

On the Existence of Dioxygen Adducts of Ruthenium (II) Tertiary-Arsine and -Phosphine Complexes

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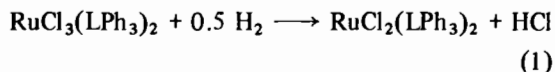
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An often quoted [1] example of the only isolated and well-characterized dioxygen adduct of a d^6 transition metal, outside that of heme systems [2] [iron(II) porphyrins], is the ruthenium(II) complex $\text{RuCl}_2(\text{AsPh}_3)_3\text{O}_2$ [3], which is said to be formed by reaction of O_2 with $\text{RuCl}_2(\text{AsPh}_3)_3$. We show here the non-existence of both of these complexes, and also report on our efforts to detect the more likely $\text{RuCl}_2(\text{LPh}_3)_2\text{O}_2$ complexes ($\text{L} = \text{As}, \text{P}$), often postulated as intermediates in catalytic oxidation reactions [4]. It should be pointed out that we consider the dioxygen complexes [5] $\text{Ru}(\text{NO})\text{X}(\text{PPh}_3)_2\text{O}_2$ to be formally derivatives of ruthenium(0).

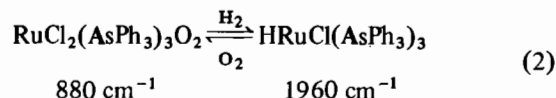
Experimental and Discussion

Solutions containing $\text{RuCl}_2(\text{LPh}_3)_2$ can be made by treatment of $\text{RuCl}_3(\text{LPh}_3)_2 \cdot \text{CH}_3\text{OH}$ complexes [6] with 1 atm H_2 in NN-dimethylacetamide at 25°C . The stoichiometry of reaction (1) has been demonstrated, and in the coordinating solvent, the $\text{RuCl}_2(\text{LPh}_3)_2$ complexes could be present as solvated monomers [7], although ^{31}P nmr data in other solvents [8] suggest the presence of five-coordinate chloride-bridged dimers.

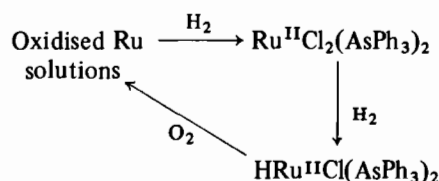


The visible spectrum of the $\text{RuCl}_2(\text{PPh}_3)_2$ solution is identical with that obtained during our study [7] of PPh_3 dissociation from $\text{RuCl}_2(\text{PPh}_3)_3$, and addition of PPh_3 to the resulting solution of reaction (1) gives the tris-phosphine complex. However, $\text{RuCl}_2(\text{AsPh}_3)_2$ solutions are completely unreactive toward AsPh_3 (possibly because the arsine fails to cleave a chloride bridge), and we have also been unable to synthesize $\text{RuCl}_2(\text{AsPh}_3)_3$ by the reported procedure [9] from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and AsPh_3 , or via various precursors such as ruthenium(II) sulphoxides [10], the blue ruthenium solutions [11], or $\text{RuCl}_2(\text{PPh}_3)_3$ [6]. Such procedures give rise to $\text{RuCl}_3(\text{AsPh}_3)_3$, $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{solvent}$, or $[\text{RuCl}_2(\text{AsPh}_3)_2]_2$, or mixtures of these [12].

The reported [3] 1:1 O_2 absorption by $\text{RuCl}_2(\text{AsPh}_3)_3$ must be due to oxidation of 2 mol of coordinated arsine in complexes such as those listed above. The so-called 880 cm^{-1} peroxide band is attributable to $\nu_{\text{As}-\text{O}}$, and the paramagnetism and esr signals (assigned to a $\text{Ru}^{\text{III}}-\text{O}_2^-$ moiety) are likely due to Ru(III) arsine oxide complexes, which are known [12]. Infrared data ascribed [3] to reaction (2) may be accounted for by the



sequence shown below:



The solutions containing triphenylarsine oxide complexes can be reduced by H_2 in solution back to $\text{RuCl}_2(\text{AsPh}_3)_2$, and this can undergo reaction with a further mol of H_2 to give the chlorohydro complex. Again we find that solutions of $\text{HRuCl}(\text{AsPh}_3)_2$ are unreactive toward excess arsine, although the corresponding phosphine system readily forms the trisphosphine complex (see also ref. 13), and we have been unable to synthesize the $\text{HRuCl}(\text{AsPh}_3)_3$ complex.

