Experimental and Theoretical Study of the Reactivity of Cluster-bound Dicarbon: Synthesis and Structures of Novel Electron-rich Ru_5 Clusters

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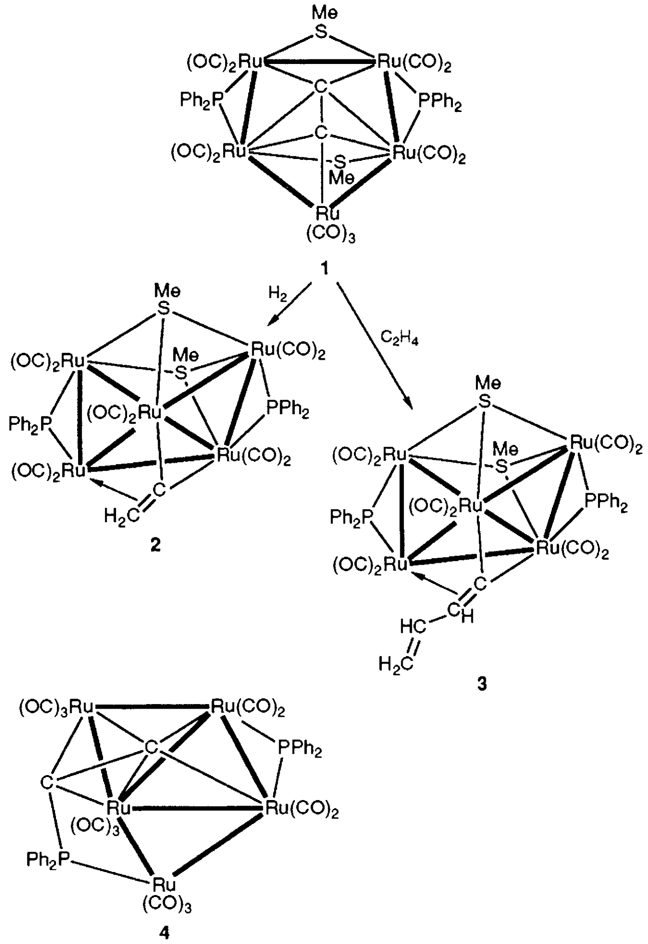
An EHMO (extended Hückel molecular orbital) study of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SH)_2(\mu\text{-}PH_2)_2(CO)_{11}]$ suggests that C_β should behave as a nucleophile; this is found experimentally in the reactions of the SMe–PPh_2 derivative with H_2 or C_2H_4, in which C_β inserts into H–H or C–H bonds to give μ_3-CCHR ligands (R = H or CH=CH_2, respectively), as shown by X-ray structure determinations carried out on $[Ru_5(\mu_3\text{-}CCHR)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ (R=H and CH=CH_2).

With both diamond and C_{60} recently being nominated as successive 'molecules of the year',[1] attention has focused on the synthesis and reactivity of all-carbon molecules. We have recently described[2] a high-yield route to the pentanuclear cluster $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **1** (Scheme 1) containing a multi-site bound C_2 ligand, which gives the opportunity to determine the reactivity patterns for this ligand. Previous examples of clusters containing C_2 include the unreactive $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}]$,[3a] and the decanuclear systems $[Ni_{10}(C_2)(CO)_{16}]^{2-}$ [ref. 3(*b*)] and $[Co_3Ni_7(C_2)(CO)_{15}]^3$ [ref. 3(*c*)] in which the C_2 ligand is encapsulated by the M_{10} cluster. The heterolytic cleavage of CO by early transition metals followed by coupling to give C_2 ligands[4] was suggested to mimic the early stages of the Fischer–



Scheme 1

Tropsch process; complex **1** may be a reasonable model for later C–H and C–C insertion reactions involving the C_2 ligand. The open Ru_5 framework in **1** is related to the 'step-site' analogues found in other ruthenium clusters.[5] We have found that **1** reacts readily with many substrates, undergoing a series of insertion reactions, of which we describe those with H_2 and C_2H_4 in this communication.

