A novel route to butatrienylidene complexes: stabilisation of $:C{=}C{=}C{=}CH_2$ on Ru_5 clusters

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Addition of $C_2(SiMe_3)_2$ to $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{11}]$ 1 affords an isomeric mixture of $[Ru_5\{\mu_4\text{-}CCCCH(SiMe_3)\}(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)(\mu_3\text{-}SMe)(CO)_{10}]$ 2, alkaline hydrolysis of which gives the first stable butatrienylidene complex $[Ru_5(\mu_4\text{-}CCCCH_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)(\mu_3\text{-}SMe)(CO)_{10}]$ 3; carbonylation of 3 affords produces the spiked-rhomboidal pentanuclear complex $[Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{11}]$ 4; the X-ray structures of 3 and 4 are reported.

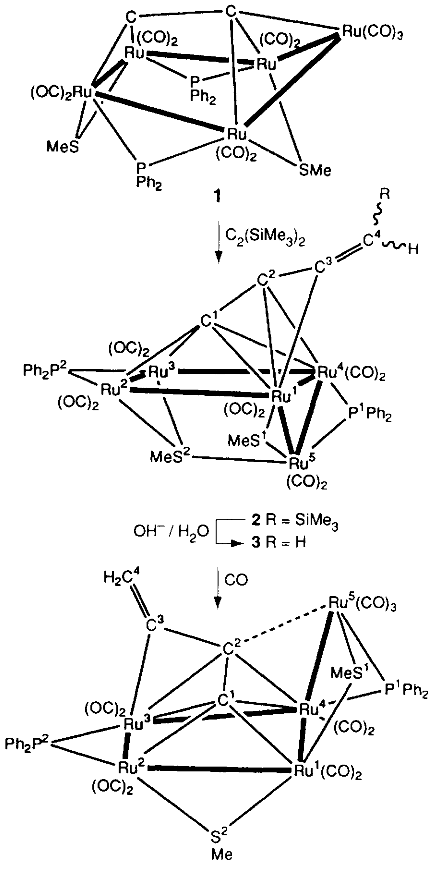
The stabilisation of unsaturated carbenes, such as vinylidene, $:C{=}CH_2$, and allenylidene, $:C{=}C{=}CH_2$, by complex formation at transition-metal centres is now well established, and vigorous development of their chemistry continues.[1] Extension to longer unsaturated carbon chains presents a greater challenge because of the increased reactivity resulting from spatial extension beyond the protection afforded by bulky ligands, such as PPh_3. Although there appears to be no authenticated example of a complex containing the unsubstituted butatrienylidene ligand ($:C{=}C{=}C{=}CH_2$), we recently described a reactive ruthenium complex, obtained from buta-1,3-diyne, which from its method of synthesis and reactions appears to contain this ligand.[2]

The coupling of unsaturated carbon systems on metal clusters presents an alternative approach to the synthesis of longer unsaturated carbon chains.[3] In this regard, we were interested to explore the possibility of coupling a vinylidene ligand (from an alk-1-yne by 1,2-H shift) with the dicarbon ligand present in $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{11}]$ **1** (Scheme 1).[4] While experiments with several alk-1-ynes such as $HC{\equiv}CR$ (R = Ph, Me, Bu^t) afforded ligands formed by coupling without rearrangement of the alk-1-yne,[5] we have now found that reactions of **1** with $C_2(SiMe_3)_2$, followed by removal of the $SiMe_3$ groups, provides a route to complexes of the sought-after C_4 ligand.

Thus reactions of **1** with $C_2(SiMe_3)_2$ (PhMe, 110 °C, 26 h) afforded red crystals of $[Ru_5\{\mu_4\text{-}CCCCH(SiMe_3)\}(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}]$ **2** in 94% yield as a mixture of geometrical isomers.† Alkaline hydrolysis of **2** (KOH in aq. $MeOH–CH_2Cl_2$, 1 h, room temp.) gave a red crystalline solid (84%) which was shown to be the first structurally characterised‡ butatrienylidene complex, $[Ru_5(\mu_4\text{-}CCCCH_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}]$ **3**.† The IR ν(CO) spectra of **2** and **3** were similar, suggesting that conversion of **2** into **3** involves only replacement of $SiMe_3$ by H without any skeletal rearrangement.

