Synthesis and Characterisation of the Diphenylfulvene Derivative $[Ru_6C(CO)_{14}(\mu_3\text{-}\sigma:\eta^2:\eta^3\text{-}C_5H_4CPh_2)]$, showing an Unusual Facial Bonding Mode and Fluxionality on the NMR Timescale

Alexander J. Blake, Paul J. Dyson, Brian F. G. Johnson*, David Reed and Douglas S. Shephard

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

The molecular structure of the octahedral cluster, $[Ru_6C(CO)_{14}(\mu_3\text{-}\sigma:\eta^2:\eta^3\text{-}C_5H_4CPh_2)]$, prepared from the reaction of $[Ru_6C(CO)_{17}]$ with diphenylfulvene in the presence of trimethylamine-*N* oxide, has been established by low-temperature single-crystal X-ray diffraction analysis; the coordination mode is unique and the compound displays highly unusual fluxional behaviour on the NMR timescale.

The characterisation of molecular counterparts of chemisorbed organic and inorganic substrates presents an interesting challenge. Over the past few years the isolation of cluster compounds which provide good models for the threefold chemisorption site for benzene has enabled workers in this field to investigate aspects of the cluster-surface vibrational spectroscopic analogy.[1–6] On multimetal sites organic substrates undergo profound modification to their bonding modes and this has been clearly demonstrated for benzene. In this communication we wish to report a further extension of our studies of cluster-bound organic moieties to the chemistry of coordinated diphenylfulvene and the isolation and full characterisation of a hexaruthenium cluster containing a face-bonding cyclopentadienyl unit. To date, work with fulvenes has been limited to single- and di-metal systems,[7–10] and in general the terminal η^5-coordination mode is usually preferred by the cyclopentadienyl ligand and its derivatives.

The oxidative removal of three carbonyl groups from the parent cluster $[Ru_6C(CO)_{17}]$ by reaction with 3 molar equiv. of trimethylamine-*N* oxide (Me_3NO) in the presence of an excess of diphenylfulvene yields $[Ru_6C(CO)_{14}(\mu_3\text{-}\sigma:\eta^2:\eta^3\text{-}C_5H_4CPh_2)]$ as the major product. After separation by TLC using CH_2Cl_2–hexane (3:7) as eluent, the red compound was initially characterised on the basis of its mass spectrum which exhibited a parent ion peak at *m*/*z* 1240.

The molecular structure of $[Ru_6C(CO)_{14}(\mu_3\text{-}\sigma:\eta^2:\eta^3\text{-}C_5H_4CPh_2)]$, as determined by single-crystal X-ray diffraction, is shown in Fig. 1 together with some relevant structural parameters. The metal framework consists of an octahedral arrangement of six ruthenium atoms with an interstitial carbon atom at the centre, a feature common to the majority of organoderivatives of the $[Ru_6C(CO)_{17}]$ cluster. Of primary importance is the facially bonded fulvene ligand, formally replacing three adjacent terminal CO ligands. On close inspection, three different modes of coordination of the five-membered carbocyclic ring to the three ruthenium atoms constituting the triangular metal face are observed.

First, a σ-type (η^1) mode, producing the Ru(4)–C(3z) bond. Secondly, a π-type (η^2) mode giving the Ru(1)–C(4z) and Ru(1)–C(5z) bonds. Thirdly, and perhaps most interestingly, there is a π-allyl (η^3) mode produced by coordination of C(1),