The reaction between **1** and H_2 was carried out in refluxing toluene (1 atm, 7 h) and afforded black crystalline $[Ru_5(\mu_3\text{-}CCH_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **2** in 94% yield. A similar reaction with C_2H_4 (25 atm, 90 °C, 20 h) gave black crystalline $[Ru_5\{\mu_3\text{-}CCH(CH{=}CH_2)\}(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **3** in 78% yield.† Both complexes were fully characterised by single-crystal X-ray studies. Their molecular structures are shown in Figs. 1 and 2 and significant bond parameters are given in the captions.‡

Both clusters contain an Ru_5 core which consists of three edge-fused triangles, as found in $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ **4**,[6] the precursor of **1**. The two SMe groups bridge three Ru atoms each [Ru (1 or 2)–Ru(4)–Ru(5)] while the outer edges of the cluster [Ru(1)–Ru(2) and Ru(3)–Ru(4)] are bridged by the PPh_2 groups. The organic ligands in **2** and **3** are vinylidenes, formed by insertion of C_β of **1** into the H–H or a C–H bond of the substrates. The geometries of these ligands are similar to those found in other μ_3-CCHR ligands, summarised elsewhere.[7]

The most surprising feature of these clusters is that they are 80-valence-electron (v.e.) systems, instead of the 76-v.e. clusters that would have been predicted on the basis of the skeletal geometry. This electron-rich character is reflected in the Ru–Ru separations, many of which are greater than 3.0 Å; the average is 3.03_7 Å, which may be compared with those in **4** (av. 2.86_9 Å)[6] and in $[Ru_3(CO)_{12}]$ (av. 2.85_4 Å),[8] both of which are electron-precise. The propensity for medium-sized clusters to accept extra electron density by expanding the cluster, presumably as a result of the extra electrons occupying M–M antibonding orbitals, has been noted before.[9] In hexanuclear raft clusters, long transannular interactions {3.003–3.034(1) Å in $[Ru_6(\mu\text{-}H)(\mu_3\text{-}S)_3(CO)_{15}]^-$ (ref. 10) and 3.213–3.242(2) Å in $[Ru_6H(\mu\text{-}O{=}CNMe_2)(\mu\text{-}CO)_4(CO)_{14}]^-$ (ref. 11)} have been interpreted as partial interactions resulting from a balance between the electronic and steric requirements of the clusters.

The spectroscopic properties of **2** and **3** are in accord with their solid-state structures. In particular, the vinylidene protons are found at δ 5.12, 5.22 (2 × s, in **2**) or 5.31 (s, in **3**) and the SMe resonances are found at δ −0.22 and 3.17 in **2** or −0.24 and 3.40 in **3** (^{1}H). In the ^{13}C NMR spectrum of **2**, the SMe resonances are at δ 20.1 and 22.6, while C_α and C_β resonate at δ 285.4 and 70.2, respectively, the former showing the usual large downfield shift associated with cluster-bound vinylidene carbons.[7]

The reactivity of **1**, as illustrated by these initial results with H_2 and C_2H_4, has encouraged us to look at the electronic structure of the model complex $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SH)_2(\mu\text{-}PH_2)_2(CO)_{11}]$ **1a** at the EHMO level. Previous theoretical treatments of organometallic C_2 complexes include the EH study of $[Ta_2(\mu\text{-}C_2)(OSiBu^t{}_3)_6]$ where the C_2 ligand was found to be in a Ta=C=C=Ta bonding mode involving appreciable $d\pi \rightarrow C_2(\pi^*)$ backbonding[4] and the SCF-DV-X$_\alpha$ (self-consistent field discrete variational α) study of $[Re_2(\mu\text{-}C_2)(CO)_{10}]$ where the ReC≡CRe bonding resulted from a dominant

