

Heteronuclear Metal Complexes with Bridging Methoxymethylidyne Ligands: X-Ray Crystal Structures of $[\text{AuRu}_3(\mu_2\text{-COMe})(\text{CO})_{10}(\text{PPh}_3)]$ and $[\text{Fe}_3\text{Pt}(\mu_3\text{-H})(\mu_3\text{-COMe})(\text{CO})_{10}(\text{PPh}_3)]$

Michael Green, Kevin A. Mead, Rona M. Mills, Ian D. Salter, F. Gordon A. Stone, and Peter Woodward

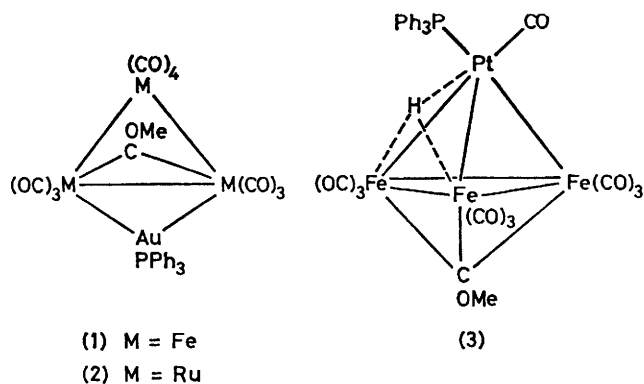
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.

Heteronuclear cluster compounds can be prepared from reactions between $[\text{M}_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}]$ ($\text{M} = \text{Fe}$ or Ru) and $[\text{AuMePPh}_3]$, or between the tri-iron compound and $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$; the structures of $[\text{AuRu}_3(\mu_2\text{-COMe})(\text{CO})_{10}(\text{PPh}_3)]$ and $[\text{Fe}_3\text{Pt}(\mu_3\text{-H})(\mu_3\text{-COMe})(\text{CO})_{10}(\text{PPh}_3)]$ have been established by X-ray diffraction.

Cluster complexes containing the bridging ligand $\mu\text{-COMe}$ are attracting interest in the context of CO reduction at di- or tri-metal centres.¹⁻³ All species so far reported involve homopolynuclear metal compounds. Herein we describe the

first examples of heteronuclear metal complexes containing the methoxymethylidyne group.

We have previously shown⁴ that $[\text{AuMe}(\text{PPh}_3)]$ reacts with $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ to give $[\text{AuOs}_3(\mu\text{-H})(\text{CO})_{10}(\text{PPh}_3)]$, the



structure of which was recently established.⁵ We have now found that the compounds $[M_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}]^{6,7}$ react with $[\text{AuMe}(\text{PPh}_3)]$ in diethyl ether at room temperature, evidently with loss of methane, to give the purple complex (1) and the orange complex (2) in 60% yield. Proton and $^{13}\text{C}\{^1\text{H}\}$ n.m.r. measurements† on these clusters showed the presence of a $\mu\text{-COMe}$ ligand and the absence of any hydrido-metal linkage. Moreover, the ^{13}C chemical shifts of the ligated carbon atoms of the former groups, δ 361 p.p.m. in (1) and δ 382 p.p.m. in (2), are little shifted from those reported^{6,7} for the $\mu\text{-COMe}$ resonances in their precursors $[M_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}]$, suggesting that the methoxyalkylidyne group retains its edge-bridging environment in the tetranuclear metal compounds. In order to establish the structures of these complexes an X-ray diffraction study was carried out on (2) for which a suitable crystal was available.

