

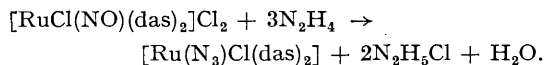
## A Di(tertiary arsine)-stabilized Dinitrogen Complex of Ruthenium

By P. G. DOUGLAS, R. D. FELTHAM,\* and H. G. METZGER

(Department of Chemistry, University of Arizona, Tucson, Arizona 85721)

**Summary** *trans*-[RuCl(N<sub>2</sub>)(das)<sub>2</sub>]PF<sub>6</sub> has been prepared by the reaction of a co-ordinated azide with NOPF<sub>6</sub> [(das) = *o*-phenylenebis(dimethylarsine)].

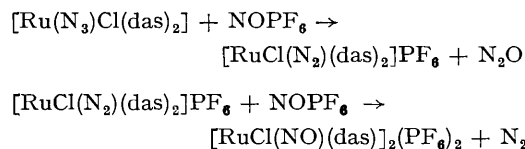
THE reaction of *trans*-[RuCl(NO)(das)<sub>2</sub>]Cl<sub>2</sub> with hydrazine has been reported<sup>1</sup> to yield [RuCl<sub>2</sub>N<sub>2</sub>(das)<sub>2</sub>]. We have now shown that the product is *trans*-[Ru(N<sub>3</sub>)Cl(das)<sub>2</sub>]. The reaction may be represented by the equation:



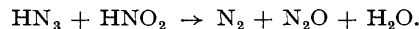
The azido-complex is characterized by elemental analysis† and i.r. absorptions at 2038 and 1317 cm<sup>-1</sup> (KBr pellet) due to antisymmetric and symmetric stretching frequencies of the azide ligand. Furthermore, *trans*-[Ru(N<sub>3</sub>)Cl(das)<sub>2</sub>] may be obtained independently by the reaction of *trans*-[RuCl<sub>2</sub>(das)<sub>2</sub>] with NaN<sub>3</sub> in boiling 2-methoxyethanol.

When the azido-complex is treated with an excess of NOPF<sub>6</sub> in methanol a mixture is obtained which contains

unchanged *trans*-[Ru(N<sub>3</sub>)Cl(das)<sub>2</sub>], *trans*-[RuCl(N<sub>2</sub>)(das)<sub>2</sub>]PF<sub>6</sub>, and *trans*-[RuCl(NO)(das)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, the relative proportions depending upon the reaction conditions. The reactions are thought to be:



The reaction of a co-ordinated azide with NO<sup>+</sup> is analogous to the known reaction:<sup>2</sup>



Other methods have been described for the conversion of co-ordinated azide ligands into N<sub>2</sub>.<sup>3,4</sup>

*trans*-[RuCl(NO)(das)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was isolated and had  $\nu(\text{N}\equiv\text{O})$  at 1865 cm.<sup>-1</sup> This complex may also be prepared

† All compounds had satisfactory elemental analyses.

directly by the reaction of *trans*-[RuCl(NO)(das)<sub>2</sub>]Cl<sub>2</sub> [ $\nu(\text{N}\equiv\text{O}) = 1883 \text{ cm}^{-1}$ ] with KPF<sub>6</sub> in water.