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† *Selected spectroscopic data.* For **2**: IR: ν(CO)/cm^{-1} (cyclohexane) 2050m, 2045m, 2026vs, 2023vs, 2008m, 1992m, 1970m, 1957m, 1948w and 1936m. ^{1}H NMR: δ(CDCl$_3$) −0.22 (3 H, s, SMe), 3.17 (3 H, s, SMe), 5.12, 5.22 (2 × 1 H, br s, CH$_2$) and 6.78–8.03 (20 H, m, Ph). ^{13}C NMR: δ(CDCl$_3$ 20.09, 22.63 (2 × s, SMe), 70.22 (d, J_{CP} 9.8 Hz, C_β), 127.61–135.85 (m, Ph), 137.93–142.86 (m, *ipso* C), 190.79–204.47 (CO) and 285.43 (d, J_{CP} 10.6 Hz, C_α). FAB MS (*m/z*): 1277, M$^+$; 1249–997 [M − *n*CO]$^+$ (*n* = 1–10). For **3**: IR: ν(CO)/cm^{-1} (cyclohexane) 2043m, 2026vs, 2023sh, 2006m, 1988s, 1971s, 1966m, 1946w and 1943m. ^{1}H NMR: δ(CDCl$_3$) −0.24 (3 H, s, SMe), 3.40 (3 H, t, J_{HP} 2.0 Hz, SMe), 5.31 (1 H, d, J_{HH} 10.8 Hz, CH), 5.61 (1 H, d, J_{HH} 16.2 Hz, =CH$_2$), 6.48 (1 H, dt, J_{HH} 9.6, 16.5 Hz, =CH), 6.58 (1 H, d, J_{HH} 9.3 Hz, =CH$_2$) and 6.8–7.95 (20 H, m, Ph). FAB MS (*m/z*): 1303, M$^+$; 1275–1023, [M − *n*CO]$^+$ (*n* = 1–10).

‡ *Crystal data.* For **2**: $Ru_5(\mu_3\text{-}CCH_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10} \equiv C_{38}H_{28}O_{10}P_2Ru_5S_2$, *M* = 1276.1. Monoclinic, space group $P2_1/c$, *a* = 11.992(9), *b* = 12.896(4), *c* = 28.432(9) Å, β = 93.50(4)°, *V* = 4389 Å^3, *Z* = 4, D_c = 1.93 g cm^{-3}. CAD4 diffractometer, $2\theta_{max}$ = 55°, μ(Mo-Kα) = 16.9 cm^{-1}. Crystal dimensions 0.38 × 0.20 × 0.48 mm. 7425 'observed' data [$I > 3\sigma(I)$] from 10086 data measured and absorption-corrected were refined to *R* = 0.038, R_w = 0.041. Organic ligand hydrogen atoms were refined in (*x*, *y*, *z*, U_{iso}). A second triclinic phase ($P\bar{1}$) was isolated as a toluene hemisolvate but afforded a less precise determination: *a* = 23.725(7), *b* = 17.049(10), *c* = 13.981(3) Å, α = 69.09(3), β = 72.10(2), γ = 69.83(3)°, *V* = 4848 Å^3, *Z* = 4; *R* was 0.081 for 6625 'observed' reflections.

For **3**: $Ru_5\{\mu_3\text{-}CCH(CH{=}CH_2)\}(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}\cdot 0.104CH_2Cl_2 \equiv C_{40}H_{30}O_{10}P_2Ru_2S_2\cdot 0.104CH_2Cl_2$, *M* = 1311.1. Monoclinic, space group $P2_1/c$, *a* = 11.499(4), *b* = 28.482(12), *c* = 15.077(12) Å, β = 113.65(5)°, *V* = 4523.0 Å^3, *Z* = 4, D_c = 1.93 g cm^{-3}. CAD4 diffractometer, $2\theta_{max}$ = 50°, μ(Mo-Kα) = 16.8 cm^{-1}. Crystal dimensions 0.11 × 0.13 × 0.24 mm. 5319 'observed data' [$I > 3\sigma(I)$] from 7942 data measured and absorption-corrected were refined to *R* = 0.043, R_w = 0.043.

