$-CR)$_2$(CO)$_8$L$_4$] [M = M′ = Pt, R = C_6H_4Me-4, L = η-C_5H_5 (**6a**); R = Me, L = η-C_5Me_5 (**6b**); M = M′ = Ni, R = Me, L = η-C_5Me_5 (**6c**); M = Pt, M′ = Ni, R = Me, L = η-C_5Me_5 (**6d**)].[1]

The complexes with four to seven metal atoms exist in solution as mixtures of diastereoisomers resulting from different conformations of the metal atom chains. All the possible conformations are not always observed, due presumably to the steric effects of the ligands encasing the metal chains. However, it was anticipated that with a sufficiently long metal-atom chain a stereochemical arrangement might be favoured which would result in chain cyclisation rather than growth. This occurred during attempts to prepare compounds containing chains of eight metal atoms from precursors containing seven. Moreover, it was also found that metallacycles with eight metal atoms could be prepared by dimerisation of species with four metal atoms, and that addition of an excess of [Ni(cod)$_2$] to certain PtW_2 compounds afforded clusters containing NiWPtWNiWPtW rings. Preliminary accounts of the work have been given.[6]

Results and Discussion

Addition of [Pt(cod)$_2$], dissolved in ethylene-saturated tetrahydrofuran (thf), to a solution of (**6a**) in the same solvent gave the black crystalline complex [Pt_4W_4(μ-CC_6H_4Me-4)(μ$_3$-CC_6H_4Me-4)$_3$(μ-CO)(CO)$_7$(η-C_5H_5)$_4$] (**7a**). Data characterising this complex are summarised in Tables 1—3. Compound (**7a**) is also formed in the reaction between [Pt(C_2H_4)$_3$] and (**1a**), or by treating (**2a**) in CH_2Cl_2 with ethylene (*ca.* 50 atm). Yields in these syntheses are variable, and the reaction mixtures contain other products not separable by column chromatography, as well as unreacted starting materials.

The previously reported[1] *X*-ray diffraction study on (**6a**) revealed a configuration of the Pt_3W_4 spine not conducive to

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

Compound[b]	Yield (%)	$\nu_{max.}$(CO)[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(7a) $[Pt_4W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$	42	1 851s br, 1 811m br (sh)	29.6 (29.9)	2.0 (2.0)
(7b) $[Pt_4W_4(\mu_3\text{-}CC_6H_4Me\text{-}4)_4(CO)_8(\eta\text{-}C_5H_5)_4]$	88[d]	1 840s br	30.0 (29.9)	2.2 (2.0)
(8a) $[Ni_2Pt_2W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7\text{-}(\eta\text{-}C_5H_5)_4]$	89	1 842s br, 1 815m (sh), 1 775m (sh)	33.6 (33.7)	2.3 (2.3)
(8b) $[Ni_2Pt_2W_4(\mu_3\text{-}CC_6H_4Me\text{-}4)_4(CO)_8(\eta\text{-}C_5H_5)_4]$	90[d]	1 832s br	33.5 (33.7)	2.2 (2.3)
(9a) $[Ni_2Pt_2W_4(\mu\text{-}CPh)(\mu_3\text{-}CPh)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$	45	1 847s br, 1 814m (sh), 1 780m (sh)	32.5 (32.3)	2.3 (1.9)
(9b) $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$	90[d]	1 838s br	32.3 (32.3)	2.2 (1.9)
(10) $[NiPt_3W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7\text{-}(\eta\text{-}C_5H_5)_4]$	44	1 848s br, 1 815m (sh), 1 780m (sh)	32.8 (31.7)	2.6 (2.1)

[a] Calculated values are given in parentheses. [b] All the compounds are black in colour. [c] Measured in CH_2Cl_2. [d] Essentially quantitative yield *via* thermal isomerisation of the precursor (see text).

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

Complex	^{1}H (δ)[b]	^{13}C (δ)[c]
(7a)	[d]2.17 (s, 3 H, Me-4), 2.19 (s, 3 H, Me-4), 2.25 (s, 3 H, Me-4), 2.43 (s, 3 H, Me-4), 4.66 (s, 5 H, C_5H_5), 5.03 (s, 5 H, C_5H_5), 5.18 (s, 5 H, C_5H_5), 5.41 (s, 5 H, C_5H_5), 6.37—7.64 (m, 16 H, C_6H_4)	[d]313.0 [μ-C, *J*(WC) 160, *J*(PtC) 920], 279.3 [μ_3-C, *J*(WC) 120, *J*(PtC) 545, 612], 268.9 [μ_3-C, *J*(WC) 115, *J*(PtC) 603, 670], 265.2 [μ_3-C, *J*(WC) 112, *J*(PtC) 582], 240.7 [CO, *J*(WC) 160], 234.5, 233.8, 232.9, 229.2 (CO), 228.7 (2 × CO), 222.4 [CO, *J*(WC) 154], 155.9, 154.7, 153.6, 153.5 [$C^1(C_6H_4)$], 136.3—123.2 (C_6H_4), 94.4 (2 × C_5H_5), 94.0, 93.9 (C_5H_5), 21.6, 21.5 (Me-4), 21.4 (2 × Me-4)
(7b)	[d]2.21 (s, 12 H, Me-4), 5.07 (s, 20 H, C_5H_5), 6.55, 6.93 [(AB)$_2$, 16 H, C_6H_4, *J*(AB) 8]	[e]95.0 (C_5H_5), 27.3 (Me-4)
(8a)	2.12—2.41 (m, 24 H, Me-4), 4.60 (s, 5 H, C_5H_5), 4.84 (s, 5 H, C_5H_5), 5.05 (s, 5 H, C_5H_5), 5.09 (s, 5 H, C_5H_5), 5.10 (s, 5 H, C_5H_5), 5.12 (s, 5 H, C_5H_5), 5.34 (s, 5 H, C_5H_5), 5.37 (s, 5 H, C_5H_5), 6.23—7.93 (m, 32 H, C_6H_4)	326.4, 314.0 (μ-C), 297.6, 297.2, 290.8, 288.2, 288.0, 284.8 (μ_3-C), 264.4, 248.2, 247.7, 246.6, 246.0, 245.7, 242.0, 241.0, 236.4, 235.3, 234.3, 233.8, 232.9, 229.7, 228.6, 228.2 (CO), 160.1, 159.3, 159.2 [$C^1(C_6H_4)$], 157.8 [2 × $C^1(C_6H_4)$], 157.3, 156.7, 156.3 [$C^1(C_6H_4)$], 136.9—122.4 (C_6H_4), 95.1 (4 × C_5H_5), 94.7, 94.3 (C_5H_5), 94.2 (2 × C_5H_5), 21.8 (8 × Me-4)
(8b)	2.19 (s, 12 H, Me-4), 5.04 (s, 20 H, C_5H_5), 6.56, 7.19 [(AB)$_2$, 16 H, C_6H_4, *J*(AB) 8]	305.7 (μ_3-C), 246.7, 233.9 (CO), 157.9 [$C^1(C_6H_4)$], 136.1, 127.7, 127.0 (C_6H_4), 95.5 (C_5H_5), 27.3 (Me-4)
(9a)	[d]4.58 (s, 5 H, C_5H_5), 4.81 (s, 5 H, C_5H_5), 5.09 (s, 5 H, C_5H_5), 5.13 (s, 5 H, C_5H_5), 5.14 (s, 5 H, C_5H_5), 5.15 (s, 5 H, C_5H_5), 5.35 (s, 5 H, C_5H_5) 5.38 (s, 5 H, C_5H_5), 6.40—8.10 (m, 40 H, Ph)	325.6, 313.6 (μ-C), 297.6, 297.3, 290.7, 287.7, 287.0, 284.5 (μ_3-C), 264.1, 248.3, 247.4, 246.1, 245.0, 241.8, 240.1, 239.9, 236.2, 235.1, 234.1, 233.6, 232.7, 229.3, 227.9, 227.5 (CO), 162.8, 161.4, 161.3, 159.5, 159.2, 159.1 [C^1(Ph)], 158.2 [2 × C^1(Ph)], 128.5–122.1 (Ph), 95.3 (2 × C_5H_5), 95.1 (3 × C_5H_5), 94.7 (C_5H_5), 94.3 (2 × C_5H_5)
(9b)	5.05 (s, 20 H, C_5H_5), 6.75—7.35 (m, 20 H, Ph)	299.4 (μ_3-C), 246.3, 233.3 (CO), 159.3 [C^1(Ph)], 126.9, 126.7, 126.5 (Ph), 95.2 (C_5H_5)
(10)	2.09 (s, 3 H, Me-4), 2.12 (s, 3 H, Me-4), 2.18 (s, 3 H, Me-4), 2.22 (s, 3 H, Me-4), 2.28 (s, 3 H, Me-4), 2.35 (s, 3 H, Me-4), 2.38 (s, 3 H, Me-4), 2.46 (s, 3 H, Me-4), 4.74 (s, 5 H, C_5H_5), 4.80 (s, 5 H, C_5H_5), 5.00 (s, 5 H, C_5H_5), 5.09 (s, 5 H, C_5H_5), 5.12 (s, 5 H, C_5H_5), 5.18 (s, 5 H, C_5H_5), 5.35 (s, 5 H, C_5H_5), 5.42 (s, 5 H, C_5H_5), 6.36—7.85 (m, 32 H, C_6H_4)	316.0, 315.8 (μ-C), 297.7, 287.2, 283.2, 280.4, 271.0, 268.6 (μ_3-C), 263.9, 246.5, 246.3, 240.3, 240.0, 235.8 (CO), 235.5 (2 × CO), 234.3, 232.8, 231.2, 230.8, 230.5, 229.6, 227.5, 223.9 (CO), 159.3, 157.7, 156.7, 156.5, 155.4, 155.3, 153.9, 153.6 [$C^1(C_6H_4)$], 137.4—123.9 (C_6H_4), 95.3, 95.2, 95.1, 95.0, 94.7, 94.5, 94.4, 94.3 (C_5H_5), 21.9, 21.8 (Me-4), 21.7 (2 × Me-4), 21.6 (3 × Me-4), 21.5 (Me-4)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD_2Cl_2 unless otherwise stated. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. Measurements are in CD_2Cl_2–CH_2Cl_2 unless otherwise stated. [d] Measured in $CDCl_3$. [e] Quality of spectrum limited by very poor solubility, hence all peaks are not listed.

