by the addition of cyclohexanol, while the rate of the PCA–Ni^{2+} catalyzed reaction is unaffected by added cyclohexanol. Also consistent with this interpretation is the observation that 8-acetoxy-5-quinolinesulfonate (AQS), a molecule which does not fit into the cyclohexaamylose cavity, is only 57% as reactive toward II as toward PCA–Ni^{2+}. That in fact AQS is not bound into the cavity of II is further evident from the inability of cyclohexanol to inhibit the reaction of II with AQS. The dissociation constant for the II–*p*NPA complex must be greater than 0.05 *M* since saturation kinetics were not observed. Accordingly V_{max} for the acyl transfer under our conditions is at least 1 min^{-1}. Turnover occurs, and at pH 5.17 and 30.0° the overall pseudo-first-order rate constant, corresponding to the hydrolysis of the acetylated intermediate, is $3.95 \pm 0.60 \times 10^{-3}$ min^{-1}.

It should be pointed out that in contrast to the intracomplex reaction[4] of *m*-nitrophenyl acetate with cycloamylose at high pH, the present reaction occurs rapidly near neutrality (both the acylation and deacylation are base catalyzed,[5] and the rate of hydrolysis at pH 7.0 would be even greater than that observed at pH 5.1). However, the extent to which the very effective catalysis by our functional group has been increased by hydrophobic binding is only modest, of the same general magnitude as Cramer has observed[6] for some imidazole-substituted cycloamyloses. Presumably the difficulty is that even though models show that the PCA oxygen can reach the acetyl group of bound *p*NPA, several degrees of rotational freedom must be frozen for this to occur. As greater rigidity is built into the catalyst this problem should diminish.[7,8]

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(6) F. Cramer and G. Mackensen, *Angew. Chem. Intern. Ed. Engl.*, **5**, 601 (1966).

(7) Support of the work by the National Institutes of Health, through a research grant and a postdoctoral fellowship to L. E. O., is gratefully acknowledged.

(8) NOTE ADDED IN PROOF. We have recently found a related phenomenon in the observation that the copper(II) complex of I is a six fold better catalyst for the hydrolysis of the *p*-nitrophenyl ester of glycine than is an equivalent concentration of copper(II) or the copper(II) pyridine-2,5-dicarboxylic acid complex. This acceleration is also competitively inhibited by added cyclohexanol.

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A Molecular Palladium(II) Complex Containing Both Sulfur- and Nitrogen-Bonded Thiocyanate Groups

Sir:

Metal complexes containing both S- and N-bonded nonbridging thiocyanate ions have been difficult to prepare. Although preparation of S- and N-bonded complexes has been claimed on the basis of infrared and other evidence,[1] no X-ray studies have been carried out on these compounds.[2] Since the bonding of thiocyanate to palladium appears to be strongly influenced by the other ligands,[3] mixed chelating ligands have been utilized to prepare the elusive mixed thiocyanate complexes.[4] We report herein the first X-ray structural study of a mixed thiocyanato–isothiocyanato complex, Pd(PN)(NCS)(SCN), where PN is $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$.[5]

The complex Pd(PN)(NCS)(SCN) is a nonelectrolyte in nitromethane ($\Lambda_M = 4.2$ cm^2 ohm^{-1} mol^{-1}). The infrared spectrum of the solid (Nujol mull) has a very sharp peak at 2120 cm^{-1} and a relatively broader peak at 2080 cm^{-1}, while in dichloromethane the sharp peak is at 2125 cm^{-1} and the broad peak at 2087 cm^{-1}. These results suggest that the mixed mode of thiocyanate coordination is present in both the solid and in solution.

The orange, polyhedral crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions of a = 11.684 (3), b = 12.961 (4), c = 14.641 (3) Å, and β = 110.04 (1)°. The density calculated for four molecules per unit cell is 1.574 g/cm^3, and the observed density is 1.567 g/cm^3. Three-dimensional intensity data were measured using Cu Kα radiation and an automatic diffractometer. All the unique reflections with $2\theta \leq 135°$ were measured followed by a measurement of all the reflections within these limits in a hemisphere defined by our quarter-circle single-crystal orienter. After averaging the equivalent reflections, 2176 reflections were considered to be observed and used in the analysis.

The structure was solved by locating the palladium atom in the Patterson function and the light atoms in successive Fourier syntheses. The structure was refined by least-squares methods using individual isotropic and then anisotropic thermal parameters for all atoms. The refinement converged to an *R* (the usual residual) of 4.1%. No attempt was made to locate the hydrogen atoms.

The palladium atom is square planar with the four donor atoms being the phosphorus and nitrogen atoms from the PN ligand and one nitrogen and one sulfur atom from each thiocyanate group. The molecule projected onto the plane of the four coordinated atoms is illustrated in Figure 1. The two palladium thiocyanate linkages are different, and thus the compound is correctly formulated as Pd(PN)(SCN)(NCS), isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane)palladium(II).

