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Preliminary Communication

Formal insertion of carbon into a C=C double bond on an Ru_5 cluster. X-Ray structure of $Ru_5(\mu_4\text{-}CC_{11}H_{12})(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_9$

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Abstract

Addition of cyclopentadiene to $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{13}$ (**1**) resulted in the selective formation of $Ru_5(\mu_4\text{-}CC_{11}H_{12})(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_9$ (**2**), in 85% yield. Formation of the tricyclic $\mu_4\text{-}CC_{11}H_{12}$ ligand is consistent with a carbene-type addition of one of the C_2 carbons in **1** to a C=C double bond of the cyclopentadiene, followed by ring enlargement.

We have previously described the reactions of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{11}$ (**1**; Scheme 1) with dihydrogen or ethene, in which one of the C_2 carbons formally inserts into H–H or C–H bonds, respectively [1]. These reactions are consistent with the polarisation of the C_2 ligand as suggested by Extended Huckel MO calculations. In developing this chemistry further with cyclic olefins, we have found a modification of this behaviour, namely an unusual insertion of one of the C_2 carbons into a C=C double bond.

The reaction between **1** and freshly distilled cyclopentadiene (toluene, 100°C, 20 h) afforded $Ru_5(\mu_4\text{-}CC_{11}H_{12})(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_9$ (**2**) in high yield (84%) as black crystals [2*]. Complex **2** has been characterised by a single-crystal X-ray study. The molecular structure of **2** is shown in Fig. 1 and important bond distances and angles are given in the caption.

The Ru_5 core adopts the open-envelope conformation, the flap being held open [dihedral 96.45(3)°] by the two μ_3-SMe groups; Ru(5) is attached to both [Ru(5)–S(1,2) 2.379(2), 2.479(1) Å]. Two of the Ru–Ru edges are bridged by PPh_2 groups. Unusually long Ru–Ru separations in this and related complexes appear to be the result of geometrical constraints imposed by the ligands, although we are investigating these features in more detail as other examples become available. The organic ligand, which has been formed by combination of the C_2 unit in **1** with two molecules of cyclopentadiene, is a tricyclic hydrocarbon consisting of fused five- and six-membered rings. One of the carbons of the latter is attached to a μ_4-C atom [C(0)–C(1) 1.424(7) Å], this separation indicating some multiple-bond character in this bond; C(0) is somewhat more strongly bonded to Ru(1,2) [2.120(5), 2.114(5) Å] than to Ru(3,4) [2.292(5), 2.266(4) Å]. However, the two carbons attached to this atom also interact with two of the Ru atoms of the square face.

The best description of the hydrocarbon ligand is a tricyclo[5.3.1^{2,6}.0]undeca-3,8-dien-4-yl-substituted μ_4-methylidyne, with an η^3-allylic interaction of C(2)–C(1)–C(10) with Ru(3) and Ru(4). The latter resembles the bonding of the allyl ligand in $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}C_3H_5)(CO)_8$ [4]. Although the separation of the central carbon, C(1), from Ru(3,4) is relatively long [Ru(3,4)–C(1) 2.419(4), 2.427(3) Å)], recent calculations have shown that the primary bonding of the allyl group to an $Ru_3(CO)_{10}$ cluster is via the allyl non-bonding orbital; the significant lengthening of the C(1)–Ru(3,4) separation is consistent with this picture [5]. Some disorder in atoms C(5)–C(6)–C(7) is presumed, resulting from the presence of isomers by virtue of the C=C double bond being located between C(5)–C(6) or C(6)–C(7). This is also consistent with the observation of a series of doubled resonances in the ^1H and ^{13}C NMR spectra [2*]; in the latter, signals at δ 125.5 and 257.2 were assigned to C(1) and C(0), respectively.

As a whole, the hydrocarbon ligand donates six electrons to the cluster, which has a total of 80 cluster valence electrons (c.v.e.); the two electrons more than the 78 c.v.e. expected for an M_5 polyhedron with six M–M bonds are probably accommodated in an orbital

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* Reference number with asterisk denotes a note in the list of references.