Fig. 1 shows a molecule of **3**, from which it can be seen that the Ru_5 cluster adopts an open envelope conformation, with a μ_3-SMe group spanning the flap and the base of the envelope. The organic ligand spans the four Ru atoms on the face of the envelope. The strongly bonded C(1) atom closely interacts with Ru(1–4); this is now a common feature of many of the reaction products of **1** and related complexes.[5,6] A plausible interpretation of the structure is that C(1) has a strong σ-type interaction with Ru(1–4); two of the three C=C double bonds of the 1,2,3-triene have η^2 interactions with Ru(1) and Ru(4). The fourth carbon of the chain is attached to C(3) by a double bond [C(3)–C(4) 1.32(1) Å] and carries two H atoms. Thus the organic ligand is the $CCCCH_2$ system, stabilised by strong bonding interactions with Ru(1–4) and donating six electrons to the cluster. Three Ru–Ru edges are bridged by the second SMe group and two PPh_2 groups, while ten terminal CO groups complete the coordination of the Ru atoms. The cluster valence electron (CVE) count is 80, two more than anticipated for an M_5 cluster with six M–M bonds. Closer examination of the Ru–Ru separations in **3** shows that, with the exception of Ru(2)–Ru(3) [2.743(1) Å], all are between 2.942 and 3.070(1) Å. This is consistent with an expansion of the cluster as a result of occupation of an Ru–Ru antibonding orbital, a feature previously found in several Ru_3 and Ru_4 clusters containing μ-PR_2 and μ-SR ligands.[7–9]

An interesting skeletal change is found on carbonylation of **3** (PhMe, 80 °C, 1.5 h, CO purge) when conversion to $[Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **4** (62%) occurs, shown crystallographically to contain a spiked rhomboidal Ru_5 core.‡ Fig. 2 shows a molecule of **4**, significant bond parameters being given in the caption. This structure is consistent with the uptake of one CO molecule resulting in cleavage of an Ru–Ru bond.



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Scheme 1

The interactions of the $CCCH_2$ ligand with Ru(1–4) are similar to those found in **3**. Considerable rearrangement of the ligands around the periphery of the clusters in **1** and **3** has occurred and further discussion of these changes will be deferred until the full account. This cluster also has a CVE count of 80, but here the Ru–Ru bonds are significantly shorter than those in **3**, ranging between 2.830 and 2.943(1) Å.

