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Cyclo-addition of buta-1,3-dene to cluster-bound dicarbon: X-ray structure of $Ru_5(\mu_3\text{-}C_6H_6)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$[1]

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Abstract

Reactions between $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**1**) and butadiene afford $Ru_5(\mu_3\text{-}C_6H_6)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ (**2**), shown by a single-crystal X-ray structure determination to contain a μ_3-η^1:η^1:η^2-cyclohex-1-en-4-yne ligand formed by cycloaddition of the diene to the C_2 fragment. The cluster has 80 c.v.e.; with only six Ru–Ru bonds a lengthening of three of them to between 3.003(2) and 3.144(2) Å is found. The structure is compared to those of two other related 80 c.v.e. clusters. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cluster; Buta-1,3-diene; Phosphido-methylthio-lato

1. Introduction

The reactions of small molecules which are attached to several metal centres provide further understanding of changes that may be wrought by multi-site bonding [1]. We have prepared an open Ru_5 cluster which supports a dicarbon molecule, namely $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{11}$ (**1**) [2]. This complex has given a rich variety of chemistry which has been reviewed recently [3]. In particular, reactions with olefins and cyclopentadiene have resulted in addition of the olefin to the C_2 ligand, to give vinylidenes [4] and a tetracyclic C_{12} ligand [5], respectively. This paper describes the major product obtained from **1** and the simplest 1,3-diene, buta-1,3-diene.

2. Results and discussion

The reaction between **1** and buta-1,3-diene was carried out in toluene at 95°C for 24 h. Separation of the products by preparative TLC gave a light brown complex, which remains unidentified, and a purple crystalline solid, identified (by means of a single-crystal X-ray structure determination) as $Ru_5(\mu_3\text{-}C_6H_6)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ (**2**), containing an unusual isomer of benzene, namely cyclohex-3-en-1-yne, stabilised by coordination to three of the five Ru atoms Scheme 1.

2.1. Molecular structure of $Ru_5(\mu_3\text{-}C_6H_6)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ (2)

A molecule of **2** is depicted in Fig. 1 and selected bond parameters are given in Table 1. The new complex is based on an Ru_5 skeleton having a highly-distorted bow-tie geometry. In the Ru(1)–Ru(2)–Ru(3) portion, the Ru–Ru separations are between 2.842 and 2.979 (**2**) Å. In the other half, comprising Ru(1)–Ru(4)–Ru(5), the Ru–Ru separations are all longer than 3.0 Å, suggesting an electron-rich cluster, as found in other complexes containing PR_2 and SR ligands. The

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[1] Dedicated to Brian Johnson on the occasion of his 60th birthday in recognition of his many contributions to organometallic and inorganic chemistry.

