The ylides from **1**, **2**, and **3** are stronger bases than hydroxide by only 2–4 pK_a units, yet react with water with limiting rates. It therefore seems likely that an Eigen plot[4a] of log k *vs.* ΔpK_a for these reactions will show an abnormally small pK_a region for which neither forward nor reverse rates are limiting. We conjecture that high rates for proton transfers with small driving forces will prove general for highly localized carbanions reacting in protic media, and that the moderate activation required for proton transfers between oxygen anions of comparable strength[4a] may reflect the strengths of hydrogen bonds to these anions, rather than a general property of aqueous proton transfers.

The above data set limits on the rates of reactions catalyzed in water by thiazolium yields. For example, for diffusion-controlled reaction of the ylide from **1** with a substrate S at pH 7, the maximum rate is $(10^{-2}–10^{-3})[S][\mathbf{1}]$ M sec^{-1} in water and $(10^{-1}–10^{-2})[S][\mathbf{1}]$ M sec^{-1} in 50% ethanol.[7] The observed rate constant for formation of benzoin from 1 M benzaldehyde at 30° in 50% ethanol containing 0.1 M **1**, pH 7.5, is 3×10^{-6} M^{-1} sec^{-1}, which is only 10^4–10^5 slower than the maximum estimated above for rate-determining ylide attack.

By contrast, yeast pyruvate decarboxylase, a thiamine pyrophosphate dependent enzyme, reacts with 0.01 M pyruvate at pH 6, 30°, with a turnover number of *ca.* 50 sec^{-1}.[8] The enzyme-mediated reaction of thiamine with pyruvate is thus seen to be at least 10^4 times faster than the maximum rate possible with **1** in water, and 10^3 times faster than the maximum possible with **3**.[9] Although this comparison involves assumptions which might result in order of magnitude errors, the scale of this rate ratio establishes the presence within the enzyme of a far higher concentration of thiamine ylide than can be realized in water. Thus a major role of the enzyme must be to change the relative thermodynamic stabilities of thiamine and its ylide, perhaps by juxtaposing an oxyanion and the thiamine cation in a relatively nonpolar environment. Conversely, the rapid uncatalyzed reaction observed in water between the ylide of **1** and the relatively unreactive carbonyl compound, benzaldehyde, together with the high β for ylide formation (which precludes general-base-catalyzed rate increases of any magnitude), independently imply that marked mechanistic catalysis during enzymatic addition of thiamine to pyruvate is rather unlikely. It appears that pyruvate decarboxylase may catalyze the initial step of its reaction sequence simply by providing a medium which shifts an equilibrium.

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(6) For discussion of a related situation, see E. A. Walters and F. A. Long, *J. Amer. Chem. Soc.*, **91**, 3733 (1969).

(7) Calculated from the observed exchange rate in 50% ethanol, assuming the ylide protonation rate to be that observed in water.

(8) J. Ullrich, J. H. Wittorf, and C. J. Gubler, *Biochim. Biophys. Acta*, **113**, 595 (1966).

(9) It should be noted that **1** may be a more appropriate model for enzymatically bound thiamine pyrophosphate than the protonated thiamine **3**.

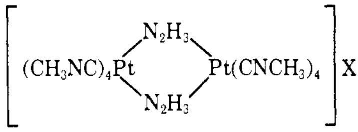
(10) A. P. Sloan Fellow, 1968–1970. Financial support from National Institute of Health Grants GM 13453 and GM 15944 and National Science Foundation Grant GP 8329 is gratefully acknowledged.

(11) National Institutes of Health Predoctoral Fellow, 1967–1969.