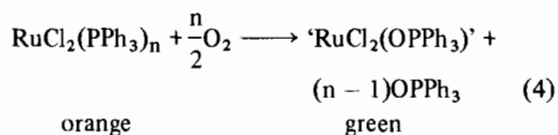
Formation of dioxygen complexes in solution is invariably exothermic [14] and is favoured at least thermodynamically at lower temperatures. Solutions of $\text{RuCl}_2(\text{AsPh}_3)_2$ or $\text{RuCl}_2(\text{PPh}_3)_2$ are completely unreactive toward O_2 in NN-dimethylformamide at -23°C or in toluene at -39°C , as studied by u.v./vis spectroscopy. A 10^{-3} M solution of $\text{RuCl}_2(\text{PPh}_3)_3$ in toluene at -39°C contains an equilibrium mixture of the tris- and bis-phosphine species [7], and under an O_2 atmosphere, the spectrum slowly changes to that of $\text{RuCl}_2(\text{PPh}_3)_2$ *i.e.* reaction (3) is pushed to the right due to removal of PPh_3 as the phosphine oxide.



By adding small amounts of O_2 from a gas-tight syringe it is possible to demonstrate that at 20°C , 0.5 mol O_2 will generate 1 mol OPPh_3 and 1 mol of $\text{RuCl}_2(\text{PPh}_3)_2$. Since neither free PPh_3 nor $\text{RuCl}_2(\text{PPh}_3)_3$ (fully formed by addition of excess phosphine) reacts with O_2 at the sub-zero temperature, the data imply that phosphine oxidation at these conditions occurs via attack of *external* phosphine

on a dioxygen moiety, presumably $\text{RuCl}_2(\text{PPh}_3)_2\text{O}_2$. Such a mechanism has been established for the related $\text{Pt}(\text{PPh}_3)_n/\text{O}_2$ systems [15].

At ambient temperatures, oxidation of $\text{RuCl}_2(\text{PPh}_3)_n$, $n = 2$ or 3 , (initially to green solutions which yield $[\text{RuCl}_2(\text{OPPh}_3)]_n$) occurs according to reaction (4) [4, 7].



and it now appears necessary to invoke an O-atom transfer mechanism [15] within $\text{RuCl}_2(\text{PPh}_3)_2\text{O}_2$, although the activation energy for this process must be greater than that for the intermolecular process. Stopped-flow measurements have failed to detect any intermediates for reaction (4) in benzene.

Acknowledgments

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References

- 1 G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **13**, 29 (1974).
- 2 L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).
- 3 M. M. Taqui Khan, R. K. Andal, and P. T. Manoharan, *Chem. Comm.*, 561 (1971); M. M. Taqui Khan and A. E. Martell, 'Homogeneous Catalysis by Metal Complexes', Vol. 1, Academic Press, New York, 1974, p. 103.
- 4 S. Cenini, A. Mantovani, A. Fusi and M. Keubler, *Gazz. Chim. Ital.*, **105**, 255 (1975).
- 5 B. W. Graham, K. R. Laing, C. J. O'Connor and W. R. Roper, *J. Chem. Soc. Dalton*, 1237 (1972).
- 6 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).
- 7 B. R. James and L. D. Markham, *Inorg. Chem.*, **13**, 97 (1974).
- 8 P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, **97**, 4221 (1975).
- 9 M. M. Taqui Khan and S. Vancheesan, *Proc. Department of Atomic Energy, India*, 1969, Vol. II, p. 58.
- 10 R. S. McMillan, A. Mercer, B. R. James and J. Trotter, *J. Chem. Soc. Dalton*, 1006 (1975).
- 11 D. Rose and G. Wilkinson, *J. Chem. Soc. A*, 1791 (1970).
- 12 R. K. Poddar and U. Agarwala, *J. Inorg. Nucl. Chem.*, **35**, 567 (1973); R. K. Poddar, I. P. Khuller and U. Agarwala, *Inorg. Nucl. Chem. Letters*, **10**, 221 (1974).
- 13 B. R. James, L. D. Markham and D. K. W. Wang, *Chem. Comm.*, 439 (1974).
- 14 B. R. James, 'Interaction of Dioxygen with Metalloporphyrins' in 'The Porphyrins', ed. D. H. Dolphin, Academic Press, New York, in press.
- 15 J. Halpern and A. L. Pickard, *Inorg. Chem.*, **9**, 2798 (1970).