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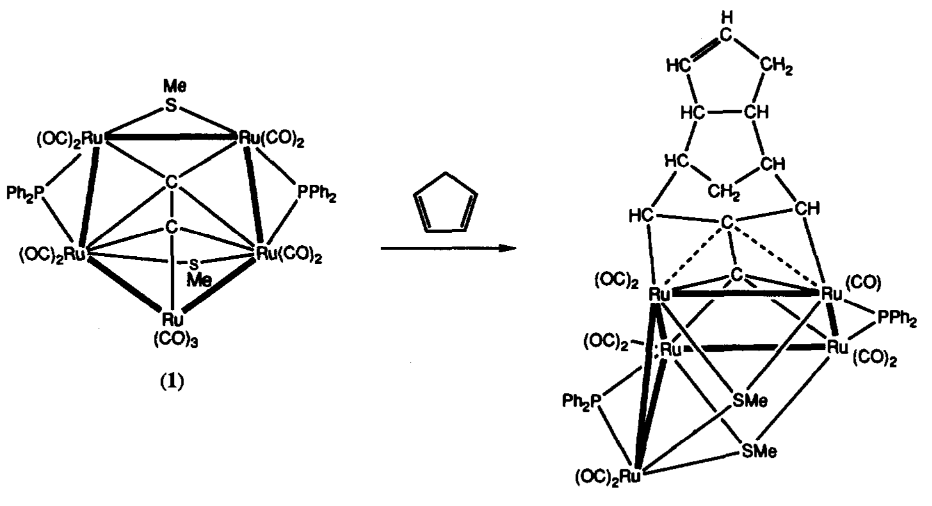


(1)

(2)

Scheme 1.

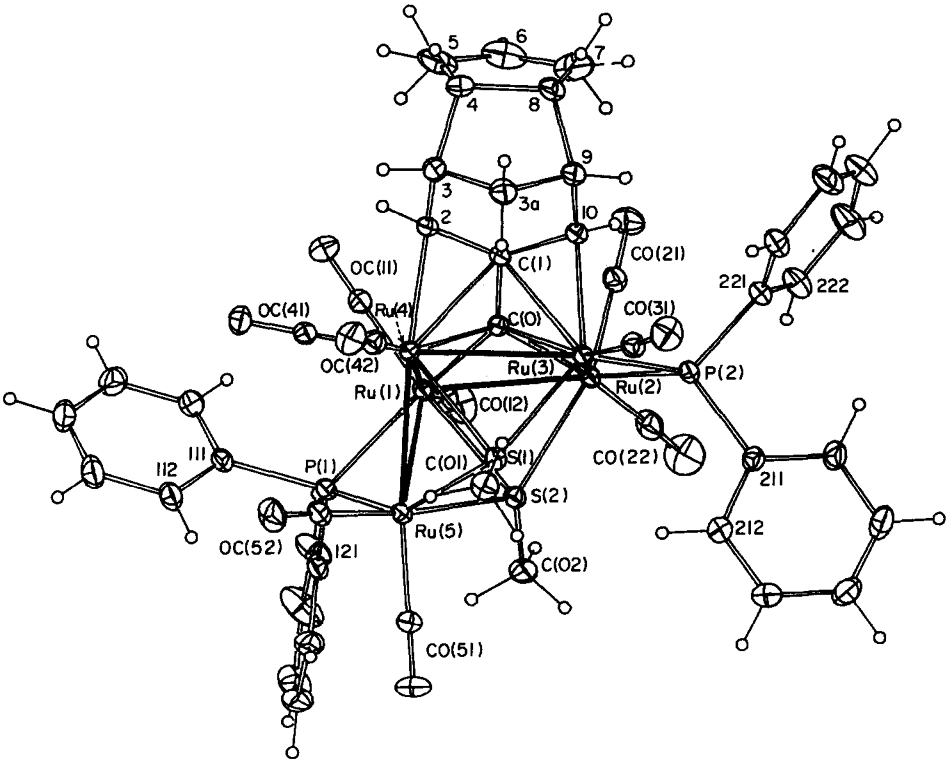
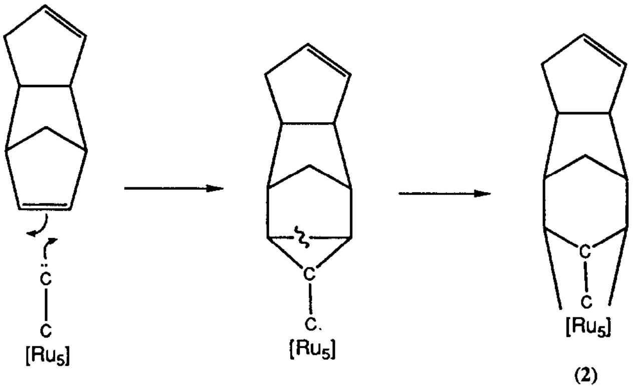