Crystal data: $\text{C}_{30}\text{H}_{18}\text{AuO}_{11}\text{PRu}_3$, $M = 1085.6$, triclinic, space group $P\bar{1}$, $a = 12.952(7)$, $b = 15.588(3)$, $c = 17.386(3)$ Å, $\alpha = 107.80(2)$, $\beta = 95.46(3)$, $\gamma = 90.37(3)^\circ$, $U = 3325(2)$ Å³, $Z = 4$, $D_m = 2.01$ g cm⁻³, $D_c = 2.17$ g cm⁻³, $F(000) = 2048$, $\mu(\text{Mo-K}\alpha) = 58.07$ cm⁻¹; current R 0.075 (R' 0.077) for 4868 independent reflections [220 K, $2\theta \leq 40^\circ$, $I \geq 4.0\sigma(I)$, Nicolet $P2_1m$ diffractometer, Mo- $K\alpha$ X-radiation, $\lambda = 0.71069$ Å].‡

The two crystallographically independent molecules in the asymmetric unit are closely similar except in the orientation of the phenyl groups of the phosphine ligand. One molecule is shown in Figure 1. This reveals the 'butterfly' arrangement of the metal atom core, the dihedral angle between the two planes defined by $\text{Au}(1)\text{Ru}(11)\text{Ru}(12)$ and $\text{Ru}(11)\text{Ru}(12)-$

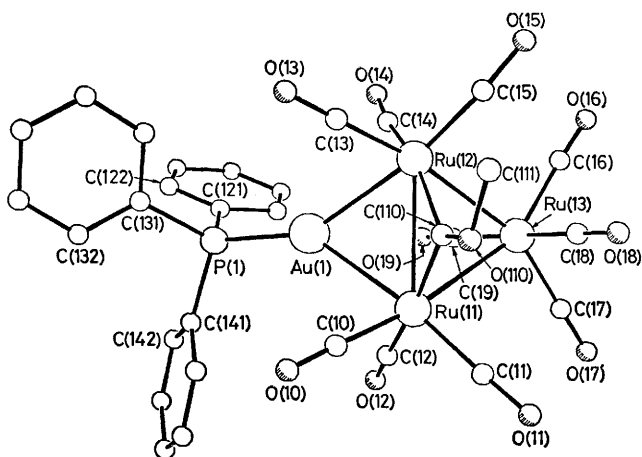


Figure 1. Molecular structure of $[\text{AuRu}_3(\mu_2\text{-COMe})(\text{CO})_{10}(\text{PPh}_3)]$ (2). Dimensions of one of the two essentially equivalent molecules in the asymmetric unit are as follows: $\text{Au}(1)\text{-Ru}(11)$ 2.760(2), $\text{Au}(1)\text{-Ru}(12)$ 2.762(2), $\text{Ru}(11)\text{-Ru}(12)$ 2.879(2), $\text{Ru}(11)\text{-Ru}(13)$ 2.845(2), $\text{Ru}(12)\text{-Ru}(13)$ 2.839(3), $\text{Au}(1)\text{-P}(1)$ 2.301(6), $\text{Ru}(11)\text{-C}(110)$ 1.94(3), $\text{Ru}(12)\text{-C}(110)$ 1.99(2) Å. Torsion angle $\text{Au}(1)\text{-Ru}(11)\text{Ru}(12)\text{Ru}(13) = 124.1(1)^\circ$.

$\text{Ru}(13)$ being 117° . The COMe ligand bridges $\text{Ru}(11)\text{-Ru}(12)$, the body of the 'butterfly', and the PPh_3 group is terminally bound to the gold atom. The structure of (2) is thus comparable with that of $[\text{Ru}_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}]$,⁷ the hydrido-ligand in the latter having been replaced by the isolobal AuPPh_3 group. A similar substitution occurs in the formation of $[\text{AuOs}_3(\mu\text{-H})(\text{CO})_{10}(\text{PPh}_3)]$ from $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}]$.^{4,5}

