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A Zwitterionic Cluster Compound: Synthesis and Characterisation of the Triphenylphosphoniocyclopentadienide Derivative $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$

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The crystal and molecular structure of the zwitterionic octahedral cluster, $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$, prepared from the reaction of $[Ru_6C(CO)_{17}]$ with trimethylamine *N*-oxide in the presence of triphenylphosphoniocyclopentadienide, has been established by low-temperature single-crystal X-ray diffraction analysis, and shows intermolecular interactions typical of zwitterionic compounds.

Here we report, as part of our investigation into the chemistry of cluster-co-ordinated carbocycles, the synthesis and full characterisation of the new zwitterionic cluster compound $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$. Our interest in these molecules is three-fold. First, the study of electron-transfer reactions between a redox-active cluster centre and a closely bound cation. Secondly, the elucidation of interactions in the solid state in order to establish a systematic approach to the synthesis of crystalline materials with desired redox properties, and finally the development of the synthetic potential of such systems to macromolecular clusters containing redox-active, cluster centres.

We have previously reported that the reaction of C_5H_6 with the parent cluster $[Ru_6C(CO)_{17}]$ yields only the bis-cyclopentadienyl derivative in moderate yield.[1] We now report that the utilisation of triphenylphosphoniocyclopentadienide, $C_5H_4PPh_3$, gives a direct route to the mono-cyclopentadienyl cluster derivative $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$ which is related to the mono-cyclopentadienyl mixed-metal cluster $[RhRu_5C(CO)_{14}(\eta^5\text{-}C_5H_5)]$.[2] Others[3] have shown that reaction of $C_5H_4PPh_3$ with $[Os_3(CO)_{10}(MeCN)_2]$ gives two products with interesting bonding modes, but as far as we are aware η^5-co-ordination has not been previously observed in a cluster compound. Monometal species bound to the $C_5H_4PPh_3$ ligand display a variety of bonding modes[4–7] and some have shown extraordinary homogeneous catalytic capability.[8,9]

The oxidative-removal of three carbonyl groups from the parent cluster $[Ru_6C(CO)_{17}]$ (150 mg) by reaction with three molar equivalents of Me_3NO (30 mg) in the presence of a slight excess of $C_5H_4PPh_3$ gives $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$ as the only product in good yield (64%). After separation by TLC on silica plates using CH_2Cl_2(40%)–hexane(55%)–ethyl acetate(5%) as eluent, the deep red compound was initially characterised on the basis of its mass spectrum which exhibited a strong parent peak at *m*/*z* 1338.

The infrared spectrum† of $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$ (in CH_2Cl_2) is consistent with its formulation as a zwitterionic compound, exhibiting a shift to lower energy of the main CO band of *ca.* 17 cm^{-1}, compared to the value for $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$[10] and is similar to the anionic cluster $[NMe_4][Ru_6H(C)(CO)_{18}]$.[11] The ^{31}P NMR signal shows a shift to higher frequency compared to that of the free ylide[12,13] and the ^1H NMR spectrum is consistent with that of comparable cluster-co-ordinated unsaturated carbocycles. Single crystals suitable for structure determination‡ were grown from CH_2Cl_2 by slow evaporation at 248 K.

The molecular structure of $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$ is shown in Fig. 1 together with some key structural parameters. The metal framework consists of an octahedral arrangement of six ruthenium atoms with an interstitial carbon atom, a feature common to the majority of organo derivatives of the $[Ru_6C(CO)_{17}]$ cluster (Fig. 2). The interstitial carbon atom is displaced slightly towards Ru(1) bonded to the cyclopentadienyl group, a feature previously observed in other similar systems.[2,10] Of primary importance is the apically co-ordinated cyclopentadienyl fragment, formally replacing three adjacent terminal CO ligands and thus donating a total of six electrons to the cluster core. The five-membered ring is planar to within estimated error. Its centroid does not lie directly over the Ru(1)–Ru(3) vector but is tilted to one side, probably due to a combination of steric interaction of the bulky PPh_3 group with CO(52) and CO(53) and intermolecular interactions (see above). The phosphorus atom occupies a slightly distorted tetrahedral environment and is bent out of the plane of the

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† Spectroscopic data for $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$. IR ($CH_2Cl_2$) $\tilde{\nu}$(CO)/cm^{-1}: 2068m, 2060s, 2018 (sh), 2008vs, 1945m, 1794w (br); NMR [$(CD_3)_2CO$]: ^1H, δ 7.96 (m, 3 H), 7.77 (m, 9 H), 7.69 (m, 3 H), 5.16 (m, 2 H), 4.92 (m, 2 H); ^{31}P, δ 21.46 (s). Positive-ion FAB mass spectrum: M^+ 1338 (calc. 1337).

