Notes

Synthesis of *cis*-$[Ru(NH_3)_4(acetone)_2]^{2+}$: A Valuable Precursor for *cis*-Tetraammineruthenium(II) Chemistry

T. Sugaya and M. Sano*

Graduate School of Human Informatics and College of General Education, Nagoya University and Presto21,[†] Nagoya 464-01, Japan

Received July 2, 1993

The chemistry of ruthenium ammine complexes has been an area of considerable activity in the last three decades.[1] The $[Ru(NH_3)_5(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4(SO_2)Cl]^+$ complexes are useful synthetic intermediates for the preparation of a variety of pentaammine and *trans*-tetraammine complexes, respectively.[2]

In the preparation of *cis*-tetraammineruthenium complexes, the usual precursor is *cis*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$, which is prepared by the reduction of $[Ru(NH_3)_4Cl_2]^+$ with Zn/Hg in acidic aqueous solution. However, this must be used immediately after the preparation without any storage. A desired product frequently contains impurities, and its purification involves empirical and complex techniques.

Below we present the synthesis of *cis*-$[Ru(NH_3)_4(acetone)_2](PF_6)_2$, which we find to be a versatile precursor for *cis*-tetraammineruthenium(II) chemistry.

Synthesis of *cis*-$[Ru(NH_3)_4(acetone)_2](PF_6)_2$ (1)

A 150-mg amount of *cis*-$[Ru(NH_3)_4Cl_2]Cl$[3] was dissolved in 9 mL of water adjusted to approximately pH 2 with CF_3COOH. To this was added 2.0 g of Zn(Hg), and the solution was stirred for 8 min. The resulting brown solution was filtered. Addition of 4.5 g of NH_4PF_6 precipitated the light yellow solid *cis*-$[Ru(NH_3)_4(H_2O)_2](PF_6)_2$. The solid was filtered off, washed with ethanol, and dried under vacuum. Then 174 mg of *cis*-$[Ru(NH_3)_4(H_2O)_2](PF_6)_2$ was dissolved in 2 mL of acetone, and the solution was stirred for 10 min. When 2 mL of ether was added slowly to the solution, an orange flake-like solid *cis*-$[Ru(NH_3)_4(acetone)_2](PF_6)_2$ formed. After further addition of 2 mL of ether, the solid was filtered off, washed with ether, and dried under vacuum. At 0 °C, **1** can be stored for several weeks as a solid under argon. Anal. Calcd for $[Ru(NH_3)_4(OC(CH_3)_2)_2](PF_6)_2$: C, 12.53; H, 4.21; N, 9.74. Found: C, 12.72, H, 4.19; N, 9.89. ^1H NMR (270 MHz, acetone-d_6): δ 2.68 (cis NH_3, 6H, br), 3.08 (cis NH_3, 6H, br). Cyclic voltammetry (acetone, 0.1 M *n*-Bu_4NPF_6, 100 mV s^{-1}): $E_{1/2} = 0.52$ V (NHE).

Electrochemical data for **1** showed a reversible couple which suggested that the acetones are bound to the metal center in an η^1-fashion at the O-position.[4] A dynamic NMR experiment yields as k for exchange of the coordinated acetones with solvent acetone the value 13 s^{-1} (30 °C).

We find that **1** reacts efficiently with dienes, isonitriles, and sulfoxides, as well as more conventional ligands[5] (Figure 1). General methods for the preparation of *cis*-tetraammineruthenium(II) derivatives are described as follows.

General Preparation of *cis*-$[Ru(NH_3)_4(ligand)_2](PF_6)_2$

In a typical preparation, 100 mg of **1** was dissolved in 2 mL of acetone. An excess of the desired ligand was added (200 mg), and the solution was stirred for 30 min. The solution was filtered, and the filtrate was treated with CH_2Cl_2. The resulting precipitate was filtered off and washed with CH_2Cl_2. The solid was redissolved with acetone, and then the solution was treated with CH_2Cl_2. The resulting precipitate was filtered off and washed with CH_2Cl_2 and ether.

General Preparation of *cis*-$[Ru(NH_3)_4(ligand)(ligand)](PF_6)_2$

One hundred milligrams of **1** was dissolved in 2 mL of acetone. A desired ligand (1:1 molar ratio) was added, and the solution was stirred for 30 min. The solution was filtered, and the filtrate was treated with CH_2Cl_2. The resulting precipitate was filtered off and washed with CH_2Cl_2. The solid was redissolved with acetone, and the solution was treated with CH_2Cl_2. The resulting precipitate was filtered off and was confirmed as a salt of approximate formula *cis*-$[Ru(NH_3)_4(ligand)(acetone)]^{2+}$ by NMR.

