Inorganica Chimica Acta, 20 (1976) L25 - L26
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

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

B. R. JAMES, L. D. MARKHAM, A. D. RATTRAY and D. K. W. WANG

Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1W5

(Received August 18, 1975)

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 $RuCl_2(AsPh_3)_3O_2$ [3]. which is said to be formed by reaction of O_2 with $RuCl_2(AsPh_3)_3$. We show here the non-existence of both of these complexes, and also report on our efforts to detect the more likely $RuCl_2(LPh_3)_2O_2$ complexes (L = As, P), often postulated as intermediates in catalytic oxidation reactions [4]. It should be pointed out that we consider the dioxygen complexes [5] $Ru(NO)X(PPh_3)_2O_2$ to be formally derivatives of ruthenium(0).

Experimental and Discussion

Solutions containing $RuCl_2(LPh_3)_2$ can be made by treatment of $RuCl_3(LPh_3)_2 \cdot CH_3OH$ 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 $RuCl_2(LPh_3)_2$ 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.

$$RuCl_3(LPh_3)_2 + 0.5\ H_2 \longrightarrow RuCl_2(LPh_3)_2 + HCl \qquad (1)$$

The visible spectrum of the $RuCl_2(PPh_3)_2$ solution is identical with that obtained during our study [7] of PPh_3 dissociation from $RuCl_2(PPh_3)_3$, and addition of PPh_3 to the resulting solution of reaction (1) gives the tris-phosphine complex. However, $RuCl_2(AsPh_3)_2$ 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 $RuCl_2(AsPh_3)_3$ by the reported procedure [9] from $RuCl_3 \cdot 3H_2O$ and $AsPh_3$, or via various precursors such as ruthenium(II) sulphoxides [10], the blue ruthenium solutions [11], or $RuCl_2(PPh_3)_3$ [6]. Such procedures give rise to $RuCl_3(AsPh_3)_3$, $RuCl_3(AsPh_3)_2 \cdot$solvent, or $[RuCl_2(AsPh_3)_2]_2$, or mixtures of these [12].

The reported [3] 1:1 O_2 absorption by $RuCl_2(AsPh_3)_3$ 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 $\nu_{As—O}$, and the paramagnetism and esr signals (assigned to a $Ru^{III}—O_2^-$ 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

$$\underset{880\ cm^{-1}}{RuCl_2(AsPh_3)_3O_2} \underset{O_2}{\overset{H_2}{\rightleftharpoons}} \underset{1960\ cm^{-1}}{HRuCl(AsPh_3)_3} \qquad (2)$$

sequence shown below:

$$\begin{tikzcd}
\text{Oxidised Ru solutions} \arrow[r, "H_2"] & Ru^{II}Cl_2(AsPh_3)_2 \arrow[d, "H_2"] \\
& HRu^{II}Cl(AsPh_3)_2 \arrow[ul, "O_2"]
\end{tikzcd}$$

The solutions containing triphenylarsine oxide complexes can be reduced by H_2 in solution back to $RuCl_2(AsPh_3)_2$, and this can undergo reaction with a further mol of H_2 to give the chlorohydrido complex. Again we find that solutions of $HRuCl(AsPh_3)_2$ 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 $HRuCl(AsPh_3)_3$ complex.

Formation of dioxygen complexes in solution is invariably exothermic [14] and is favoured at least thermodynamically at lower temperatures. Solutions of $RuCl_2(AsPh_3)_2$ or $RuCl_2(PPh_3)_2$ 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 $RuCl_2(PPh_3)_3$ 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 $RuCl_2(PPh_3)_2$ *i.e.* reaction (3) is pushed to the right due to removal of PPh_3 as the phosphine oxide.

$$RuCl_2(PPh_3)_3 \rightleftharpoons RuCl_2(PPh_3)_2 + PPh_3 \qquad (3)$$

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 $RuCl_2(PPh_3)_2$. Since neither free PPh_3 nor $RuCl_2(PPh_3)_3$ (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 $\mathrm{RuCl_2(PPh_3)_2O_2}$. Such a mechanism has been established for the related $\mathrm{Pt(PPh_3)_n/O_2}$ systems [15].

At ambient temperatures, oxidation of $\mathrm{RuCl_2(PPh_3)_n}$, n = 2 or 3, (initially to green solutions which yield $[\mathrm{RuCl_2(OPPh_3)}]_n$) occurs according to reaction (4) [4, 7].

$$\underset{\text{orange}}{\mathrm{RuCl_2(PPh_3)_n}} + \frac{n}{2}\mathrm{O_2} \longrightarrow \underset{\text{green}}{\text{‘}\mathrm{RuCl_2(OPPh_3)}\text{’} + (n-1)\mathrm{OPPh_3}} \qquad (4)$$

and it now appears necessary to invoke an O-atom transfer mechanism [15] *within* $\mathrm{RuCl_2(PPh_3)_2O_2}$, 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

We thank the N.R.C. for financial support, and Johnson, Matthey Ltd. for the loan of ruthenium.

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).