Transformations of μ-Methylene-diruthenium Complexes into Tetranuclear Metal Clusters with μ_4-Methylidyne and μ_4-Carbido Groups: *X*-Ray Crystal Structures of $[Ru_2Pt_2(\mu\text{-}H)(\mu_4\text{-}CH)(\mu\text{-}CO)(CO)_2(PPr^i{}_3)_2(\eta\text{-}C_5H_5)_2]$ and $[Ru_2Pt_2(\mu\text{-}H)_2(\mu_4\text{-}C)(\mu\text{-}CO)_2(PPr^i{}_3)_2(\eta\text{-}C_5H_5)_2]$

David L. Davies, John C. Jeffery, Daniel Miguel, Paul Sherwood, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.

The diruthenium compounds $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(L)(\eta\text{-}C_5H_5)_2]$ (L = CO or NCMe) react under mild conditions with the platinum complexes $[Pt(C_2H_4)_2(PR_3)]$ (R = cyclo-C_6H_{11} or Pr^i) to afford tri- and tetranuclear metal compounds $[Ru_2Pt(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(PR_3)(\eta\text{-}C_5H_5)_2]$, $[Ru_2Pt_2(\mu\text{-}H)(\mu_4\text{-}CH)(\mu\text{-}CO)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)_2]$, and $[Ru_2Pt_2(\mu\text{-}H)_2(\mu_4\text{-}C)(\mu\text{-}CO)_2(PR_3)_2(\eta\text{-}C_5H_5)_2]$; the species $[Ru_2Pt_2(\mu\text{-}H)(\mu_4\text{-}CH)(\mu\text{-}CO)(CO)_2(PPr^i{}_3)_2(\eta\text{-}C_5H_5)_2]$ and $[Ru_2Pt_2(\mu\text{-}H)_2(\mu_4\text{-}C)(\mu\text{-}CO)_2(PPr^i{}_3)_2(\eta\text{-}C_5H_5)_2]$ have been structurally characterised by *X*-ray diffraction.

In transition metal complex chemistry the C_1 fragments CH_2, CH, and C have become well established ligands, and their reactivity towards alkenes, alkynes, carbon monoxide, hydrogen, and other small molecules has been extensively investigated.[1] This work has in part been stimulated by the expectation that such studies might provide an insight into certain catalytic processes which occur on surfaces.[2] Irrespective of whether or not such an analogy has any validity for small clusters,[3] the interconversion of the three C_1 fragments at metal centres is of interest.

Acting on the premise that the addition of unsaturated metal centres would facilitate C–H bond dissociation of μ-CH_2 groups in dimetal complexes, we have studied reactions between the di-ruthenium compounds (**1**)[4] and the co-ordinatively unsaturated platinum fragments $Pt(PR_3)$ (R = cyclo-C_6H_{11} or iso-C_3H_7).[5]

Treatment of (**1a**) with the complexes $[Pt(C_2H_4)_2(PR_3)]$ in diethyl ether at room temperature affords a mixture of the tri- and tetra-nuclear metal cluster compounds (**2**) (*ca.* 70%) and (**3**) (*ca.* 10%).† The molecular structures of (**2a**) and (**3b**) have been established by *X*-ray diffraction, and that of (**3b**)‡ is shown in Figure 1. The four metal atoms form a non-planar ring§ with the Pt–Pt edge bridged by a CO group, and one Ru–Pt edge bridged by a hydrido ligand. A novel feature of the structure is the presence of the μ_4-CH group, the hydrogen atom of which was located from an electron density difference synthesis. Its presence was fully confirmed from the ^1H n.m.r. spectrum.† Moreover, in a fully coupled ^{13}C n.m.r. spectrum of (**3b**) the μ_4-C resonance at δ 248.1 p.p.m. showed ^1H–^{13}C coupling of 140 Hz.

To our knowledge the only previously reported tetranuclear metal cluster compound with a μ_4-CH ligand is the 62 valence electron species $[Fe_4(\mu\text{-}H)(\mu_4\text{-}CH)(CO)_{12}]$[1h] in which the methylidyne group acts formally as a five electron donor with a three-centre two-electron C–H–Fe interaction, the Fe_4 core in this molecule adopting a butterfly configuration. In contrast, in (**3b**) the μ_4-CH ligand contributes three electrons in a 60 valence electron cluster, and although the metal atoms deviate from coplanarity there is an analogy with a C_1 fragment located on the fourfold symmetry axis of a (100) surface plane of a body-centred cubic metal.