Atomic coordinates, bond lengths and angles, and thermal parameters for **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

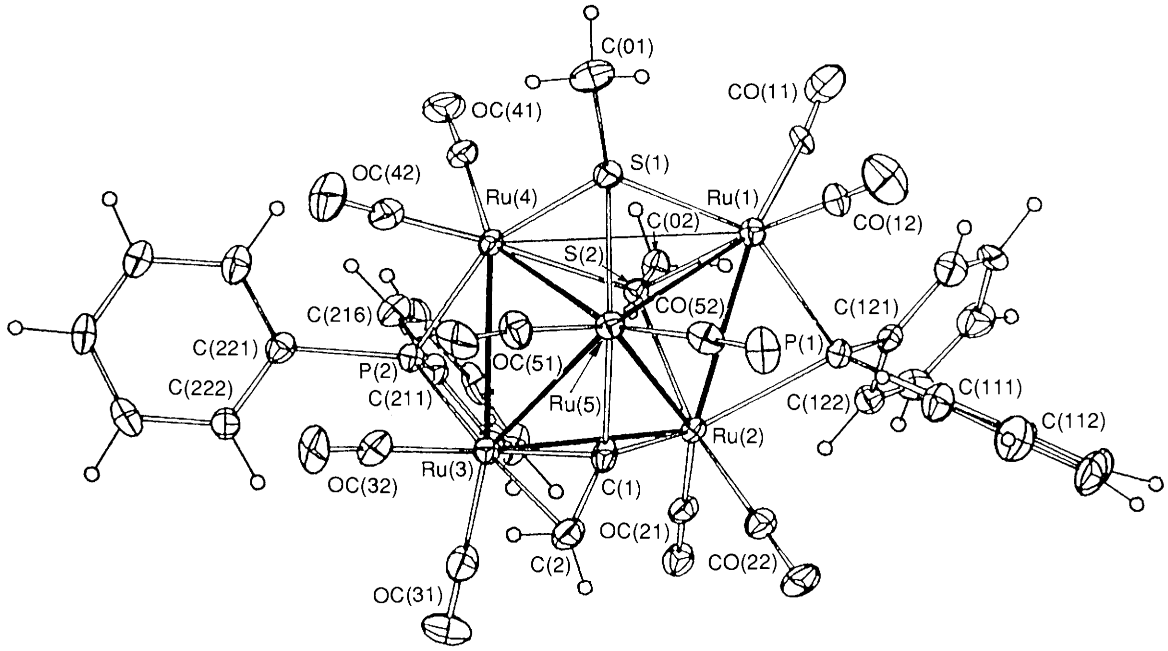


Fig. 1 A molecule of $[Ru_5(\mu_3\text{-}CCH_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **2**, showing atom numbering scheme. Selected bond distances (Å): Ru(1)-Ru(2) 3.095(1), Ru(1)···Ru(4) 3.729(1), Ru(1)-Ru(5) 2.992(1), Ru(2)-Ru(3) 2.9802(9), Ru(2)-Ru(5) 2.937(2), Ru(3)-Ru(4) 3.139(1), Ru(3)-Ru(5) 3.080(1), Ru(4)-Ru(5) 3.039(1), Ru(1)-S(1) 2.394(3), Ru(4)-S(1) 2.410(3), Ru(5)-S(1) 2.356(3), Ru(1)-S(2) 2.396(2), Ru(4)-S(2) 2.391(2), Ru(2)-S(2) 2.417(1), Ru(1)-P(1) 2.313(2), Ru(2)-P(1) 2.373(2), Ru(3)-P(2) 2.319(2), Ru(4)-P(2) 2.303(2), Ru(2)-C(1) 2.144(6), Ru(3)-C(2) 2.308(7), Ru(3)-C(1) 2.052(6), Ru(5)-C(1) 1.964(6), C(1)-C(2) 1.37(1). Angles (°): Ru(1)-Ru(2)-Ru(3) 110.26(3), Ru(2)-Ru(3)-Ru(4) 80.78(3), Ru(1)-Ru(5)-Ru(3) 110.36(5), Ru(1)-Ru(5)-Ru(4) 76.39(3), Ru(2)-Ru(5)-Ru(4) 83.17(4). Dihedrals (°): Ru(1)-Ru(2)-Ru(5)/Ru(2)-Ru(3)-Ru(5) 139.25(4), Ru(2)-Ru(3)-Ru(5)/Ru(3)-Ru(4)-Ru(5) 99.32(4).