ring closure to form **(7a)** without a significant rearrangement of the metal atom framework. It may be that a different diastereoisomer of **(6a)** is involved in the ring-closure process upon addition of $[Pt(cod)_2]$. It cannot be assumed that the structure established for **(6a)** in the solid state corresponds to the most abundant species in solution, since relative solubilities of isomers and their ease of crystallisation will have an indeterminate effect on the crystals isolated. The ^{13}C-{^{1}H} n.m.r. studies on solutions of **(6a)** indicated that only one isomer was present. However, surprisingly the ^{195}Pt-{^{1}H} spectrum clearly showed the presence of two isomers in solution. Hence the mechanism of formation of **(7a)** must remain obscure.

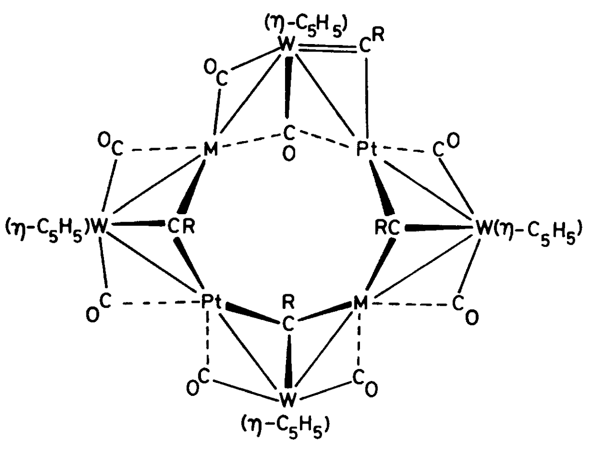
Examination of the n.m.r. data for compound **(7a)** revealed that the complex had an unsymmetrical structure. The ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra (Table 2) showed that the four tolylmethylidyne groups were in different environments. Thus the ^{13}C-{^{1}H} spectrum showed resonances for the ligated carbon nuclei of the alkylidyne ligands at δ 265.2, 268.9, 279.3, and 313.0 p.p.m. The latter signal is in the region expected for a tolylmethylidyne group bridging two metal centres, while the other three peaks are in the range for the ligand bridging three metal atoms.[7] The ^{195}Pt-{^{1}H} n.m.r. spectrum (Table 3) showed the presence of four distinct platinum environments. However, the spectrum is complicated, and discussion is deferred until the results of the *X*-ray diffraction study are presented.

The structure of **(7a)** is shown in Figure 1, and selected bond distances and angles are listed in Table 4. It will be immediately apparent that the structure is based on a ring of eight metal atoms. Moreover, three of the CC_6H_4Me-4 groups triply bridge Pt_2W triangles, while the fourth such group edge-bridges a

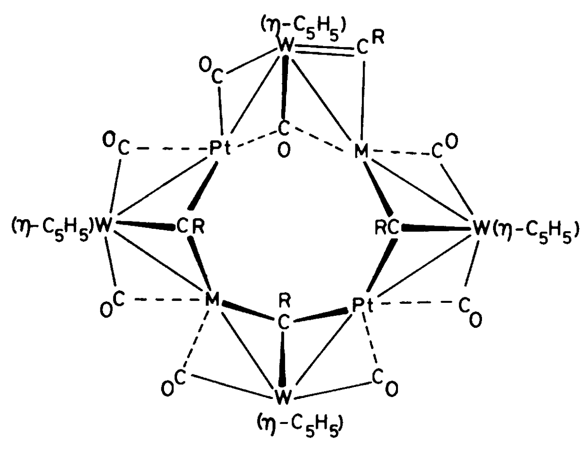
Table 3. Platinum-195 n.m.r. data[a] for the new complexes

Compound[b]	δ[c]	J(WPt)	J(PtPt)	Compound	δ[c]	J(WPt)	J(PtPt)
(7a)[d]	1 693 (A)		2 522 (AB)	**(9a)**	1 740	126	413
	1 665 (B)		1 216 (AC)		1 648	410	242
	947 (C)		−508 (AD)		1 138	100	413
	859 (D)		−295 (BC)		1 004	121	242
			1 194 (BD)	**(9b)**	1 245	73,105	
			1 467 (CD)	**(10)**	1 604 (A)	137	361 (AB)
(8a)	1 726	136	410		1 062 (B)		1 338 (AC)
	1 641	420	234		904 (C)		1 553 (BC)
	1 138	117	410				
	1 002	108	234				
(8b)	1 236						

[a] Chemical shifts are in p.p.m., coupling constants are in Hz. Measurements are in CD_2Cl_2–CH_2Cl_2 unless otherwise indicated. [b] Compound **(7b)** too insoluble for measurement. [c] δ Values are to high frequency of Ξ(^{195}Pt) = 21.4 MHz. [d] Measured in $CDCl_3$.



(i)



(ii)

	M	R
(7a)	Pt	C_6H_4Me-4
(8a)	Ni	C_6H_4Me-4
(9a)	Ni	Ph

platinum–tungsten bond [Pt(2)–W(2)]. The n.m.r. data, which revealed non-equivalent platinum sites, and three μ_3-C and one μ-C environments, are thus readily explained.

Compound **(7a)** contains three μ_3-CPt_2W groups, a fragment first observed by *X*-ray analysis in the complex [Pt_2W(μ_3-CC_6H_4Me-4)$(CO)_4(PMePh_2)_2$(η-C_5H_5)] [Pt ··· Pt 2.989(3), Pt–W 2.785(3), μ_3-C–Pt 2.05(4), and μ_3-C–W 2.04(4) Å].[8] In **(7a)** the mean values of the corresponding distances are very similar: Pt ··· Pt 2.954, Pt–W 2.754, μ_3-C–Pt 2.07, and μ_3-C–W 2.01 Å. The Pt(2)[μ-C(21)]W(2) ring in **(7a)** [Pt(2)–W(2) 2.792(2), Pt(2)–C(21) 1.99(2), W(2)–C(21), 1.90(3) Å] is found also in [PtW(μ-CC_6H_4Me-4)$(CO)_2(PMe_2Ph)_2$(η-C_5H_5)] with similar internuclear separations: Pt–W 2.751(1), μ-C–Pt 1.997(9), and μ-C–W 1.967(6) Å.[5]

The Pt ··· Pt distances in **(7a)** (mean 2.954 Å) most probably result from the bonding requirements of the various μ-C–W fragments, rather than from direct metal–metal interactions. The eight metal atoms in the metallacycle are not coplanar. Atoms W(2) and W(4) show the maximum deviations, 0.43 and 0.35 Å, respectively, from the best mean plane through the metal atoms.

It will be observed that two of the μ_3-CC_6H_4Me-4 ligands lie on one side of the metal ring, with one μ_3-CC_6H_4Me-4 group on the other. On this side also is a carbonyl group [C(2)O(2)], which asymmetrically bridges the Pt(2)Pt(3)W(2) triangle [W(2)–C(2)–O(2) 168(3)°, W(2)–C(2) 1.99(2), Pt(2)–C(2) 2.58(3), Pt(3)–C(2) 2.43(4) Å]. Another carbonyl ligand [C(20)O(20)] bridges the Pt(3)–W(2) bond [W(2)–C(20)–O(20) 153(3)°, W(2)–C(20) 2.10(4), Pt(3)–C(20) 2.12(2) Å]. The remaining carbonyl groups semi-bridge the various Pt–W bonds, as shown, with W–C–O angles of 160—169°.

At Pt(1), Pt(4), and Pt(2) the angles between the Pt(μ-C)W planes are 80, 82, and 89°, respectively. The corresponding angle between the planes Pt(3)[μ_3-C(31)]W(3) and Pt(3)[μ-C(20)]W(2) is 89°.

The observation that **(7a)** could also be obtained from **(1a)** and [$Pt(C_2H_4)_3$] prompted a study of the reaction between **(1a)** and [$Ni(cod)_2$], in an attempt to obtain a compound structurally akin to **(7a)**, but with three different transition elements in the ring. Treatment of **(1a)** with an excess of [$Ni(cod)_2$] in thf afforded the black crystalline complex [$Ni_2Pt_2W_4$(μ-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)$_3$(μ-CO)$(CO)_7$(η-C_5H_5)$_4$] **(8a)**, data for which are given in Tables 1—3.

