Oligomerisation of Phenylacetylene at a Polynuclear Site; the Molecular Structure of $[Ru_6C(CO)_{12}(\mu_2\text{-}CO)(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$

Jane L. Haggitt, Brian F. G. Johnson,* Alexander J. Blake and Simon Parsons

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ

The structure of the octahedral cluster $[Ru_6C(CO)_{12}(\mu_2\text{-}CO)(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$ **1** is established by single crystal X-ray diffraction study, revealing both C≡C bond scission of an acetylene ligand and oligomerisation to form a five-membered ring.

Interest in the reactions of alkynes with transition metal carbonyl clusters was initially fuelled by their potential as models for processes occurring at metal surfaces.[1] We have been interested in the reactions of alkynes with the ruthenium carbido cluster compound $[Ru_6C(CO)_{17}]$, with a view to studying potential cyclo-trimerisation and -dimerisation, as observed with some mononuclear metal complexes (*e.g.* formation of $[(\eta^4\text{-}Ph_4C_4)PdCl_2]_2$ from $PdCl_2$ and diphenylacetylene,[2] formation of $[(\eta^5\text{-}C_5H_5)Co(\eta^6\text{-}Me_6C_6)]$ from $(\eta^5\text{-}C_5H_5)Co(C_2H_4)_2$ and dimethylacetylene).[3] Although coordination of one or more alkynes to cluster compounds often leads to the formation of coordinated oligomers generated by linkage of the ligands, so far, studies of $[Ru_6C(CO)_{17}]$ with a range of alkynes have resulted in the formation of only mono-, bis-, tris- or tetrakis-alkyne substituted clusters.[4–6] In these compounds the alkynes bond to triangular ruthenium faces in $\mu_2:\eta^3$ modes and show no evidence of oligomerisation. In this communication we report the reaction of $[Ru_6C(CO)_{17}]$ with phenylacetylene, in which C≡C bond scission and oligomerisation occur to form a hexanuclear ruthenium carbido cluster containing both an η^5-bound diphenylcyclopentadienyl ligand and a μ_3-bound C–Ph alkylidyne ligand.

Treatment of $[Ru_6C(CO)_{17}]$ with 2 equiv. of Me_3NO in the presence of excess phenylacetylene results primarily in the formation of $[Ru_6C(CO)_{15}(PhC_2H)]$ **2**, and three minor products, including $[Ru_6C(CO)_{12}(\mu_2\text{-}CO)(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$ **1** in 7% yield. The products were separated by TLC and characterised on the basis of IR, ^1H NMR and FAB-MS for **2**[5] and IR, ^1H NMR† and X-ray diffraction analysis‡ for **1**.

The molecular structure of compound **1** is shown in Fig. 1. The metal framework consists of the familiar octahedron of ruthenium atoms and interstitial C carbido atom common to $[Ru_6C(CO)_{17}]$[9,10] and its arene[11–13] and alkyne[4–6] derivatives. The cluster compound is characterised by the presence of a diphenylcyclopentadienyl group η^5-bound to a single ruthenium atom Ru(3) and a μ_3-bound C–Ph alkylidyne ligand. There are thirteen carbonyl ligands: one bridging CO group spanning the Ru(4)–Ru(5) edge and 12 terminally bound carbonyls which are essentially linear. The compound contains a total of 86 valence electrons, characteristic of these octahedral clusters. The structure reveals a wide range of Ru–Ru bond lengths [2.755(1)–2.973(1) Å] with the three metal atoms bridged by the alkylidyne ligand exhibiting the shortest distances. The interstitial carbido atom is displaced towards the η^5-coordinated Ru(3) atom, the Ru(3)–C(1) distance being 1.983(7) Å, noticeably shorter than the remaining five distances [2.029(6)–2.068(7) Å]. This behaviour has also been observed in arene substituted hexanuclear clusters such as $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$,[11] $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)]$[12] and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$[13] where there is a shift towards the Ru atom bearing the η^6-bound arene. The bridging CO group is highly asymmetric as shown by the Ru(4)–C(51) and Ru(5)–C(51) [2.56(1) and 1.92(1) Å, respectively] bond distances, the longer Ru–C bond involving the Ru atom bound to the alkylidyne ligand. The five-membered ring is essentially planar with the phenyl rings positioned slightly above plane of the C_5 ring [C(331) elevation = 0.16 Å, C(351) elevation = 0.26 Å]. The two phenyl rings lie such that they form dihedral angles of 15.9° [C(331)–C(336)] and 18.3° [C(351)–C(356)] with respect to the cyclopentadienyl ring. The Ru–C(ring) distances range from 2.222(7) to 2.276(7) Å with the bonds to the carbon atoms connected to the phenyl rings being the longest [Ru(3)–C(33) = 2.262(6), Ru(3)–C(35) = 2.276(7) Å]. The coordination of the μ_3-alkylidyne ligand is slightly asymmetric [Ru(3)–C(2) = 2.066(7), Ru(4)–C(2) = 2.110(7), Ru(3)–C(2) = 2.040(7) Å] with the longest bond associated with the ruthenium atom bonded to the bridging CO ligand.

