A Reversible Metal Framework Rearrangement in High-nuclearity Osmium–Platinum Cluster Compounds. *X*-Ray Crystal Structures of $[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})]$, $[Os_6Pt(CO)_{17}(\mu_4\text{-}NCMe)(C_8H_{12})]$ (C_8H_{12} = Cyclo-octa-1,5-diene), and $[Os_6(CO)_{19}(\mu_3\text{-}NCMe)]$:[†] Compounds with Novel Metal–Acetonitrile Bonding Modes

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The reaction of $[Os_6(CO)_{17}(NCMe)]$ with $[Pt(C_8H_{12})_2]$ (C_8H_{12} = cyclo-octa-1,5-diene) results in the formation of $[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})]$ (**1**). The geometry of (**1**) may be derived from that of $[Os_6(CO)_{18}]$ by breaking one Os–Os edge and adding a terminal $Pt(C_8H_{12})$ fragment to one of the Os atoms constituting the central tetrahedron. Upon standing in CH_2Cl_2, cluster (**1**) isomerizes to a different geometry, $[Os_6Pt(CO)_{17}(\mu_4\text{-}NCMe)(C_8H_{12})]$ (**2**). The isomerization process is first order with $\Delta H^\ddagger$ = 28.7 kcal mol^{-1} and $\Delta S^\ddagger$ = 13 cal K^{-1} mol^{-1}. The structure of isomer (**2**) may be derived from its precursor (**1**) by breaking one more Os–Os edge and by moving the $Pt(C_8H_{12})$ unit into a bridging position. Substitution of the C_8H_{12} ligand in (**1**) or (**2**) by 1,2-bis(diphenylphosphino)ethane or $P(OMe)_3$ results in clusters having a metallic framework analogous to (**1**). The extrusion of the Pt moiety results from reaction of CO with either isomer giving a product characterized as $[Os_6(CO)_{19}(\mu_3\text{-}NCMe)]$ (**3**).

We have recently reported[1] that the activated complexes $[Os_6(CO)_{18-n}(NCMe)_n]$ (*n* = 1 or 2) react with $[Pt(C_8H_{12})_2]$ (C_8H_{12} = cyclo-octa-1,5-diene) to give a mixture of compounds from which the mixed-metal clusters $[Os_6Pt_2(CO)_{17}(C_8H_{12})_2]$ and $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ can be isolated. *X*-Ray crystallographic studies showed that upon addition of the $Pt(C_8H_{12})$ fragments the bicapped tetrahedral geometry of the parent cluster $[Os_6(CO)_{18}]$[2] had rearranged to different metallic cores. The cluster $[Os_6Pt_2(CO)_{17}(C_8H_{12})_2]$ has the six Os atoms rearranged in an octahedral geometry with two opposed faces Pt-capped, while $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ has two edge-fused Os tetrahedra, one of which is Pt-bicapped. These two metallic frameworks were found reversibly to interconvert upon reaction with CO.

We now present the molecular structures of the heterometallic cluster $[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})]$ (**1**) and its isomeric form $[Os_6Pt(CO)_{17}(\mu_4\text{-}NCMe)(C_8H_{12})]$ (**2**). Isomer (**1**) was isolated from the reaction of $[Os_6(CO)_{17}(NCMe)]$ with $[Pt(C_8H_{12})_2]$ where the acetonitrile ligand was not displaced by the incoming $Pt(C_8H_{12})$ fragment. Upon standing in solution (**1**) isomerizes to a different metallic framework (**2**). The metallic framework rearrangement can be reversed by substitution of the C_8H_{12} ligand in the Pt moiety with phosphorus-donor ligands. Both isomeric forms react with CO, eliminating the Pt fragment, and yielding the homometallic cluster $[Os_6(CO)_{19}(\mu_3\text{-}NCMe)]$ (**3**).

Results and Discussion

The green complex $[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})]$ (**1**) was isolated in 20% yield from the reaction of $[Os_6(CO)_{17}(NCMe)]$ with $[Pt(C_8H_{12})_2]$ after separation of the reaction mixture by thin-layer chromatography (t.l.c.). The reactions are summarized in the Scheme and i.r. data are presented in Table 1. Dark green crystals of (**1**) suitable for *X*-ray analysis were obtained by recrystallization from CH_2Cl_2–cyclohexane at 0 °C.

The molecular structure of (**1**) is shown in Figure 1 and selected intramolecular distances and angles are listed in Table 2. The structure may be derived from that of $[Os_6(CO)_{18}]$[2] by breaking one Os–Os edge [Os(2)–Os(5)], adding a terminal

Table 1. Infrared carbonyl stretching bands (cm^{-1})

	Complex	ν(CO)(CH_2Cl_2)
(**1**)	$[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})]$	2 089m, 2 061s, 2 036m, 2 020s, 2 000m (sh), 1 984w (sh), 1 957w
(**1a**)	$[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)\{P(OMe)_3\}_2]$	2 086m, 2 057s, 2 030m, 2 015s, 2 000m (sh), 1 993w, 1 980w
(**1b**)	$[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(dppe)]$	2 084m, 2 055s, 2 032m (sh), 2 013s, 1 992w, 1 977w, 1 950w
(**2**)	$[Os_6Pt(CO)_{17}(\mu_4\text{-}NCMe)(C_8H_{12})]$	2 090m, 2 063vs, 2 051s, 2 019s (sh), 1 980w, 1 954w
(**3**)	$[Os_6(CO)_{19}(\mu_3\text{-}NCMe)]$	2 128w, 2 092m, 2 068s, 2 051m, 2 029s, 2 014w (sh), 1 989w, 1 954w br

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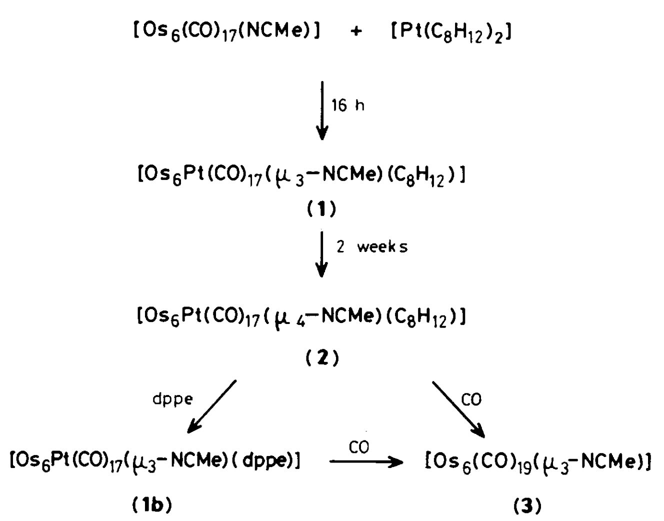
[†] μ_3-[Acetonitrile-*C*(Pt^1)*N*($Os^{2,7}$)]-2,2,2,3,3,3,4,4,4,5,5,5,6,6,6,7,7-heptadecacarbonyl-1-(η^4-cyclo-octa-1,5-diene)-*cyclo*-platinumhexaosmium(*Pt–Os*)(11 *Os–Os*), μ_4-[acetonitrile-*C*(Pt^1,Os^2)*N*($Os^{2,3,7}$)]-2,2,2,3,3,3,4,4,4,5,5,5,6,6,6,7,7-heptadecacarbonyl-1-(η^4-cyclo-octa-1,5-diene)-*cyclo*-platinumhexaosmium(2 *Pt–Os*)(10 *Os–Os*), and μ_3-[acetonitrile-*C*(Os^1)*N*($Os^{2,3}$)]-1,1,1,1,2,2,2,3,3,3,4,4,4,5,5,5,6,6,6-nonadecacarbonyl-*cyclo*-hexaosmium(9 *Os–Os*) respectively.

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

Non-S.I. unit employed: cal = 4.184 J.