It was apparent from the n.m.r. measurements that **(8a)** was formed as a mixture of two isomers, and that these isomers were

Table 4. Selected interatomic distances (Å) and angles (°) for the compound $[Pt_4W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]\cdot CH_2Cl_2$ (**7a**)

Pt(1)···Pt(2)	3.020(2)	Pt(2)···Pt(3)	2.888(2)	Pt(3)···Pt(4)	2.970(2)	Pt(1)···Pt(4)	2.937(2)
Pt(1)–W(1)	2.733(2)	Pt(2)–W(1)	2.745(2)	Pt(2)–W(2)	2.792(2)	Pt(3)–W(2)	2.735(2)
Pt(3)–W(3)	2.781(2)	Pt(4)–W(3)	2.737(2)	Pt(4)–W(4)	2.765(1)	Pt(1)–W(4)	2.745(2)
W(1)–C(11)	2.02(3)	Pt(1)–C(11)	2.12(2)	Pt(2)–C(11)	2.05(2)	W(3)–C(31)	2.00(2)
Pt(3)–C(31)	2.01(3)	Pt(4)–C(31)	2.10(2)	W(4)–C(41)	2.00(3)	Pt(4)–C(41)	2.11(3)
Pt(1)–C(41)	2.04(2)	W(2)–C(21)	1.90(3)	Pt(2)–C(21)	1.99(2)	W(1)–C(1)	1.96(2)
Pt(1)–C(1)	2.27(3)	W(1)–C(10)	2.05(3)	Pt(2)–C(10)	2.41(3)	W(3)–C(3)	1.97(2)
Pt(4)–C(3)	2.39(3)	W(3)–C(30)	2.04(4)	Pt(3)–C(30)	2.56(3)	W(4)–C(4)	1.98(4)
Pt(4)–C(4)	2.30(3)	W(4)–C(40)	1.99(3)	Pt(1)–C(40)	2.42(3)	W(2)–C(2)	1.99(2)
Pt(2)–C(2)	2.58(3)	Pt(3)–C(2)	2.43(4)	W(2)–C(20)	2.10(4)	Pt(3)–C(20)	2.12(2)
W(1)–C(cp)*	2.35	W(2)–C(cp)*	2.34	W(3)–C(cp)*	2.37	W(4)–C(cp)*	2.36
Pt(1)–Pt(2)–Pt(3)	87.7(1)	Pt(2)–Pt(3)–Pt(4)	93.1(1)	Pt(3)–Pt(4)–Pt(1)	87.7(1)	Pt(4)–Pt(1)–Pt(2)	91.1(1)
Pt(1)–W(1)–Pt(2)	66.9(1)	Pt(2)–W(2)–Pt(3)	63.0(1)	Pt(3)–W(3)–Pt(4)	65.1(1)	Pt(4)–W(4)–Pt(1)	64.4(1)
W(1)–Pt(2)–W(2)	154.1(1)	W(2)–Pt(3)–W(3)	150.9(1)	W(3)–Pt(4)–W(4)	155.4(1)	W(4)–Pt(1)–W(1)	154.3(1)
W(1)–C(11)–C(12)	140(2)	Pt(2)–C(11)–C(12)	122(2)	Pt(2)–C(11)–C(12)	121(1)	W(3)–C(31)–C(32)	133(2)
Pt(3)–C(31)–C(32)	125(1)	Pt(4)–C(31)–C(32)	121(1)	W(4)–C(41)–C(42)	138(1)	Pt(4)–C(41)–C(42)	120(1)
Pt(1)–C(41)–C(42)	125(2)	W(2)–C(21)–C(22)	144(2)	Pt(2)–C(21)–C(22)	124(1)	W(1)–C(1)–O(1)	160(2)
W(1)–C(10)–O(10)	165(2)	W(3)–C(3)–O(3)	166(3)	W(3)–C(30)–O(30)	166(3)	W(4)–C(4)–O(4)	164(2)
W(4)–C(40)–O(40)	169(2)	W(2)–C(2)–O(2)	168(3)	W(2)–C(20)–O(20)	153(3)	C(1)–W(1)–C(10)	91(1)
C(1)–W(1)–C(11)	104(1)	C(10)–W(1)–C(11)	106(1)	C(2)–W(2)–C(20)	106(1)	C(2)–W(2)–C(21)	105(1)
C(20)–W(2)–C(21)	101(1)	C(3)–W(3)–C(30)	92(1)	C(3)–W(3)–C(31)	105(1)	C(30)–W(3)–C(31)	106(1)
C(4)–W(4)–C(40)	94(1)	C(4)–W(4)–C(41)	105(1)	C(40)–W(4)–C(41)	106(1)		

* Mean distance to cyclopentadienyl ring-carbon atoms.

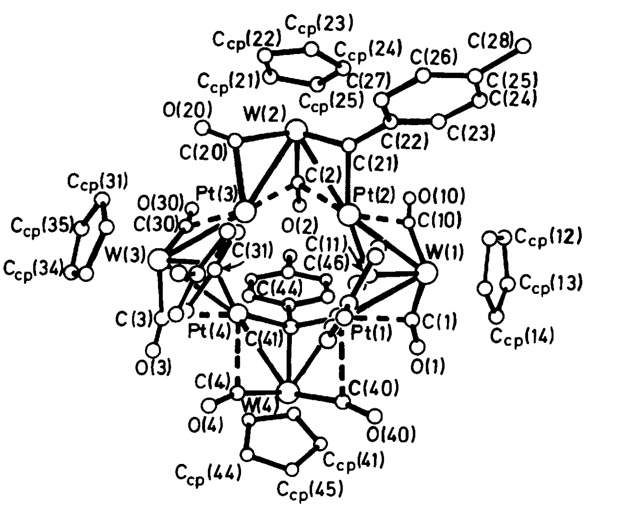


Figure 1. The molecular structure of $[Pt_4W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ (**7a**) showing the atom labelling scheme

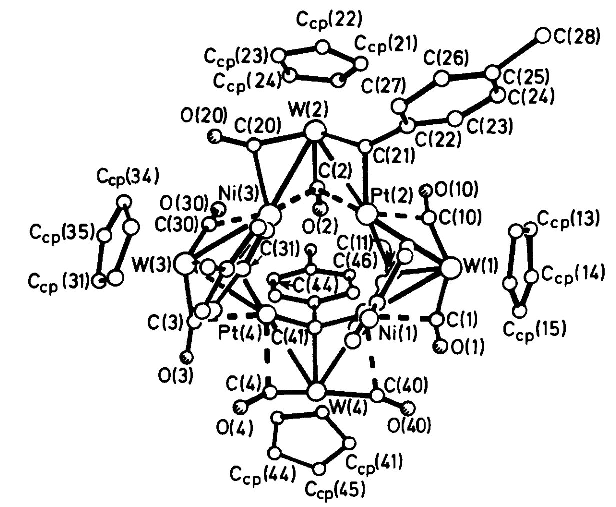


Figure 2. The molecular structure of $[Ni_2Pt_2W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ (**8a**) showing the atom labelling scheme

produced in approximately equal amounts, based on relative peak intensities in the spectra. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum was particularly informative (Table 2) showing two signals for alkylidyne carbon nuclei spanning two metal centres (δ 326.4 and 314.0 p.p.m.), and six resonances for alkylidyne carbons bridging three metal atoms (δ 297.6, 297.2, 290.8, 288.2, 288.0, and 284.8 p.p.m.). Moreover, there were 16 CO peaks in the spectrum of the mixture, eight corresponding to each isomer. In the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum two pairs of platinum signals are observed (Table 3) corresponding to the presence of two inequivalent platinum nuclei in each isomer. The data strongly suggested that the two isomers should be formulated as (**8a**)(i) and (**8a**)(ii), *i.e.* with *trans*-Ni···Ni and *trans*-Pt···Pt configurations, but with a tolylmethylidyne group bridging a Pt–W bond in isomer (i) and a Ni–W bond in (ii).

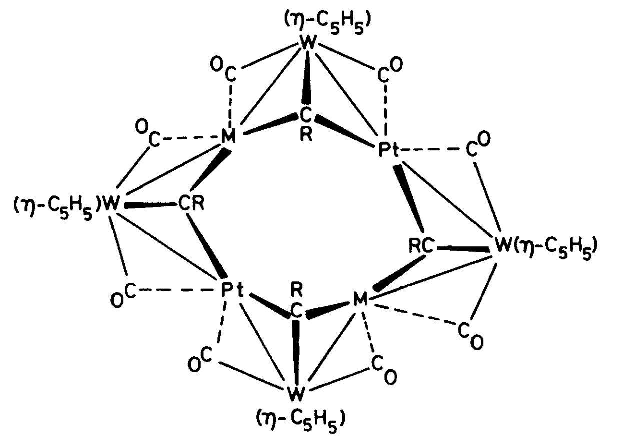
An *X*-ray diffraction study was carried out on a suitable crystal of (**8a**). The structure was disordered (60:40) with alternating nickel and platinum sites. Data for the major component (60%) are given in Table 5; Figure 2 shows the structure of this form, with the tolylmethylidyne ligand bridging the Pt(2)–W(2) bond [*i.e.* isomer (**8a**)(i), the other form in the crystal being (**8a**)(ii)].