‡ Crystal data for $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)]$. $C_{38}H_{19}O_{14}PRu_6$, $M = 1336.92$, monoclinic, space group $P2_1/c$, $a = 10.646(4)$, $b = 26.823(8)$, $c = 14.278(4)$ Å, $\beta = 104.53(3)°$, $U = 3947(2)$ Å^3, $D_c = 2.250$ g cm^{-3}, $Z = 4$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 2.512$ mm^{-1}, $T = 150$ K. Stöe-Stadi 4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[14] Total of 5529 reflections collected, including 5186 independent reflections $5 < 2\theta < 45°$ ($R_{int} = 0.0215$), semi-empirical absorption correction[15] applied (minimum and maximum transmission factors 0.680 and 0.713 respectively). Structure solved by direct methods[16] (Ru) and completed by full-matrix least-squares refinement on F^2.[17] Hydrogen atoms placed in calculated positions (C–H 0.93 Å) and refined riding on their respective C atoms [$U_{iso}(H) = 1.2U_{eq}(C)$]. Refinement converged at $R = 0.0536$ [based on F and 3836 reflections with $F > 4\sigma(F)$], $wR_2 = 0.1219\%$ (based on F^2 and 5095 data), $S = 1.094$, for 340 parameters, including anisotropic displacement parameters for all non-H atoms. In final difference synthesis no feature lay outwith +1.11 and −0.82 e Å^{-3}. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

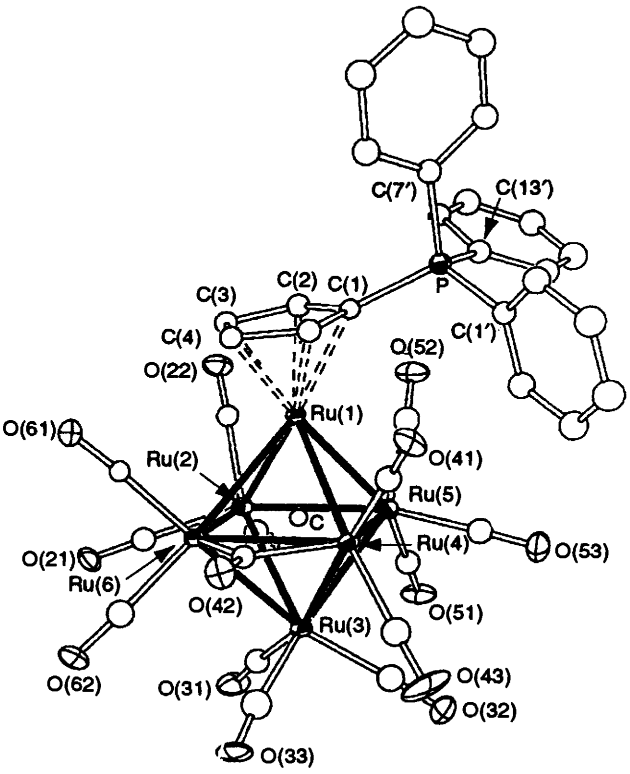

Fig. 1 Molecular structure of $[\mathrm{Ru_6C(CO)_{14}}(\eta^5\text{-}\mathrm{C_5H_4PPh_3})]$. Relevant structural parameters (Å): Ru(1)–C 1.917(11), Ru(1)–C(1) 2.201(11), Ru(1)–C(2) 2.158(11), Ru(1)–C(3) 2.190(11), Ru(1)–C(4) 2.214(12), Ru(1)–C(5) 2.202(11), Ru(3)–C 2.106(11), C(1)–C(2) 1.39(2), C(2)–C(3) 1.42(2), C(3)–C(4) 1.40(2), C(4)–C(5) 1.41(2), C(1)–C(5) 1.43(2), C(1)–P 1.793(12), C(1')–P 1.801(12), C(7')–P 1.805(12), C(13')–P 1.752(13), C–O(av.) 1.125(1). The hydrogen atoms have been removed for clarity

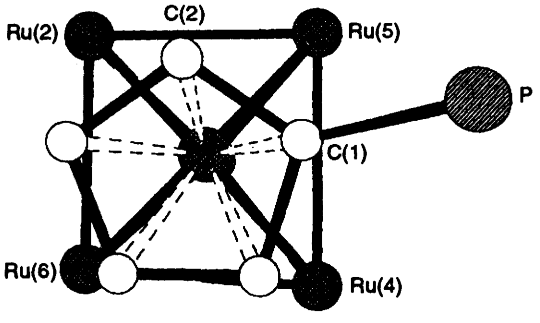

Fig. 2 The core geometry of $[\mathrm{Ru_6C(CO)_{14}}(\eta^5\text{-}\mathrm{C_5H_4PPh_3})]$ viewed along the Ru(1)–Ru(3) vector

cyclopentadienyl ring, the C(1)–P vector producing an angle of 19.4(6)° at its intersection with the plane. The P–C(1) bond length of 1.793(12) Å is consistent with that of a single P–C bond. This is considerably longer than that quoted for the free ylide [1.718(2)].[18] The remaining P–C bond lengths are within the normal range. The observed Ru–Ru contacts are just within the normal range, the longest being Ru(4)–Ru(5) 3.131(2) Å and the shortest Ru(2)–Ru(5) 2.806(2) Å. There are thirteen terminal carbonyl ligands and a bridging carbonyl triangulating the Ru(4)–Ru(6) vector.