The steric constraints imposed by the PN ligand require the thiocyanate groups to be *cis* coordinated. The observed structure has the Pd–SCN bond *trans* to the amine nitrogen atom and the Pd–NCS linkage *trans* to the phosphorus atom. The Pd–S–CN angle is 107.3 (3)° and the Pd–N–CS angle is 177.7 (6)°. Other metal isothiocyanates have M–N–CS angles as low as 156°, whereas metal thiocyanates have M–S–CN angles up to 120°.[6] These results suggest that $Pd{-}N{\equiv}C{-}S$ and $Pd{-}S{-}C{\equiv}N$ are the major resonance forms in

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(1) (a) I. Bertini and A. Sabatini, *Inorg. Chem.*, **5**, 1025 (1966); (b) G. C. Kulasingam and W. R. McWhinnie, *Chem. Ind.* (London), 2200 (1966); (c) K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966); (d) P. E. Nicpon and D. W. Meek, *ibid.*, **6**, 145 (1967); (e) A. J. Carty and A. Efraty, *Can. J. Chem.*, **47**, 2573 (1969).

(2) A referee pointed out that the formulation of Cu(tren)(NCS)(SCN)[1c] was contrary to the infrared and conductance data which suggested an ionic five-coordinated species. Subsequently, P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, **89**, 6131 (1967), demonstrated that the compound was indeed $[Cu(tren)(NCS)]^+SCN^-$.

(3) D. J. Hewkins and A. J. Poe, *J. Chem. Soc., A*, 1884 (1967), and J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966), and references contained therein.

(4) D. W. McPeek, P. E. Nicpon, and V. I. Meek, *J. Amer. Chem. Soc.*, in press; C. A. McAuliffe and D. W. Meek, *ibid.*, in press.

(5) *Anal.* Calcd for $C_{19}H_{22}N_3PPdS_2$: C, 46.20; H, 4.49; S, 12.98. Found: C, 46.19; H, 4.68; S, 13.10.

(6) A summary of the dimensions can be found in ref 2.

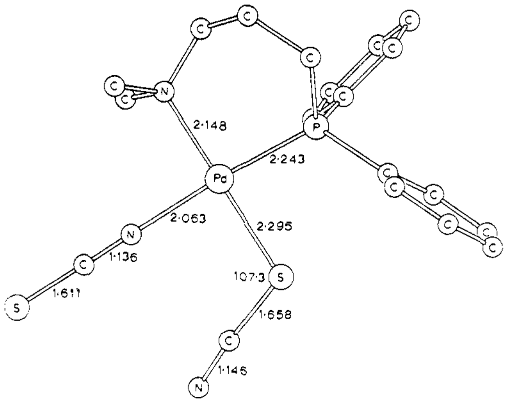

Figure 1. A view of the isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane)palladium(II) molecule normal to the plane of the four donor atoms. The estimated standard deviations for the bond lengths are Pd–S or –P, 0.002 Å; P–N, 0.007 Å; C–S, 0.008 Å; and C–N, 0.011 Å.

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.

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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$_2$R)

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**).

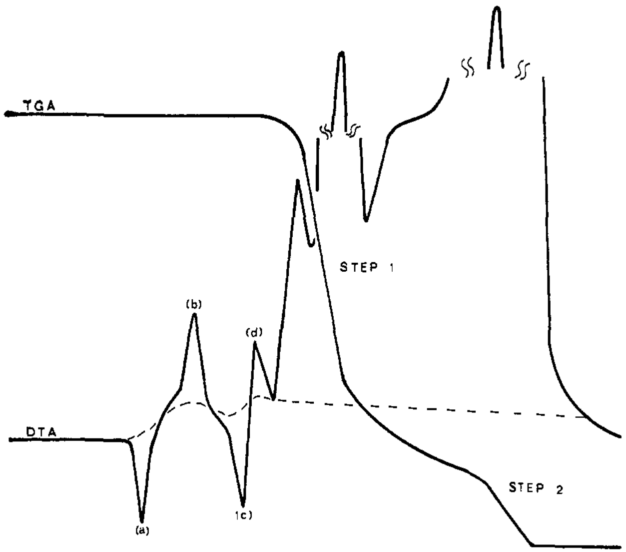

Figure 1. DTA/TGA curve of *trans*-PtCl$_2$ (CO)(NH$_2$CH(CH$_3$)C$_6$H$_5$): step 1, loss of CO and NH$_2$CH(CH$_3$)C$_6$H$_5$; step 2, decomposition of PtCl$_2$. (Steps refer to TGA curve: step 1, 200–350°; step 2, >350°.)

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$_2$R) 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$_2$CH(CH$_3$)C$_6$H$_5$] to the *cis* isomer.

In a study of the thermal behavior of *trans*-**1** [L = (+)-NH$_2$CH(CH$_3$)C$_6$H$_5$], 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).