$Pt(C_8H_{12})$ fragment to Os(2), and inserting a triply bridging acetonitrile ligand thus linking Os(2), Os(5), and Pt. There are 17 carbonyl ligands; Os(2) possesses two and each of the remaining Os atoms have three terminal carbonyl ligands. The mean Os–C and C–O distances are 1.86(2) and 1.17(3) Å, respectively, and the average Os–C–O angle is 174(3)° (the range of Os–C–O angles spans 3.5σ). These values are typical for linear carbonyls. The Os–Os distances vary from 2.728(1) to 2.890(1) Å and the Os(2)–Pt separation is 2.783(1) Å. The geometry about the Pt atom is close to square planar. Typical Os–Pt distances observed in previous structures[1] are 2.6—2.8 Å for interactions in the plane defined by the metal and the C_8H_{12} ligand and 2.9—3.0 Å for the out-of-plane interaction. The out-of-plane distances tend to be longer as the higher energy Pt $6p_z$ atomic orbital is used in this interaction.



Scheme. Summary of reactions; all were performed in CH_2Cl_2

The C_8H_{12} ligand is not symmetrically bound to the Pt atom, the Pt–C(olefinic) bond lengths vary from 2.20(2) to 2.43(3) Å, and the largest separations [Pt–C(5) and Pt–C(6)] are *trans* to the Pt–C(acetonitrile) bond. The bond parameters of the C_8H_{12} ligand fall within the ranges previously observed in $Pt(C_8H_{12})$ fragments.[1,3] The acetonitrile ligand symmetrically bridges the Os(2)–Os(5) edge through the N atom [Os(2)–N 2.06(2), Os(5)–N 2.11(2) Å] and this results in elongation of the edge Os(2)–Os(5) to 3.350(1) Å. The distance between the unsaturated carbon, C(9), of the MeCN group and the Pt atom is 2.01(3) Å, which is typical for a Pt–C σ bond.[3] The C(9) and N atoms can be considered as sp^2 hybridized with a C=N bond [C–N 1.22(3) Å and N–C(9)–C(10) 124(4)°].

To our knowledge this is the first example of a triply bridging acetonitrile ligand in a metallic complex. A similar linkage is observed in the homometallic cluster $[Os_6(CO)_{18}(CNC_6H_4\text{-}Me\text{-}p)_2]$[4] in which one of the isocyanide groups triply bridges three different metallic centres and acts as a four-electron donor ligand.

Upon standing in CH_2Cl_2 for several days, the green complex (**1**) converts to a brown compound (**2**). Complex (**2**) also is observed in the reaction of $[Os_6(CO)_{17}(NCMe)]$ with $[Pt(C_8$-

Table 2. Selected internuclear distances (Å) and angles (°) for $[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})]$ (**1**)*

Os(2)–Os(1)	2.728(1)	Os(3)–Os(1)	2.804(1)	C(33)–Os(3)	1.88(2)	Os(6)–Os(4)	2.774(1)
Os(4)–Os(1)	2.829(1)	Os(6)–Os(1)	2.806(1)	C(41)–Os(4)	1.88(3)	C(42)–Os(4)	1.87(2)
C(11)–Os(1)	1.84(3)	C(12)–Os(1)	1.86(2)	C(43)–Os(4)	1.88(2)	Os(6)–Os(5)	2.890(1)
C(13)–Os(1)	1.85(2)	Os(3)–Os(2)	2.828(1)	C(51)–Os(5)	1.87(2)	C(52)–Os(5)	1.85(2)
Os(6)–Os(2)	2.815(1)	Pt–Os(2)	2.783(1)	C(53)–Os(5)	1.88(3)	N–Os(5)	2.11(2)
C(21)–Os(2)	1.87(2)	C(22)–Os(2)	1.84(2)	C(61)–Os(6)	1.88(2)	C(62)–Os(6)	1.85(2)
N–Os(2)	2.06(2)	Os(4)–Os(3)	2.853(1)	C(63)–Os(6)	1.88(2)	C(9)–Pt	2.01(3)
Os(5)–Os(3)	2.856(1)	Os(6)–Os(3)	2.802(1)	C(1)–Pt	2.20(2)	C(2)–Pt	2.22(3)
C(31)–Os(3)	1.88(3)	C(32)–Os(3)	1.83(2)	C(5)–Pt	2.43(3)	C(6)–Pt	2.38(2)
				C(9)–N	1.22(3)		
C(9)–Pt–Os(2)	69.4(7)	C(1)–Pt–Os(2)	156.9(7)	Os(6)–Os(3)–Os(5)	61.4(1)	C(7)–C(6)–Pt	98(2)
C(1)–Pt–C(9)	98.1(9)	C(2)–Pt–Os(2)	160.4(7)	C(33)–Os(3)–C(31)	90(1)	C(32)–Os(3)–C(31)	99(1)
C(2)–Pt–C(9)	98(1)	C(2)–Pt–C(1)	35(1)	Os(3)–Os(4)–Os(1)	59.1(1)	C(33)–Os(3)–C(32)	94.9(9)
C(5)–Pt–Os(2)	111.6(7)	C(5)–Pt–C(9)	168.7(9)	Os(6)–Os(4)–Os(3)	59.7(1)	Os(6)–Os(4)–Os(1)	60.1(1)
C(5)–Pt–C(1)	84(1)	C(5)–Pt–C(2)	78(1)	C(43)–Os(4)–C(41)	95(1)	C(42)–Os(4)–C(41)	92(1)
C(6)–Pt–Os(2)	103.4(6)	C(6)–Pt–C(9)	161.7(9)	Os(6)–Os(5)–Os(3)	58.4(1)	C(43)–Os(4)–C(42)	91(1)
C(6)–Pt–C(1)	82.3(8)	C(6)–Pt–C(2)	93(1)	C(53)–Os(5)–C(51)	91(1)	C(52)–Os(5)–C(51)	94(1)
C(6)–Pt–C(5)	29.5(9)	Os(3)–Os(1)–Os(2)	61.5(1)	N–Os(5)–Os(3)	84.9(5)	C(53)–Os(5)–C(52)	92(1)
Os(4)–Os(1)–Os(2)	111.0(1)	Os(4)–Os(1)–Os(3)	60.9(1)	Os(2)–Os(6)–Os(1)	58.1(1)	N–Os(5)–Os(6)	82.5(4)
Os(6)–Os(1)–Os(2)	61.1(1)	Os(6)–Os(1)–Os(3)	59.9(1)	Os(3)–Os(6)–Os(2)	60.5(1)	Os(3)–Os(6)–Os(1)	60.0(1)
Os(6)–Os(1)–Os(4)	59.0(1)	C(12)–Os(1)–C(11)	92(1)	Os(4)–Os(6)–Os(2)	110.0(1)	Os(4)–Os(6)–Os(1)	60.9(1)
C(13)–Os(1)–C(11)	92(1)	C(13)–Os(1)–C(12)	91(1)	Os(5)–Os(6)–Os(1)	114.9(1)	Os(4)–Os(6)–Os(3)	61.5(1)
Os(1)–Os(2)–Pt	153.4(1)	Os(3)–Os(2)–Pt	142.2(1)	Os(5)–Os(6)–Os(3)	60.2(1)	Os(5)–Os(6)–Os(2)	71.9(1)
Os(3)–Os(2)–Os(1)	60.6(1)	Os(6)–Os(2)–Pt	136.1(1)	C(62)–Os(6)–C(61)	91(1)	Os(5)–Os(6)–Os(4)	108.2(1)
Os(6)–Os(2)–Os(1)	60.8(1)	Os(6)–Os(2)–Os(3)	59.5(1)	C(63)–Os(6)–C(62)	89(1)	C(63)–Os(6)–C(61)	96(1)
C(22)–Os(2)–C(21)	106(1)	N–Os(2)–Pt	65.4(5)	Os(5)–N–Os(2)	106.8(8)	C(9)–N–Os(2)	115(2)
N–Os(2)–Os(1)	140.9(5)	N–Os(2)–Os(3)	86.6(6)	C(9)–N–Os(5)	138(2)	N–C(9)–Pt	110(2)
N–Os(2)–Os(6)	85.2(5)	Os(2)–Os(3)–Os(1)	57.9(1)	C(10)–C(9)–Pt	126(2)	C(10)–C(9)–N	124(4)
Os(4)–Os(3)–Os(1)	60.0(1)	Os(4)–Os(3)–Os(2)	107.4(1)	C(2)–C(1)–Pt	74(2)	C(8)–C(1)–Pt	111(2)
Os(5)–Os(3)–Os(1)	116.1(1)	Os(5)–Os(3)–Os(2)	72.2(1)	C(8)–C(1)–C(2)	124(3)	C(1)–C(2)–Pt	71(2)
Os(5)–Os(3)–Os(4)	107.0(1)	Os(6)–Os(3)–Os(1)	60.1(1)	C(3)–C(2)–Pt	110(2)	C(4)–C(5)–Pt	106(2)
Os(6)–Os(3)–Os(2)	60.0(1)	Os(6)–Os(3)–Os(4)	58.8(1)	C(6)–C(5)–Pt	73(2)	C(5)–C(6)–Pt	78(2)

* Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

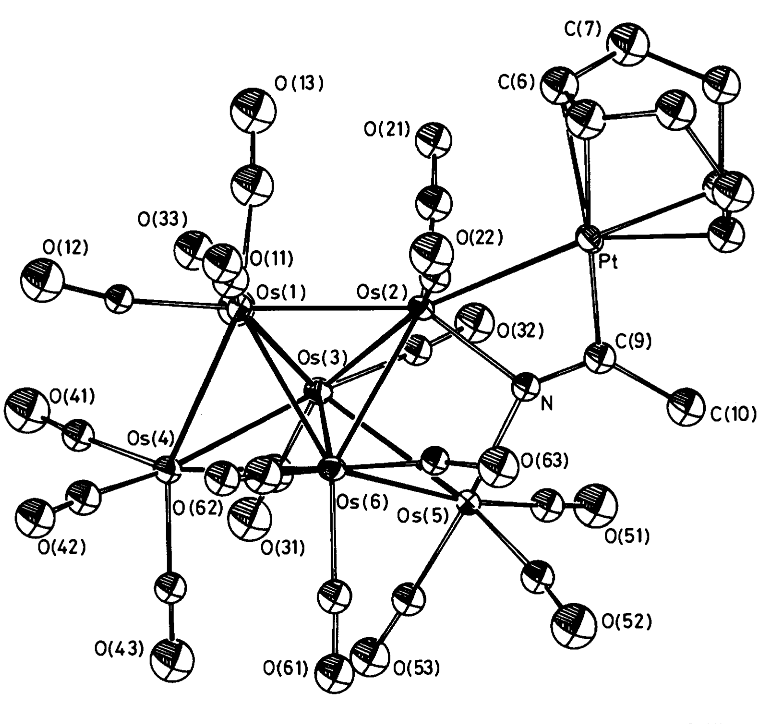


Figure 1. The molecular structure of $[Os_6Pt(CO)_{17}(\mu_3\text{-NCMe})(C_8H_{12})]$ (**1**)

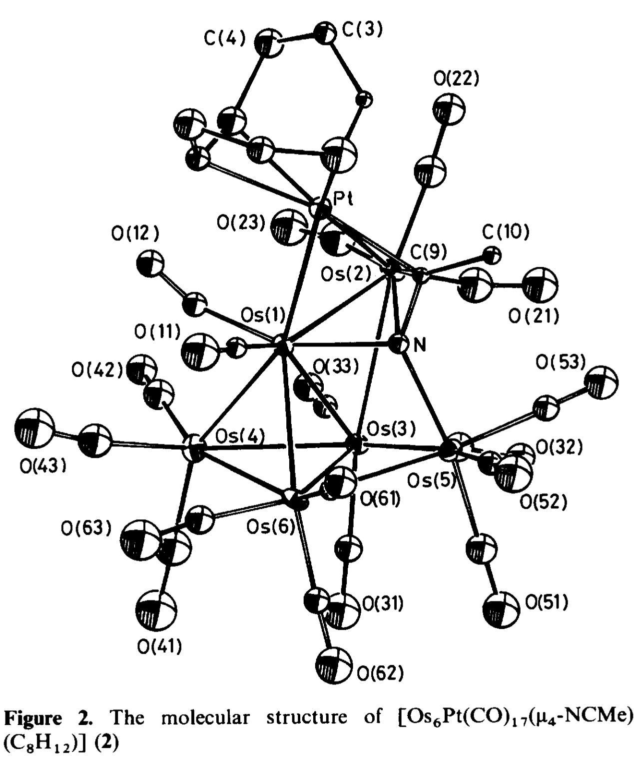


Figure 2. The molecular structure of $[Os_6Pt(CO)_{17}(\mu_4\text{-NCMe})(C_8H_{12})]$ (**2**)

$H_{12})_2]$ but in very low yield. In order to establish the molecular structure of compound (**2**) a single-crystal *X*-ray analysis was undertaken and this revealed that (**2**) is a geometric isomer of cluster (**1**). Figure 2 shows the molecular structure of isomer (**2**) and Table 3 contains selected internuclear distances and angles.

The metal core geometry of (**2**) can be derived from that of its precursor (**1**) by breaking one Os–Os edge, Os(2)–Os(6), and bringing the $Pt(C_8H_{12})$ unit into a bridging position between Os(1) and Os(2). The MeCN ligand triply bridges Os(1), Os(2), and Os(5) through the N atom and doubly bridges Os(2) and Pt through the C atom. The C_8H_{12} ligand is now symmetrically bound to the Pt atom, and the mean Pt–C distance is 2.27(2) Å. There are no significant differences in the bond parameters of the C_8H_{12} groups in the two isomers (**1**) and (**2**).

All of the carbonyl ligands are linear and terminal with the exception of C(12)–O(12), Os(1)–C(12)–O(12) 161(4)°, which semi-bridges the Os(1)–Os(4) edge. The Os(1)–C(12) and Os(4)–C(12) distances are 1.92(4) and 2.57(6) Å respectively. The mean Os–C and C–O distances are 1.85(5) and 1.18(6) Å, respectively, and the Os–C–O angles vary from 161(4) to 179(4) °. The Os–Os distances vary from 2.617(3) to 3.175(2) Å, the shortest separation is the edge bridged by the $Pt(C_8H_{12})$ fragment and the longest is between Os(2) and Os(3). The Os(1)–Pt and Os(2)–Pt internuclear distances are 2.696(2) and 2.903(2) Å respectively, Os(1) being closer to the plane defined by the metal and the C_8H_{12} olefinic groups. The values also are comparable to the Pt–Os separations reported for the 'butterfly' complex $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(\text{cyclo-}C_6H_{11})_3\}]$ [5] in which the Pt atom is positioned at one of the 'wing tips'.

The co-ordination about the Pt atom in isomer (**2**) defines a distorted trigonal-bipyramidal geometry. A variation in the geometry also is evident about the MeCN ligand which changes from planar in cluster (**1**) to tetrahedral environments at the C and N atoms in complex (**2**). The C–N bond distance in isomer (**2**) is still typical of a C=N bond and is not statistically longer (1.4σ) than in (**1**) [C(9)–N 1.30(5) in (**2**) and 1.22(3) Å in (**1**)].