Examination of the molecular packing within the crystal structure of $[\mathrm{Ru_6C(CO)_{14}}(\eta^5\text{-}\mathrm{C_5H_4PPh_3})]$ provides two additional solid-state intermolecular interactions for organocluster compounds. Fig. 3 shows two molecular arrangements involving short ion-pair contacts of the C–H(*p*-phenyl) ··· O type: A (2.559 Å) and B (2.510 Å). Type A shows a 'dipole–dipole'-type interaction between two molecules related by an inversion centre, while type B shows a unidimensional 'nose-to-tail' arrangement. Previously, interactions of the type C–H(coordinated arene) ··· O short contacts (the oxygen often being that of a μ-CO) and arene–arene (graphitic) have been found to dictate the solid-state orientations of arene-cluster compounds.[19]

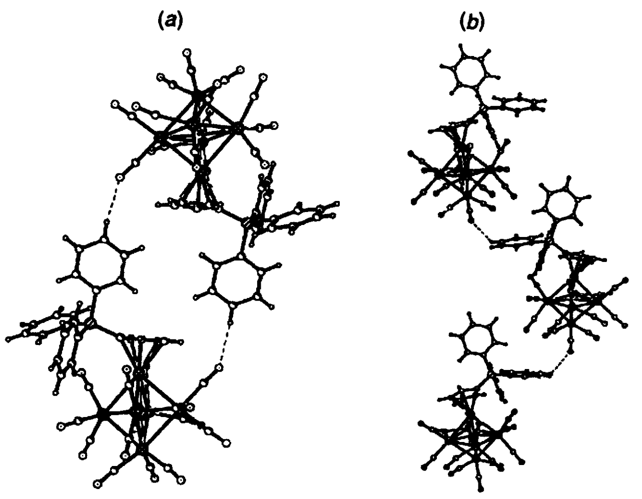

Fig. 3 The intermolecular close contacts, types A (*a*) and B (*b*), present in crystalline $[\mathrm{Ru_6C(CO)_{14}}(\eta^5\text{-}\mathrm{C_5H_4PPh_3})]$

The new complex $[\mathrm{Ru_6C(CO)_{14}}(\eta^5\text{-}\mathrm{C_5H_4PPh_3})]$ is an example of an organocluster containing an apically coordinated cyclopentadienyl unit. Of significance in these studies is the formal description of this compound as a zwitterionic complex $[\overset{-}{\mathrm{Ru}}_6\mathrm{C(CO)_{14}}(\eta^5\text{-}\mathrm{C_5H_4}\overset{+}{\mathrm{P}}\mathrm{Ph_3})]$.

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References

1 A. J. Blake, P. J. Dyson, R. C. Gash, B. F. G. Johnson and P. Trickey, *J. Chem. Soc., Dalton Trans.*, 1994, 1105.
2 P. J. Bailey, A. J. Blake, P. J. Dyson, B. F. G. Johnson, J. Lewis and E. Parisini, *J. Organomet. Chem.*, 1993, **452**, 175.
3 A. J. Deeming, N. I. Powell and C. Whittaker, *J. Chem. Soc., Dalton Trans.*, 1991, 1875.
4 T. Debaerdemaeker, *Z. Kristallogr.*, 1979, **149**, 91.
5 G. Tresoldi, A. Recca, P. Finocchiaro and F. Farone, *Inorg. Chem.*, 1981, **20**, 3103.
6 C. G. Pierpoint, H. H. Downs, K. Itoh, H. Nishiyama and Y. Ishii, *J. Organomet. Chem.*, 1977, **124**, 93.
7 N. C. Baenziger, R. M. Flynn, D. C. Swenson and N. L. Holy, *Acta Crystallogr., Sect. B*, 1978, **34**, 2300.
8 N. C. Baenziger, R. M. Flynn, D. C. Swenson and N. L. Holy, *Acta Crystallogr., Sect. B*, 1979, **35**, 741.
9 N. C. Baenziger, R. M. Flynn, D. C. Swenson and N. L. Holy, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 686.
10 B. F. G. Johnson, R. D. Johnson and J. Lewis, *Chem. Commun.*, 1967, 1057.
11 C. R. Eady, P. F. Johnson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383.
12 O. Kock, F. Edelmann and U. Behrens, *Chem. Ber.*, 1982, **115**, 1313.
13 R. Drews and U. Behrens, *Chem. Ber.*, 1984, **118**, 888.
14 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
15 A. C. T. North, D. C. Philips and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
16 G. M. Sheldrick, SHELXS 86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
17 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
18 H. L. Ammon, G. L. Wheeler and P. H. Watts, *J. Am. Chem. Soc.*, 1973, **95**, 6158.
19 D. Braga, P. J. Dyson, F. Grepioni, B. F. G. Johnson and M. J. Calhorda, *Inorg. Chem.*, 1994, **33**, 3218.

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