The complex (**1b**), which contains a weakly co-ordinated acetonitrile ligand, reacts with the compounds $[Pt(C_2H_4)_2(PR_3)]$ in diethyl ether at room temperature to give chromatographically separable mixtures of the tetranuclear

---

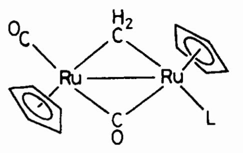
† Selected spectroscopic data [i.r. measured in Et_2O, n.m.r. measured in $CDCl_3$ (^1H and $^{31}P\text{-}\{^1H\}$) or CD_2Cl_2–CH_2Cl_2 ($^{13}C\text{-}\{^1H\}$), coupling constants in Hz, chemical shifts are to high frequency and relative to 85% H_3PO_4 (external) for $^{31}P\text{-}\{^1H\}$]. Compound (**2a**), ν_{CO} (max.) at 1 934w, 1 913s, and 1 799m cm^{-1}. N.m.r.: ^1H, δ 7.85 [br, 2 H, μ-CH_2, *J*(PtH) 18]; $^{13}C\text{-}\{^1H\}$, δ 244.1 [d, μ-CO, *J*(PC) 5, *J*(PtC) 858], 208.5 [CO, *J*(PtC) 49], 142.8 [μ-CH_2, *J*(PtC) 576], 86.3, 86.1 (C_5H_5), 35—27 p.p.m. (C_6H_{11}); $^{31}P\text{-}\{^1H\}$, δ 59.7 p.p.m. [*J*(PtP) 3 433]. Compound (**2b**), ν_{CO} (max.) at 1 936w, 1 914s, and 1 800m cm^{-1}. $^{13}C\text{-}\{^1H\}$ n.m.r.: δ 244.5 (μ-CO), 208.4 (CO), 142.9 [μ-CH_2, *J*(PtC) 573], 86.4, 86.1 p.p.m. (C_5H_5). Compound (**3a**), ν_{CO} (max.) at 1 918s and 1 763s cm^{-1}. N.m.r.: ^1H, δ 14.87 [d of d, 1 H, μ_4-CH, *J*(PH) 6 and 2, *J*(PtH) 60 and 25], 5.12, 5.06 (s × 2, 10 H, C_5H_5), 0.80—0.20 (m, 66 H, C_6H_{11}), −12.61 [d of d, 1 H, μ-H, *J*(PH) 14 and 4, *J*(PtH) 627 and 75]; $^{13}C\text{-}\{^1H\}$, δ 248.9 [d of d, μ_4-CH, *J*(PC) 45 and 36], 235.5 (μ-CO), 223.3 (CO), 202.9 p.p.m. [CO, *J*(PtC) 76]. Compound (**3b**), ν_{CO} (max.) at 1 914s and 1 760s cm^{-1}. N.m.r.: ^1H, δ 14.89 [d of d, 1 H, μ_4-CH, *J*(PH) 6 and 2, *J*(PtH) 56 and 22], −12.51 [d of d, 1 H, μ-H, *J*(PH) 14 and 4, *J*(PtH) 74 and 622]; $^{13}C\text{-}\{^1H\}$, δ 248.1 [d of d, μ_4-CH, *J*(PC) 44 and 35, *J*(PtC) 262 and 192], 236.2 [μ-CO, *J*(PtC) 1 087 and 1 011], 221.0 (CO), 201.8 [CO, *J*(PtC) 74], 84.8, 83.0 p.p.m. (C_5H_5); $^{31}P\text{-}\{^1H\}$, δ 55.5 [d, *J*(PP) 12, *J*(PtP) 5 650 and 347] and 36.9 p.p.m. [d, *J*(PP) 12, *J*(PtP) 4 023 and 287. Compound (**4a**), ν_{CO} (max.) at 1 763 cm^{-1}. N.m.r.: ^1H, δ −13.00 [d, 2 H, μ-H, *J*(PH) 15, *J*(PtH) 604 and 23]; $^{13}C\text{-}\{^1H\}$, δ 438.9 p.p.m. (μ_4-C). Compound (**4b**), ν_{CO} (max.) at 1 765 cm^{-1}. N.m.r.: ^1H, δ −12.89 [d, 2 H, μ-H, *J*(PH) 15, *J*(PtH) 609 and 23]; $^{13}C\text{-}\{^1H\}$, δ 439.5 [t, μ_4-C, *J*(PC) 23, *J*(PtC) 104], 250.3 [μ-CO, *J*(PtC) 1 002], 85.3 p.p.m. (C_5H_5); $^{31}P\text{-}\{^1H\}$, δ 41.9 p.p.m. [*J*(PtP) 5 227].