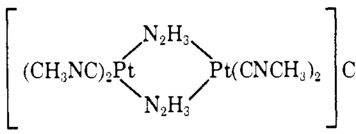
Palladium and Platinum Complexes Resulting from the Addition of Hydrazine to Coordinated Isocyanide

Sir:

In 1925 Chugaev and coworkers reported[1] that treatment of tetrakis(methyl isocyanide)platinum(II) with hydrazine produced a red, crystalline complex, A, which was formulated on the basis of analytical and conductivity data as **1**. Treatment of this salt with hydrochloric acid led to the evolution of methyl isocyanide and the formation of yellow crystals, B, which were formulated as **2**. The yellow crystals, B, could be converted back into the the red form, A, by treatment with methyl isocyanide and aqueous base. Since compounds containing coordinated molecular nitrogen[2a] or diazene[2b] have been prepared by treating certain transition metal complexes with hydrazine, we suspected that Chugaev's nitrogen-rich compounds might also contain an oxidized form of hydrazine. However, investigation has revealed that these complexes contain a novel ligand which is formed by the insertion of hydrazine into two methyl isocyanide moieties.



1, X = Cl^-, I^-, ClO_4^-, N_3^-



2

We have confirmed the experimental findings of Chugaev, *et al.*[1] In addition analogous complexes have been prepared with palladium(II), but not with nickel(II). Methylhydrazine, phenylhydrazine, or hydroxylamine also react with tetrakis(methyl isocyanide)-platinum(II) to produce analogs of A; these complexes also yield analogs of B on treatment with hydrochloric acid. Both A and B and their analogs exhibit infrared absorptions in the 3400–3300-cm^{-1} region which indicate the presence of N–H groups. The infrared spectra of A and its analogs also exhibit two bands in the 2330–2370-cm^{-1} region which are assigned to the CN stretch of two *cis* methyl isocyanide ligands, but no infrared absorptions are found in the region 3000–1650 cm^{-1} for B and its analogs. Consequently it is apparent that the formation of these compounds has involved a reaction of the isocyanide triple bond. In order to ascertain the nature of the product, an X-ray study has been carried out on the palladium analog of B.

The complex $[(CH_3)_2C_2N_4H_4]PdCl_2$ crystallizes as very fine, yellow needles in the orthorhombic space

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(1) L. Chugaev, M. Skanavy-Grigorieva, and A. Posniak, *Z. Anorg. Allg. Chem.*, **148**, 37 (1925).

(2) (a) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967); Yu. G. Borod'ko, V. S. Bukreev, G. I. Kozub, M. L. Khideke', and A. E. Shilov, *Zh. Strukt. Khim.*, **8**, 542 (1967); A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967); J. E. Fergusson and J. L. Love, *ibid.*, 399 (1969); J. T. Moelwyn-Hughes and A. W. B. Garner, *ibid.*, 1309 (1969); (b) G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini, and F. Bonati, *ibid.*, 739 (1967).

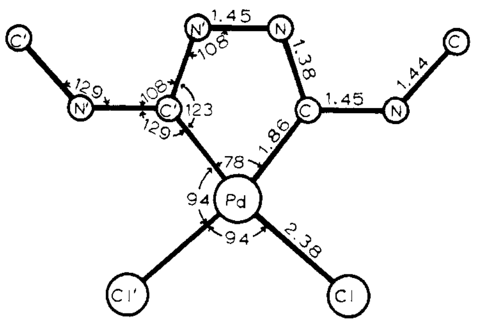
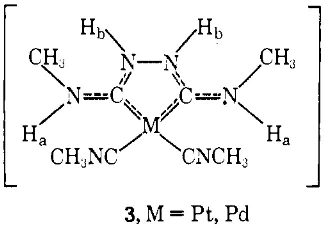


Figure 1. Structure of $PdCl_2C_4N_4H_{10}$; hydrogen atoms are not shown. The primed atoms are related to the unprimed atoms by a mirror plane. The standard deviations on bond distances are: Pd-Cl, 0.01; Pd-C, 0.03; C-N, 0.04; and N-N, 0.05 Å.