The dinitrogen complex *trans*-[RuCl(N<sub>2</sub>)(das)<sub>2</sub>]PF<sub>6</sub> was separated from the mixture by recrystallization from acetone-water. It is a white, diamagnetic solid, stable towards aerial oxidation, and thermally stable to 100°. On heating to 200° *in vacuo*, 93% of the theoretical amount of nitrogen is evolved. A  $5.5 \times 10^{-4}\text{M}$ -solution of the dinitrogen complex in acetone has an equivalent conductivity of  $156 \text{ ohm}^{-1}\text{mole}^{-1}\text{cm}^2$ , typical for a 1:1 electrolyte (*e.g.* for NPr<sup>n</sup><sub>4</sub>I,  $\Lambda = 152 \text{ ohm}^{-1}\text{mole}^{-1}\text{cm}^2$ ). The i.r. spectrum of [RuCl(N<sub>2</sub>)(das)<sub>2</sub>]PF<sub>6</sub> shows  $\nu(\text{N}\equiv\text{N})$  at  $2130 \text{ cm}^{-1}$  and  $\nu(\text{Ru}-\text{N})$  at  $494 \text{ cm}^{-1}$ , similar to the values found for other dinitrogen complexes of ruthenium(II).<sup>5</sup> The <sup>1</sup>H n.m.r. spectrum of [RuCl(N<sub>2</sub>)(das)<sub>2</sub>]PF<sub>6</sub> in (CD<sub>3</sub>)<sub>2</sub>SO shows two methyl singlets at  $\tau$  8.11 and 8.17 and hence is the *trans*-isomer. The *cis*-isomer would be expected to give a maximum of 8 lines in the <sup>1</sup>H n.m.r. spectrum.<sup>6</sup>

A <sup>15</sup>N-enriched sample of [RuCl(NO)(das)<sub>2</sub>]Cl<sub>2</sub> has been prepared and has  $\nu(\text{N}\equiv\text{O})$  at  $1851 \text{ cm}^{-1}$  (isotopic shift,  $\Delta = 32 \text{ cm}^{-1}$ , calc. =  $32 \text{ cm}^{-1}$ ). Treatment of [RuCl(<sup>15</sup>NO)(das)<sub>2</sub>]Cl<sub>2</sub> with hydrazine gives <sup>15</sup>N-enriched [Ru(N<sub>3</sub>)Cl(das)<sub>2</sub>] in which the <sup>15</sup>N atom is thought to be bonded to ruthenium. The antisymmetric azide stretch is found at  $2026 \text{ cm}^{-1}$  ( $\Delta = 12 \text{ cm}^{-1}$ ; observed for the free azide ion,<sup>7</sup>  $12 \text{ cm}^{-1}$ ). When this azido-complex is treated with NOPF<sub>6</sub>, the dinitrogen-containing product is [RuCl(<sup>15</sup>N<sup>14</sup>N)(das)<sub>2</sub>]PF<sub>6</sub> with  $\nu(\text{N}\equiv\text{N})$  at  $2095 \text{ cm}^{-1}$  ( $\Delta = 35 \text{ cm}^{-1}$ ; calc. =  $36 \text{ cm}^{-1}$ ). These i.r. data suggest that the nitrogen atom in [RuCl(NO)(das)<sub>2</sub>]Cl<sub>2</sub> remains bonded to ruthenium during the formation of the azido and dinitrogen complexes. Since both [RuCl(NO)(das)<sub>2</sub>]Cl<sub>2</sub> and [RuCl(N<sub>2</sub>)(das)<sub>2</sub>]PF<sub>6</sub> have the *trans*-configuration (from <sup>1</sup>H n.m.r.) the intermediate [Ru(N<sub>3</sub>)Cl(das)<sub>2</sub>] is also assumed to be *trans*.

We thank the National Science Foundation for support of this research.

(Received, June 1st, 1970; Com. 835.)

<sup>1</sup> R. D. Feltham, H. G. Metzger, and R. Singler, Proceedings XII International Conference on Co-ordination Chemistry, Sydney, 1969.

<sup>2</sup> L. F. Audrieth, *Chem. Rev.*, 1934, **15**, 169.

<sup>3</sup> L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 5295.

<sup>4</sup> L. A. P. Kane-Maguire, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 4609.

<sup>5</sup> A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.

<sup>6</sup> B. K. W. Bayliss and J. C. Bailar, *Inorg. Chem.*, 1970, **9**, 641.

<sup>7</sup> T. Theophanides and G. C. Turrell, *Spectrochim. Acta*, 1967, **23**, A, 1927.