At room temperature, in diethyl ether, $[\text{Fe}_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}]$ reacts with $[\text{Pt}(\text{C}_2\text{H}_5)_2(\text{PPh}_3)]^8$ to give (50% yield) black crystals of compound (3). The $^{13}\text{C}\{^1\text{H}\}$ n.m.r. data† showed that (3) contained a CO group terminally bound to platinum and a bridging COMe ligand. The chemical shift (δ 343 p.p.m.) of the ligated carbon atom of the $\mu\text{-COMe}$ group in (3) is at higher field than the corresponding signal (δ 356 p.p.m.)⁶ in the spectrum of $[\text{Fe}_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}]$, as would be expected⁹ for a triply bridging methoxymethylidyne ligand. The high field resonance in the ^1H n.m.r. spectrum of (3), with $J(\text{PtH})$ 440 Hz, indicated the existence of a $\text{Fe}(\mu\text{-H})\text{Pt}$ hydrido-bridge system.¹⁰ To establish the molecular structure an X-ray diffraction study was undertaken.

Crystal data: $\text{C}_{30}\text{H}_{19}\text{Fe}_3\text{O}_{11}\text{PPT}$, $M = 949.0$, monoclinic, space group $P2_1/c$, $a = 17.977(9)$, $b = 11.193(3)$, $c = 18.137(8)$ Å, $\beta = 117.89(3)^\circ$, $U = 3226(2)$ Å³, $Z = 4$, $D_m = 1.88$ g cm⁻³, $D_c = 1.95$ g cm⁻³, $F(000) = 1832$, $\mu(\text{Mo-K}\alpha) = 58.0$ cm⁻¹. Current R 0.065 (R' 0.066) for 5212 absorption-corrected intensities [220 K, $2\theta \leq 55^\circ$, $I \geq 6\sigma(I)$].‡

The molecule (Figure 2) has a distorted tetrahedral core of four metal atoms, and in confirmation of the ^{13}C n.m.r. data transfer of a CO group from iron to platinum has evidently taken place, as previously observed.¹⁰ The methoxymethylidyne ligand triply bridges the $\text{Fe}(1)\text{Fe}(2)\text{Fe}(3)$ face. A similar face capping by this ligand occurs in the anion $[\text{Fe}_4(\mu_3\text{-COMe})(\mu\text{-CO})(\text{CO})_{11}]^-$ (refs. 2 and 3.) Although the location of the hydrido-ligand could not be established by electron density difference syntheses, its presence as a triply bridging ligand on the $\text{Fe}(2)\text{Fe}(3)\text{Pt}$ face of the cluster can be inferred from the enlargement of this face compared with $\text{Fe}(1)\text{Fe}(3)\text{Pt}$ or $\text{Fe}(1)\text{Fe}(2)\text{Pt}$, and from potential energy minima calculations.¹¹ Moreover, a triply bridging hydrido-ligand in the position indicated is supported by the ^1H n.m.r. data† since the high-field signal shows no $^{31}\text{P}\text{-}^1\text{H}$ coupling, in accord with a *cis*-(Ph_3P) HPt arrangement. Complex (3) appears to be the first example of a metal cluster molecule containing both hydrido-