The structure is identical in most respects with that of (**7a**), apart from the substitution of two platinum by two nickel atoms. Thus one carbonyl ligand [C(2)O(2)] asymmetrically bridges the Ni(3)W(2)Pt(2) triangle, which is edge-bridged by another carbonyl group [C(20)O(20)]. The triply bridging carbonyl ligand is on the same side of the metal ring as one of the tolylmethylidyne groups, while the other two lie on the other side. Six of the CO groups semi-bridge Pt–W or Ni–W bonds. As with (**7a**), the tungsten atoms W(2) and W(4) deviate most from the mean plane of the eight metal atoms, by 0.35 and 0.30 Å, respectively.

Table 5. Selected interatomic distances (Å) and angles (°) for the compound $[Ni_2Pt_2W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]\cdot CH_2Cl_2$ **(8a)**[a]

Ni(1) ··· Pt(2)	2.843(5)	Ni(3) ··· Pt(2)	2.717(4)	Ni(3) ··· Pt(4)	2.788(5)	Ni(1) ··· Pt(4)	2.796(4)
Ni(1)–W(1)	2.654(4)	Pt(2)–W(1)	2.701(3)	Pt(2)–W(2)	2.733(4)	Ni(3)–W(2)	2.644(5)
Ni(3)–W(3)	2.716(4)	Pt(4)–W(3)	2.687(3)	Pt(4)–W(4)	2.711(3)	Ni(1)–W(4)	2.684(5)
W(1)–C(11)	1.98(3)	Ni(1)–C(11)	1.99(5)	Pt(2)–C(11)	1.96(4)	W(3)–C(31)	2.01(6)
Ni(3)–C(31)	2.02(5)	Pt(4)–C(31)	2.13(5)	W(4)–C(41)	1.94(5)	Pt(4)–C(41)	2.02(4)
Ni(1)–C(41)	2.00(6)	W(2)–C(21)	1.84(8)	Pt(2)–C(21)	1.94(8)	W(1)–C(1)	2.05(6)
Ni(1)–C(1)	2.26(4)	W(1)–C(10)	2.03(9)	Pt(2)–C(10)	2.44(7)	W(3)–C(3)	1.92(6)
Pt(4)–C(3)	2.30(5)	W(3)–C(30)	1.99(5)	Ni(3)–C(30)	2.45(6)	W(4)–C(4)	1.97(4)
Pt(4)–C(4)	2.29(6)	W(4)–C(40)	2.09(5)	Ni(1)–C(40)	2.34(5)	W(2)–C(2)	2.15(5)
Pt(2)–C(2)	2.49(5)	Ni(3)–C(2)	2.30(4)	W(2)–C(20)	2.03(5)	Ni(3)–C(20)	2.07(6)
W(1)–C(cp)[b]	2.36	W(2)–C(cp)[b]	2.32	W(3)–C(cp)[b]	2.35	W(4)–C(cp)[b]	2.38
Ni(1)–Pt(2)–Ni(3)	88.8(1)	Pt(2)–Ni(3)–Pt(4)	92.3(1)	Ni(3)–Pt(4)–Ni(1)	88.4(1)	Pt(4)–Ni(1)–Pt(2)	89.5(1)
Ni(1)–W(1)–Pt(2)	64.1(1)	Pt(2)–W(2)–Ni(3)	60.7(1)	Ni(3)–W(3)–Pt(4)	62.1(1)	Pt(4)–W(4)–Ni(1)	62.4(1)
W(1)–Pt(2)–W(2)	151.8(1)	W(2)–Ni(3)–W(3)	148.5(2)	W(3)–Pt(4)–W(4)	152.3(2)	W(4)–Ni(1)–W(1)	152.6(1)
W(1)–C(11)–C(12)	136(3)	Ni(1)–C(11)–C(12)	124(3)	Pt(2)–C(11)–C(12)	121(2)	W(3)–C(31)–C(32)	140(3)
Ni(3)–C(31)–C(32)	127(4)	Pt(4)–C(31)–C(32)	122(3)	W(4)–C(41)–C(42)	139(4)	Pt(4)–C(41)–C(42)	122(3)
Ni(1)–C(41)–C(42)	120(3)	W(2)–C(21)–C(22)	144(6)	Pt(2)–C(21)–C(22)	121(4)	W(1)–C(1)–O(1)	163(4)
W(1)–C(10)–O(10)	169(9)	W(3)–C(3)–O(3)	164(4)	W(3)–C(30)–O(30)	170(6)	W(4)–C(4)–O(4)	161(5)
W(4)–C(40)–O(40)	166(5)	W(2)–C(2)–O(2)	165(4)	W(2)–C(20)–O(20)	157(6)	C(1)–W(1)–C(10)	92(3)
C(1)–W(1)–C(11)	102(2)	C(10)–W(1)–C(11)	106(2)	C(2)–W(2)–C(20)	103(2)	C(2)–W(2)–C(21)	103(3)
C(20)–W(2)–C(21)	102(3)	C(3)–W(3)–C(30)	94(2)	C(3)–W(3)–C(31)	105(2)	C(30)–W(3)–C(31)	108(2)
C(4)–W(4)–C(40)	92(2)	C(4)–W(4)–C(41)	104(2)	C(40)–W(4)–C(41)	105(2)		

[a] Distances and angles refer to the major disordered component shown in Figure 2. [b] Mean distance to cyclopentadienyl carbons.



(iii)

	M	R
(7b)	Pt	C_6H_4Me-4
(8b)	Ni	C_6H_4Me-4
(9b)	Ni	Ph

During the syntheses of **(7a)** and **(8a)** evidence was obtained for the formation of small amounts of the symmetrical isomers $[Pt_4W_4(\mu_3\text{-}CC_6H_4Me\text{-}4)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ **(7b)** and $[Ni_2Pt_2W_4(\mu_3\text{-}CC_6H_4Me\text{-}4)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ **(8b)**. Thus during chromatography of reaction mixtures which afforded **(7a)** a trace of a pink coloured band was sometimes observed preceding **(7a)** on the alumina column, but it was only obtained in amounts sufficient for i.r. identification. This same product was observed on repurification of samples of **(7a)** which had been stored for several weeks. Similarly in preparations of **(8a)** traces of the species **(8b)** were sometimes detected by n.m.r. measurements.

These results suggested that **(7b)** and **(8b)** were the thermodynamically more stable isomers, and prompted studies in which **(7a)** and **(8a)** were refluxed in thf. Isomerisation to the symmetric isomers **(7b)** and **(8b)** occurred quantitatively under these conditions. Compound **(7b)** proved to be exceedingly insoluble and hence satisfactory n.m.r data could not be obtained even when using a 400-MHz spectrometer. However, satisfactory n.m.r. studies on **(8b)** were possible and the results (Tables 2 and 3) were in agreement with the complex having the structure indicated, with four symmetrically disposed triply bridging alkylidyne groups, two on either side of the eight-membered metal ring. Thus in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum the ligated carbon nuclei of the tolylmethylidyne groups show a single resonance at δ 305.7 p.p.m., and in accord with the symmetrical structure, the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum also shows a single peak at δ 1 236 p.p.m.

It was thought important to carry out an *X*-ray diffraction study on an eight-membered-ring metal complex having four symmetrically disposed triply bridging alkylidyne groups. However, neither **(7b)** nor **(8b)** afforded suitable crystals, and this led to experiments using **(1c)** and **(1d)** as precursors to an eight-membered-ring metallacycle. It was thought that a change from CC_6H_4Me-4 to CPh substituents in a cluster might improve the chance of obtaining crystals suitable for *X*-ray diffraction studies.

The reaction between **(1c)** and an excess of $[Ni(cod)_2]$ in thf gave a *ca.* 1 : 1 mixture of the isomeric compounds $[Ni_2Pt_2W_4(\mu\text{-}CPh)(\mu_3\text{-}CPh)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ **(9a)** and $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ **(9b)**, separable as two distinct fractions by column chromatography. Moreover, when dissolved in refluxing thf, **(9a)** was quantitatively converted into **(9b)**. A mixture of **(9a)** and **(9b)** is also obtained by treating **(1d)** with $[Pt(C_2H_4)_3]$, but the yields of product are much lower. Also formed are brown products which could not be characterised, and which revert to **(1d)**. It is tempting to assign these brown species as unstable Ni_2PtW_4 chain compounds, intermediates on the way to **(9)**.