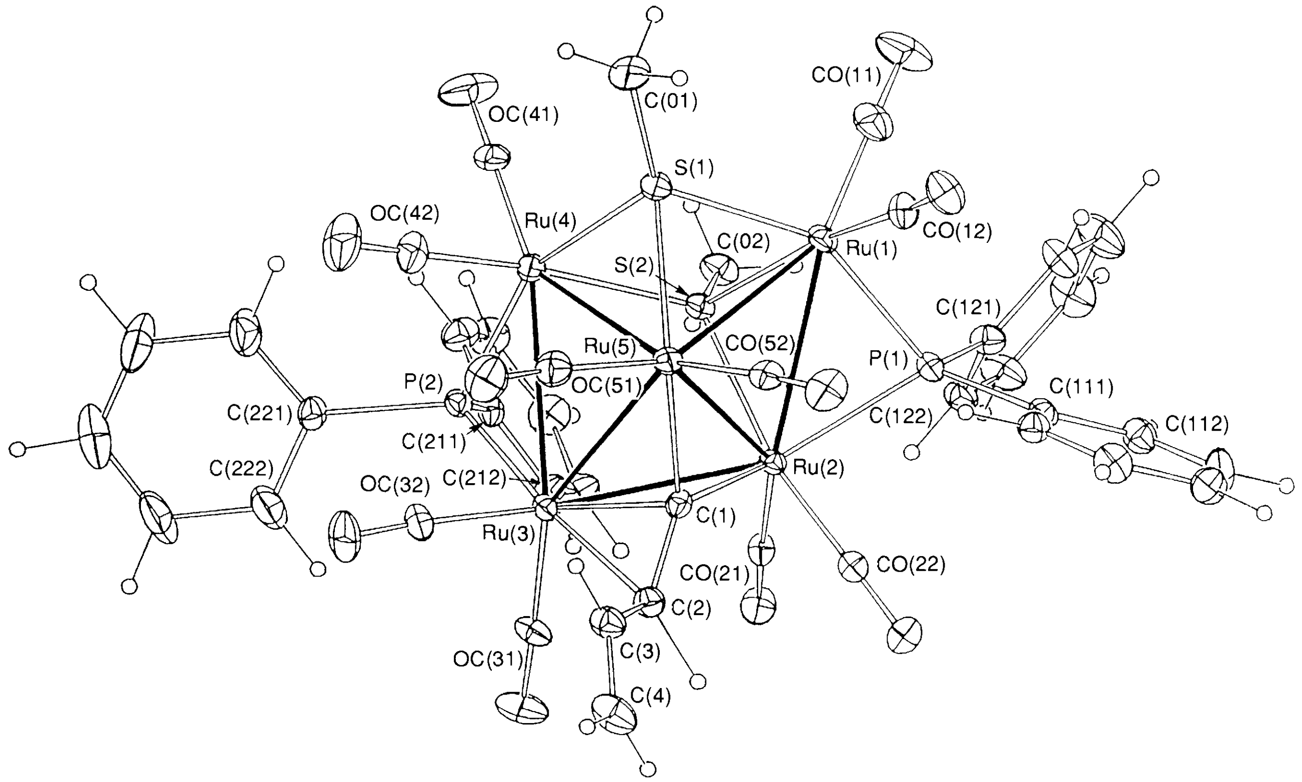


Fig. 2 A molecule of $[Ru_5\{\mu_3\text{-}CCH(CH{=}CH_2)\}(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **3**, showing atom-numbering scheme. Selected bond distances (Å): Ru(1)-Ru(2) 3.053(3), Ru(1)···Ru(4) 3.723(2), Ru(1)-Ru(5) 2.993(1), Ru(2)-Ru(3) 2.948(1), Ru(2)-Ru(5) 2.983(1), Ru(3)-Ru(4) 3.162(3), Ru(3)-Ru(5) 3.062(2), Ru(4)-Ru(5) 3.024(2), Ru(1)-S(1) 2.384(3), Ru(4)-S(1) 2.395(2), Ru(5)-S(1) 2.351(3), Ru(1)-S(2) 2.394(2), Ru(2)-S(2) 2.419(3), Ru(4)-S(2) 2.406(3), Ru(1)-P(1) 2.313(3), Ru(2)-P(1) 2.377(2), Ru(3)-P(2) 2.316(3), Ru(4)-P(2) 2.300(2), Ru(2)-C(1) 2.164(8), Ru(3)-C(1) 2.063(8), Ru(5)-C(1) 1.975(8), Ru(3)-C(2) 2.39(1), C(1)-C(2) 1.38(1), C(2)-C(3) 1.47(1), C(3)-C(4) 1.31(2). Angles (°): Ru(1)-Ru(2)-Ru(3) 110.94(3), Ru(2)-Ru(3)-Ru(4) 80.37(3), Ru(1)-Ru(5)-Ru(3) 109.51(4), Ru(1)-Ru(5)-Ru(4) 76.45(3), Ru(2)-Ru(5)-Ru(4) 82.12(4). Dihedrals (°): Ru(1)-Ru(2)-Ru(5)/Ru(2)-Ru(3)-Ru(5) 141.40(4), Ru(2)-Ru(3)-Ru(5)/Ru(3)-Ru(4)-Ru(5) 97.93(4).