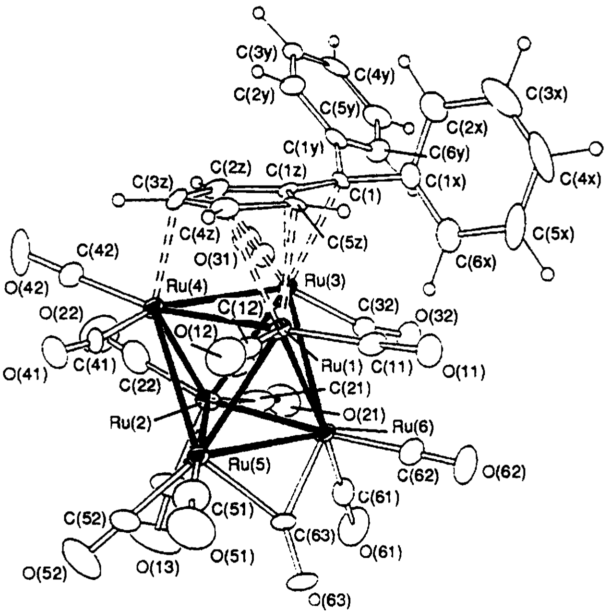

Fig. 1 The molecular structure of $[Ru_6C(CO)_{14}(\mu_3\text{-}\sigma:\eta^2:\eta^3\text{-}C_5H_4CPh_2)]$. Relevant structural parameters (Å), Ru(1)–C(4z) 2.381(19), Ru(1)–C(5z) 2.245(18), Ru(3)–C(1z) 2.215(17), Ru(3)–C(2z) 2.470(19), Ru(3)–C(1) 2.357(16), Ru(4)–C(3z) 2.160(19), C(1z)–C(2z) 1.471(25), C(1z)–C(5z) 1.461(24), C(1z)–C(1) 1.437(23), C(2z)–C(3z) 1.40(3), C(3z)–C(4z) 1.46(3), C(4z)–C(5z) 1.42(3), C(1)–C(1y) 1.519(25), C(1)–C(1x) 1.54(3), C–C(y)$_{av}$ 1.37(3), C–C(x)$_{av}$ 1.38(4).

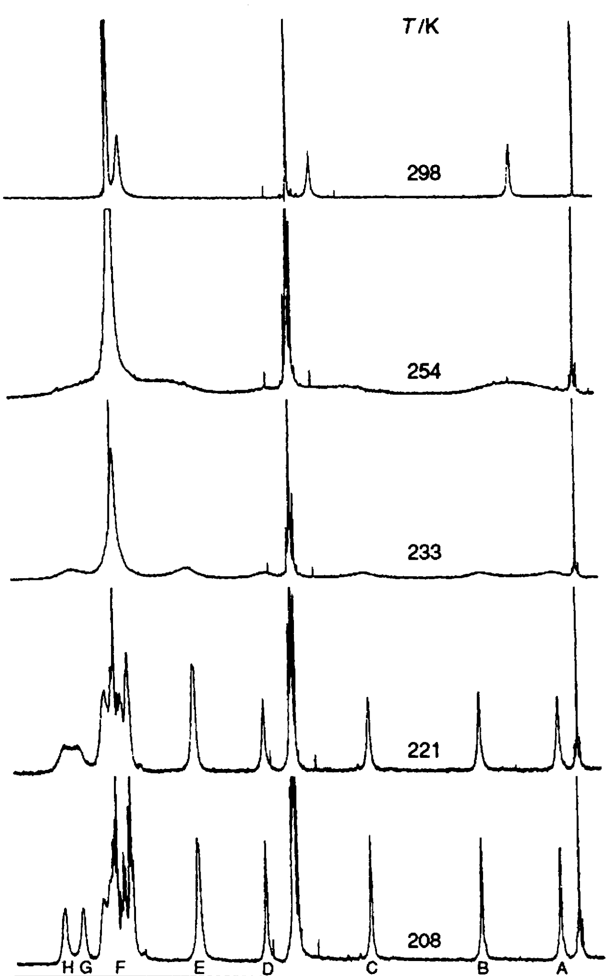

Fig. 2 360.13 MHz ^{1}H NMR spectra recorded over a range of temperatures. The coalescence of signals C and D at 254 K gives $\Delta G^\ddagger$ 47.43 kJ mol^{-1} for the ligand 'swivel' process.

C(1z) and C(2z) to Ru(3). The two pendant phenyl groups are in distinctly non-equivalent environments. One is in a most sterically constrained position with respect to rotation about the C(1)–Ph axis, the other less so. This concurs with ^1H NMR spectroscopic data for the compound recorded over a range of temperatures. These spectra are not straightforward and require careful delineation.

The ^1H NMR spectrum of $[Ru_6C(CO)_{14}(\mu_3\text{-}\sigma:\eta^2:\eta^3\text{-}C_5H_4CPh_2)]$ in $CDCl_3$ obtained at room temperature comprises three sets of signals at *ca.* δ 7.2, 5.0 and 2.8. The simplicity of this spectrum is consistent with some kind of fluxional process, and this was confirmed by recording spectra over a range of temperatures, the results of which are presented in Fig. 2.