The n.m.r. data for **(9a)** and **(9b)** are summarised in Tables 2 and 3. Those for **(9b)** indicated the symmetrical structure, with

Table 6. Selected interatomic distances (Å) and angles (°) for the compound $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ (**9b**)[a]

Ni ••• Pt	2.777(4)	Ni′ ••• Pt	2.749(3)	Ni–W(1)	2.657(4)	Pt–W(1)	2.711(2)
Ni–W(2)	2.634(4)	Pt′–W(2)	2.771(2)	W(1)–C(11)	1.98(2)	Ni–C(11)	2.01(3)
Pt–C(11)	2.12(3)	W(2)–C(21)	1.93(3)	Ni–C(21)	2.00(3)	Pt′–C(21)	2.05(3)
W(1)–C(1)	2.09(3)	Pt–C(1)	2.44(3)	W(1)–C(10)	2.00(3)	Ni–C(10)	2.20(3)
W(2)–C(2′)	1.88(3)	Pt′–C(2′)	2.38(3)	W(2)–C(20)	1.89(3)	Ni–C(20)	2.19(4)
W(1)–C(cp)[b]	2.36	W(2)–C(cp)[b]	2.34				
Pt–Ni–Pt′	81.7(1)	Ni–Pt–Ni′	96.9(1)	Ni–W(1)–Pt	62.3(1)	Ni–W(2)–Pt′	61.1(1)
W(1)–Ni–W(2)	155.2(1)	W(1)–Pt–W(2′)	147.6(1)	W(1)–C(11)–C(12)	137(2)	Ni–C(11)–C(12)	124(2)
Pt–C(11)–C(12)	128(2)	W(2)–C(21)–C(22)	133(2)	Ni–C(21)–C(22)	127(2)	Pt′–C(21)–C(22)	124(2)
W(1)–C(1)–O(1)	164(2)	W(1)–C(10)–O(10)	163(2)	W(2)–C(2′)–O(2′)	165(2)	W(2)–C(20)–O(20)	162(3)
C(1)–W(1)–C(10)	90(1)	C(1)–W(1)–C(11)	110(1)	C(10)–W(1)–C(11)	103(1)	C(2′)–W(2)–C(20)	94(1)
C(2′)–W(2)–C(21)	105(1)	C(20)–W(2)–C(21)	101(1)				

[a] Atoms with a prime label are related to those without by a two-fold rotation axis. [b] Mean distance to cyclopentadienyl ring-carbon atoms.

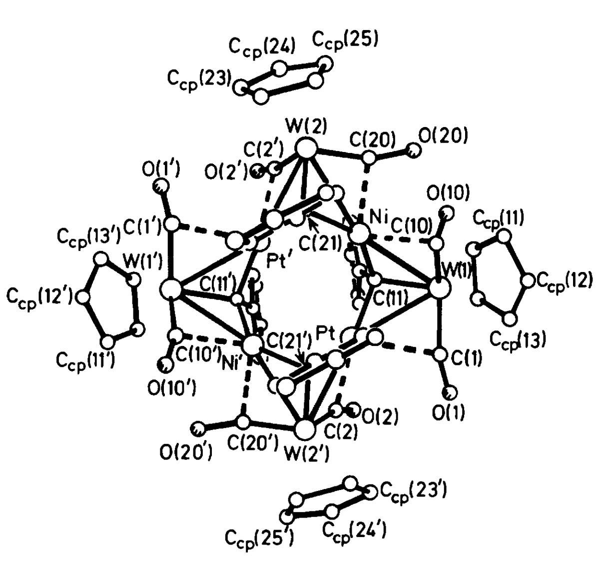


Figure 3. The molecular structure of $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ (**9b**) showing the atom labelling scheme

the appearance of only one resonance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at δ 299.4 p.p.m., for the μ_3-C nuclei, and correspondingly one peak in the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum at δ 1 245 p.p.m. The n.m.r. data for (**9a**), however, were similar to those of (**7a**) and (**8a**), showing resonances due to the presence in solution of isomers with *trans* Ni ••• Ni and *trans* Pt ••• Pt arrangements in the metallacycle, but with a phenylmethylidyne group bridging a Pt–W bond in one isomer (**9a**)(i) and a Ni–W bond in the other (**9a**)(ii). Thus the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table 2) shows two resonances for edge-bridging *C*Ph groups, six signals for triply bridging *C*Ph ligands, and 16 peaks for CO groups. In agreement, the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum shows (Table 3) two sets of two resonances, the platinum atoms in each isomer being in different environments.

Suitable crystals of (**9b**) became available, and the results of an *X*-ray diffraction study are summarised in Table 6, with the molecular structure shown in Figure 3. The eight metal atoms form a ring, as inferred for (**9a**)(i) and (**9a**)(ii), and the four triply bridging phenylmethylidyne groups lie alternately above and below the ring. The conformation is highly symmetric, displaying a crystallographic two-fold axis of symmetry through the centre of and perpendicular to the metal ring. We have used the description 'star cluster' to describe such polynuclear metal species.[6] As with the compounds (**7a**) and (**8a**), the metal atoms in (**9b**) only approximate to coplanarity. The atoms deviating most from the mean plane are W(1) (0.37 Å) and W(2) (0.33 Å), being directed away from their associated CPh groups.

The eight carbonyl ligands semi-bridge the Ni–W and Pt–W bonds, with W–C–O angles of 162—165°. The ligating μ_3-C–W groups at the Ni or Pt centres occupy sites which lead to dihedral angles between the respective $M(\mu_3\text{-}C)W$ planes of 76° at M = Ni and 81° at M = Pt.

The central Ni_2Pt_2 fragment is slightly distorted from a square arrangement with Ni–Pt 2.777(4) and Ni′–Pt 2.749(3) Å, and with Pt–Ni–Pt′ 81.7(1) and Ni–Pt–Ni′ 96.9(1)°. The W(1)–Ni–W(2) angle [155.2(1)°] is less than the W(1)–Pt–W(2′) angle [147.6(1)°]. As expected, the Pt–W bonds (mean 2.741 Å) are somewhat longer than the Ni–W (mean 2.646 Å).

The reaction between (**6a**) and $[Ni(cod)_2]$ was investigated with the object of obtaining a cluster with a $NiPt_3W_4$ core. In this manner the complex $[NiPt_3W_4(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)_3(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ (**10**) was isolated, after chromatography of the crude reaction mixture. The yield of (**10**) was relatively low and variable, and other unidentified products were observed. As mentioned earlier, when discussing the synthesis of (**7a**) from (**6a**), it is possible that only one isomer of the latter can ring-close effectively. Data for (**10**) are given in Tables 1—3. It was apparent from the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum that (**10**) was formed as a mixture of two isomers. It is likely that in one form the tolylmethylidyne group edge-bridges a Ni–W bond [**10**(i)], and in the other a Pt–W bond [**10**(ii)]. However, it was evident from relevant peak intensities that one isomer predominated. Moreover, in the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum, discussed below, only one predominant isomer was observed and the resonances assigned.

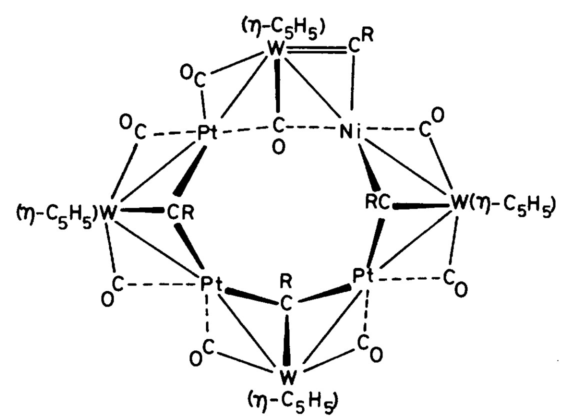
Refluxing thf solutions of (**10**) affords a black insoluble compound [ν_{CO}(max.) at 1 834s br cm^{-1} (in CH_2Cl_2)], but n.m.r. data for this species could not be obtained. The insolubility, and i.r. spectrum in the CO region compared with that of (**7b**) (Table 1), suggest that this product is an isomer of (**10**) with a symmetrical $NiPt_3W_4(\mu_3\text{-}C)_4$ framework.

The $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectra (Table 3) of the unsymmetrical complexes (**7a**), (**8a**), (**9a**), and (**10**) are complicated, due to the various $^{195}Pt\text{-}^{195}Pt$ couplings (Table 3). For (**7a**) a complete analysis and simulation of the spectrum has been possible, leading to classification of the spin system as ABXY.[9] For (**7a**) it will be seen that the observed chemical shifts fall into two groups with resonances in the vicinity of *ca.* δ 1 670 or 900 p.p.m. It has not been possible to assign unambiguously each Pt signal to a particular platinum site (Figure 1). However, consideration of the spectrum of (**10**) is helpful, since one isomer predominates in solution with only three well resolved $^{195}Pt\text{-}\{^1H\}$ n.m.r. resonances being observed. The method used to prepare (**10**),

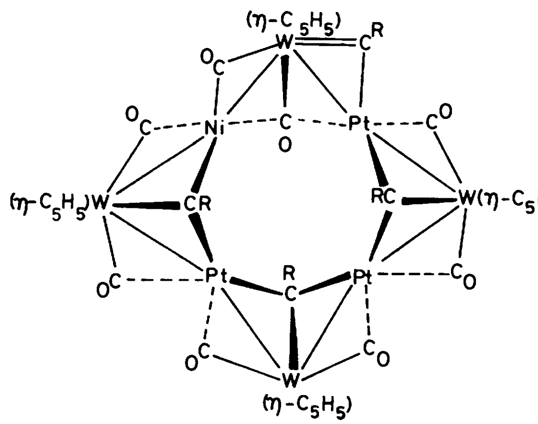
Table 7. Crystal data and experimental parameters*