The most striking feature in this structure is the presence of both an η^5-diphenylcyclopentadienyl ligand and an alkylidyne C–Ph ligand, the formation of which requires the cleavage of a phenylacetylene C≡C triple bond. The C_5 ring is formed by the condensation of two phenylacetylene ligands and the incorporation of a C–H fragment derived from the cleavage of a third alkyne ligand. The remaining C–Ph fragment from the C≡C scission process forms the μ_3-bound alkylidyne ligand capping a triangular ruthenium face. Although oligomerisation and/or C≡C bond cleavage of alkynes in cluster compounds are common, most processes involve the formation metallacyclic rings, allyl ligands or alkylidyne ligands.[14–18] There are very

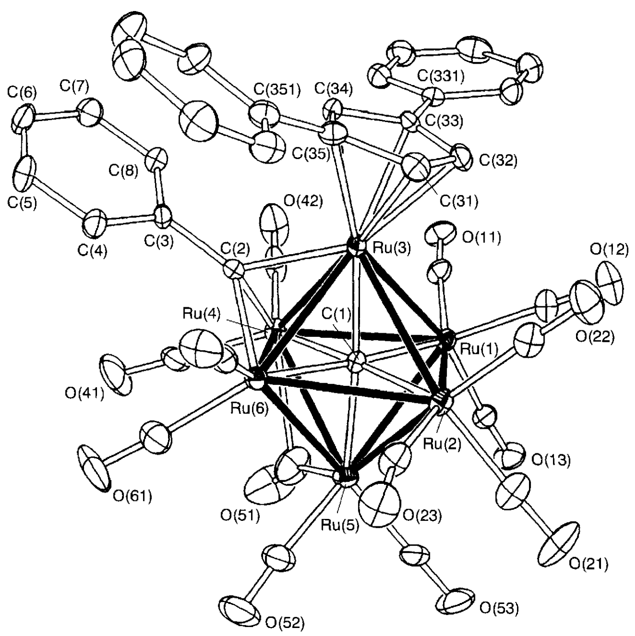

Fig. 1 Molecular structure of $[Ru_6C(CO)_{12}(\mu_2\text{-}CO)(\eta^5\text{-}C_5H_3Ph_2)(\mu_3\text{-}CPh)]$ **1** with the hydrogen atoms omitted for clarity. The C atoms of the CO groups bear the same numbering as the corresponding O atoms. Selected bond lengths (Å): Ru(1)–Ru(2) 2.8607(11), Ru(1)–Ru(3) 2.8902(10), Ru(1)–Ru(4) 2.9360(11), Ru(1)–Ru(5) 2.9321(12), Ru(2)–Ru(3) 2.9502(10), Ru(2)–Ru(5) 2.8965(12), Ru(2)–Ru(6) 2.9727(11), Ru(3)–Ru(4) 2.8299(11), Ru(3)–Ru(6) 2.7552(11), Ru(4)–Ru(5) 2.8245(10), Ru(4)–Ru(6) 2.7952(11), Ru(5)–Ru(6) 2.9317(10), Ru(1)–C(1) 2.049(7), Ru(2)–C(1) 2.029(6), Ru(3)–C(1) 1.983(7), Ru(4)–C(1) 2.057(6), Ru(5)–C(1) 2.068(7), Ru(6)–C(1) 2.043(7), Ru(3)–C(2) 2.066(7), Ru(4)–C(2) 2.110(7), Ru(6)–C(2) 2.040(7), C(2)–C(3) 1.465(9), Ru(3)–C(31) 2.233(7), Ru(3)–C(32) 2.232(7), Ru(3)–C(33) 2.262(6), Ru(3)–C(34) 2.222(7), Ru(3)–C(35) 2.276(7), C(33)–C(331) 1.484(10), C(35)–C(351) 1.465(11), mean C(ring)–C(ring) 1.42, mean Ru–C(CO terminal) 1.885, mean C–O(CO terminal) 1.14.

few examples where the alkyne oligomerises to give an organic cyclic ligand coordinated to the metals.[19,20]

We wish to thank the EPSRC for financial support.