The question of the number of electrons that the acetonitrile ligand contributes to the metallic framework in each isomer arises naturally from electron counting. Isomer (**2**) has a more open skeleton than its parent cluster (**1**) and thus more electrons are required from the MeCN ligand. In (**2**) there is a total of five metal–acetonitrile interactions as opposed to three found in compound (**1**). The Pt atom in (**1**) can be considered as a 16-electron square-planar centre while an 18-electron trigonal-bipyramidal Pt centre is more consistent with the geometry of

Table 3. Selected internuclear distances (Å) and angles (°) for $[Os_6Pt(CO)_{17}(\mu_4\text{-}NCMe)(C_8H_{12})]$ (**2**)

Os(1)–Pt	2.696(2)	Os(2)–Pt	2.903(2)	N–Os(2)	2.31(3)	Os(4)–Os(3)	2.876(3)
C(9)–Pt	2.10(3)	C(1)–Pt	2.24(6)	Os(5)–Os(3)	2.870(2)	Os(6)–Os(3)	2.821(3)
C(2)–Pt	2.26(4)	C(5)–Pt	2.27(4)	C(31)–Os(3)	1.87(5)	C(32)–Os(3)	1.88(5)
C(6)–Pt	2.30(4)	Os(2)–Os(1)	2.617(3)	C(33)–Os(3)	1.87(4)	Os(6)–Os(4)	2.754(2)
Os(3)–Os(1)	2.881(2)	Os(4)–Os(1)	2.777(2)	C(41)–Os(4)	1.87(6)	C(42)–Os(4)	1.85(5)
Os(6)–Os(1)	2.760(2)	C(11)–Os(1)	1.85(4)	C(43)–Os(4)	1.91(6)	Os(6)–Os(5)	2.842(3)
C(12)–Os(1)	1.92(4)	N–Os(1)	2.11(3)	C(51)–Os(5)	1.87(5)	C(52)–Os(5)	1.92(4)
Pt–Os(2)	2.903(2)	Os(3)–Os(2)	3.175(2)	C(53)–Os(5)	1.88(5)	N–Os(5)	2.10(3)
C(21)–Os(2)	1.78(6)	C(22)–Os(2)	1.83(5)	C(61)–Os(6)	1.84(4)	C(62)–Os(6)	1.84(4)
C(23)–Os(2)	1.70(5)	C(9)–Os(2)	2.39(4)	C(63)–Os(6)	1.81(5)		
				N–C(9)	1.30(5)		

Os(2)–Pt–Os(1)	55.6(1)	C(9)–Pt–Os(1)	72(1)	Os(4)–Os(3)–Os(2)	100.3(1)	Os(5)–Os(3)–Os(1)	74.3(1)
C(9)–Pt–Os(2)	54(1)	C(1)–Pt–Os(1)	141(2)	Os(5)–Os(3)–Os(2)	75.9(1)	Os(5)–Os(3)–Os(4)	114.7(1)
C(1)–Pt–Os(2)	146(2)	C(1)–Pt–C(9)	97(2)	Os(6)–Os(3)–Os(1)	57.9(1)	Os(6)–Os(3)–Os(2)	103.0(1)
C(2)–Pt–Os(1)	173.0(9)	C(2)–Pt–Os(2)	120.1(9)	Os(6)–Os(3)–Os(4)	57.8(1)	Os(6)–Os(3)–Os(5)	59.9(1)
C(2)–Pt–C(9)	100.5(1)	C(2)–Pt–C(1)	39(2)	C(32)–Os(3)–C(31)	88(2)	C(33)–Os(3)–C(31)	97(2)
C(5)–Pt–Os(1)	107(1)	C(5)–Pt–Os(2)	106(1)	C(33)–Os(3)–C(32)	90(2)	Os(3)–Os(4)–Os(1)	61.3(1)
C(5)–Pt–C(9)	158(2)	C(5)–Pt–C(1)	96(2)	Os(6)–Os(4)–Os(1)	59.9(1)	Os(6)–Os(4)–Os(3)	60.1(1)
C(5)–Pt–C(2)	79(2)	C(6)–Pt–Os(1)	100(1)	C(42)–Os(4)–C(41)	101(2)	C(43)–Os(4)–C(41)	90(2)
C(6)–Pt–Os(2)	130(1)	C(6)–Pt–C(9)	167(2)	C(43)–Os(4)–C(42)	91(2)	Os(6)–Os(5)–Os(3)	59.2(1)
C(6)–Pt–C(1)	82(2)	C(6)–Pt–C(2)	87(1)	C(52)–Os(5)–C(51)	91(2)	C(53)–Os(5)–C(51)	93(2)
C(6)–Pt–C(5)	34(2)	Os(2)–Os(1)–Pt	66.2(1)	C(53)–Os(5)–C(51)	93(2)	N–Os(5)–Os(3)	78.8(8)
Os(3)–Os(1)–Pt	134.9(1)	Os(3)–Os(1)–Os(2)	70.3(1)	N–Os(5)–Os(6)	81.7(9)	Os(3)–Os(6)–Os(1)	62.2(1)
Os(4)–Os(1)–Pt	156.5(1)	Os(4)–Os(1)–Os(2)	119.1(1)	Os(4)–Os(6)–Os(1)	60.5(1)	Os(4)–Os(6)–Os(3)	62.1(1)
Os(4)–Os(1)–Os(3)	61.1(1)	Os(6)–Os(1)–Pt	139.9(1)	Os(5)–Os(6)–Os(1)	76.6(1)	Os(5)–Os(6)–Os(3)	60.9(1)
Os(6)–Os(1)–Os(2)	121.7(1)	Os(6)–Os(1)–Os(3)	60.0(1)	Os(5)–Os(6)–Os(4)	119.6(1)	C(63)–Os(6)–C(61)	90(2)
Os(6)–Os(1)–Os(4)	59.6(1)	C(12)–Os(1)–C(11)	93(2)	C(62)–Os(6)–C(61)	95(2)	C(63)–Os(6)–C(62)	92(2)
N–Os(1)–Pt	68.5(8)	N–Os(1)–Os(2)	57.3(9)	Os(2)–C(9)–Pt	80(1)		
N–Os(1)–Os(3)	78.4(8)	N–Os(1)–Os(4)	134.7(8)	N–C(9)–Pt	105(2)	N–C(9)–Os(2)	71(2)
N–Os(1)–Os(6)	83.6(8)	Os(1)–Os(2)–Pt	58.2(1)	C(10)–C(9)–Pt	123(2)	C(10)–C(9)–Os(2)	130(3)
Os(3)–Os(2)–Pt	115.8(1)	Os(3)–Os(2)–Os(1)	58.7(1)	C(10)–C(9)–N	128(3)	Os(2)–N–Os(1)	72.5(9)
C(22)–Os(2)–C(21)	84(2)	C(23)–Os(2)–C(21)	93(2)	Os(5)–N–Os(1)	111(2)	Os(5)–N–Os(2)	115(1)
C(23)–Os(2)–C(22)	89(2)	C(9)–Os(2)–Pt	45.6(8)	C(9)–N–Os(1)	113(2)	C(9)–N–Os(2)	77(2)
C(9)–Os(2)–Os(1)	70.0(9)	C(9)–Os(2)–Os(3)	101.6(9)	C(9)–N–Os(5)	136(2)	C(2)–C(1)–Pt	71(3)
N–Os(2)–Pt	62.4(7)	N–Os(2)–Os(1)	50.2(8)	C(8)–C(1)–Pt	108(4)	C(1)–C(2)–Pt	70(3)
N–Os(2)–Os(3)	69.6(8)	N–Os(2)–C(9)	32(1)	C(3)–C(2)–Pt	112(3)	C(4)–C(5)–Pt	108(3)
Os(2)–Os(3)–Os(1)	50.9(1)	Os(4)–Os(3)–Os(1)	57.7(1)	C(6)–C(5)–Pt	74(3)	C(5)–C(6)–Pt	72(3)
				C(7)–C(6)–Pt	110(3)		

isomer (**2**). This ability of platinum to act as a 16-electron or 18-electron system was previously observed in the mixed-metal clusters $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3\}]$ and $[Os_3Pt(\mu\text{-}H)_4(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$.[5] The effective atomic number (e.a.n.) rule for each Os atom is obeyed if the acetonitrile ligand provides four electrons to the metal centres in compound (**1**) and six electrons in isomer (**2**). This effort to resolve the electron-counting problem in both isomers shows the relevance of molecular orbital studies since the clusters do not possess regular polyhedral frameworks and thus electron-counting procedures such as Wade's rules,[6] the condensed polyhedra approach of Mingos,[7] and the topological electron-counting rules of Teo[8] are not as useful in rationalizing the metallic cores. An alternative way of considering these mixed-metal clusters is to break the structures into $Os_6(CO)_{17}$ and $Pt(C_8H_{12})(MeCN)$ fragments. In cluster (**1**) the $Pt(C_8H_{12})(MeCN)$ fragment must provide four electrons to the $Os_6(CO)_{17}$ unit and in isomer (**2**) the former fragment must provide a total of six electrons. This is in agreement with the suggestion that the addition of a pair of electrons to an Os cluster is concomitant with the breaking of a metal–metal bond.[9]

In both (**1**) and (**2**) a network of incipient bridging carbonyl ligands is observed between metal atoms with different formal electron counts.