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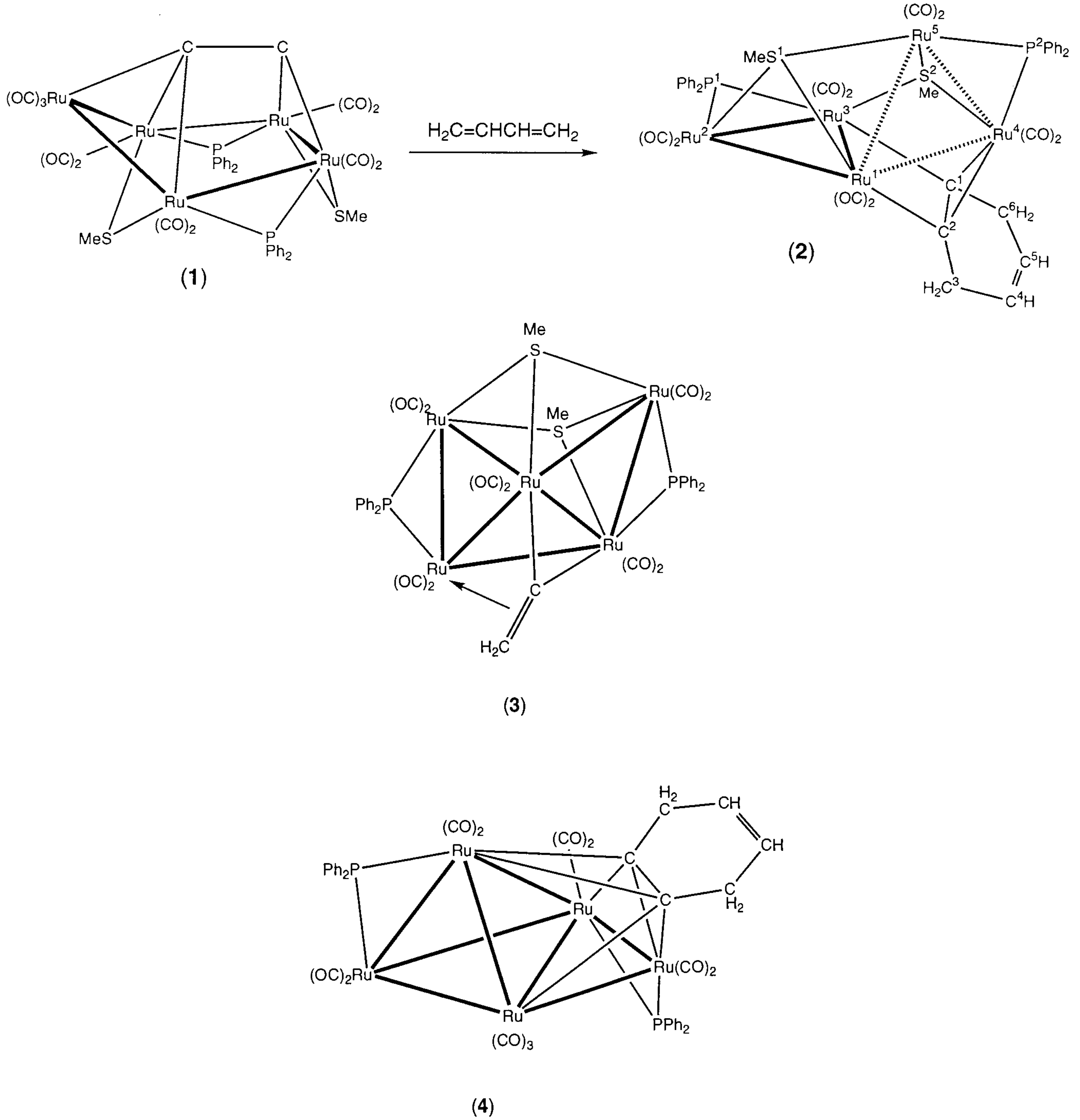

Scheme 1.

angle subtended at Ru(1) by the lines connecting that atom with the mid-points of Ru(2)–Ru(3) and Ru(4)–Ru(5) is 85.44°, while the two Ru_3 planes are twisted by 39.81° relative to one another. The two μ-PPh_2 groups bridge the Ru(2)–Ru(3) and Ru(4)–Ru(5) vectors [Ru–P, 2.260–2.343(3) Å, av. 2.312 Å] and the two SMe groups, both now in the μ_3 bonding mode, span Ru(2)–Ru(l)...Ru(5) and Ru(3)...Ru(4)–Ru(5) [Ru–S, 2.332–2.408(3) Å, av. 2.384 Å].

The organic ligand is a six-membered ring [χ^2 (C_6 plane) 589; deviations δC(1–6) $-0.05(1)$, $-0.08(1)$, 0.18(1), $-0.12(1)$, $-0.12(1)$, 0.17(1) Å; δRu(1–4) $-0.02(1)$, 1.64(2), 0.62(1), $-2.261(7)$ Å; torsions in bonds C(1)–C(2) et seq. $-2(1)$, 23(1), $-23(2)$, 0.4(2), 21(2), $-20(1)$°]. It is attached by the C(1)–C(2) atoms to Ru(1) and Ru(3) by two Ru–C σ-bonds [Ru(1)–C(2) 2.05(1), Ru(3)–C(1) 2.202(9) Å] and to Ru(4) by a π-bond [Ru(4)–C(1, 2) 2.359(9), 2.35(1) Å]. Both the