Fig. 1. Molecular structure of Ru$_5$(μ_4-CC$_{11}$H$_{12}$)(μ_3-SMe)$_2$(μ-PPh$_2$)$_2$(CO)$_9$ (2), projected oblique to the Ru(1–4) 'plane' ($\chi^2 = 1.4 \times 10^4$; Ru deviations ±0.07 Å). Atom labelling and 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Bond distances (Å): Ru(1)–Ru(2) 2.821(1), Ru(1)–Ru(4) 3.014(1), Ru(1)–Ru(5) 2.983(1), Ru(2)–Ru(3) 2.881(1), Ru(3)–Ru(4) 2.935(1), Ru(4)–Ru(5) 2.867(2), Ru(1)–P(1) 2.350(2), Ru(5)–P(1) 2.332(1), Ru(2)–P(2) 2.315(2), Ru(3)–P(2) 2.214(2), Ru(3)–S(1) 2.364(1), Ru(4)–S(1) 2.426(1), Ru(5)–S(1) 2.379(2), Ru(1)–S(2) 2.443(1), Ru(2)–S(2) 2.423(2), Ru(5)–S(2) 2.479(1), Ru(1)–C(0) 2.120(5), Ru(2)–C(0) 2.114(5), Ru(3)–C(0) 2.292(5), Ru(4)–C(0) 2.266(4), Ru(3)–C(1) 2.419(4), Ru(4)–C(1) 2.427(3), Ru(3)–C(10) 2.160(3), Ru(4)–C(2) 2.217(3), C(0)–C(1) 1.424(7). Bond angles (°): Ru(1)–Ru(2)–Ru(3) 91.34(3), Ru(2)–Ru(3)–Ru(4) 90.99(3), Ru(1)–Ru(4)–Ru(3) 86.58(3), Ru(2)–Ru(1)–Ru(4) 90.54(3), Ru(1)–Ru(4)–Ru(5) 60.91(3), Ru(1)–Ru(5)–Ru(4) 61.97(3), Ru(4)–Ru(1)–Ru(5) 57.11(4). Dihedral angle (°): Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(1)–Ru(4)–Ru(5) 96.45(3).



(1) (2)

Scheme 2.

with significant M–M anti-bonding character, as suggested by the long separations between Ru(1) and Ru(4) and Ru(5) [3.014(1), 2.983(1), Å, respectively]. Similar effects in the tetranuclear clusters $Ru_4(\mu\text{-}PPh_2)_2(CO)_{13}$ and $Ru_4(\mu\text{-}PPh_2)_4(CO)_{10}$ have been noted previously [6].

Formation of this unusual complex can be envisaged by addition of one of the C_2 carbons to a C=C double bond of one molecule of cyclopentadiene to give a bicyclo[3.1.0]hexene, which then undergoes ring expansion to the six-membered cyclohexadiene system (Scheme 2). As the reaction proceeds, release of C(1) from Ru(5) allows the latter to bend to the opposite side of the Ru_4 rhombus where μ_3 interaction with the SMe groups is possible. Addition of the second molecule of cyclopentadiene may occur before or after this ring-opening reaction; separate experiments have shown that dicyclopentadiene also reacts with **1** at 100°C to give **2** as the main product.