The above compound was dissolved in 2 mL of acetone. A desired ligand (1:1 molar ratio) was added, and the solution was

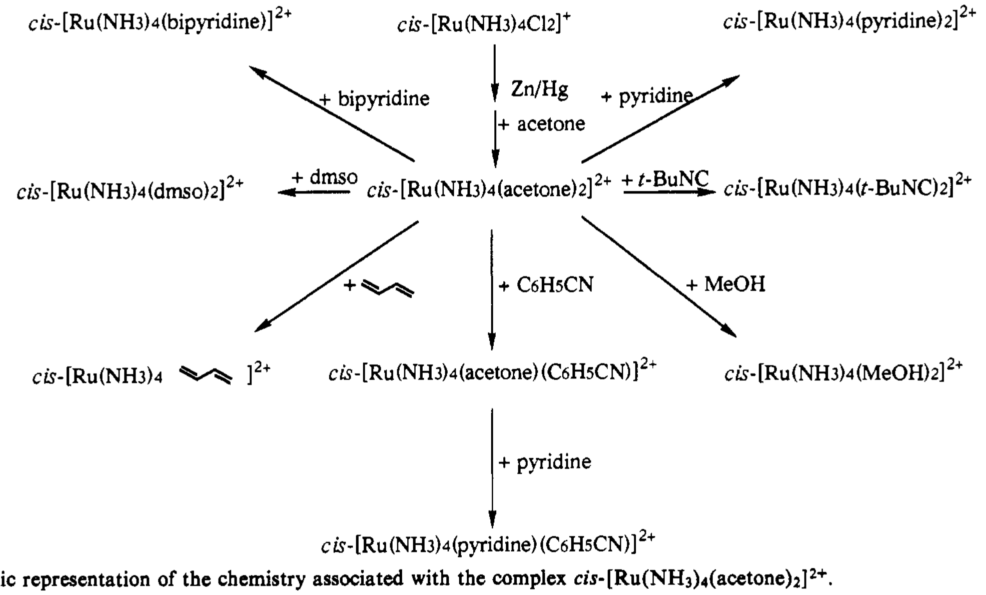

Figure 1. Schematic representation of the chemistry associated with the complex *cis*-$[Ru(NH_3)_4(acetone)_2]^{2+}$.

0020-1669/93/1332-5878$04.00/0

stirred for 30 min. The solution was filtered, and the filtrate was treated with CH_2Cl_2. The resulting precipitate was filtered off and washed with CH_2Cl_2. The solid was redissolved with acetone, and the solution was treated with CH_2Cl_2. The resulting precipitate was filtered off and washed with CH_2Cl_2 and ether.

In the addition of an excess ligand to the bis(acetone) complex, the monosubstituted complex was formed within 3 min and the bis complex was generated within 10 min at room temperature.[6] The reaction of a 1:1 molar ratio was even completed within 10 min[6] to form *cis*-$[Ru(NH_3)_4(ligand)(acetone)]^{2+}$.[7] However, we could not obtain bis-substituted tetraammine compounds with bulky ligands such as diphenyl sulfoxide because of ligand–ligand repulsion.

A desired product was easily precipitated by the addition of CH_2Cl_2 and/or ether. The resulting solid was redissolved in acetone and was reprecipitated by the addition of CH_2Cl_2, a procedure which results in adequate purification.

For the vast majority of reactions that we have investigated,[8] we find **1** to be a convenient precursor for *cis*-tetraammineruthenium(II) chemistry.

Acknowledgment. Support of this work by the Yazaki Foundation and the Nihon Shoken Foundation is gratefully acknowledged.

[†] Presto21 is a department of the Research Development Corp. of Japan.

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 887.

(2) Gleu, K.; Rehm, K. *Z. Anorg. Allg. Chem.* **1936**, *227*, 237.

(3) Pell, S. D.; Sherban, M. M.; Tramontano, V.; Clarke, M. J. *Inorg. Synth.* **1989**, *26*, 65. There are some impurities in this method. We usually pufified *cis*-$[Ru(NH_3)_4Cl_2]Cl$ by SP-Sephadex C-25 column chromatography (0.1 M HCl).

(4) Powell, D. W.; Lay, P. A. *Inorg. Chem.* **1992**, *31*, 3542.

(5) The products were analyzed in situ by electrochemical and NMR techniques. A more complete characterization of the diene and sulfoxide complexes will be reported separately.

(6) The reaction was followed by cyclic volammetry.

(7) A reaction yield of 90% was obtained for *cis*-$[Ru(NH_3)_4(C_6H_5CN)(acetone)]^{2+}$ by NMR.

(8) Sugaya, T.; Sano, M. To be published. Tomita, A.; Sano, M. To be published.