Compound	**(7a)**	**(8a)**	**(9b)**
Formula	$C_{60}H_{48}O_8Pt_4W_4 \cdot CH_2Cl_2$	$C_{60}H_{48}Ni_2O_8Pt_2W_4 \cdot CH_2Cl_2$	$C_{56}H_{40}Ni_2O_8Pt_2W_4$
M	2 497.7	2 224.9	2 083.9
Crystal system	Triclinic	Triclinic	Monoclinic
Crystal habit	Prisms	Prisms	Hexagonal prisms
Colour	Black	Black	Black
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	12.122(4)	11.853(4)	12.977(10)
b/Å	13.658(5)	12.796(5)	22.134(15)
c/Å	22.068(9)	21.758(15)	19.306(14)
α/°	105.01(3)	105.85(5)	
β/°	90.56(3)	89.80(4)	93.77(6)
γ/°	59.52(2)	114.06(3)	
U/Å^3	3 009(2)	2 877(3)	5 533(7)
Z	2	2	4
D_c/g cm^{-3}	2.76	2.57	2.50
$F(000)$	2 244	2 044	3 792
T/K	293	190	293
μ(Mo-K_α)/cm^{-1}	172.82	138.22	142.70
Crystal size (mm)	0.10 × 0.175 × 0.25	0.20 × 0.20 × 0.50	0.40 × 0.50 × 0.50
$2\theta_{min.,max.}$/°	2.9, 50	3.0, 50	3.0, 40
Data recorded	7 436	10 345	3 469
Data unique	7 054	9 868	2 614
Data used	4 619	5 556	2 356
n in $I \geq n\sigma(I)$	4	4	1
Absorption correction	Empirical	Empirical	Empirical
Mean μR used	1.6	3.05	3.00
No. of refined parameters	335	295	257
g in weighting scheme $w^{-1} = [\sigma^2(F) + g\|F\|^2]$	0.001 5	0.001 0	0.000 8
R (R')	0.041 (0.044)	0.100 (0.106)	0.068 (0.072)

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



(i)



(ii)

(10)

and the established structure of **(8a)**, suggests that the nickel atoms are disposed as indicated, *viz.* **(10)**(i) or **(10)**(ii). It is to be expected that isomer (ii) would be the more readily formed, since in a ring-closure process to produce (i) from **(6a)** breaking of a μ-C-Pt bond and forming of a μ-C–Ni bond would be required, steps which could be energetically less favourable. The observed ^{195}Pt-{^{1}H} resonances for **(10)** may thus be reasonably assigned, with their associated ^{195}Pt–^{195}Pt coupling constants, as in Figure 4. Based on these assignments, it is possible to make tentative ^{195}Pt-{^{1}H} n.m.r. assignments for **(7a)** also, as depicted in Figure 4.

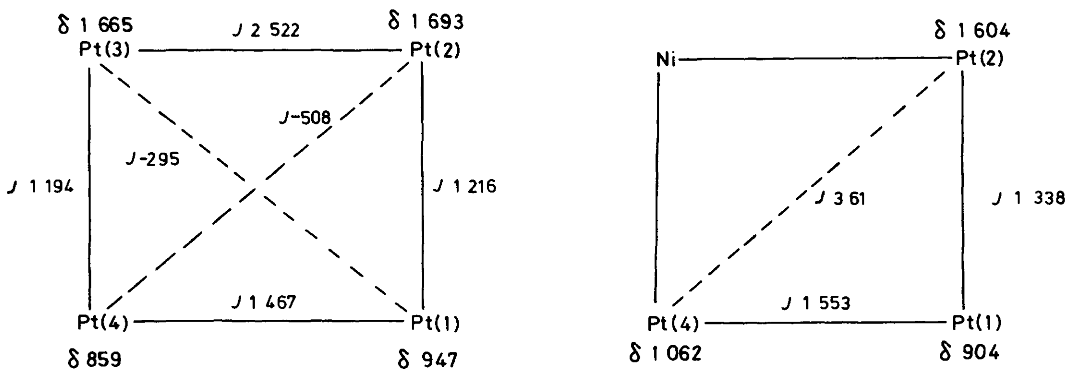
Thus for **(7a)** the ^{195}Pt resonances at δ 1 693 and 1 665 p.p.m. are assigned to nuclei at the 'asymmetric' end of the molecule, while those at 947 and 859 p.p.m. are assigned to ^{195}Pt atoms ligated by two μ_3-C groups. The Pt(2)–Pt(3) coupling (2 522 Hz) also differs the greatest from the other coupling constants and relates to the shortest Pt••• Pt separation (Table 4).

As discussed above, the compounds **(8a)** and **(9a)** exist as two distinct isomers, corresponding to an interchange of the nickel and platinum sites. The observed ^{195}Pt-{^{1}H} chemical shifts for these species, and the ^{195}Pt–^{195}Pt couplings, are either very similar, or in one instance the same. This is not surprising, since

Table 8. Atomic positional parameters (fractional co-ordinates) (× 10[4]) with estimated standard deviations in parentheses for (**7a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	−957(1)	−2 422(1)	−3 236(1)	C_{cp}(24)	−7 505	875	−1 610
Pt(2)	−3 811(1)	−705(1)	−2 769(1)	C_{cp}(25)	−6 823	330	−1 150
Pt(3)	−3 101(1)	445(1)	−1 682(1)	C(31)	−1 745(20)	736(18)	−1 955(9)
Pt(4)	−298(1)	−1 071(1)	−2 190(1)	C(33)[a]	−3 114(13)	2 181(14)	−2 557(8)
W(1)	−2 847(1)	−2 551(1)	−3 872(1)	C(34)	−3 318	3 053	−2 838
W(2)	−5 529(1)	785(1)	−1 647(1)	C(35)	−2 308	3 222	−2 958
W(3)	−1 225(1)	771(1)	−1 092(1)	C(36)	−1 095	2 520	−2 796
W(4)	1 557(1)	−3 200(1)	−3 038(1)	C(37)	−892	1 649	−2 514
C(11)	−2 577(22)	−1 174(19)	−3 561(10)	C(32)	−1 902	1 480	−2 394
C(13)[a]	−3 701(12)	555(14)	−3 958(8)	C(38)	−2 542(29)	4 291(24)	−3 205(13)
C(14)	−3 711	1 338	−4 261	C(3)	534(26)	−632(23)	−1 236(12)
C(15)	−2 573	1 315	−4 391	O(3)	1 612(20)	−1 307(18)	−1 221(9)
C(16)	−1 425	509	−4 218	C(30)	−1 993(24)	2(22)	−710(11)
C(17)	−1 415	−274	−3 915	O(30)	−2 313(20)	−370(17)	−394(8)
C(12)	−2 553	−251	−3 786	C_{cp}(31)[a]	−2 532(18)	2 657(21)	−373(11)
C(18)	−2 562(29)	2 138(25)	−4 725(13)	C_{cp}(32)	−2 084	2 819	−909
C(1)	−1 238(24)	−3 919(22)	−3 771(11)	C_{cp}(33)	−723	2 298	−943
O(1)	−355(19)	−4 942(16)	−3 865(9)	C_{cp}(34)	−331	1 815	−427
C(10)	−3 821(23)	−2 523(21)	−3 108(11)	C_{cp}(35)	−1 449	2 037	−75
O(10)	−4 416(21)	−2 662(18)	−2 783(10)	C(41)	1(21)	−2 797(19)	−2 486(10)
C_{cp}(11)[a]	−4 399(18)	−1 807(15)	−4 548(10)	C(43)[a]	−111(17)	−2 995(14)	−1 389(7)
C_{cp}(12)	−4 363	−2 815	−4 458	C(44)	−324	−3 525	−978
C_{cp}(13)	−3 112	−3 824	−4 719	C(45)	−727	−4 330	−1 199
C_{cp}(14)	−2 375	−3 439	−4 970	C(46)	−917	−4 604	−1 831
C_{cp}(15)	−3 170	−2 193	−4 864	C(47)	−704	−4 073	−2 241
C(21)	−5 642(24)	637(22)	−2 523(11)	C(42)	−300	−3 269	−2 020
C(23)[a]	−6 906(17)	214(11)	−3 352(8)	C(48)	−987(29)	−4 909(26)	−774(13)
C(24)	−7 769	539	−3 788	C(4)	1 543(26)	−1 696(23)	−2 847(12)
C(25)	−8 310	1 665	−3 870	O(4)	1 794(21)	−969(16)	−2 835(12)
C(26)	−7 987	2 466	−3 516	C(40)	1 043(26)	−3 140(24)	−3 895(12)
C(27)	−7 124	2 141	−3 080	O(40)	965(19)	−3 214(18)	−4 425(8)
C(22)	−6 584	1 015	−2 998	C_{cp}(41)[a]	3 092(20)	−5 223(17)	−3 451(8)
C(28)	−9 281(26)	2 014(24)	−4 320(12)	C_{cp}(42)	2 752	−5 021	−2 798
C(2)	−4 017(25)	−758(22)	−1 619(11)	C_{cp}(43)	3 155	−4 262	−2 441
O(2)	−3 261(17)	−1 697(17)	−1 539(9)	C_{cp}(44)	3 744	−3 995	−2 875
C(20)	−4 944(28)	2 025(25)	−1 406(13)	C_{cp}(45)	3 706	−4 589	−3 499
O(20)	−5 143(22)	3 014(19)	−1 215(11)	C_{sol}[b]	4 595(39)	3 063(35)	1 279(18)
C_{cp}(21)[a]	−6 685(22)	1 183(22)	−684(9)	Cl(1)[b]	4 976(13)	2 322(12)	459(6)
C_{cp}(22)	−7 283	2 255	−855	Cl(2)[b]	4 401(15)	4 452(11)	1 408(7)
C_{cp}(23)	−7 790	2 065	−1 427				

[a] Atom of a rigid group; remaining atoms of group have identical standard deviations. [b] Solvent molecule.