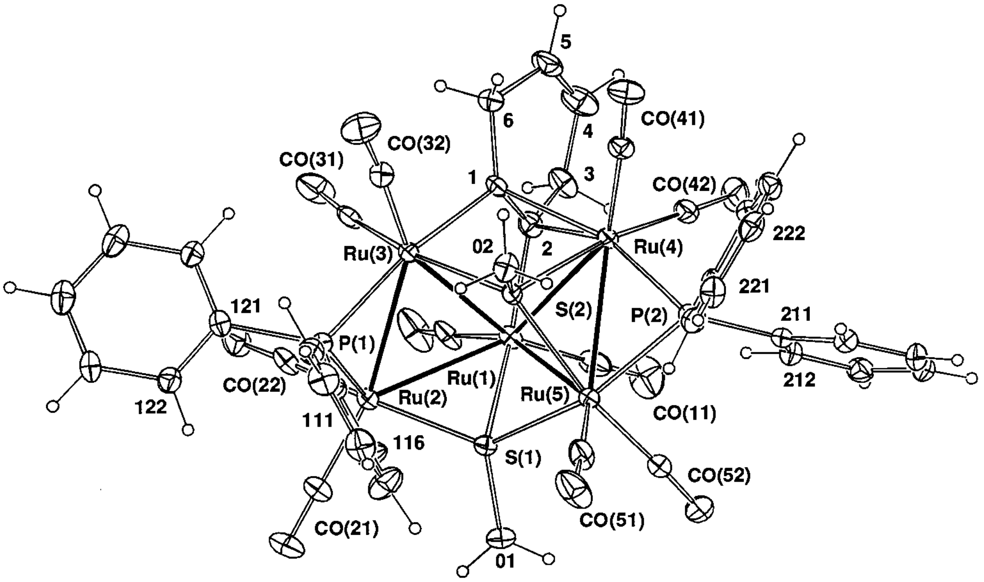

Fig. 1. Plot of a molecule of $Ru_5(\mu_3\text{–}C_6H_6)(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{10}$ (**2**) showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

latter separations and Ru(3)–C(1) are rather long [c.f. values of 2.092, 2.099(5) Å (Ru–C σ-bond), 2.250, 2.276(4) Å (Ru C_2 π-bond) in $Ru_3(\mu_3\text{-}C_2Me_2)(\mu\text{–}CO)(CO)_9$] [6] although in the related complex, $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-PPh}_2)_2(CO)_{12}$ (**3**), containing the same ligand attached to four Ru atoms, similar lengthening is found [7]. Around the ring, the C–C separations are consistent with a cyclohex-1-yn-4-ene formulation [c.f. especially C(1)–C(2) 1.33(1) Å for a coordinated C≡C triple bond and C(4)–C(5) 1.29(2) Å for the double bond; the C–C single bonds are between 1.50 and 1.56(2) Å].

Table 1
Selected bond parameters for $Ru_5(\mu_3\text{-}C_6H_6)(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{10}$ (**2**)

