Synthesis, Dynamic Behaviour, and Molecular Structures of μ-Methylene Platinumtriosmium Complexes; *X*-Ray Crystal Structures of Two Isomers of $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(C_6H_{11})_3\}]$

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Summary Treatment of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(C_6H_{11})_3\}]$ with diazomethane affords, under kinetic control, a single isomer $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(C_6H_{11})_3\}]$, which in solution isomerises (days) to a second isomer; the structures in the solid state of both isomers have been determined by *X*-ray crystallography, and those in solution by ^1H and ^2H n.m.r. spectroscopy.

METAL complexes containing bridging methylene (μ-CH_2) ligands are still relatively rare, and except for $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$[1] are limited to bimetallic compounds of Mn,[2] Co,[3] Rh,[4] Fe,[5] Ru,[6] and Pt.[7] Interest in these species has been stimulated by the idea that μ-CH_2 groups on a metal surface are intermediates in the conversion of CO into hydrocarbons in Fischer–Tropsch chemistry.[8] The observation[9] that the 58-electron (unsaturated) *closo*-cluster $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(C_6H_{11})_3\}]$ (**1a**) readily adds a molecule of CO suggested that it would also react with CH_2N_2 to afford the first tetranuclear metal complex with a μ-CH_2 ligand.

Treatment of (**1a**) [0 °C, tetrahydrofuran (THF)] with excess of CH_2N_2 in Et_2O led to rapid nitrogen evolution. Chromatography of the mixture gave a product which on recrystallisation (toluene–light petroleum) afforded two isomeric complexes $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(C_6H_{11})_3\}]$ which were separated as orange (**3a**) and red (**3b**) crystals

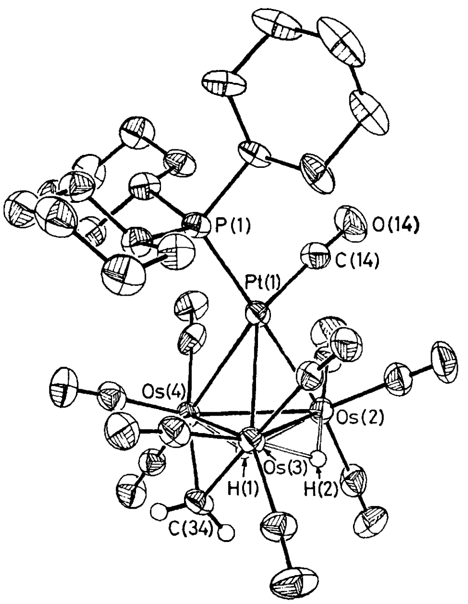


FIGURE 1. Molecular structure of (**3a**) (orange isomer). Bond lengths Pt(1)–Os(2) 2·730(1), Pt(1)–Os(3) 2·814(1), Pt(1)–Os(4) 2·826(1), Os(2)–Os(3) 2·954(1), Os(2)–Os(4) 2·941(1), Os(3)–Os(4) 2·826(1), Os(3)–C(34) 2·143(8), Os(4)–C(34) 2·118(8), mean Os–H 1·8(1) Å; ∠ Os(3)–C(34)–Os(4) 83·1(3)°.

and identified by n.m.r.† and single-crystal *X*-ray diffraction studies.‡

Crystal data for (**3a**): $C_{29}H_{37}O_{10}Os_3PPt$, $M = 1341{\cdot}7$, triclinic, space group $P\bar{1}$, $a = 12{\cdot}244(5)$, $b = 9{\cdot}533(4)$, $c = 16{\cdot}239(7)$ Å, $\alpha = 77{\cdot}00(3)$, $\beta = 72{\cdot}79(3)$, $\gamma = 75{\cdot}84(3)°$, $U = 1\ 731(1)$ Å^3, $Z = 2$, $D_c = 2{\cdot}57$ g cm^{-3}, $F(000) = 1\ 224$, Mo-K_α radiation ($\bar{\lambda} = 0{\cdot}710\ 69$ Å), μ(Mo-K_α) $= 149{\cdot}8$ cm^{-1}.

Crystal data for (**3b**): $C_{29}H_{37}O_{10}Os_3PPt$, $M = 1341{\cdot}7$, monoclinic, space group $P2_1/c$, $a = 18{\cdot}708(4)$, $b = 16{\cdot}664(3)$, $c = 22{\cdot}875(5)$ Å, $\beta = 101{\cdot}82(2)°$, $U = 6\ 890(2)$ Å^3, $Z = 8$, $D_c = 2{\cdot}55$ g cm^{-3}, $F(000) = 4\ 896$, Mo-K_α radiation ($\bar{\lambda} = 0{\cdot}710\ 69$ Å), μ(Mo-K_α) $= 148{\cdot}6$ cm^{-1}.