A kinetic study of the isomerization of isomer (**1**) to isomer (**2**) was undertaken and this has shown that the process obeys a first-order rate law. From the linear dependence of ln k/T on $1/T$ the enthalpy and the entropy of activation, $\Delta H^{\ddagger} = 28.7 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 13 \pm 4$ cal K^{-1} mol^{-1}, were determined in 1,2-dichloroethane. These values are typical of a slow process involving a substantial reorganization in the transition state.

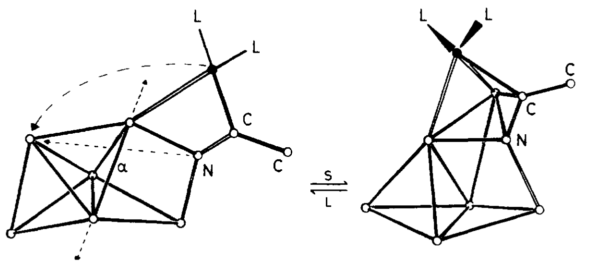


Figure 3. Transformation from cluster $[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})]$ (**1**) to isomeric form $[Os_6Pt(CO)_{17}(\mu_4\text{-}NCMe)(C_8H_{12})]$ (**2**): (●) Pt atoms, (○) Os atoms; L = dppe, S = CH_2Cl_2

We have examined the reactivity of both isomeric forms with ligands such as dppe ($Ph_2PCH_2CH_2PPh_2$), $P(OMe)_3$, and CO. Upon the exchange of the C_8H_{12} ligand of the Pt fragment in isomer (**1**) for dppe or $P(OMe)_3$, the metallic framework is retained (based on spectroscopic data, see Table 1 for details) and no longer isomerizes to the geometry of (**2**). Substitution of

Table 4. Intermetallic distances (Å) and angles (°) for $[Os_6(CO)_{19}(\mu_3\text{-NCMe})]$ (**3**)

Os(2)–Os(1)	2.845(5)	Os(3)–Os(1)	2.842(5)	Os(5)–Os(3)	2.837(5)	Os(6)–Os(3)	2.742(5)
Os(4)–Os(1)	2.848(5)	Os(5)–Os(1)	3.458(5)	Os(6)–Os(4)	2.783(5)	Os(6)–Os(5)	2.909(6)
Os(6)–Os(1)	2.838(5)	Os(4)–Os(3)	2.745(5)				

Os(3)–Os(1)–Os(2)	144.0(2)	Os(4)–Os(1)–Os(2)	156.7(2)	Os(6)–Os(3)–Os(4)	60.9(1)	Os(6)–Os(3)–Os(5)	62.8(1)
Os(4)–Os(1)–Os(3)	57.7(1)	Os(5)–Os(1)–Os(2)	102.8(2)	Os(3)–Os(4)–Os(1)	61.0(1)	Os(6)–Os(4)–Os(1)	60.5(1)
Os(5)–Os(1)–Os(3)	52.4(1)	Os(5)–Os(1)–Os(4)	99.7(1)	Os(6)–Os(4)–Os(3)	59.5(1)	Os(3)–Os(5)–Os(1)	52.5(1)
Os(6)–Os(1)–Os(2)	133.6(2)	Os(6)–Os(1)–Os(3)	57.7(1)	Os(6)–Os(5)–Os(1)	52.1(1)	Os(6)–Os(5)–Os(3)	57.0(1)
Os(6)–Os(1)–Os(4)	58.6(1)	Os(6)–Os(1)–Os(5)	54.0(1)	Os(3)–Os(6)–Os(1)	61.2(1)	Os(4)–Os(6)–Os(1)	60.9(1)
Os(4)–Os(3)–Os(1)	63.1(1)	Os(5)–Os(3)–Os(1)	75.0(1)	Os(4)–Os(6)–Os(3)	59.6(1)	Os(5)–Os(6)–Os(1)	74.1(1)
Os(5)–Os(3)–Os(4)	120.1(2)	Os(6)–Os(3)–Os(1)	61.0(1)	Os(5)–Os(6)–Os(3)	60.2(1)	Os(5)–Os(6)–Os(4)	116.4(2)

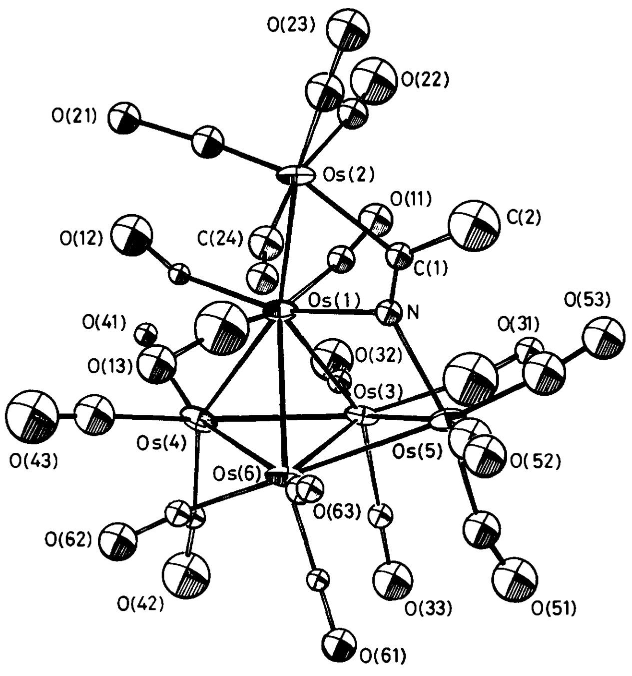


Figure 4. The molecular structure of $[Os_6(CO)_{19}(\mu_3\text{-NCMe})]$ (**3**)

the C_8H_{12} group for dppe in isomer (**2**) produces the same product and thus reversion to the geometry of (**1**) has occurred. The transformation from cluster geometry (**1**) to (**2**) is depicted in Figure 3. Elongation of bond α, Os(2)–Os(6), with movement of the Pt atom into a bridging position, Os(1)–Os(2), brings the N atom into interaction with a third metallic centre, Os(1), and the unsaturated C atom to a second metallic centre, Os(2). A carbonyl ligand must migrate [probably from Os(1) to Os(2)] in order to maintain the correct co-ordination number for Os(1) and Os(2) in complex (**2**).