‡ *Crystal data for* (**3b**): $C_{32}H_{54}O_3P_2Pt_2Ru_2$, $M = 1\,141.1$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.833(2)$, $b = 15.270(2)$, $c = 20.486(4)$ Å, $\beta = 112.71(1)°$, $U = 3\,703(1)$ Å^3, $Z = 4$, $D_c = 2.05$ g cm^{-3}, $F(000) = 2\,176$, $\mu(\text{Mo-}K_\alpha) = 85.1$ cm^{-1}, $R = 0.041$, ($R_w = 0.038$) for 5 122 unique absorption corrected intensities [293 K, ω–2θ scans, $2\theta \leqslant 50°$, $I \geqslant 2.0\sigma(I)$, Mo-K_α ($\bar{\lambda} = 0.710\,69$ Å)]. Data were collected on a Nicolet *P*3m diffractometer, and the structure was solved by Patterson and Fourier methods, with refinement by blocked-cascade least squares. The atoms μ-H and H(1) were located and refined with fixed isotropic thermal parameters.

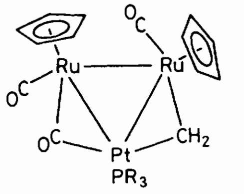
Crystal data for (**4b**): $C_{31}H_{54}O_2P_2Pt_2Ru_2$, $M = 1\,113.0$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.471(2)$, $b = 13.476(3)$, $c = 14.038(4)$ Å, $\alpha = 76.51(2)$, $\beta = 88.56(2)$, $\gamma = 68.74(2)°$, $U = 1\,791(1)$ Å^3, $Z = 2$, $D_c = 2.06$ g cm^{-3}, $F(000) = 1\,060$, $\mu(\text{Mo-}K_\alpha) = 87.9$ cm^{-1}, $R = 0.029$, ($R_w = 0.029$) for 3 282 unique absorption corrected intensities [293 K, Wyckoff ω scans, $2\theta \leqslant 42°$, $I \geqslant 2.0\sigma(I)$]. Structure solution and refinement as for (**3b**), but data were of insufficient quality to locate the μ-H positions.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, see Notice to Authors, Issue No. 1.

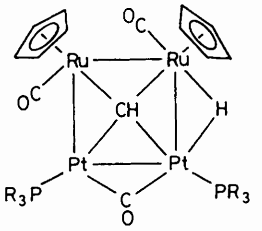
§ The deviation of Pt(1) from the plane defined by Pt(2), Ru(1), and Ru(2) is 0.594 Å. The torsion angle P(1)–Pt(1)–Pt(2)–P(2) is 8.8°.