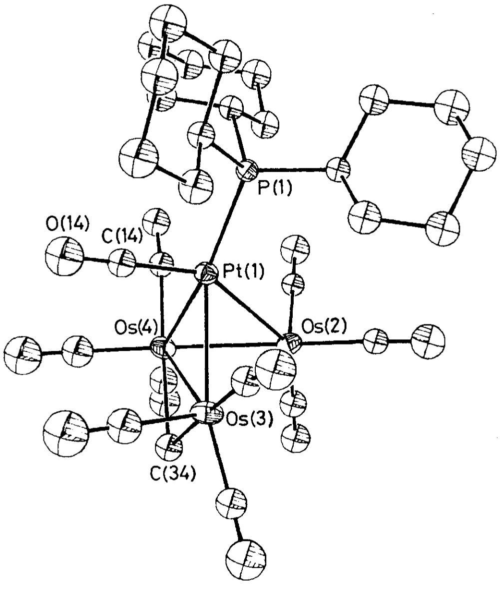
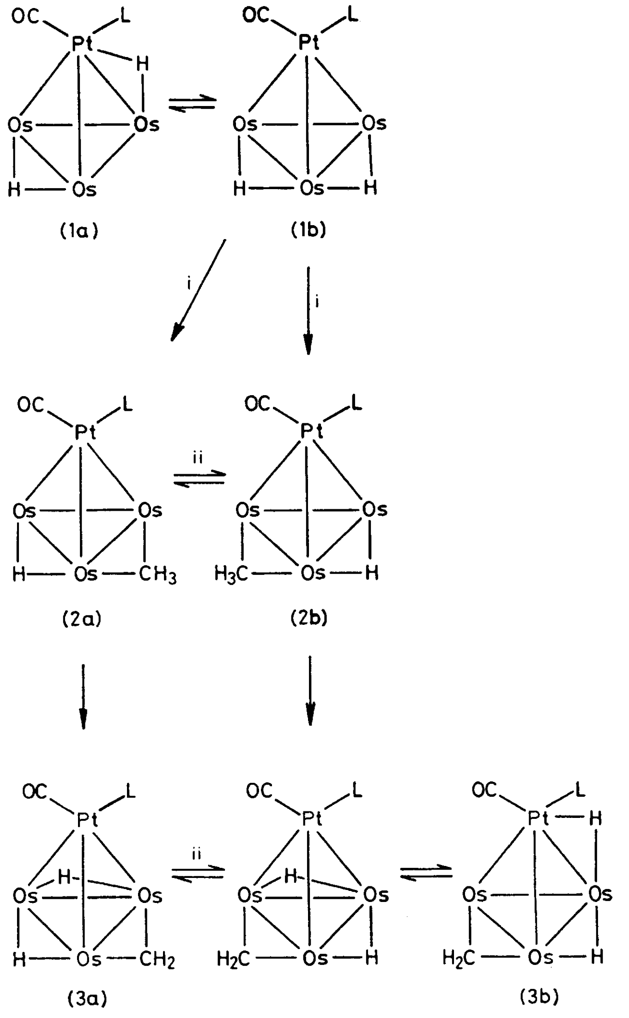


FIGURE 2. Molecular structure of (**3b**) (red isomer). Bond lengths (averaged over two independent molecules): Pt(1)–Os(2) 2·867(2), Pt(1)–Os(3) 2·854(1), Pt(1)–Os(4) 2·777(2), Os(2)–Os(3) 2·975(1), Os(2)–Os(4) 2·808(2), Os(3)–Os(4) 2·866(1), Os(3)–C(34) 2·13(2), Os(4)–C(34) 2·20(2) Å; ∠ Os(3)–C(34)–Os(4) 83·0(6)°.