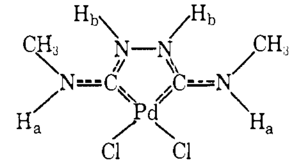
group Cmcm. Unit cell data are a = 18.05 (1) Å, b = 7.33 (1) Å, c = 6.84 (1) Å. The measured density of 2.141 (7) g cm^{-3} yields a molecular weight of 291.5 ± 1.0 (calcd 291.4) for $Z = 4$. A crystal of dimensions 0.025 × 0.075 × 0.225 mm was mounted about c, the needle axis, and six levels of data ($hk0$–$hk5$) were collected by Weissenberg photography using Mo Kα radiation. The 188 nonzero intensity data were estimated visually and the structure was solved by Patterson and difference Fourier methods. Least-squares refinement was carried out with the Pd atom allowed to vibrate anisotropically. The final value of the conventional R factor is 0.074. A drawing of the molecule, which is required crystallographically to have C_{2v} symmetry, is shown in Figure 1. Because the small size of the available crystals allowed only a limited number of nonzero intensity data to be collected, the X-ray data do not distinguish C from N with certainty nor do they locate the hydrogen atoms. The results, however, do indicate the mode of hydrazine addition and the basic molecular geometry.[3]

Further evidence pertinent to the structure of these complexes comes from their nmr spectra. Unfortunately neither B nor its palladium analog have sufficient solubility for nmr spectroscopic observation. However, treatment of the fluoroborate salt of A or its palladium analog with aqueous fluoroboric acid produces a new complex C in which protonation occurs without loss of methyl isocyanide. The salt C is formulated as **3** on the basis of its ir spectrum, which indicates the presence of coordinated methyl isocyanide, its nmr spectrum, and its relation to B. The complex C may be converted into A by treatment with base; consequently A and C are related by a one-proton transfer, and A and B are related by a one-proton transfer and substitution of chloride for methyl isocyanide.



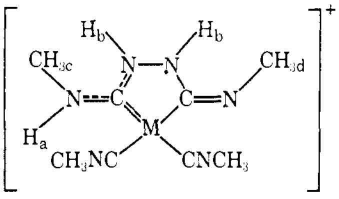
3, M = Pt, Pd

The nmr spectrum of C shows a methyl doublet at τ 6.97 (J = 4.0 Hz, relative intensity (ri) 6) which is assigned to the terminal methyl groups of the chelating ligand, a singlet at 6.40 (ri 6) which is assigned to the coordinated methyl isocyanide, a broad quartet at 2.75 (J = 4.0 Hz, ri 2) which is assigned to the H_a protons in **3**, and a very broad resonance centered at 0.5 (ri 2) which is assigned to the inner protons H_b.[4] The assignment of resonances to H_a and the terminal methyl groups has been confirmed by double resonance experiments; in addition the J_{H-CH_3} coupling constant of 4.0 Hz is consistent which the values found in N-methylacetamide and the carbene complex, $(CO)_5CrC(CH_3)NHCH_3$.[5] The relationship between B and C allows the structure **4** to be assigned to B.



4

Deprotonation of the chelating ligand to form B appears to occur predominantly at the H_a sites in **3** and **4**; the structure **5** is assigned to A.[5a] The nmr spectrum of A as the tetraphenylborate salt in perdeuterioacetone shows a doublet at τ 7.25 (J = 5.0 Hz, ri 3) which is assigned to methyl group c, a singlet, at 7.26 (ri 3) which is assigned to the methyl group d, a singlet at 6.92 (ri 6) which is assigned to the methyl groups of the coordinated isocyanide, and a broad



5, M = Pt, Pd

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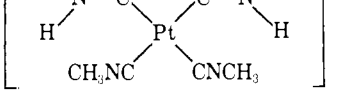
(3) The ionic formulation of B as **2** was based on its conductivity in aqueous solution.[1] We also find that B and its palladium analog are electrolytes in aqueous solution but nonelectrolytes in acetonitrile solution. Free chloride ions have been detected in the aqueous solutions of B; consequently it appears that either the hydrolysis or condensation to split off chloride ion and produce chloride-bridged polymers occurs in aqueous solution.

