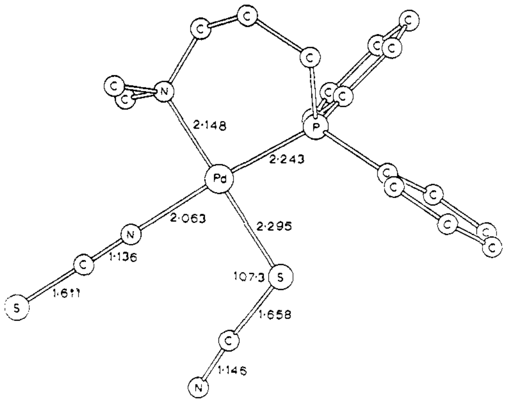

Figure 1. A view of the isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane)palladium(II) molecule normal to the plane of the four donor atoms. The estimated standard deviations for the bond lengths are Pd–S or –P, 0.002 Å; P–N, 0.007 Å; C–S, 0.008 Å; and C–N, 0.011 Å.

the molecule. The near equality of the C–S and C–N bonds support this view.

The two Pd–N bonds[7] are both significantly longer than the Pd–N distances found in other palladium complexes.[8] The fact that the Pd–P distance is slightly shorter than the Pd–S distance, and both are shorter than expected when compared with the Pd–N distances,[9] suggests a *trans* effect. The relative "softness" and "hardness" of the four donor atoms is in agreement with this hypothesis. Therefore, the mixed thiocyanato coordination may be rationalized on the basis of a competition for π back-bonding between the amino and phosphino donors and the N and S ends of the thiocyanate ions.

Acknowledgment. We wish to acknowledge support of this research by the National Science Foundation (Grants No. GP-5729 and GP-8365 to D. W. M.) and the National Research Council of Canada (Grant A3707 to G. J. P.).

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(7) The difference in the two Pd–N bond lengths may be accounted for in part by a difference in hybridization in the two atoms.

(8) A summary of Pd–N bond lengths has been given by R. C. Braun and E. C. Lingafelter, *Acta Cryst.*, 22, 787 (1967).

(9) A comparison of the corresponding C–N, C–P, and C–S bonds, where no π bonding is possible, suggests that Pd–N would be 0.37 Å shorter than Pd–P and 0.35 Å shorter than Pd–S in the absence of any other effects.

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Thermal *trans* to *cis* Rearrangement of $(CO)PtCl_2(NH_2R)$

Sir:

The catalytic activity of the platinum group metals in homogeneous systems depends either on the external attack of a reagent on a coordinated ligand or the interaction between two ligands simultaneously coordinated.[1] In the latter process, the interacting ligands are probably *cis* in the square-planar complexes $(CO)PtCl_2(L)$ (**1**).

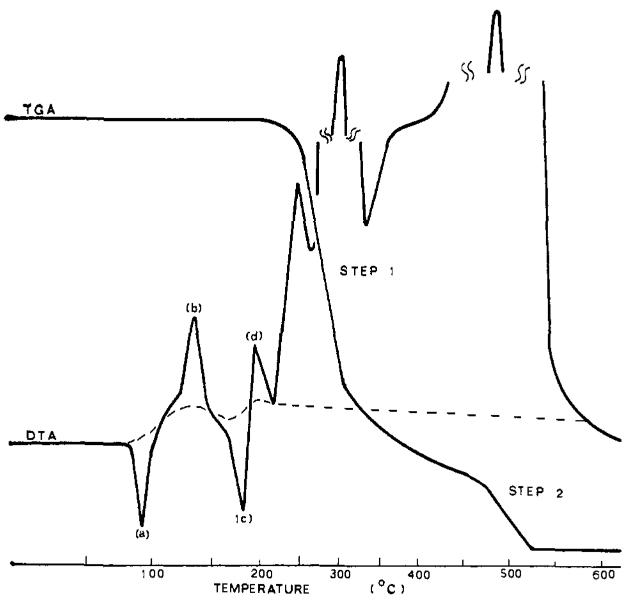

Figure 1. DTA/TGA curve of *trans*-$PtCl_2(CO)(NH_2CH(CH_3)C_6H_5)$: step 1, loss of CO and $NH_2CH(CH_3)C_6H_5$; step 2, decomposition of $PtCl_2$. (Steps refer to TGA curve: step 1, 200–350°; step 2, >350°.)