(**10**)(ii)

(**7a**)

Figure 4. Platinum-195 n.m.r. assignments for complexes (**7a**) and (**10**) (ii) with chemical shifts (δ) in p.p.m. and coupling constants in Hz

(**8a**) and (**9a**) differ only by the former containing tolylmethylidyne groups and the latter phenylmethylidyne groups. Each isomer of each complex has two pairs of resonances, due to the two inequivalent platinum nuclei. In Table 3 the members of each pair are assigned on the basis of their ^{195}Pt–^{195}Pt coupling constants. Although no unambiguous assignment of the ^{195}Pt resonances to particular platinum sites can be made, in the light of the above discussions it is likely that signals in the range *ca.* δ

Table 9. Atomic positional parameters (fractional co-ordinates) (× 10^4) with estimated standard deviations in parentheses for (**8a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	6 590(3)	2 555(3)	1 778(2)	C_{cp}(22)	4 503	7 163	3 599
Ni(1)	6 590(3)	2 555(3)	1 778(2)	C_{cp}(23)	5 108	7 237	4 182
Pt(2)	5 569(2)	4 239(2)	2 255(1)	C_{cp}(24)	4 502	6 115	4 305
Ni(2)	5 569(2)	4 239(2)	2 255(1)	C_{cp}(25)	3 522	5 348	3 798
Pt(3)	7 333(3)	5 293(3)	3 296(2)	C(31)	9 047(47)	5 748(43)	3 012(26)
Ni(3)	7 333(3)	5 293(3)	3 296(2)	C(33) [a]	10 765(26)	6 659(25)	2 465(16)
Pt(4)	8 570(2)	3 877(2)	2 768(1)	C(34)	11 420	7 558	2 186
Ni(4)	8 570(2)	3 877(2)	2 768(1)	C(35)	10 843	8 210	2 012
W(1)	4 572(2)	2 398(2)	1 161(1)	C(36)	9 610	7 962	2 117
W(2)	5 357(2)	5 769(2)	3 356(1)	C(37)	8 955	7 063	2 396
W(3)	9 548(2)	5 666(2)	3 874(1)	C(32)	9 532	6 411	2 570
W(4)	8 331(2)	1 778(2)	1 925(1)	C(38)	11 663(51)	9 307(46)	1 764(26)
C(11)	6 247(32)	3 732(30)	1 464(18)	C(3)	9 812(44)	4 230(40)	3 679(24)
C(13) [a]	8 375(27)	4 692(25)	1 085(16)	O(3)	10 241(32)	3 530(30)	3 652(18)
C(14)	9 155	5 484	774	C(30)	8 005(47)	4 995(43)	4 274(26)
C(15)	8 757	6 231	567	O(30)	7 222(34)	4 562(31)	4 554(18)
C(16)	7 579	6 187	671	C_{cp}(31) [a]	11 513(35)	6 674(35)	4 511(21)
C(17)	6 798	5 396	982	C_{cp}(32)	11 538	7 192	4 008
C(12)	7 196	4 648	1 189	C_{cp}(33)	10 684	7 724	4 105
C(18)	9 692(53)	7 159(49)	240(30)	C_{cp}(34)	10 130	7 535	4 668
C(1)	4 852(42)	954(39)	1 233(23)	C_{cp}(35)	10 642	6 886	4 919
O(1)	4 756(29)	9(27)	1 155(16)	C(41)	7 227(43)	2 185(40)	2 506(24)
C(10)	3 632(77)	2 415(69)	1 945(42)	C(43) [a]	6 863(22)	1 956(26)	3 611(14)
O(10)	2 986(41)	2 400(36)	2 304(22)	C(44)	6 140	1 431	4 045
C_{cp}(11) [a]	4 586(29)	2 721(31)	155(22)	C(45)	4 897	622	3 848
C_{cp}(12)	3 693	3 099	453	C(46)	4 376	337	3 218
C_{cp}(13)	2 707	2 087	556	C(47)	5 098	862	2 784
C_{cp}(14)	2 991	1 083	323	C(42)	6 341	1 672	2 981
C_{cp}(15)	4 152	1 475	75	C(48)	4 063(42)	187(42)	4 286(25)
C(21)	5 151(64)	5 601(58)	2 492(35)	C(4)	9 795(46)	3 319(42)	2 060(25)
C(23) [a]	3 379(30)	5 145(23)	1 688(18)	O(4)	10 800(33)	4 003(30)	2 094(18)
C(24)	2 802	5 478	1 266	C(40)	7 721(37)	1 816(35)	1 035(21)
C(25)	3 425	6 583	1 152	O(40)	7 570(31)	1 751(28)	538(17)
C(26)	4 626	7 354	1 459	C_{cp}(41) [a]	7 874(27)	−267(28)	1 514(14)
C(27)	5 202	7 021	1 880	C_{cp}(42)	7 673	−67	2 172
C(22)	4 579	5 916	1 995	C_{cp}(43)	8 837	709	2 552
C(28)	2 829(43)	7 117(41)	683(24)	C_{cp}(44)	9 757	990	2 130
C(2)	5 314(39)	4 077(36)	3 368(22)	C_{cp}(45)	9 162	386	1 489
O(2)	5 087(29)	3 197(27)	3 443(16)	C_{sol} [b]	12 299(46)	1 782(42)	3 751(26)
C(20)	7 189(50)	6 913(46)	3 608(27)	Cl(1) [b]	12 704(19)	2 681(21)	4 536(11)
O(20)	8 062(38)	7 839(34)	3 822(20)	Cl(2) [b]	11 067(25)	488(20)	3 583(15)
C_{cp}(21) [a]	3 523(47)	5 995(47)	3 362(22)				

[a] Atom of a rigid group; remaining atoms of group have identical standard deviations. [b] Solvent molecule.

1 600—1 700 p.p.m. correspond to platinum atoms in the more asymmetric part of these molecules, while those resonances in the range *ca.* δ 1 000—1 100 **p.p.m.** correspond to platinum atoms each ligated by two μ_3-**C groups**. As mentioned earlier, on heating, the asymmetric isomers convert to the symmetric species $[Ni_2Pt_2W_4(\mu_3\text{-}CR)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ (R = C_6H_4-Me-4 or Ph), and the platinum environments become equivalent giving rise to one ^{195}Pt n.m.r. resonance.

The relative rates of these conversions are such that longer reflux times are needed when R = C_6H_4Me-4 (**8a**) compared with R = Ph (**9a**). Similarly, for the Pt_4W_4 compound (**7a**, R = C_6H_4Me-4) thermal isomerisation to the symmetric compound (**7b**) requires the longest reflux time of all (*ca.* 8 h). Such observations, along with the fact that the symmetric isomer (**9b**) (R = Ph) is formed in substantial amounts in the initial reaction of (**1c**) with [Ni(cod)$_2$], may indicate that steric factors play an important part in determining the observed isomer ratios. The kinetic products (**7a**), (**8a**), and (**9a**) predominate in these reactions, with the ease of isomerisation to the thermodynamic products (**7b**), (**8b**), and (**9b**) facilitated when nickel is present in the metallacycle or when R = Ph is the substituent compared with R = C_6H_4Me-4.

The results described herein report for the first time the synthesis and characterisation of a new type of metallacyclic ring cluster compound incorporating eight metal atoms. It is to be hoped that such compounds may show interesting reactivity features. Studies are also in progress to extend the syntheses of such compounds to afford examples containing molybdenum in conjunction with tungsten, platinum, or nickel, and to afford compounds with a variety of substituent groups. It is envisaged that such 'fine tuning' of substituent group and metal centre may afford clusters with unique reactivities.

Experimental

The techniques employed and the instrumentation used have been described previously.[1] Light petroleum refers to that fraction of b.p. 40—60 °C. The complexes (**1c**), (**1d**), (**2a**),[2] (**6a**),[1] [Pt(cod)$_2$], and [Pt(C$_2$H$_4$)$_3$][10] were prepared as described earlier. The compound [Ni(cod)$_2$] used was a commercial sample (Strem Chemicals Inc.). Analytical and other data for the complexes are given in Table 1.