Bond lengths (Å)			
Ru(1)–Ru(2)	2.842(2)	Ru(3)–P(1)	2.343(3)
Ru(l)–Ru(3)	2.979(2)	Ru(4)–P(2)	2.331(3)
Ru(l)–Ru(4)	3.003(2)	Ru(S)–P(2)	2.314(2)
Ru(l)–Ru(S)	3.144(2)		
Ru(2)–Ru(3)	2.937(2)	Ru(3)–C(1)	2.202(9)
Ru(3)...Ru(4)	3.515(2)	Ru(4)–C(1)	2.359(9)
Ru(4)–Ru(5)	3.004(2)	Ru(1)–C(2)	2.05(1)
Ru(1)–S(1)	2.408(3)	Ru(4)–C(2)	2.35(1)
Ru(2)–S(1)	2.332(3)	C(1)–C(2)	1.33(1)
Ru(S)–S(1)	2.378(2)	C(1)–C(6)	1.53(1)
Ru(3)–S(2)	2.401(3)	C(2)–C(3)	1.56(2)
Ru(4)–S(2)	2.406(3)	C(3)–C(4)	1.51(2)
Ru(S)–S(2)	2.384(2)	C(4)–C(5)	1.29(2)
Ru(2)–P(1)	2.260(3)	C(s)–C(6)	1.50(2)
Bond angles (°)			
Ru(l)–Ru(2)–Ru(3)	62.02(2)	Ru(3)–Ru(l)–Ru(4)	71.98(5)
Ru(l)–Ru(3)–Ru(2)	57.43(5)	Ru(l)–Ru(5)–Ru(4)	58.42(3)
Ru(2)–Ru(l)–Ru(3)	60.55(5)	Ru(l)–Ru(4)–Ru(5)	63.11(4)
Ru(l)–Ru(3)–Ru(4)	54.33(4)	Ru(4)–Ru(l)–Ru(5)	58.47(3)
Ru(1)–Ru(4)–Ru(3)	53.69(3)		

The infra-red spectrum of **2** contains a plethora of terminal ν(CO) bands, but none in the μ–CO region. The ^{1}H-NMR spectrum contains resonances assigned to two inequivalent SMe groups at δ 0.33 and 3.83 and a multiplet between δ 6.96–7.92 for the PPh_2 protons. In addition, two sets of resonances at δ 3.32, 3.40 and 5.81, and at 4.00, 4.02 and 5.92 arise from the six protons attached to the C_6 ring.

Depending on the distribution of electrons from the bridging groups, individual Ru atoms have electron counts between 18 and 20. As a whole, the cluster is an 80 c.v.e. system, which for five metal atoms requires only five Ru–Ru bonds. The normal electron count for a bow-tie cluster is 78. The apparent electron-richness in **2** is accounted for by accommodation of extra electrons in Ru–Ru antibonding orbitals in the enlarged Ru_3 portion, as found previously in other complexes derived from **1**, such as $Ru_5(\mu_2,\mu_3\text{-}C_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{13}$ [8], and several other related systems [9–11]. There are many examples of μ_3-alkyne-Ru_3 cluster carbonyls, including several μ_3-benzyne complexes [12]. However, this appears to be the first occasion on which a monocyclic μ_3-cycloalkyne derivative has been characterised. Complexes containing bicyclic ligands (bicyclo[2.2.1]hept-2-yne [13], bicyclo[2.2.1]hept-5-en-2-yne [14] and 7-oxabicyclo[2.2.1]hept-5-yn-2-one [15]) have been described.

It is interesting to compare the cores of three of the 80 c.v.e. clustes obtained from **1**, namely **1** itself (with five Ru–Ru bonds, **2** (with six Ru–Ru bonds) and **3** (with seven Ru–Ru bonds), obtained from **1** and dihydrogen [4]. The average Ru–Ru separations in these three complexes are 2.885, 2.985 and 3.037 Å, respectively. Both **2** and **3** have several Ru–Ru separations in excess of 3.0 Å. While in **1**, this reduction in bond order is manifested in there being only five bonding vectors around the periphery of a pentagon, with no cross-ring interactions, more condensed cores are found in the other two complexes. This difference can be traced to the presence of the 6-e donor C_2 ligand in **1** which spans the five Ru atoms. In **2** and **3**, the hydrocarbon ligands are both 4-e donors, interacting with only three metal atoms. In both cases, this results in the SMe groups adopting μ_3 bridging modes, the increase in electron density having to be taken up in the M–M antibonding orbitals, with concomitant reduction in bond order, as discussed above. These complexes provide further examples of the 'softness' of the metal cores in medium-sized clusters, which alter their geometry to accommodate the steric and bonding requirements of the organic ligands [16,17].