In conclusion, we have shown a further example of the carbenic reactivity of **1** found in earlier studies [1] in a reaction of the C_2 unit which is reminiscent of the addition of reactive carbenes to C=C double bonds, and further emphasizes the unusual chemistry of this complex. The nature of the interaction of the $CC_{11}H_{12}$ ligand with the square face depends on the formation of the μ_4-CRu_4 system, now a familiar structural feature of the reaction products from **1** [7].

Acknowledgements

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References and notes

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2 Selected spectroscopic data for **2**. ν(CO) (cyclohexane) 2071vw, 2057vw, 2051w, 2043vw, 2033m, 2027w, 2021m, 2014vs, 2002m, 1991s, 1982m, 1980m, 1969s, 1961m, 1949m, 1924m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.20 (3H, s, SMe), 1.52 (1H, m, CH/CH_2), 1.79 (1H, m, CH/CH_2), 2.04 (2H, m, CH/CH_2), 2.16–2.54 (4H, m, CH/CH_2), 2.92 (1H, m, CH/CH_2), 3.23 (3H, s, SMe), 3.45 (1H, m, CH/CH_2), 5.28 (0.5H, m, =CH), 5.49 (1H, m, =CH), 5.61 (0.5H, m, =CH), 7.05–8.05 (20H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 22.57 (s, 2×SMe), 28.13 (s, CH), 29.43 (s, CH), 30.91 (s, CH_2), 31.52 (s, CH_2), 32.92 (s, CH), 33.24 (s, CH_2), 33.30 (s, CH_2), 33.44 (s, CH), 35.88 (s, CH), 42.65 (s, CH), 43.02 (s, CH), 43.39 (s, CH), 47.75 (s, CH), 48.31 (s, CH), 57.41 (s, CH), 58.25 (s, CH), 125.50 (d, J(CP) = 3.1 Hz, C(1)), 127.74–134.02 (m, Ph), 140.10 (d, J(CP) = 27.7 Hz), 142.52 (d, J(CP) = 28.3 Hz), 144.44 (d, J(CP) = 22.5 Hz), 144.48 (d, J(CP) = 22.8 Hz) (*ipso*-C), 193.50–209.71 (m, CO), 257.19 (t, J(CP) = 23 Hz, C(0)). The ^{13}C multiplicities were assigned from standard DEPT experiments. FAB MS (m/z): 1378, $[M]^+$; 1350–1126, $[M-nCO]^+$ (n = 1–9).

3 (**2**) $Ru_5(\mu_4\text{-}CC_{11}H_{12})(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_9 \cdot 0.75CH_2Cl_2 \equiv C_{47}H_{38}O_9P_2Ru_5S_2 \cdot 0.75CH_2Cl_2$, M = 1441.9. Triclinic, space group $P\bar{1}$, $a = 15.357(11)$, $b = 14.946(5)$, $c = 14.535(4)$ Å, $\alpha = 105.47(2)$, $\beta = 101.08(4)$, $\gamma = 118.30(4)°$, $V = 2624$ Å^3, $Z = 2$, $\rho_c = 1.82$ g cm^{-3}. CAD4 diffractometer, $2\theta_{max} = 60°$, μ(Mo Kα) = 14.9 cm^{-1}. $F(000)$ 1415; A^* (min, max) = 1.32, 1.40. Crystal dimensions 0.34×0.26×0.22 mm. 10848 observed absorption-corrected data ($I \geq 3\sigma(I)$) from 13881 data measured were refined to $R = 0.039$, $R_w = 0.054$ (statistical weights). The X-ray result is unable to determine the location or confirm the existence of any localised or disordered double bond at the periphery of the hydrocarbon ligand; following the mass spectral and NMR results, one double bond is presumed, disordered between C(6)–C(5,7) in the final refinement model. Solvent population was estimated from refinement and constrained.

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