tertiary phosphines affect in diverse ways the reductive elimination of alkanes from transition-metal dialkyl complexes.[5,6a,c]

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Platinum(II) Complexes of Tridentate Bis(2-aminoethyl)methylamine

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In the course of preparing the trans-spanned platinum(II) complex [Pt(*sym*-medien·HCl)$(NH_3)_2$]Cl_2,[1] the iodo iodide [Pt (*sym*-medien)I]I was prepared by the method of Watt and Cude.[2]

By the methylation of iodo(diethylenetriamine)platinum(II) iodide, [Pt(dien)I]I, Watt and Cude obtained what they believed to be symmetrical product [Pt(medien)I]I. They attributed this rather surprising result to the secondary trans effect in the I–Pt–N–H chain. Their identification of the product was based on the fact that their product was different from the analogous compound prepared from a commercial sample of the diamine that was said to be the unsymmetrical isomer.

Our results do not agree with those of Watt and Cude in regard to the position of the methyl group in the triamine ligand. The discrepancies are important because the position at which methylation occurred in the complex is the crux of their discussion concerning the secondary trans effect in platinum(II) complexes.

We have synthesized the symmetrical isomer of [Pt(medien)X]X by using the triamine of which the structure had been fully determined by the method of synthesis, as well as NMR and IR spectra.

Experimental Section

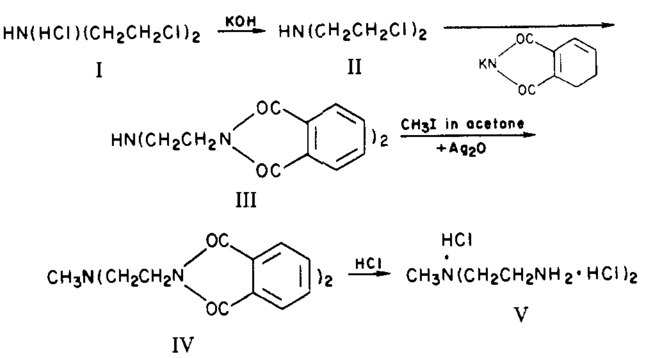
Symmetrical *N*-methyldiethylenetriamine was synthesized by the phthalamide synthesis as described by Mann (Scheme I).[3] Anal. Calcd for $C_5H_{18}N_3Cl_3$ (V): C, 26.65; H, 8.00; N, 18.50; Cl, 46.95. Found: C, 26.46; H, 8.05; N, 18.25; Cl, 46.62.

[Pt(*sym*-medien)I]I. Symmetrical *N*-methyldiethylenetriamine trihydrochloride (medien·3HCl) was converted to the free amine by treatment with Ag_2O, and the amine was made to react with $PtI_2\cdot H_2O$ to form [Pt(medien)I]I according to the method of Watt and Cude.[2] Anal. Calcd for $C_5H_{15}N_3I_2Pt$: C, 10.70; H, 2.66; N, 7.44; I, 44.60; Pt, 34.50. Found: C, 10.63; H, 2.71; N, 7.49; I, 44.72; Pt, 34.35.

Results and Discussion

The formation of $CH_3N(CH_2CH_2NH_2)_2$ through the phthalimide synthesis shows that methylation occurs exclusively on the central nitrogen atom of the triamine. This is confirmed by the NMR spectrum, which was compared with that of 1,4,7-trimethyldiethylenetriamine, in which the peaks of the methyl groups are easily identified by their relative intensities. The chemical shift values of the methyl group in the *N*-methyldiethylenetriamine synthesized in this way agree very well with that of the central methyl group of 1,4,7-trimethyldiethylenetriamine. Also, the IR spectrum of our *N*-methyldiethylenetriamine trihydrochloride shows an absorption band of medium intensity at 1990 cm^{-1}, which is attributed to the stretching vibration of the N–H bond in the tertiary amine.[4] No peak was found in the 2700-cm^{-1} region, where the absorption due to the N–H stretching vibration of a secondary ammonium ion would be expected.[4]

Scheme I



Platinum Complexes of *N*-Methyldiethylenetriamine. Watt and Cude[2] reported that one of the nitrogen atoms in [Pt(dien)I]I is methylated by methyl iodide in liquid ammonia at −70 °C in the presence of potassium amide. From the NMR spectrum of the product and a comparison of its IR spectrum with that of supposed unsymmetrical [Pt(medien)I]I, but without comparison with that of the isomer containing symmetrical medien, they concluded that the product was [Pt(*sym*-medien)I]I, in other words that the methylation occurred on the central nitrogen atom of the ligand, *trans to the coordinated iodine atom*.

Watt and Cude obtained their medien from K & K Laboratories, Inc., and used it without further purification. We also obtained a sample of medien from K & K Laboratories; the NMR data indicate that it is a mixture of the two isomers in the ratio of *sym* to *unsym* of 1.24 to 1.0, although it is labeled "*N′*-medien". On the basis of the greater reactivity of the primary amine groups as compared with that of the secondary amine, it is possible that only the symmetrical medien reacts with PtI_2 in spite of the presence of the unsymmetrical isomer in the mixture. This suggestion is supported by the fact that our attempts to prepare [Pt(*unsym*-medien)I]I by the same method that we used to make [Pt(*sym*-medien)I]I were unsuccessful.

Secondary Trans Effect. The data on the secondary trans effect which Watt and Cude[2] give and which led to their conclusions must be reconsidered; although they tried to determine on which nitrogen atom the methylation occurred, they unfortunately had the wrong triamine for comparison. The results of the present investigation indicate that the methyl group was on a terminal nitrogen atom rather than on the central one. This is what would be expected, for the terminal primary nitrogen atoms are more reactive than the secondary ones, and in this case, they offer four reaction sites instead of one. Moreover, in the free ligand, methylation occurs on the primary amine.[5]

We must conclude that in Watt and Cude's experiment methylation occurred on the nitrogen atom cis to the iodo group and that the trans effect is not strong enough to provoke the change in the relative reactivities of N–H bonds of coordinated dien.

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