The formation of **2** can be understood by considering the organic ligand to be the product of a formal cycloaddition of the buta-1,3-diene to the C_2 ligand in **1**. Formation of two new C–C bonds is accompanied by cleavage of two C–Ru bonds and rearrangement of the cluster; the SMe groups now each interact with three Ru atoms, while one CO ligand has been lost.

It is interesting to recall that the precursor of **1**, $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$, reacts with buta-1,3-diene to give the complex $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{12}$ (**4**) which contains the same cyclohexenyne ligand bridging four Ru atoms in a pseudo-octahedral C_2Ru_4 cluster [7]. In this reaction, cleavage of the P–C bond in the C_2PPh_2 ligand must occur, although it is not possible to say whether this reaction occurs before or after the addition of the diene to the C_2 fragment.

3. Conclusion

Cycloaddition of buta-1,3-diene to the C_2 ligand in **1** occurs to give a reactive isomer of benzene, namely cyclohex-1-en-4-yne, which is trapped by coordination to three of the Ru atoms in a pentanuclear cluster in the 2σ, π-bonding mode favoured by alkynes on trinuclear ruthenium cluster carbonyls.

4. Experimental

General experimental conditions were similar to those described earlier [7]. Complex **1** was prepared by the literature method [2]. Butadiene (Matheson) was used as received.

*4.1. Reaction of **1** with butadiene*

A solution of **1** (60 mg, 0.046 mmol) and butadiene (1.2 g, 22 mmol) in toluene (10 ml) were heated (95°C) in a Carius tube for 24 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone, 10/3) to yield two products. The major purple band (R_f 0.50) was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_3\text{–}C_6H_6)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ (**2**) (49 mg, 80%). Found: C, 37.74; H, 2.46%; M, 1329 (mass spectrometry). $C_{42}H_{32}O_{10}P_2Ru_5S_2$ requires C, 37.98; H, 2.43%; M, 1329. IR: ν(CO) (cyclohexane) 2039m, 2023vs, 2018s, 1998m, 1984m, 1976s, 1968m, 1962m, 1947m, 1923w cm^{-1}. ^{1}H-NMR: ($CDCl_3$) 0.33, 3.83 (2 × 3H, 2 × s, SMe), 3.32, 3.40 [2 × 1H, 2 × m, H(61), H(62)], 4.00, 4.02 [2 × 1H, 2 × m, H(31), H(32)], 5.81 [1H, dm, $J = 9$ Hz, H(5)], 5.92 [1H, dm, $J = 9$ Hz, H(4)], 6.96–7.92 (20H, m, Ph). [The set of resonances assigned to H(31), H(32) and H(4) are interchangeable with those of H(61), H(62) and H(5)]. FAB, MS (m/z): 1329, M$^+$; 1301–1049, [M–nCO]$^+$ ($n = 1$–10). A light brown band (R_f 0.45; 5 mg) was not identified.

5. Crystallography

A unique data set was measured at ca. 295 K to $2\theta_{max} = 50°$ using an Enraf-Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo–K$_\alpha$ radiation, λ 0.7107$_3$ Å); 7659 independent reflections were obtained, 4902 with $I > 3\sigma,(I)$ being considered 'observed' and used in the full matrix least squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the nonhydrogen atoms; $(x, y, z, U_{ISO})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are 0.040, 0.038, respectively, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.0 program system [18] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables.

5.1. Crystal data and refinement details

(**2**) $Ru_5(\mu_3\text{-}C_6H_6)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10} \equiv C_{42}H_{32}O_{10}P_2Ru_5S_2$, $M = 1328.1$. Monoclinic, space group $P2_1/c$, $a = 11.410(6)$, $b = 27.974(18)$, $c = 16.496(10)$ Å, $\beta = 119.79(4)°$. $V = 4569$ Å^3, $Z = 4$. $\rho_c = 1.93$ g cm^{-3}. $F(000) = 2584$, μ(Mo–K$_\alpha$) = 17.9 cm^{-1}, A^*(min, max) = 1.20, 1.26, respectively. Specimen: 0.10 × 0.10 × 0.44 mm.

Acknowledgements

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