Received, 31st March 1995; Com. 5/02059J

Footnotes

† *Spectroscopic data* for **1**: IR (CH_2Cl_2) ν(CO)/cm^{-1}: 2073m, 2031s, 2019(sh)m, 2000w, 1982(sh)w, 1959w; ^{1}H NMR (CD_2Cl_2): δ 7.77–7.49 (m), 7.32–7.11 (m), 5.64(t), 5.45(d).

‡ *Crystal data* for **1**: $C_{38}H_{18}O_{13}Ru_6$, M = 1288.9, triclinic, space group $P\bar{1}$, a = 10.875(2), b = 11.595(2), c = 15.324(3) Å, α = 92.87(2), β = 95.69(4), γ = 99.76(2)°, U = 1891 Å^3, Z = 2, D_c = 2.264 g cm^{-3}, μ(Mo-Kα) = 2.403 mm^{-1}, F(000) = 1228. Data collection on a Stoë Stadi-4 four-circle diffractometer with graphite-monochromated Mo-Kα X-radiation yielded 4980 unique, absorption-corrected reflections ($2\theta_{max}$ = 45°), of which 4960 were used in all calculations. Following solution by direct methods,[7] the structure was refined by full matrix least squares on F^2 with anisotropic temperature factors for all non-H atoms and with H atoms riding on their respective C atoms.[8] At final convergence $R[F_o > 4\sigma(F_o)$, 4000 data] = 0.0318, $wR[F^2$, all data] = 0.1135, $S[F^2]$ = 1.433 for 514 parameters. Residual ΔF extrema lay in the range −0.97 to +0.68 e Å^{-3}.

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

References

1 E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203.

2 P. M. Maitlis, *Acc. Chem. Res.*, 1976, **9**, 93.

3 K. Jonas, E. Deffense and D. Habermann, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 716.

4 R. Mallors, The University of Edinburgh, unpublished results.

5 S. R. Drake, B. F. G. Johnson, J. Lewis, G. Conole and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1990, 995.

6 R. D. Adams and W. Wu, *Organometallics*, 1993, **12**, 1238.

7 G. M. Sheldrick, SHELXL-86, *Acta Crystallogr., Sect. A, Fund. Crystallogr.*, 1990, **46**, 467.

8 G. M. Sheldrick, SHELXL-93, *Program for structure refinement, University of Göttingen, 1993.*

9 A. Sirigu, M. Bianchi and E. Benedetti, *J. Chem. Soc., Chem. Commun.*, 1969, 596.

10 D. Braga, F. Grepioni, P. J. Dyson, B. F. G. Johnson, P. Frediani, M. Bianchi and F. Piacenti, *J. Chem. Soc., Dalton Trans.*, 1992, 2565.

11 P. J. Dyson, B. F. G. Johnson, J. Lewis, M. Martinelli, D. Braga and F. Grepioni, *J. Am. Chem. Soc.*, 1993, **115**, 9062.

12 D. Braga, F. Grepioni, E. Parisini, P. J. Dyson, A. J. Blake and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1993, 2951.

13 D. Braga, F. Grepioni, B. F. G. Johnson, H. Chen and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1991, 2559.

14 J.-S. Song, G. L. Geoffroy and A. L. Rheingold, *Inorg. Chem.*, 1992, **31**, 1505.

15 J. T. Park, B. W. Woo, J.-H. Chung, S. C. Shim, J.-H. Lee, S.-S. Lim and I.-H. Suh, *Organometallics*, 1994, **13**, 3384.

16 R. D. Adams and J. A. Belinski, *Organometallics*, 1991, **10**, 2114.

17 Y. Chi and J. R. Shapley, *Organometallics*, 1985, **4**, 1900.

18 C. P. Casey, R. A. Widenhoefer and S. L. Hallenbeck, *Organometallics*, 1993, **12**, 3788.

19 S. Aime, L. Milone, E. Sappa and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1977, 227.

20 E. Sappa, A. Tiripicchio and A. M. Manotti Lanfredi, *J. Chem. Soc., Dalton Trans.*, 1978, 552.