

Insertion of Dioxygen between Organic Ligands in a Rhodium Complex

John Jeffery,^a Roger J. Mawby,^{a*} Michael B. Hursthouse,^b and Nigel P. C. Walker^b

^a *Department of Chemistry, University of York, York YO1 5DD, U.K.*

^b *Chemistry Department, Queen Mary College, Mile End Road, London E1 4NS, U.K.*

Atmospheric oxidation of $[\text{Rh}(\text{dpf})_2]^+$ (dpf = 6,6-diphenylfulvene) in propanone solution results in the linking of the exocyclic carbon atoms in the two fulvene ligands by a peroxide bridge.

We report an unusual template reaction in which dioxygen is inserted between two organic ligands to generate an organic

peroxide. Cations $[\text{RhL}_2]^+$ (L = $\text{P}(\text{OPh})_3$ or L_2 = cyclo-octa-1,5-diene), generated by treatment of $[\text{RhClL}_2]_2$ with a

silver salt in tetrahydrofuran,¹ reacted with 6,6-diphenylfulvene (dpf) to yield intensely coloured species $[\text{Rh}(\text{dpf})\text{L}_2]^+$, isolable as PF_6^- or ClO_4^- salts. In these complexes, the fulvene appears to act as an η^4 -diene ligand. The cation $[\text{Rh}(\text{CO})_2]^+$, however, yielded deep blue $[\text{Rh}(\text{dpf})_2]^+$. The colour of a propanone solution of $[\text{Rh}(\text{dpf})_2](\text{ClO}_4)$ faded rapidly on exposure to air. Colourless crystals [of compound (1)] were obtained from the solution, and analytical data suggested that the reaction had simply involved uptake of O_2 by the complex. It seemed unlikely, however, that (1) was a dioxygen complex $[\text{Rh}(\text{dpf})_2(\text{O}_2)](\text{ClO}_4)$, first because it was colourless whereas both free dpf and the other dpf complexes were strongly coloured, and secondly because all five carbon atoms in the fulvene rings were equally coupled to rhodium in the ^{13}C n.m.r. spectrum ($J_{\text{Rh-C}} = 7.3$ Hz), implying that the rings were now η^5 -bonded to the metal. We believed that O_2 might have been added across the exocyclic carbon atoms of the two fulvene ligands, thus destroying delocalization between five- and six-membered rings (hence the loss of colour). To obtain proof of the presence of oxygen in the complex and to determine how the oxygen had been incorporated into the structure, we undertook a single-crystal X-ray diffraction study of (1).†

The structure of the complex cation is shown in Figure 1 (the ClO_4^- anion is not co-ordinated to the metal). The rhodium is sandwiched between staggered and essentially planar cyclopentadienyl-rings, with Rh–C distances varying between 2.148(4) and 2.185(5) Å. Within the rings, C–C bond lengths range from 1.395(9) to 1.437(6) Å, and C–C–C angles from 106.4(4) to 110.1(5)°. Bond lengths (Å) and angles (°) across the peroxide bridge between the cyclopentadienyl rings are as follows: C(31)–C(1), 1.531(6); C(1)–O(1), 1.454(4); O(1)–O(2), 1.487(4); O(2)–C(2), 1.458(5); C(2)–C(61), 1.521(6); C(31)–C(1)–O(1), 110.6(3); C(1)–O(1)–O(2), 106.7(2); O(1)–O(2)–C(2), 108.2(3); O(2)–C(2)–C(61), 110.8(3).

† *Crystal data*: $\text{C}_{36}\text{H}_{28}\text{O}_2\text{Rh}\cdot\text{ClO}_4$, $M = 695.0$, rhombohedral (hexagonal setting), space group $R\bar{3}$, $a = b = 35.989(6)$, $c = 12.118(1)$ Å, $Z = 18$, $D_c = 1.528$ g cm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 6.9$ cm $^{-1}$, 3164 observed out of 4738 measured reflections [$I > 1.5\sigma(I)$], data measured to $\sin\theta/\lambda = 0.572$ Å $^{-1}$, $R = 0.042$ (anisotropic thermal parameters for non-hydrogen atoms, isotropic parameters for all hydrogen atoms). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

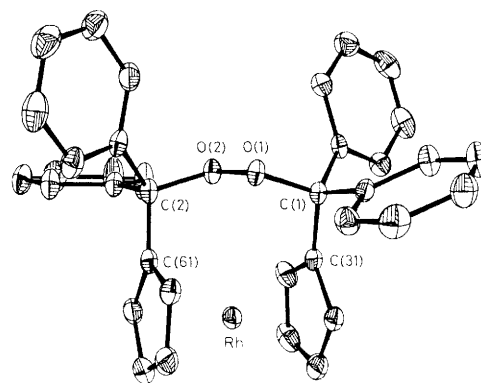


Figure 1. The crystal structure of the complex cation $[\text{Rh}((\text{dpf})_2\text{O}_2)]^+$, (1).

It seems probable that (1) is formed by way of an intermediate dioxygen complex $[\text{Rh}(\text{dpf})_2(\text{O}_2)]^+$. The subsequent rearrangement might simply be envisaged as a nucleophilic attack by a peroxide ligand on the (probably somewhat positively charged) exocyclic carbon atoms of the fulvene ligands, but a parallel might also be drawn with the reaction in which singlet O_2 adds across the 9 and 10 positions in anthracene.² As Mason³ and Vaska⁴ have pointed out, dioxygen complexes are commonly diamagnetic, and the complexed O_2 might be envisaged as being in the singlet state and hence activated for the subsequent addition reaction.

Some years ago, Fischer and Weimann claimed to have obtained $[\text{Rh}(\text{dpf})_2](\text{PF}_6)$ in tiny yield by an entirely different route.⁵ Since their compound was beige, and air was used as an oxidant during the reaction, it may well be that the compound actually contained the same cation as (1).

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