Syntheses of the Complexes $[M_2Pt_2W_4(\mu\text{-}CR)(\mu_3\text{-}CR)_3\text{-}(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)_4]$ (M = Pt, R = C_6H_4Me-4; M = Ni,

Table 10. Atomic positional parameters (fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for (**9b**)

Atom	x	y	z	Atom	x	y	z
Pt	−421(1)	3 103(1)	1 589(1)	C(10)	−2 714(21)	3 731(14)	2 137(14)
Ni	−1 518(2)	3 239(1)	2 767(2)	O(10)	−3 065(16)	4 128(10)	2 400(11)
W(1)	−2 507(1)	3 005(1)	1 547(1)	C(2)	591(19)	2 586(16)	793(14)
W(2)	−1 320(1)	3 318(1)	4 131(1)	O(2)	256(15)	2 084(9)	613(10)
C(11)	−1 446(18)	2 539(12)	2 108(12)	C(20)	−2 460(26)	2 970(15)	3 615(18)
C(12)	−1 284(20)	1 926(10)	2 317(14)	O(20)	−3 388(15)	2 827(11)	3 403(11)
C(13)	−966(22)	1 509(12)	1 889(17)	C(21)	−675(20)	3 768(13)	3 421(13)
C(14)	−1 061(23)	901(13)	2 010(21)	C(22)	−463(20)	4 424(11)	3 331(13)
C(15)	−1 383(27)	677(14)	2 601(21)	C(23)	−1 279(21)	4 841(14)	3 308(12)
C(16)	−1 697(24)	1 097(15)	3 059(22)	C(24)	−1 068(29)	5 420(15)	3 336(15)
C(17)	−1 628(22)	1 702(12)	2 930(16)	C(25)	−71(25)	5 659(12)	3 361(16)
$C_{cp}(11)$*	−4 238(19)	2 764(11)	1 702(11)	C(26)	705(23)	5 260(13)	3 403(18)
$C_{cp}(12)$	−4 177	2 998	1 021	C(27)	561(21)	4 663(12)	3 357(13)
$C_{cp}(13)$	−3 586	2 588	642	$C_{cp}(21)$*	−2 004(18)	4 132(11)	4 737(13)
$C_{cp}(14)$	−3 283	2 101	1 089	$C_{cp}(22)$	−929	4 133	4 929
$C_{cp}(15)$	−3 686	2 209	1 743	$C_{cp}(23)$	−680	3 578	5 269
C(1)	−1 799(18)	3 547(13)	830(13)	$C_{cp}(24)$	−1 601	3 233	5 286
O(1)	−1 605(16)	3 780(10)	364(10)	$C_{cp}(25)$	−2 420	3 576	4 957

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

R = C_6H_4Me-4 *or* Ph).—(*i*) A cold (*ca.* 0 °C) solution of [Pt(cod)$_2$] (0.04 g, 0.09 mmol), in ethylene-saturated thf (10 cm^3), was added to a cold ethylene-saturated solution of (**6a**) (0.20 g, 0.09 mmol) in the same solvent (15 cm^3). After stirring the mixture at room temperature under nitrogen for 2 h, solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (*ca.* 8 cm^3) and chromatographed on an alumina column (*ca.* 15 × 2.5 cm). Elution with neat CH_2Cl_2 afforded a black eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from light petroleum gave black *crystals* of [Pt_4W_4(μ-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)$_3$(μ-CO)(CO)$_7$(η-C_5H_5)$_4$] (**7a**) (0.09 g).

(*ii*) The compound [Ni(cod)$_2$] (0.21 g, 0.80 mmol) was added to a solution of (**1a**) (0.20 g, 0.20 mmol) in thf (10 cm^3), and the mixture stirred for 2 h under nitrogen. Solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 (*ca.* 5 cm^3) and chromatographed on alumina. Removal of solvent *in vacuo* from the brown-black eluate, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:5) yielded black *crystals* of [$Ni_2Pt_2W_4$(μ-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)$_3$(μ-CO)(CO)$_7$-(η-C_5H_5)$_4$] (**8a**) (0.19 g).

(*iii*) Similarly, [Ni(cod)$_2$] (0.14 g, 0.50 mmol) was added to (**1c**) (0.20 g, 0.20 mmol), dissolved in thf (20 cm^3), and the mixture stirred for 3 h. Removal of solvent *in vacuo*, dissolving the residue in CH_2Cl_2–light petroleum (*ca.* 10 cm^3, 2:1) and column chromatography on alumina, eluting with the same solvent mixture, gave initially a green band followed by a black band. Removal of solvent *in vacuo*, and crystallisation of the separate fractions from CH_2Cl_2–light petroleum (1:5) gave black *crystals* of [$Ni_2Pt_2W_4$(μ-CPh)(μ_3-CPh)$_3$(μ-CO)(CO)$_7$-(η-C_5H_5)$_4$] (**9a**) (0.10 g) from the second eluate, and green-black *crystals* of [$Ni_2Pt_2W_4$(μ_3-CPh)$_4$(CO)$_8$(η-C_5H_5)$_4$] (**9b**) (0.07 g) from the first eluate.

Formation of the Complexes [$M_2Pt_2W_4$(μ_3-CR)$_4$(CO)$_8$-(η-C_5H_5)$_4$] (M = Pt, R = C_6H_4Me-4; M = Ni, R = C_6H_4Me-4 *or* Ph).—The symmetrical eight-membered-ring metallacycles may be obtained in essentially quantitative yield by refluxing the species (**7a**), (**8a**), or (**9a**) in thf. Thus (**7a**) (0.20 g, 0.08 mmol) refluxed in thf (10 cm^3) for *ca.* 8 h gave highly insoluble black *crystals* of [Pt_4W_4(μ_3-CC_6H_4Me-4)$_4$(CO)$_8$(η-C_5H_5)$_4$] (**7b**) (0.19 g). Similarly, (**8a**) (0.20 g, 0.09 mmol) after *ca.* 4 h reflux in thf (30 cm^3) gave black *crystals* of [$Ni_2Pt_2W_4$(μ_3-CC_6H_4Me-4)$_4$(CO)$_8$(η-C_5H_5)$_4$] (**8b**) (0.18 g), recrystallised from CH_2Cl_2–light petroleum (1:5).

The compound [$Ni_2Pt_2W_4$(μ_3-CPh)$_4$(CO)$_8$(η-C_5H_5)$_4$] (**9b**) (0.18 g) was obtained from (**9a**) (0.20 g, 0.10 mmol) after a 2 h reflux in thf (10 cm^3). The former was also isolated after chromatography, eluting with CH_2Cl_2, removing solvent *in vacuo*, and crystallising the residue from CH_2Cl_2–light petroleum (1:5).

Preparation of the Complex [$NiPt_3W_4$(μ-CC_6H_4Me-4)-(μ_3-CC_6H_4Me-4)$_3$(μ-CO)(CO)$_7$(η-C_5H_5)$_4$].—The compound [Ni(cod)$_2$] (0.10 g, 0.36 mmol) was added to a thf (15 cm^3) solution of (**6a**) (0.10 g, 0.05 mmol), and the mixture stirred (3 h) at room temperature under nitrogen. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (*ca.* 10 cm^3) and chromatographed on alumina. Elution with CH_2Cl_2 removed a black-grey band. Removal of solvent *in vacuo*, and recrystallisation of the residue from CH_2Cl_2–light petroleum (1:4) gave black *crystals* of [$NiPt_3W_4$(μ-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)$_3$-(μ-CO)(CO)$_7$(η-C_5H_5)$_4$] (**10**) (0.05 g).

Crystal Structure Determinations.—The crystal and other experimental data for the compounds (**7a**), (**8a**), and (**9b**) are summarised in Table 7. All data were corrected for Lorentz, polarisation, and *X*-ray absorption effects. The asymmetric units of (**7a**) and (**8a**) each contained a molecule of CH_2Cl_2. The structures were solved by Patterson and Fourier methods by which all the non-hydrogen atoms were located. In (**7a**) and (**8a**) the metal atoms and the chlorine atoms of the CH_2Cl_2 molecules were refined anisotropically, as were the oxygen atoms in (**7a**), all other non-hydrogen atoms being refined isotropically. In (**9b**) the C_5H_5 carbon atoms were refined isotropically, all other non-hydrogen atoms being refined with anisotropic thermal parameters. The C_5H_5 and aromatic rings in (**7a**) and (**8a**) were treated as rigid groups, the aromatic and methyl hydrogen atoms being included in calculated positions [C–H 0.96 Å, $U_{iso.}$(H) *ca.* 1.2 × $U_{iso.}$(parent carbon)]. In (**9b**), the C_5H_5 ring was treated as a rigid group and the phenyl group hydrogen atoms were incorporated using the riding model. The structure of (**8a**) is disordered at the nickel and platinum sites such that 60% of these sites are occupied as shown in Figure 2, with the nickel and platinum sites interchanged (40%) in the remaining molecule. Common atomic positional and displacement parameters were successfully refined for the metal sites, each of fixed, total unit occupancy. However, the high proportion of weak data for (**8a**), consequent upon the solid-state disorder, did not support a fully anisotropic model in the refinement. The deficiencies in the data are reflected in the high R value and residual electron density near the disordered metal atom sites, but these do not suggest any gross misinterpretations.

At convergence the electron-density difference maps showed maxima near the metal atoms of 2 [for (**7a**)], 4 [for (**8a**)], and 2 e $Å^{-3}$ [for (**9b**)]. All computations were carried out using an 'Eclipse' (Data General) computer with the SHELXTL system of programs.[11] Scattering factors and corrections for anomalous dispersion were taken from ref. 12. Atomic coordinates for (**7a**), (**8a**), and (**9b**) are listed in Tables 8—10.

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