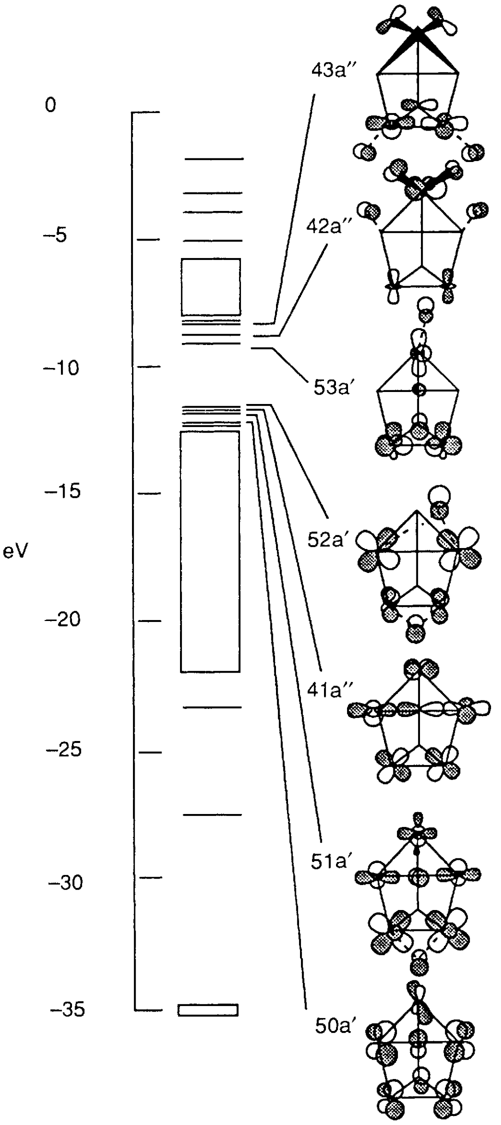
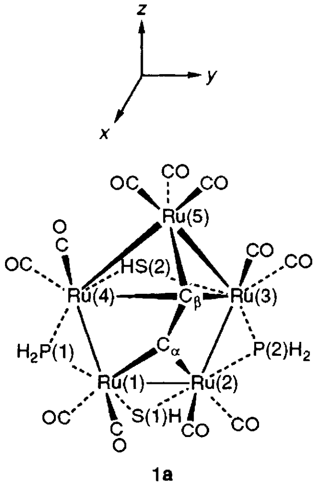


Fig. 3 Frontier MOs of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SH)_2(\mu\text{-}PH_2)_2(CO)_{11}]$ **1a** (weightings from the population analyses are included in the MO representations)

σ-interaction of the C_2 ligand with the Re atoms, with negligible dπ → $C_2(\pi^*)$ effects.[12]

The C–C distance in **1** (1.30_6 Å) is intermediate between those of typical C≡C (≈ 1.21 Å) and C=C bonds (≈1.34 Å). The bond distances Ru(5)–C_β (1.92_8 Å), Ru(1,2)–C_α (2.13_3 Å) and Ru(3,4)–C_β (2.24_7 Å), atomic overlap populations and MO interactions suggest that a cumulene description explains the most important interactions of the C_2 ligand with the cluster. We have performed a FMO (frontier molecular orbital) analysis of **1a** based on the fragments $[Ru_5(\mu\text{-}SH)_2(\mu\text{-}PH_2)(CO)_{11}]^{2+}$ and $[C_2]^{2-}$. From this we have found that metal character is predominant for all the frontier orbitals (Fig. 3) and that for MOs 41a″ and 50a′ there is significant interplay of forward and back donation between the fragments.