An orange-red product, characterized as $[Os_6(CO)_{19}(\mu_3\text{-NCMe})]$ (**3**) (m/e = 1 741) is isolated from the reaction of CO with solutions of isomers (**1**) or (**2**) but in differing yields and product distributions. With isomer (**1**), the reaction affords nearly 100% of (**3**), while isomer (**2**) gave a mixture of products from which compound (**3**) was isolated in 30% yield. The dppe derivative (**1b**) also was treated with CO, however only a trace amount of cluster (**3**) was observed after 48 h. Crystals of (**3**) were grown from a CH_2Cl_2–cyclohexane solution at 0 °C. Despite crystal twinning, an *X*-ray analysis was undertaken, and the molecular structure of compound (**3**) is illustrated in Figure 4. The poor quality of the data precludes a detailed discussion of the bond parameters although selected values are given in Table 4. The *X*-ray analysis shows that the $Pt(C_8H_{12})$ fragment has been eliminated and the acetonitrile ligand has remained co-ordinated to the Os core. The overall metal core geometry of (**3**) closely resembles the related *p*-tolyl isocyanide–osmium derivative $[Os_6(CO)_{18}(CNC_6H_4Me\text{-}p)_2]$.[4] The structure of (**3**) can be best derived from isomeric form (**2**) resulting from removal of the $Pt(C_8H_{12})$ fragment and movement of Os(2) into the plane defined by Os(1), Os(4), and Os(5).

These results suggest that the electronic unsaturation of the 16-electron square-planar Pt in (**1**) is responsible for the isomerization process, and if the electron deficiency is partially relieved by a better σ-donor ligand the metallic framework of cluster (**1**) is stable. Formation and stabilization of an isomeric form has been observed in the cluster $[Fe_4(A)(CO)_{13}]^-$,[10] where A is a Lewis-acid ligand. It was shown that $[Fe_4(A)(CO)_{13}]^-$ exhibits two isomeric forms in solution (Fe_4 butterfly and Fe_4 tetrahedron) and that the butterfly cluster is favoured when A is a strong acceptor.

Experimental

All reactions were performed under nitrogen using dry, freshly distilled solvents. Product separation was carried out in air, using t.l.c. (plates 0.25 mm thick, Merck Kieselgel 60); R_f values are not quoted as all the plates were continuously eluted until acceptable separation was achieved. Infrared spectra were recorded on a Nicolet 5DXFTIR spectrophotometer. Kinetic studies were performed using a Varian 2300 spectrophotometer. Microanalysis was performed by Alfred Bernhart Mikroanalytisches Laboratorium, West Germany. The fast-atom bombardment mass spectrum of (**3**) was recorded on a VG 70S-250 spectrometer.

The reaction of $[Os_6(CO)_{17}(NCMe)]$ with $[Pt(C_8H_{12})_2]$ and the product separation have been previously described.[1] On the t.l.c. plate the isomer (**2**) is the brown band that tails the mauve compound $[Os_6Pt_2(CO)_{17}(C_8H_{12})_2]$[1] (sixth band from the top) and the green compound $[Os_6Pt(CO)_{17}(\mu_3\text{-NCMe})(C_8H_{12})]$ (**1**), obtained in 20% yield, is the major band of lowest R_f value. *X*-Ray quality crystals of the two isomers were obtained by recrystallization from CH_2Cl_2–cyclohexane at 0 °C for (**1**) and from thf at 0 °C for (**2**) [Found for (**2**): C, 16.7; H, 0.8; N, 0.6; O, 13.7. Calc. for $C_{27}H_{15}NO_{17}Os_6Pt$: C, 16.5; H, 0.8; N, 0.7; O, 13.9%].

Reactions of $[Os_6Pt(CO)_{17}(\mu_3\text{-NCMe})(C_8H_{12})]$ (**1**) *with* $P(OMe)_3$ *and* 1,2-*Bis*(*diphenylphosphino*)*ethane*.—Addition of a CH_2Cl_2 solution containing two equivalents of $P(OMe)_3$ to $[Os_6Pt(CO)_{17}(\mu_3\text{-NCMe})(C_8H_{12})]$ (**1**) (5 mg) in CH_2Cl_2 (10 cm^3) at room temperature immediately gave two green compounds which were separated by t.l.c. using hexane–CH_2Cl_2 (3:1) as eluant. The first green band, obtained in 20% yield, was not fully characterized but its i.r. spectrum suggests

Table 5. Positional parameters (× 10^4) for the non-H atoms of $[Os_6Pt(CO)_{17}(\mu_3\text{-NCMe})(C_8H_{12})]$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	3 593(1)	3 305(1)	1 180(1)	O(42)	−2 016(14)	525(8)	−390(12)
Os(1)	1 143(1)	1 282(1)	1 102(1)	C(43)	−2 128(18)	1 819(11)	1 063(15)
Os(2)	2 036(1)	2 465(1)	1 243(1)	O(43)	−2 874(15)	2 063(9)	1 077(13)
Os(3)	644(1)	2 199(1)	2 217(1)	C(51)	633(19)	4 080(11)	2 408(16)
Os(4)	−905(1)	1 378(1)	1 135(1)	O(51)	827(15)	4 464(9)	2 973(14)
Os(5)	225(1)	3 465(1)	1 496(1)	C(52)	−223(19)	4 072(12)	601(17)
Os(6)	−70(1)	2 346(1)	353(1)	O(52)	−566(16)	4 409(10)	−14(14)
C(11)	1 374(20)	1 029(12)	54(18)	C(53)	−1 078(19)	3 412(10)	1 657(16)
O(11)	1 562(13)	838(8)	−598(12)	O(53)	−1 860(14)	3 388(7)	1 801(11)
C(12)	607(17)	485(10)	1 263(15)	C(61)	−1 359(18)	2 745(10)	4(15)
O(12)	440(15)	−59(9)	1 372(12)	O(61)	−2 162(15)	2 983(8)	−251(12)
C(13)	2 441(21)	1 032(12)	1 782(18)	C(62)	−448(18)	1 814(11)	−642(16)
O(13)	3 239(16)	818(9)	2 226(13)	O(62)	676(13)	1 492(7)	−1 287(11)
C(21)	3 181(19)	2 315(11)	2 234(17)	C(63)	544(17)	2 906(10)	−282(15)
O(21)	3 812(13)	2 159(7)	2 868(11)	O(63)	773(13)	3 277(8)	−761(12)
C(22)	2 469(15)	2 333(9)	253(13)	N	1 715(14)	3 423(8)	1 371(11)
O(22)	2 701(16)	2 160(9)	−374(14)	C(9)	2 405(19)	3 791(11)	1 360(16)
C(31)	−449(20)	2 265(11)	2 709(17)	C(10)	2 334(20)	4 513(12)	1 428(17)
O(31)	−1 056(17)	2 303(10)	3 104(14)	C(1)	4 773(19)	4 046(11)	1 669(17)
C(32)	1 524(16)	2 764(10)	2 955(14)	C(2)	4 392(23)	4 133(14)	784(20)
O(32)	2 100(13)	3 114(8)	3 559(12)	C(3)	4 806(23)	3 939(13)	41(20)
C(33)	1 134(20)	1 477(11)	2 940(17)	C(4)	5 364(22)	3 290(13)	222(19)
O(33)	1 516(14)	1 059(9)	3 456(13)	C(5)	4 885(23)	2 772(14)	652(20)
C(41)	−1 025(19)	789(11)	2 008(17)	C(6)	5 047(18)	2 625(11)	1 440(16)
O(41)	−1 032(16)	428(9)	2 558(13)	C(7)	5 772(23)	3 002(14)	2 231(20)
C(42)	−1 586(19)	827(11)	201(17)	C(8)	5 857(21)	3 727(12)	2 145(18)