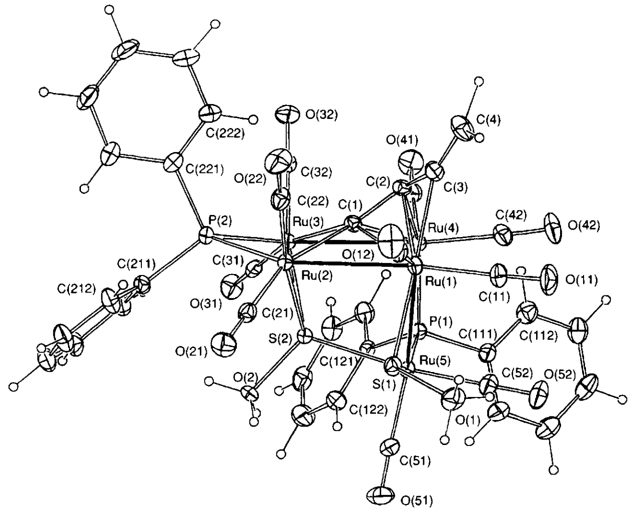

Fig. 1 Molecular structure of $[Ru_5(\mu_4\text{-CCCCH}_2)(\mu\text{-PPh}_2)_2(\mu\text{-SMe})(\mu_3\text{-SMe})(CO)_{10}\cdot CH_2Cl_2]$ **3**. Bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.9242(9), Ru(1)–Ru(4) 3.009(1), Ru(1)–Ru(5) 3.074(1), Ru(2)–Ru(3) 2.745(1), Ru(3)–Ru(4) 2.9345(9), Ru(4)–Ru(5) 3.0904(9), Ru(1)–C(1) 2.219(6), Ru(2)–C(1) 2.117(7), Ru(3)–C(1) 2.126(8), Ru(4)–C(1) 2.187(8), Ru(1)–C(2) 2.228(7), Ru(4)–C(2) 2.094(9), Ru(1)–C(3) 2.195(8), Ru(1)–S(1) 2.394(2), Ru(5)–S(1) 2.387(3), Ru(2)–S(2) 2.432(3), Ru(3)–S(2) 2.405(2), Ru(5)–S(2) 2.437(2), Ru(4)–P(1) 2.317(3), Ru(5)–P(1) 2.325(2), Ru(2)–P(2) 2.306(2), Ru(3)–P(2) 2.302(2), C(1)–C(2) 1.37(1), C(2)–C(3) 1.35(1), C(3)–C(4) 1.32(1); Ru(2)–Ru(1)–Ru(4) 87.05(3), Ru(4)–Ru(1)–Ru(5) 61.06(2), Ru(1)–Ru(2)–Ru(3) 93.20(3), Ru(2)–Ru(3)–Ru(4) 91.97(3), Ru(1)–Ru(4)–Ru(3) 87.78(3), Ru(1)–Ru(4)–Ru(5) 60.49(3), Ru(1)–Ru(5)–Ru(4) 58.44(2), C(1)–C(2)–C(3) 131.0(8), C(2)–C(3)–C(4) 148.6(8). Dihedral angle (°): Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(1)–Ru(4)–Ru(5) 86.26(3).

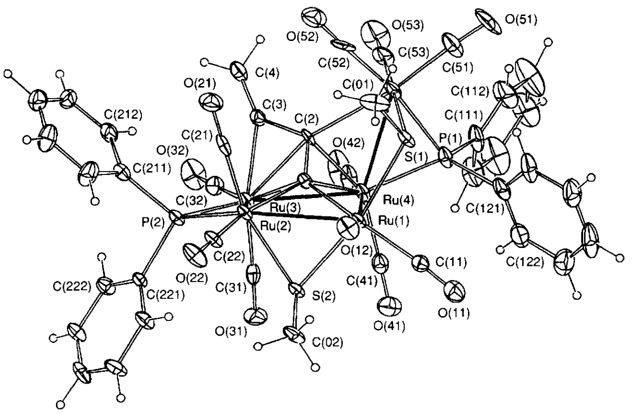

Fig. 2 Molecular structure of $[Ru_5(\mu_5\text{-CCCCH}_2)(\mu\text{-PPh}_2)_2(\mu\text{-SMe})_2(CO)_{11}]$ **4**. Bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.830(1), Ru(1)–Ru(4) 2.943(2), Ru(2)–Ru(3) 2.874(2), Ru(3)–Ru(4) 2.877(1), Ru(4)–Ru(5) 2.861(2), Ru(1)–C(1) 2.08(1), Ru(2)–C(1) 2.10(1), Ru(3)–C(1) 2.21(1), Ru(4)–C(1) 2.19(1), Ru(3)–C(2) 2.337(9), Ru(4)–C(2) 2.10(1), Ru(5)–C(2) 2.430(9), Ru(3)–C(3) 2.11(1), Ru(1)–S(1) 2.396(3), Ru(5)–S(1) 2.428(4), Ru(1)–S(2) 2.386(3), Ru(2)–S(2) 2.399(4), Ru(4)–P(1) 2.267(3), Ru(5)–P(1) 2.382(4), Ru(2)–P(2) 2.281(3), Ru(3)–P(2) 2.257(3), C(1)–C(2) 1.37(2), C(2)–C(3) 1.44(2), C(3)–C(4) 1.28(2); Ru(2)–Ru(1)–Ru(4) 91.31(5), Ru(1)–Ru(2)–Ru(3) 89.00(5), Ru(2)–Ru(3)–Ru(4) 91.76(5), Ru(1)–Ru(4)–Ru(3) 86.77(5), Ru(1)–Ru(4)–Ru(5) 83.14(5), Ru(3)–Ru(4)–Ru(5) 109.14(6).