The frontier orbitals of **1a** may be grouped into a low-lying set of unoccupied orbitals (42a″, 53a′) and a high lying set of occupied orbitals (52a′, 41a″, 51a′).§ The separation of the unoccupied frontier orbitals from the rest of the unoccupied manifold (0.34 eV) is similar to the separation of the frontier occupied group from the rest of the occupied orbitals (0.36 eV). The net charges on the carbon atoms of the C_2 moiety are quite negative (−0.30, −0.44 at C_α, C_β, respectively) while C_α is sterically protected from incoming reagents. π-Electron density is reduced at C_α as this is extensively involved in bonding with Ru(1) and Ru(2), whereas C_β is involved with (π,σ) forward and (xz → π*) back-donation with Ru(5) and in weak π-interactions with Ru(3) and Ru(4). The ligand crowding on the cluster face opposite the C_2 ligand and the way the C_2 ligand sits above the Ru_4 plane (0.89 Å-C_α, 1.39 Å-C_β) suggest that the β-carbon will be in a relatively exposed and hence more reactive position. Consequently, assuming that the frontier group are the orbitals which will control the reactivity of the molecule[13] we would expect that C_β would act as a nucleophile, reactions being directed by orbital 41a″. Nucleophilic attack on the C_2 fragment is likely to occur on C_α owing to the character of orbital 53a′.



1a

The stability of the C_2 ligand in **1a** (and by extension in **1**) is quite understandable as there is significant C–Ru bonding character in eight occupied orbitals. The presence of orbitals with Ru → C_2 π* character clearly contributes to the ability of the cluster to 'trap' the C_2 ligand effectively. From overlap populations it is seen that the bridging ligands (PH_2, SH) contribute effectively to the stability of the cluster framework. Net charges at all the Ru atoms are very similar suggesting the envelope geometry successfully optimises the electron distribution. From PSEP theory the cluster valence electron (c.v.e.) count for **1** is 80 c.v.e. (obtained for a 5-ring)[14] while the precursor **4** has 76 c.v.e. This electron count requires that the C_2 ligand is behaving as a six-electron donor, a result which is supported by the EH calculations (only two σ-electrons are strictly localised on the C_2 ligand). The appreciable HOMO–LUMO gap (1.96 eV) and near degeneracy of the two HOMOs suggests that lower electron counts might be expected for this type of cluster. We would expect that with fewer electrons there will be the possibility of Jahn–Teller effects or a triplet ground state.

We relate the ability of the C_β carbon to insert into HX (X = H, C) bonds to the nature of the 41a″ orbital. Electron donation from the p_y lobe on C_β into antibonding HX orbitals in the incoming reactant causes the cleavage of the HX bond and insertion of C_β. The ability of C_β to insert into both H–H and C–H bonds suggests a flexibility of electron density in the cluster allowing expansion/contraction of the orbital in different electronic environments.

The bridging sulfur atom [S(2)] apparently should be susceptible to electrophilic attack (based on a net charge of −0.10 and a sizeable coefficient in MO 52a′); however, the crowded ligand sphere in the local environment and the higher reactivity of the C_2 ligand may limit reactions involving S(2). Note, though, that in the reactions described above, the SMe groups each interact with a third Ru atom in the products. The

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§ The orbital nomenclature is based on the valence space.

non-planarity of the cluster may be related to the bonding of the C_2 ligand to Ru(5) and of S(2) to Ru(3) and Ru(5). In the related planar form (with the C_2 ligand parallel to the cluster plane), the non-bonding C_β-Ru(5) distance is now 2.62 Å, the overlap population of S(2) with Ru(3), Ru(4) is reduced by 5% and the energy of the system is increased with respect to that of **1a**.

In conclusion, we have shown that complex **1** shows a novel reactivity towards H_2 or ethene which derives from the electron-rich character of the C_β atom, a result consistent with EHMO calculations of **1a**. The products are remarkably electron-rich cluster complexes containing vinylidene ligands, the chemistry of which will be described elsewhere.

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