Table 6. Positional parameters (× 10^4) for the non-H atoms of $[Os_6Pt(CO)_{17}(\mu_4\text{-NCMe})(C_8H_{12})]$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	6 402(2)	1 251(1)	3 470(1)	O(42)	5 914(31)	4 680(17)	4 583(17)
Os(1)	4 770(2)	2 387(1)	3 508(1)	C(43)	3 594(52)	3 314(31)	5 000(31)
Os(2)	6 323(2)	2 588(1)	2 617(1)	O(43)	3 678(39)	3 177(23)	5 580(24)
Os(3)	3 920(2)	3 628(1)	2 598(1)	C(51)	1 556(49)	2 895(28)	1 373(27)
Os(4)	3 747(2)	3 622(1)	4 071(1)	O(51)	708(35)	3 231(21)	1 074(20)
Os(5)	2 914(2)	2 324(1)	1 837(1)	C(52)	2 046(41)	1 416(25)	1 534(22)
Os(6)	2 213(2)	2 696(1)	3 151(1)	O(52)	1 467(37)	888(23)	1 352(21)
C(11)	4 136(38)	1 629(23)	3 995(22)	C(53)	3 719(41)	2 314(27)	1 048(24)
O(11)	3 701(37)	1 176(23)	4 347(21)	O(53)	4 199(31)	2 296(20)	584(18)
C(12)	5 754(41)	2 799(24)	4 350(24)	C(61)	1 697(36)	1 738(23)	2 925(20)
O(12)	6 511(28)	2 882(16)	4 799(15)	O(61)	1 376(30)	1 114(19)	2 886(17)
C(21)	6 450(51)	3 062(30)	1 820(30)	C(62)	696(42)	3 127(24)	2 760(24)
O(21)	6 660(36)	3 321(21)	1 206(20)	O(62)	−280(36)	3 397(21)	2 486(19)
C(22)	7 738(49)	2 088(29)	2 463(27)	C(63)	1 716(44)	2 603(27)	3 997(25)
O(22)	8 619(33)	1 740(19)	2 414(17)	O(63)	1 255(40)	2 550(24)	4 511(22)
C(23)	7 289(52)	3 209(30)	3 123(29)	C(9)	5 361(33)	1 387(20)	2 445(18)
O(23)	7 880(36)	3 746(22)	3 525(20)	N	4 500(29)	1 880(18)	2 506(16)
C(31)	2 498(45)	4 255(27)	2 463(24)	C(10)	5 369(35)	846(21)	1 883(20)
O(31)	1 682(39)	4 720(23)	2 415(21)	C(1)	6 457(54)	4(32)	3 472(29)
C(32)	4 055(44)	3 805(26)	1 654(26)	C(2)	7 679(33)	295(19)	3 293(18)
O(32)	4 040(28)	4 004(17)	1 071(16)	C(3)	8 891(39)	337(22)	3 759(21)
C(33)	5 131(40)	4 365(24)	2 885(22)	C(4)	9 217(42)	1 074(26)	4 173(24)
O(33)	5 840(29)	4 863(18)	3 027(15)	C(5)	8 020(45)	1 403(28)	4 390(25)
C(41)	2 412(57)	4 296(33)	4 062(31)	C(6)	7 087(40)	1 080(24)	4 660(22)
O(41)	1 599(43)	4 737(24)	4 089(22)	C(7)	7 057(49)	201(28)	4 854(26)
C(42)	5 118(46)	4 217(28)	4 428(26)	C(8)	6 313(43)	−270(25)	4 205(24)

another isomeric structure (see Table 1) and the second green band, obtained in 80% yield, is the $P(OMe)_3$ derivative of isomer (**1**) as suggested by its i.r. spectrum and is formulated as $[Os_6Pt(CO)_{17}(\mu_3\text{-NCMe})\{P(OMe)_3\}_2]$ (**1a**). The same procedure applies for the reaction with 1,2-bis(diphenylphosphino)ethane (dppe) except that an excess (20 equivalents) of dppe was added and the reaction mixture was stirred for 24 h. Only one product was obtained which is the dppe derivative of cluster (**1**), $[Os_6Pt(CO)_{17}(\mu_3\text{-NCMe})(dppe)]$ (**1b**), as identified by its i.r. spectrum.

Reaction of $[Os_6Pt(CO)_{17}(\mu_4\text{-NCMe})(C_8H_{12})]$ (**2**) *with* 1,2-*Bis(diphenylphosphino)ethane*.—The procedure was similar to that above. T.l.c. of the solution using hexane–CH_2Cl_2 (3:1) as eluant gave three bands. The first (brown) band was unreacted compound (**2**), below it was an uncharacterized green band (yield 20%), and the third (green) band was identified as $[Os_6Pt(CO)_{17}(\mu_3\text{-NCMe})(dppe)]$ (**1b**) (yield 60%) according to its i.r. spectrum.

Reactions of (**1**), (**2**), *and* (**1b**) *with* CO.—The same procedure

Table 7. Positional parameters (× 10^4) for the non-H atoms of $[Os_6(CO)_{19}(\mu_3\text{-NCMe})]$ (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	3 041(2)	−379(3)	8 202(2)	C(33)	1 545(49)	2 675(78)	6 529(47)
Os(2)	4 045(2)	−2 613(3)	8 532(2)	O(33)	1 000(41)	3 417(64)	6 157(39)
Os(3)	2 398(2)	1 628(3)	7 081(2)	C(41)	3 078(1)	2 753(1)	9 180(1)
Os(4)	2 277(2)	1 801(4)	8 564(2)	O(41)	3 612(30)	3 602(47)	9 532(29)
Os(5)	1 889(2)	−615(4)	6 153(2)	C(42)	1 482(49)	3 079(74)	8 241(45)
Os(6)	1 299(2)	77(4)	7 422(2)	O(42)	1 011(49)	3 866(79)	8 093(45)
C(11)	3 883(52)	597(82)	7 921(49)	C(43)	2 140(63)	1 325(98)	9 509(62)
O(11)	4 452(35)	1 028(56)	7 802(34)	O(43)	2 020(52)	1 089(85)	10 063(52)
C(12)	3 486(50)	92(74)	9 300(47)	C(51)	925(65)	367(98)	5 413(62)
O(12)	3 942(45)	338(65)	9 926(41)	O(51)	550(46)	1 060(73)	4 926(45)
C(13)	2 582(87)	−1 307(142)	8 595(82)	C(52)	1 309(67)	−2 219(107)	5 769(63)
O(13)	2 004(41)	−1 868(62)	8 991(38)	O(52)	947(45)	−3 059(69)	5 526(43)
C(21)	4 390(53)	−2 458(82)	9 498(51)	C(53)	2 456(67)	−698(101)	5 494(63)
O(21)	4 622(35)	−2 364(53)	10 372(33)	O(53)	2 862(41)	−817(64)	5 108(39)
C(22)	5 018(57)	−1 576(87)	8 356(52)	C(61)	347(48)	811(72)	6 700(46)
O(22)	5 493(51)	−1 133(80)	8 330(45)	O(61)	−271(37)	1 241(56)	6 233(35)
C(23)	4 634(63)	−4 152(98)	8 565(59)	C(62)	807(50)	48(78)	8 235(48)
O(23)	5 154(43)	−4 933(66)	8 587(39)	O(62)	449(41)	42(61)	8 653(39)
C(24)	3 014(1)	−3 669(1)	8 444(1)	C(63)	785(50)	−1 533(81)	7 137(48)
O(24)	2 483(35)	−4 276(54)	8 287(33)	O(63)	568(33)	−2 543(52)	6 992(32)
C(31)	2 847(69)	1 498(106)	6 249(67)	N	2 850(41)	−1 435(62)	7 132(38)
O(31)	3 247(37)	1 692(56)	5 855(35)	C(1)	3 274(50)	−2 364(80)	7 243(48)
C(32)	3 088(51)	3 012(80)	7 519(49)	C(2)	3 453(74)	−3 249(113)	6 646(71)
O(32)	3 529(45)	3 903(71)	7 735(40)				

was used for the three starting materials; a typical reaction was as follows. The cluster (2 mg) was dissolved in CH_2Cl_2 (2 cm^3) and the solution was then frozen. Carbon monoxide (50 cm^3) was admitted into the evacuated reaction flask. The solid reaction mixture was allowed to warm up to ambient temperature and stirred for 30 min for (**1**) and (**2**), and for 48 h for (**1b**). For (**1**), t.l.c. of the solution using hexane–CH_2Cl_2 (3:1) as eluant only showed the presence of the orange-red product $[Os_6(CO)_{19}(\mu_3\text{-NCMe})]$ (**3**) (*m*/*e* = 1 741). For (**2**), t.l.c. showed six bands. The third band was identified as $[Os_6(CO)_{19}(\mu_3\text{-NCMe})]$ (**3**) (yield 30%) and the fifth band was unreacted (**2**) (20%); the other bands are yet to be identified. For (**1b**), t.l.c. of the reaction mixture showed a trace amount of $[Os_6(CO)_{19}(\mu_3\text{-NCMe})]$ (**3**) and above this band a minute amount of $[Os_6(CO)_{18}]$ was isolated, while the lowest green band was unreacted (**1b**).