We note the migration of $SiMe_3$ groups has been observed previously in mononuclear systems based on Rh and Ir[10] and for cluster-bound alkynes[11] and that the parent vinylidene ligand has been obtained from $HC{\equiv}CSiMe_3$ on a ruthenium centre.[12] Conversion of the open pentagonal cluster in **1** to the open envelope in **2**, *i.e.* formation of another Ru–Ru bond, has previously been found in the reaction of **1** with C_2Ph_2, although not in the otherwise similar reaction with HC_2Ph.[5]

In conclusion, we have shown that the butatrienylidene ligand can be formed by a novel reaction involving coupling of a C_2 ligand with a vinylidene formed by rearrangement of an alkyne. This highly unsaturated four-carbon ligand is stabilised by attachment to four (in **3**) or five (in **4**) metal atoms. The origin of the H atom in **3** (replacement of the first $SiMe_3$ group) has not been determined, but this reaction is not unexpected.

We thank the Australian Research Council for support and Johnson Matthey Technology plc for a generous loan of $RuCl_3{\cdot}nH_2O$.

Footnotes

† *Selected spectroscopic data*: for **2**: ν(CO) (cyclohexane) 2046m, 2029s, 2021vs, 2010m, 1995m, 1993m, 1981s, 1960m, 1945m cm^{-1}.

For **3**: ν(CO) (cyclohexane) 2048m, 2031s, 2024vs, 2012m, 1997m (br), 1982s, 1961m, 1946m cm^{-1}.

For **4**: ν(CO) (cyclohexane) 2093m, 2048m, 2033m, 2022m, 2017vs, 2008m, 1995m, 1982m, 1976m, 1969s, 1961m, 1950w cm^{-1}.

‡ *Crystal data*: **3**, $[Ru_5(\mu_4\text{-CCCCH}_2)(\mu\text{-PPh}_2)_2(\mu\text{-SMe})(\mu_3\text{-SMe})(CO)_{10}]\cdot CH_2Cl_2 \equiv C_{40}H_{28}O_{10}P_2Ru_5S_2\cdot CH_2Cl_2$, M = 1385.0, triclinic, space group $P\bar{1}$, a = 15.807(2), b = 14.549(5), c = 11.302(2) Å, α = 67.33(2), β = 84.17(1), γ = 76.29(2)°, U = 2330 Å^3, Z = 2, D_c = 1.97 g cm^{-3}. CAD4 diffractometer, $2\theta_{max}$ = 50°, μ(Mo-Kα) = 18.7 cm^{-1}, $A^*_{min,max}$ = 1.23, 1.45. Crystal dimensions 0.20 × 0.10 × 0.20 mm. 5966 observed data [$I \geqslant 3\sigma(I)$] from 8204 data measured were refined to R = 0.040, R_w = 0.044 (statistical weights).

4, $[Ru_5(\mu_5\text{-CCCCH}_2)(\mu\text{-PPh}_2)_2(\mu\text{-SMe})_2(CO)_{11}] \equiv C_{41}H_{28}O_{11}P_2Ru_5S_2$, M = 1328.1, triclinic, space group $P\bar{1}$, a = 22.09(1), b = 11.957(4), c = 10.060(4) Å, α = 111.99(3), β = 95.65(4), γ = 95.59(3)°, U = 2425 Å^3, Z = 2, D_c = 1.82 g cm^{-3}. CAD4 diffractometer, $2\theta_{max}$ = 50°, μ(Mo-Kα) = 16.9 cm^{-1}, $A^*_{min,max}$ = 1.23, 1.30. Crystal dimensions 0.15 × 0.15 × 0.42 mm. 5490 observed data [$I \geqslant 3\sigma(I)$] from 8526 data measured were refined to R = 0.062, R_w = 0.064 (statistical weights). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/273.

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Received, 16th September 1996; Com. 6/06349G