However, direct synthesis of *cis*-platinum(II) carbonyl complexes is tedious if not difficult, whereas the *trans* isomers are rather readily available by the route from Zeise's salt. For example, with an amine, L

$$[(C_2H_4)PtCl_3]^- + L \longrightarrow$$

$$trans\text{-}(C_2H_4)PtCl_2(L) \xrightarrow{CO} trans\text{-}(CO)PtCl_2L$$

or alternately

$$[(C_2H_4)PtCl_3]^- + CO \longrightarrow [(CO)PtCl_3]^- \xrightarrow{L} trans\text{-}(CO)PtCl_2L$$

The direct rearrangement of *trans* → *cis* in this series has not been documented, although very recently a thermal rearrangement of $(DMSO)PtCl_2(NH_2R)$ has been established.[2] We now wish to report that we have inadvertently achieved the direct thermal rearrangement of the pure *trans* carbonyl complex **1** [L = (+)-$NH_2CH(CH_3)C_6H_5$] to the *cis* isomer.

In a study of the thermal behavior of *trans*-**1** [L = (+)-$NH_2CH(CH_3)C_6H_5$], a DTA/TGA analysis was performed. The characteristics of the analysis, Figure 1, led us to suspect the *trans* → *cis* rearrangement. The DTA curve, Figure 1, shows that on heating this complex two peaks appear below 150°, neither of which is accompanied by a weight loss. The endothermic peak (a) at ~90° is assigned to fusion of the *trans* isomer. The exothermic peak (b) at ~140° corresponds to the crystallization of the isomeric and more stable *cis* complex formed by thermal rearrangement in the liquid phase. The next (endothermic) peak (c) corresponds to fusion of the *cis* isomer. The peaks in the DTA curve which occur above 180° suggest decomposition because the TGA curve shows a sharp weight loss at about this temperature. This decomposition occurs (TGA curve) in two major steps. The per cent weight

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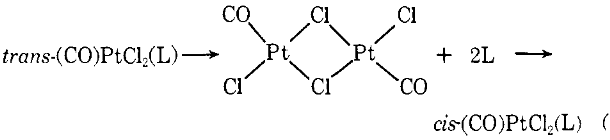
(1) For a review see E. W. Stern, *Catal. Rev.*, 1, 73 (1967).

(2) Yu. N. Kukushkin, Yu. E. Vyaz'menskii, and E. S. Postnikova, *Chem. Abstr.*, 71, 27055 (1969).

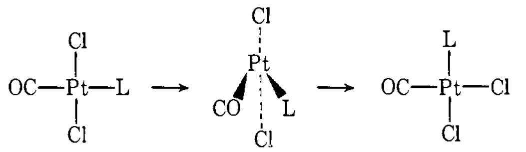
loss in the first step ($\sim$200°) corresponds very closely to the loss of both organic ligands. It is not known at this time whether the CO comes off as such, or is combined with the amine, *e.g.*, as the amide. The second stage loss corresponds to the decomposition of $PtCl_2$ to metal.

In another experiment, the heating was interrupted at about 120°, the material dissolved in acetone, and the solution examined in the infrared. The carbonyl stretching band appeared at 2109 cm^{-1}, identical in shape and position with that of authentic *cis* isomer. The original *trans* complex in acetone had $\nu_{C\equiv O}$ of 2126 cm^{-1}. Infrared examination of samples heated to 70° showed only *trans* present, while between 95 and 110° both isomers are present and at 120° only the *cis* isomer is present.

Because of the implications for catalytic reactions, the *trans* → *cis* rearrangement is of intrinsic interest. At least two possible routes (a and b) to such a rearrangement need be considered. Mechanism a or any related mechanism involving free L appears unlikely since we have been able to also achieve the rearrangement of *trans*-**1** (L = $NH_2CH_2CH_2CH_3$) to the *cis* isomer at 115°, a temperature appreciably higher than the boiling point (49°) of *n*-propylamine. Route b involves the intermediacy of a tetrahedral configuration. Even though such complexes of Pt(II) have been proposed,[3] they have never, to our knowledge, been shown to exist. Such an intermediate would provide a low-energy path to the isomerization. Studies designed to demonstrate a tetrahedral intermediate are under investigation.