Kinetic Study.—Solutions for kinetic study were prepared by dissolution of complex (**1**) in argon-purged, unpurified 1,2-dichloroethane. The visible spectra showed absorptions at 378 (ε = 19 800) for isomer (**1**) and at 640 (ε = 3 880) and 545 nm (ε = 6 200 $dm^3\ mol^{-1}\ cm^{-1}$) for isomer (**2**). The cuvettes were immersed in a thermostatted water-bath for kinetic runs. Temperatures were measured with an iron–constantan thermocouple and maintained constant to within ±0.1 °C. The isomerization process was studied at three temperatures by measuring the increasing absorbance at λ = 540 nm, one run for each temperature. The rate constants were calculated using the program KORE,[11] and the activation parameters were estimated by a least-squares fitting.

Crystal Data for (**1**)·$2CH_2Cl_2$.—$C_{29}H_{19}Cl_4N_4O_{17}Os_6Pt$, *M* = 2 131.57, monoclinic, *a* = 13.701(2), *b* = 20.808(2), *c* = 15.640(2) Å, β = 107.37(1)°, *U* = 4 255.7 $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$, *Z* = 4, D_c = 3.33 g cm^{-3}, *F*(000) = 3 752; dark green long bricks, crystal dimensions 0.067 × 0.117 × 0.292 mm; crystal faces {−010}, {010}, {011}; μ(Mo-K_α) = 215.0 cm^{-1}.

Crystal Data for (**2**).—$C_{27}H_{15}NO_{17}Os_6Pt$, *M* = 1 961.71, monoclinic, *a* = 10.709(3), *b* = 17.959(6), *c* = 19.266(6) Å, β = 100.14(2)°, *U* = 3 647.3 $Å^3$ (by least-squares refinement on diffractometer angles for 24 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$, *Z* = 4, D_c = 3.57 g cm^{-3}, *F*(000) = 3 416; dark brown blocks, crystal dimensions 0.054 × 0.075 × 0.100 mm; crystal faces {001}, {010}, {100}, {011}, {110}; μ(Mo-K_α) = 247.8 cm^{-1}.

Crystal Data for (**3**).—$C_{21}H_3NO_{19}Os_6$, *M* = 1 714.2, monoclinic, *a* = 17.25(1), *b* = 10.57(2), *c* = 17.887(4) Å, β = 112.11(3)°, *U* = 3 019.8 $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/c$, *Z* = 4, D_c = 3.73 g cm^{-3}, *F*(000) = 2 976; red blocks, crystal dimensions 0.153 × 0.109 × 0.091 mm; crystal faces {001}, {100}, {11—1}; μ(Mo-K_α) = 252.7 cm^{-1}.

Data Collection and Processing.[12]—Enraf-Nonius CAD4 diffractometer, $\theta/2\theta$ mode with scan width 0.75 + 0.35 tanθ, scan speed 1.0—11.0 ° min^{-1}; graphite-monochromated Mo-K_α radiation. For (**1**), 5 119 unique reflections measured ($2 \leqslant 2\theta \leqslant 45°$; $+h$, $+k$, $\pm l$). Gaussian absorption correction with a grid of 10 × 6 × 10 (transmission coefficients from 0.102 to 0.266), giving 3 680 with $I > 3\sigma(I)$. Crystal decay, *ca.* 1.8%, corrected during processing. For (**2**), 4 135 unique reflections measured ($2 \leqslant 2\theta \leqslant 45°$; $+h$, $+k$, $\pm l$), azimuthal scan data for 4 reflections were used in the empirical absorption correction (max., min. correction factors 0.999, 0.669), giving 2 397 with $I > 3\sigma(I)$. No decay observed. For (**3**), 2 896 unique reflections measured ($2 \leqslant 2\theta \leqslant 42°$; $+h$, $+k$, $\pm l$). Gaussian absorption correction with a grid of 12 × 8 × 6 (transmission coefficients from 0.170 to 0.251), giving 1 908 with $I > 3\sigma(I)$. Crystal decay, *ca.* 0.7%, not corrected during processing. The three data sets were corrected for Lorentz and polarization factors.

Structure Analysis and Refinement.—Structures were solved by automatic direct methods using SHELX,[13] followed by difference-Fourier syntheses. Structure (**1**) was first refined by blocked-cascade least-squares methods with Os and Pt atoms assigned anisotropic thermal parameters and the C, O, and N atoms individual isotropic thermal parameters. The structure solution then revealed the existence of two independent solvated CH_2Cl_2 molecules one of which was disordered and shown to occupy two sites. A statistical distribution between the two sites of the disordered CH_2Cl_2 molecule was considered, the occupancy factors were then correlated and refined satisfactorily by least-squares procedures to final values of 0.45 and 0.55. Consequently, the Cl atoms of both solvated CH_2Cl_2 molecules were refined for two cycles with anisotropic thermal parameters, then all of their parameters were fixed to allow convergence of the structure solution. Some of the H atoms were located in a difference-Fourier synthesis and they were included in subsequent calculations while the rest of the H atoms were calculated with idealized positional co-ordinates (either sp^2 or sp^3 geometry and C–H bond distance of 0.95 Å); all of the H atoms were not refined. The refinement converged at $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.039$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{\frac{1}{2}} = 0.042$, the fixed weighting $w = [\sigma^2(F) + p(F^2)]^{-1}$, where $p = 0.003$ (3 680 observations and 245 variables). In the final cycle no shift exceeded 0.035 of its standard deviation. A total difference-Fourier synthesis calculated from the final structure factors contained no features of chemical significance with the highest peak, of electron density 1.1 e $Å^{-3}$, at fractional co-ordinates (0.111, 0.310, −0.095), associated with O(63).

Structure (**2**) was refined by blocked-cascade least-squares methods with Os and Pt atoms assigned anisotropic thermal parameters and the C, O, and N atoms individual isotropic thermal parameters. Hydrogen atoms were not located. The refinement converged at $R = 0.054$ and $R' = 0.052$ with weighting $w = [\sigma^2(F) + p(F^2)]^{-1}$, where $p = 0.001$ (2 397 observations and 245 variables). In the final cycle no shift exceeded 0.003 of its standard deviation. A total difference-Fourier synthesis calculated from the final structure factors contained no features of chemical significance with the highest peak, of electron density 2.5 e $Å^{-3}$, at fractional co-ordinates (0.737, 0.125, 0.381), associated with Pt.

We were unable to refine structure (**3**) to convergence. The anisotropic thermal parameters U_{11} of the six Os atoms collapsed when refined. This is consistent with the crystal twinning along the *a* axis. After fixing U_{11} of the Os atoms to sensible values (0.01 $Å^2$), the non-H atoms were located in a difference-Fourier synthesis; however, the atoms of the cyano group of MeCN required their individual isotropic thermal parameters to be fixed to ideal values. Two C atoms, C(24) and C(41), were located but not refined. The least-squares calculations were stopped after the residuals reached the following values: $R = 0.099$ and $R' = 0.101$ with $p = 0.01$ (1 908 observations and 196 variables).

Complex neutral-atom scattering factors [14] were employed in all structure solutions and refinements. All computations were performed on a Gould S.E.L. computer at the University of Toronto. The molecular plots were drawn using the program ORTEP.[15] Final positional parameters for the non-H atoms for complexes (**1**), (**2**), and (**3**) are given in Table 5, 6, and 7.

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