† Selected spectroscopic data (i.r. measured in cyclohexane, ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{195}\text{Pt}\{^1\text{H}\}$ n.m.r. in CDCl_3 , $^{13}\text{C}\{^1\text{H}\}$ n.m.r. in CD_2Cl_2 or CDCl_3) are as follows: Compound (1), ν_{CO} 2068m, 2014s, 2009sh, 1996m, 1978m, 1967sh, 1959w, and 1946w cm⁻¹; n.m.r.: ^1H , δ 4.63 (s, 3 H, OMe), and 7.47–7.53 (m, 15 H, Ph); $^{31}\text{P}\{^1\text{H}\}$ (to high frequency of H_3PO_4), δ 55.6 p.p.m.; $^{13}\text{C}\{^1\text{H}\}$, δ 361.3 ($\mu\text{-COMe}$), 214.6 (CO), 134.3–129.5 (Ph), and 72.1 p.p.m. (COMe). Compound (2), ν_{CO} 2080m, 2033vs, 2027s, 2001vs, 1990m, 1971m, and 1960w cm⁻¹; n.m.r.: ^1H , δ 4.62 (s, 3 H, OMe) and 7.44–7.50 (m, 15 H, Ph); $^{31}\text{P}\{^1\text{H}\}$, δ 66.4 p.p.m.; $^{13}\text{C}\{^1\text{H}\}$, δ 381.8 ($\mu\text{-COMe}$), 210.4, 199.0, 193.6 (CO), 134.3–129.5 (Ph), and 75.2 p.p.m. (COMe). Compound (3), ν_{CO} 2067m, 2036s, 2021vs, 2009sh, 2005s, 1984m, 1978sh, 1969m, and 1952w cm⁻¹; n.m.r.: ^1H , δ -21.3 [s, 1 H, $\mu_3\text{-H}$, $J(\text{PtH})$ 440 Hz], 4.66 (s, 3 H, OMe), and 7.26–7.43 (m, 15 H, Ph); $^{31}\text{P}\{^1\text{H}\}$, δ 31.1 p.p.m. [s, $J(\text{PtP})$ 2598 Hz]; $^{13}\text{C}\{^1\text{H}\}$, δ 342.6 [$\mu\text{-COMe}$, $J(\text{PtC})$ 29 Hz], 211.0 [FeCO , $J(\text{PtC})$ 27 Hz], 188.5 [d, PtCO, $J(\text{PC})$ 17, $J(\text{PtC})$ 2031 Hz], 133.9–129.3 (Ph), and 69.9 p.p.m. (COMe); $^{195}\text{Pt}\{^1\text{H}\}$ [to high frequency of $\Xi(^{195}\text{Pt})$ 21.4 Hz], δ -116.2 p.p.m. [d, $J(\text{PPT})$ 2598 Hz].

‡ 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.

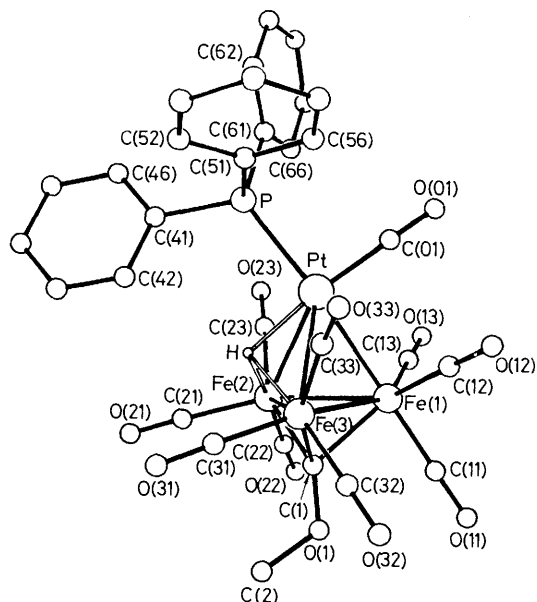


Figure 2. Molecular structure of $[\text{Fe}_3\text{Pt}(\mu_3\text{-H})(\mu_3\text{-COMe})(\text{CO})_{10}(\text{PPh}_3)]$. Important internuclear separations include: Pt-Fe(1) 2.617(2), Pt-Fe(2) 2.696(2), Pt-Fe(3) 2.739(2), Fe(1)-Fe(2) 2.556(3), Fe(1)-Fe(3) 2.543(2), Fe(2)-Fe(3) 2.694(3), C(1)-Fe(1) 2.024(10), C(1)-Fe(2) 1.919(11), C(1)-Fe(3) 1.892(12), P-Pt 2.345(3), C(01)-Pt 1.85(1), C(1)-O(1) 1.34(1) Å.

and carbyne ligands which are triply bridging, and as such is relevant to intermediates invoked in the heterogeneous reduction of CO on metal surfaces.

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