These observations may be explained in terms of the observed solid-state structure (Fig. 1) and from a consideration of the ligand movements indicated in Fig. 3. The coalescence of the signals A/B and C/D, due to the protons H(2z)/H(5z) and H(3z)/H(4z) respectively on the five-membered ring, can be explained by the swivelling movement of this ring relative to a face of the Ru_6 octahedron, as indicated in Fig. 3. At lower temperatures, the rate of this process is reduced, and as a consequence the equivalence of the two phenyl groups is lost. Additionally, one of the phenyl groups will experience restricted rotation due to its proximity to, and subsequent steric hindrance by, the cluster carbonyls, resulting in the detection of two distinct signals from the ortho protons of this ring at low temperature (coalescence at *ca.* δ 7.7 at 221 K, with signals G and H resolving out clearly at 208 K). However, it is not apparent by which pathway this process occurs. There are two possible routes: firstly through C(1z) eclipsing a ruthenium metal atom and secondly where it does not. The former seems most likely since C(1) would remain stabilised by the metal throughout the transition.

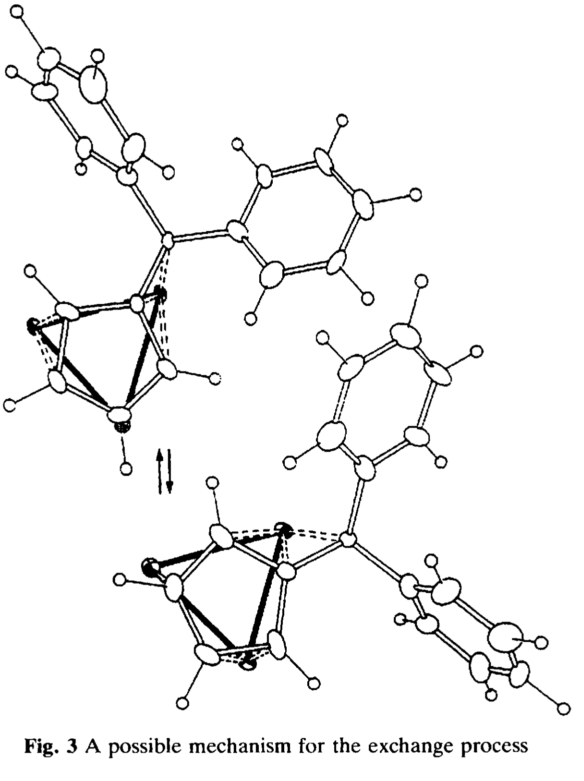

Fig. 3 A possible mechanism for the exchange process

These observations clearly indicate that fulvenes may also form facially bonded systems and exhibit sterically non-rigid behaviour reminiscent of analogous arene-bonded systems. It is interesting to note that the adopted bonding mode in this instance is through the five-membered ring system and not the available six-membered rings. This may not always be the case.

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Footnotes

[†] *Spectroscopic data* for $[Ru_6C(CO)_{14}(\mu_3\text{-}\sigma:\eta^2:\eta^3\text{-}C_5H_4CPh_2)]$: IR (CH_2Cl_2) $\nu(CO)/cm^{-1}$: 2077m, 2041s, 2025vs, 1815w br. ^1H NMR $(CDCl_3)$: δ 7.24 (m, 6H), 7.11 (s, 4H), 5.04 (s, 2H), 2.86 (s, 2H) FAB MS: *m/z* 1240 (1240, M^+)

[‡] *Crystal data* for $[Ru_6C(CO)_{14}(\mu_3\text{-}\sigma:\eta^2:\eta^3\text{-}C_5H_4CPh_2)]$: $C_{33}H_{14}O_{14}Ru_6$, $M = 1240.9$, monoclinic, space group *C2/c* (no. 15), $a = 26.046(3)$, $b = 18.674(3)$, $c = 17.016(21)$ Å, $\beta = 121.20(70)°$, $V = 7079$ Å^3, $D_c = 2.328$ g cm^{-3}, $Z = 8$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 2.512$ mm^{-1}, $T = 150$ K. Stoe-Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105), 4608 unique reflections collected $5 < 2\theta < 45°$, semi-empirical absorption correction (A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351) applied (minimum and maximum transmission factors 0.722 and 0.981 respectively), 2875 with $F > 4\sigma(F)$ used in all calculations. Structure solved by direct methods (Ru) (G. M. Sheldrick, SHELXS-86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467) and refined by full-matrix least squares (G. M. Sheldrick, SHELX-76, University of Cambridge, England, 1976). At isotropic convergence, corrections (max. 1.368, min 0.631) for absorption were applied using DIFABS (N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158). With all non-hydrogen atoms anisotropic and H atoms in fixed calculated positions refinement converged at $R = 0.053$, $R_w = 0.063$, $S = 1.090$. In the final ΔF synthesis no feature layout with $+1.13$ and -0.86e 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.

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