(a)



(b)

The DTA/TGA curves were obtained using a Mettler thermoanalyzer-2. The sample chamber was swept with air and heated at a rate of 15°/min. The complexes *cis*- (melting with decomposition from 180 to 200°) and *trans*-$(CO)PtCl_2[(+)\text{-}NH_2CH(CH_3)C_6H_5]$ (mp 71–73°) and the *trans*-$(CO)PtCl_2(NH_2CH_2CH_2CH_3)$ (mp 48–49°) are new complexes prepared using known procedures.[4-6] All complexes gave satisfactory analyses. The infrared spectrum of the *trans*-*n*-propylamine complex had $\nu_{C\equiv O}$ of 2125 cm^{-1} and after heating at 115°, $\nu_{C\equiv O}$ shifted to 2109 cm^{-1}. The carbonyl bands are essentially identical with those in the spectra of the *cis*- and *trans*-$(CO)PtCl_2[(+)\text{-}NH_2CH(CH_3)C_6H_5]$.

Acknowledgment. We are grateful to Mettler Instrument Company for determining the DTA/TGA curves and to Englehard Industries, Inc., for a generous supply of platinum. We also wish to thank the donors to the Petroleum Research Foundation of the American Chemical Society for partial support of this research. The possibility of tetrahedral intermediacy was brought out in a discussion with Dr. I. Mador. One of us (R. E.) thanks the Procter and Gamble Co. for a fellowship.

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(3) For a discussion of tetrahedral intermediates in Pt(II) complexes, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967, p 427.

(4) A. Panunzi and G. Paiaro, *J. Amer. Chem. Soc.*, **88**, 4843 (1966).

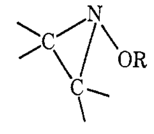
(5) G. Paiaro and A. Panunzi, *ibid.*, **86**, 5148 (1964).

(6) T. A. Weil, P. Schmidt, M. Rycheck, and M. Orchin, *Inorg. Chem.*, **8**, 1002 (1969).

Stable Nitrogen Pyramids. IV. 1-Alkoxyaziridines. A New Aziridine Synthesis *via* O-Nitrenes

Sir:

The hypothesis[1] that 1-alkoxyaziridines should exhibit high pyramidal stability at room temperature prompted the synthesis of I for nmr spectroscopic study. Since the known synthetic routes[2] to the few reported 1-alkoxyaziridines appeared unadaptable to the preparation of our model aziridines, we investigated the intriguing possibility of adding the hitherto unknown[3] O-nitrenes to alkenes, by analogy with the addition of C- and N-nitrenes to olefins.[4] In this communication, we wish to present persuasive evidence for the existence of O-nitrenes and more importantly, describe the facile addition of alkoxynitrenes to alkenes as a new route to pyramidally stable aziridines.



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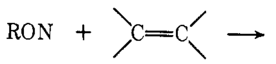
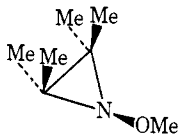


Accordingly, the oxidation of methoxyamine with lead tetraacetate in the presence of excess tetramethylethylene at −50° afforded 1-methoxy-2,2,3,3-tetramethylaziridine (II) in *ca.* 30% yield. Analytically pure product was obtained by preparative gas chromatography.



II

The 1-alkoxyaziridine (II) featured a mass spectrum which contained the molecular ion peak at *m*/*e* 129 and a base peak at *m*/*e* 98. The appearance of the latter peak indicates that the dominant mode of fragmentation of II upon electron impact involves scission of the labile nitrogen–oxygen bond. The infrared spectrum

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(1) S. J. Brois, *Trans. N. Y. Acad. Sci.*, **31**, 931 (1969).

(2) (a) H. J. Backer, *Rec. Trav. Chim. Pays-Bas*, **69**, 1223 (1950); (b) V. A. Tartakovskii, O. A. Lukyanov, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **12**, 2246 (1966).

(3) J. H. Boyer and J. D. Woodyard, *J. Org. Chem.*, **33**, 3329 (1968).

(4) (a) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964); (b) J. S. McConaghy and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 3457, 4450 (1967); (c) R. S. Atkinson and C. W. Rees, *Chem. Commun.*, 1230 (1967); (d) W. Nagata, S. Hirai, K. Kawata, and T. Aoki, *J. Amer. Chem. Soc.*, **89**, 5045 (1967); (e) D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Commun.*, 146 (1969).