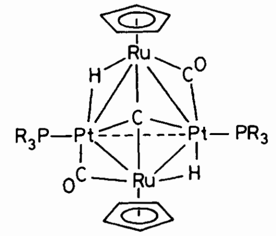
L
(**1a**) CO
(**1b**) NCMe



R
(**2a**) cyclo-C_6H_{11}
(**2b**) Pr^i



R
(**3a**) cyclo-C_6H_{11}
(**3b**) Pr^i



R
(**4a**) cyclo-C_6H_{11}
(**4b**) Pr^i

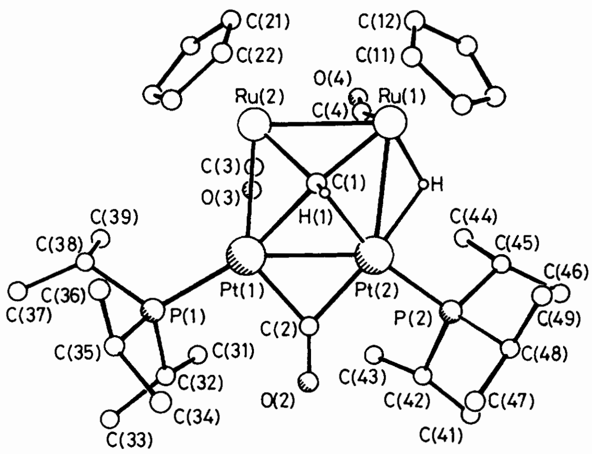


Figure 1. Molecular structure of $[\mathrm{Ru_2Pt_2(\mu\text{-}H)(\mu_4\text{-}CH)(\mu\text{-}CO)(CO)_2(PPr^i_3)_2(\eta\text{-}C_5H_5)_2}]$ (**3b**). Dimensions Pt(1)–Pt(2) 2.662(1), Pt(1)–Ru(2) 2.803(1), Pt(2)–Ru(1) 2.820(1), Ru(1)–Ru(2) 2.809(1), Pt(1)–C(1) 2.18(1), Pt(2)–C(1) 2.12(1), Ru(1)–C(1) 2.07(1), Ru(2)–C(1) 2.04(1), Ru(1)–H 1.6(1), Pt(2)–H 1.9(1), C(1)–H(1) 1.0(1) Å; Ru(1)–Pt(2)–Pt(1) 95.6(1), Pt(2)–Pt(1)–Ru(2) 85.9(1), Pt(1)–Ru(2)–Ru(1) 92.7(1), Ru(2)–Ru(1)–Pt(2) 82.9(1), Pt(1)–C(2)–O(2) 138.7(8), Pt(2)–C(2)–O(2) 139.0(7), P(1)–Pt(1)–Pt(2) 147.6(1), P(2)–Pt(2)–Pt(1) 141.6(1)°.

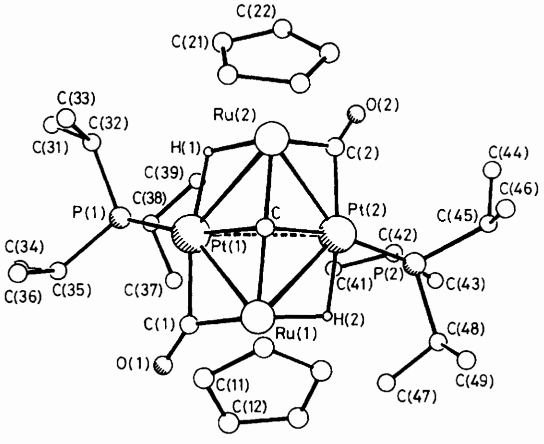


Figure 2. Molecular structure of $[\mathrm{Ru_2Pt_2(\mu\text{-}H)_2(\mu_4\text{-}C)(\mu\text{-}CO)_2(PPr^i_3)_2(\eta\text{-}C_5H_5)_2}]$ (**4b**). Dimensions Pt(1)–Ru(1) 2.707(1), Pt(2)–Ru(1) 2.858(1), Pt(1)–Ru(2) 2.850(1), Pt(2)–Ru(2) 2.707(1), Pt(1) · · · Pt(2) 3.132(1), Pt(1)–C 2.09(1), Pt(2)–C 2.08(1), Ru(1)–C 1.89(1), Ru(2)–C 1.90(1) Å; Pt(1)–C–Pt(2) 97.4(4), Ru(1)–C–Ru(2) 175.4(5), P(1)–Pt(1)–Pt(2) 137.3(1), P(2)–Pt(2)–Pt(1) 141.4(1)°. Hydrido ligands H(1) and H(2) are shown at calculated positions (see text).

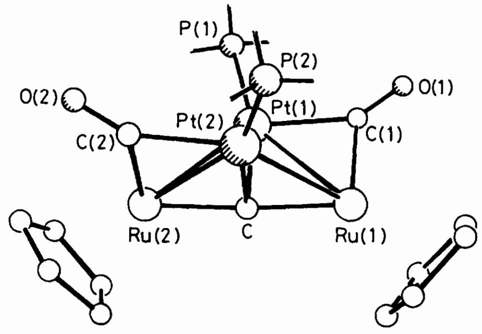


Figure 3. Molecular structure of (**4b**) showing the geometry of the μ_4-$\mathrm{CRu_2Pt_2}$ core. The Pr^i substituents on P(1) and P(2) and the hydrido ligands bridging Pt(1)–Ru(2) and Pt(2)–Ru(1) have been omitted for clarity.

cluster species (**3**) (*ca.* 5—10%) and (**4**) (*ca.* 40—50%).† The molecular structure of (**4b**) was established by *X*-ray diffraction (Figure 2).‡ A carbido ligand bridges the four metal atoms. The Pt · · · Pt separation [3.132(1) Å] implies little or no direct metal–metal bonding. The Ru(1)–Pt(1) and Ru(2)–Pt(2) edges of the metal atom array are bridged by carbonyl groups. The presence of two μ-hydrido ligands is clearly revealed by the high field signals in ^{1}H n.m.r. spectra, with strong (*ca.* 600 Hz) ^{195}Pt–^{1}H coupling. Consistent with this, a potential energy minimisation calculation[6] indicated low energy hydride sites bridging the Ru(1)–Pt(2) and Ru(2)–Pt(1) vectors.

