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

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Summary *trans*-$[RuCl(N_2)(das)_2]PF_6$ has been prepared by the reaction of a co-ordinated azide with $NOPF_6$ [(das) = *o*-phenylenebis(dimethylarsine)].

THE reaction of *trans*-$[RuCl(NO)(das)_2]Cl_2$ with hydrazine has been reported[1] to yield $[RuCl_2N_2(das)_2]$. We have now shown that the product is *trans*-$[Ru(N_3)Cl(das)_2]$. The reaction may be represented by the equation:

$$[RuCl(NO)(das)_2]Cl_2 + 3N_2H_4 \rightarrow [Ru(N_3)Cl(das)_2] + 2N_2H_5Cl + H_2O.$$

The azido-complex is characterized by elemental analysis† and i.r. absorptions at 2038 and 1317 cm^{-1} (KBr pellet) due to antisymmetric and symmetric stretching frequencies of the azide ligand. Furthermore, *trans*-$[Ru(N_3)Cl(das)_2]$ may be obtained independently by the reaction of *trans*-$[RuCl_2(das)_2]$ with NaN_3 in boiling 2-methoxyethanol.

When the azido-complex is treated with an excess of $NOPF_6$ in methanol a mixture is obtained which contains unchanged *trans*-$[Ru(N_3)Cl(das)_2]$, *trans*-$[RuCl(N_2)(das)_2]PF_6$, and *trans*-$[RuCl(NO)(das)_2](PF_6)_2$, the relative proportions depending upon the reaction conditions. The reactions are thought to be:

$$[Ru(N_3)Cl(das)_2] + NOPF_6 \rightarrow [RuCl(N_2)(das)_2]PF_6 + N_2O$$

$$[RuCl(N_2)(das)_2]PF_6 + NOPF_6 \rightarrow [RuCl(NO)(das)]_2(PF_6)_2 + N_2$$

The reaction of a co-ordinated azide with NO^+ is analogous to the known reaction:[2]

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O.$$

Other methods have been described for the conversion of co-ordinated azide ligands into N_2.[3,4]

trans-$[RuCl(NO)(das)_2](PF_6)_2$ was isolated and had $\nu(N{\equiv}O)$ at 1865 cm.$^{-1}$ This complex may also be prepared

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† All compounds had satisfactory elemental analyses.

directly by the reaction of *trans*-$[RuCl(NO)(das)_2]Cl_2$ [$\nu(N \equiv O) = 1883\ cm^{-1}$] with KPF_6 in water.

The dinitrogen complex *trans*-$[RuCl(N_2)(das)_2]PF_6$ 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 $5{\cdot}5 \times 10^{-4}$M-solution of the dinitrogen complex in acetone has an equivalent conductivity of 156 ohm^{-1}mole^{-1}cm^2, typical for a 1 : 1 electrolyte (*e.g.* for $NPr^n{}_4I$, $\Lambda = 152$ ohm^{-1}mole^{-1}cm^2). The i.r. spectrum of $[RuCl(N_2)(das)_2]PF_6$ shows $\nu(N{\equiv}N)$ at 2130 cm^{-1} and $\nu(Ru{-}N)$ at 494 cm^{-1}, similar to the values found for other dinitrogen complexes of ruthenium(II).[5] The ^1H n.m.r. spectrum of $[RuCl(N_2)(das)_2]PF_6$ in $(CD_3)_2SO$ shows two methyl singlets at τ 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 ^1H n.m.r. spectrum.[6]

A ^{15}N-enriched sample of $[RuCl(NO)(das)_2]Cl_2$ has been prepared and has $\nu(N{\equiv}O)$ at 1851 cm^{-1} (isotopic shift, $\Delta = 32$ cm^{-1}, calc. = 32 cm^{-1}). Treatment of $[RuCl(^{15}NO)(das)_2]Cl_2$ with hydrazine gives ^{15}N-enriched $[Ru(N_3)Cl(das)_2]$ in which the ^{15}N atom is thought to be bonded to ruthenium. The antisymmetric azide stretch is found at 2026 cm^{-1} ($\Delta = 12$ cm^{-1}; observed for the free azide ion,[7] 12 cm^{-1}). When this azido-complex is treated with $NOPF_6$ the dinitrogen-containing product is $[RuCl(^{15}N^{14}N)(das)_2]PF_6$ with $\nu(N{\equiv}N)$ at 2095 cm^{-1} ($\Delta = 35$ cm^{-1}; calc. = 36 cm^{-1}). These i.r. data suggest that the nitrogen atom in $[RuCl(NO)(das)_2]Cl_2$ remains bonded to ruthenium during the formation of the azido and dinitrogen complexes. Since both $[RuCl(NO)(das)_2]Cl_2$ and $[RuCl(N_2)(das)_2]PF_6$ have the *trans*-configuration (from ^1H n.m.r.) the intermediate $[Ru(N_3)Cl(das)_2]$ is also assumed to be *trans*.

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