The molecular structures (Figures 1 and 2) involve *closo* Os_3Pt cores as found in the 58-electron complex (**1a**), and thus the isomers do not have the 'butterfly' metal-framework geometry of the related 60-electron cluster $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$.[9] Complex (**3a**) is formally derived from (**1a**) by addition of CH_2 to the unusually short Os(μ-H)Os bond [2·789(1) Å] in the latter compound, with concomitant hydride migration to bridge the Os(2)–Os(3) bond. The isomerisation relating (**3a**) and (**3b**) involves rotation of the Pt(CO){$P(C_6H_{11})_3$} moiety about an axis perpendicular to the Os_3 plane and hydride transfer from a site bridging the Os(2)–Os(4) bond to one bridging the Os(2)–Pt(1) vector.¶

The n.m.r. spectra of the initial reaction mixture showed that the kinetic product was the symmetrical (C_s) orange isomer (**3a**). However, over 4 to 5 days in solution (**3a**) gives the red, unsymmetrical (C_1) isomer (**3b**) (ratio *ca.* 1 : 4). The



SCHEME. L = $P(C_6H_{11})_3$, CO ligands omitted for clarity. i, CH_2N_2; ii, rotation of Pt(CO){$P(C_6H_{11})_3$} fragment about an axis perpendicular to the Os_3 plane.

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† Selected n.m.r. data ($CDCl_3$): (**3a**), ^{1}H, δ −20·94 [d of t, 2 H, Os(μ-H)Os, *J*(PH) 5, *J*(H·CH_2) 2·5, *J*(PtH) 18 Hz], 6·4 [d of d of t, 1 H, CH_2, *J*(HH) 6 and 2·5, *J*(PH) 2 Hz], and 6·32 [d of t, 1 H, CH_2, *J*(HH) 6 and 2·5 Hz]; ^{31}P{^{1}H}, δ (p.p.m. to high frequency of H_3PO_4) 10·3 [s, *J*(PtP) 2 513 Hz]. (**3b**), ^{1}H, δ −13·57 [d, 1 H, Os(μ-H)Pt, *J*(PH) 10, *J*(PtH) 557 Hz], —21·73 [s, Os(μ-H)Os, *J*(PtH) 20 Hz], 7·46 [d, 1 H, CH, *J*(HH) 5 Hz], and 6·96 [d of d, 1 H, CH, *J*(HH) 6, *J*(H·CH_2) 2 Hz]; ^{31}P{^{1}H}, δ (p.p.m.) 65·2 [s, *J*(PtP) 2 661 Hz].

‡ Data were collected for a unique volume of reciprocal space, in the range $3 < 2\theta < 60°$, at 220 K on a Nicolet R3m diffractometer for both (**3a**) and (**3b**). Empirical absorption corrections were applied, and the structures solved by heavy-atom methods [Patterson (**3a**) and direct (**3b**)]. In (**3a**) μ-CH_2 and μ-H hydrogens were directly located and refined. There were no significant differences between two independent molecules in (**3b**). Current *R* indices are: (**3a**) 3·74% for 6 859 observed reflections [$I > 3\sigma(I)$], (**3b**) 4·66% for 8 755 observed reflections [$I > 3\sigma(I)$]. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ Hydrido-ligands in (**3b**) were assigned positions using techniques described elsewhere (A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509). The presence of an Os(μ-H)Pt bridge in (**3b**) is confirmed by the ^{1}H n.m.r. spectrum [*J*(PtH) 557 Hz].

^{1}H n.m.r. spectra of (**3**) gave no evidence for tautomers with bridging Me groups as found with $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$.[1]

Reaction of CD_2N_2 with (**1**) initially gave (**3a**), integration of the ^{2}H n.m.r. spectrum showing that *ca.* one third of the ^{2}H nuclei had transferred to the Os(μ-H)Os sites, an observation confirmed by the ^{1}H spectrum. Similar results were obtained by treating $[Os_3Pt(\mu\text{-}D)_2(CO)_{10}\{P(C_6H_{11})_3\}]$ with CH_2N_2, with *ca.* 40% of the ^{2}H nuclei transferring to the μ-CH_2 group of (**3a**). When the ^{1}H and ^{2}H n.m.r. measurements were repeated after several days, the isotopic distributions were found to have remained generally constant.§ These observations of transfer of *ca.* 30–40% of the ^{2}H nuclei from their initial sites (either μ-D or μ-CD_2) can be explained by a mechanism (Scheme) involving the participation of the species (**2a**) and (**2b**) which could be formed by attack of CH_2N_2 on (**1b**), a possible intermediate in hydride-site exchange.[9] In the deuteriation experiments the methyl groups in (**2**) would be CH_2D or CHD_2, depending on whether CH_2N_2 or CD_2N_2 was used. In either case a statistical choice of ^{1}H or ^{2}H for transfer to a μ-H site would result in transfer of one third of the deuterium from its position in (**1**).

Interestingly, reaction (toluene or THF, room temperature) of $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ with $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ affords (**3a**) which isomerises to the equilibrium mixture of (**3a**) and (**3b**).

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§ There was some evidence to show that over a period of days solvent impurities could promote transfer of deuterium from μ-H to μ-CH_2 sites.

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