The disposition of the carbido ligand is best revealed by Figure 3, which emphasises the near linearity of the Ru(1)–C–Ru(2) [175.4 (5)°] arrangement, and the non-planarity of the metal atoms. The angle between the Pt(1)Pt(2)Ru(1) and Pt(1)Pt(2)Ru(2) planes is 111°, and the P(1)Pt(1)Pt(2)P(2) torsion angle is 42.2°.

Although folded along the Pt · · · Pt vector, the metal core of (**4b**) does not have a butterfly geometry in the usual sense as there is no platinum–platinum bond. In contrast, the 'mixed metal' carbido clusters $[\mathrm{N(PPh_3)_2}][\mathrm{Fe_3Rh(\mu_4\text{-}C)(CO)_{12}}]$ and $[\mathrm{N(PPh_3)_2}][\mathrm{Fe_3Mn(\mu_4\text{-}C)(CO)_{13}}]$[7] and the homonuclear cluster $[\mathrm{Fe_4(\mu_4\text{-}C)(CO)_{13}}]$[1f,g] have conventional butterfly configurations, while the recently described $[\mathrm{Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}}]$[8] has a 'spiked triangle' configuration for the metal core.

We have previously shown that the methylidyne complex $[\mathrm{Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}}]$ affords the carbido mixed-metal clusters $[\mathrm{Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}}]$ and

$[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ on treatment with $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$.[8] This result, together with those described herein, suggest a stepwise transformation (1), with this process being facilitated by the

$$CH_2 \xrightarrow{-H} CH \xrightarrow{-H} C \qquad (1)$$

presence of additional metal sites. Considerations based on the principle of microreversibility also suggest that these results favour the carbide mechanism in Fischer–Tropsch reactions.

We thank the S.E.R.C. for support, and the Spanish Ministry of Education and Science for a Fellowship (to D. M.).

Received, 3rd November 1986; Com. 1567

References

1 (a) W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 160; (b) C. P. Casey, P. J. Fagan, W. H. Miles, and S. R. Marder, in 'Organometallic Compounds, Synthesis, Structure and Theory,' ed. B. L. Shapiro, Texas A & M University Press, 1983, pp. 86—114; (c) S. A. R. Knox, *Pure Appl. Chem.*, 1984, **56**, 81; (d) C. E. Sumner, J. A. Collier, and R. Pettit, *Organometallics*, 1982, **1**, 1350 and references therein; (e) J. W. Kolis, E. M. Holt, and D. F. Shriver, *J. Am. Chem. Soc.*, 1983, **105**, 7307 and references therein; (f) J. S. Bradley, *Adv. Organomet. Chem.*, 1983, **22**, 1; (g) M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, 1981, **28**, 203; (h) M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1981, 103, 1485 and references therein.

2 (a) E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91; E. L. Muetterties, *Bull. Soc. Chim. Belg.*, 1976, **85**, 451; (b) F. Zaera, A. J. Gellman, and G. A. Somorjai, *Acc. Chem. Res.*, 1986, **19**, 24; (c) R. P. A. Sneeden, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, vol. 8, pp. 19—100, Pergamon Press, Oxford, 1982; (d) R. H. Grubbs, *ibid.*, vol. 8, pp. 499—551; (e) W. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117.

3 (a) M. Moskovits, *Acc. Chem. Res.*, 1979, **12**, 229; (b) R. Whyman, in 'Transition Metal Clusters,' ed. B. F. G. Johnson, Wiley, Chichester, 1980, ch. 8.

4 A. P. Humphries and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1975, 1710; S. A. R. Knox and M. I. Yates, unpublished results.

5 F. G. A. Stone, *Acc. Chem. Res.*, 1981, **14**, 318; *Inorg. Chim. Acta*, 1981, **50**, 33 and references therein.

6 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

7 J. A. Hriljac, P. N. Swepston, and D. F. Shriver, *Organometallics*, 1985, **4**, 158.

8 L. J. Farrugia, A. D. Miles, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 2437.