(4) Although this spectrum has been obtained in strongly acidic media, no additional protonation of the complex appears to have occurred. It is assured that protons must occur in the positions H_b since a derivative of **3** with a methyl group substituted for an H_b proton is formed starting from methylhydrazine; in order to account for the charge on the complex, then, both H_b sites must be occupied in the acid forms B and C. The nmr spectrum of the palladium complex analogous to **3** but with a methyl group substituted for one of the two H_b hydrogens is also completely consistent with the proposed structure.

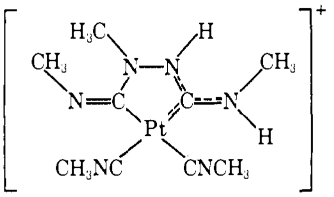
(5) E. Moser and E. O. Fischer, *J. Organometal. Chem.*, **13**, 387 (1968).

(5a) Note Added in Proof. In a recent note (G. Rouschias and B. L. Shaw, *Chem. Commun.*, 183 (1970)) the structure

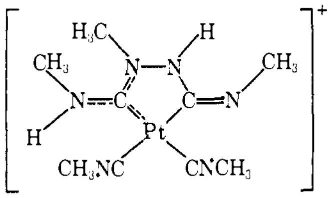


has been tentatively suggested for A on the basis of infrared and limited nmr data. Although we agree in the formulation of the basic chelating ligand skeleton, the planarity of the chelating ligand in the acid form, the preparation of 6a and 6b from methylhydrazine, and our nmr data indicate that the location of the protons is that shown in **5**. The observation of a single doublet for the terminal methyl groups of the chelating ligand of A in nitrobenzene solution could be due either to acidic impurities in the solvent which would convert A into C or to a solvent effect which alters the rate of proton exchange.

resonance at 4.0 (ri 1) which is assigned to the H_a proton. Although no structure is observed on this latter broad signal, the coupling between H_a and the CH_3 group c has been demonstrated in double resonance experiments. No resonance due to the H_b protons could be observed; the failure to observe these protons could be caused by excessive breadth or by overlap with the phenyl resonances which appear as multiplets centered at 3.1 and 2.6. The nmr spectrum of the analogous complex derived from methylhydrazine is also consistent with the loss of a proton from one of the terminal nitrogens of the chelate, but in this case the spectrum is more complicated because of the presence of two isomers **6a** and **6b** in solution.



6a



6b

Although the structures of the molecules described herein are unusual, they are not unprecedented. The addition of aniline to $PtCl_2(CNMe)(PEt_3)$ to give the related carbene complex $PtCl_2[C(NHMe)NHPh]PEt_3$ has recently been reported.[6] Several examples of insertion of alkyl groups into the triple bond of coordinated isocyanides to give the unit $MC(R){=}NR'$ have been reported,[7] but protonation reactions of this latter unit do not appear to have been described. Finally we note that the copper-catalyzed addition of amines and isocyanides to give formamidic acid derivatives[8] may involve nonchelated intermediates with metal coordination similar to that found in **4** or **5**.

Acknowledgment. This research was supported by Grant AM 12182 from the National Institutes of Health and GP12299 from the National Science Foundation.

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(6) E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Commun.*, 1322 (1969).

(7) S. Otsuka, A. Nakamura, and T. Yoshida, *J. Amer. Chem. Soc.*, **91**, 7196 (1969); P. M. Triechel and J. P. Stenson, *Inorg. Chem.*, **8**, 2563 (1969); Y. Yamamoto, H. Yamazaki, and N. Hagihara; *J. Organometal. Chem.*, **18**, 189 (1969).

(8) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Lett.*, 6121 (1966).

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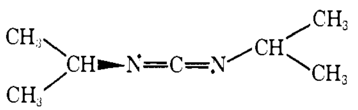
Energy Barrier of Racemization in Diisopropylcarbodiimide

Sir:

Carbodiimides are expected to exhibit the same molecular dissymmetry as do appropriately substituted allenes.[1] Although allenes have been resolved, first[2] in 1936, attempts to demonstrate experimentally the chirality of carbodiimides have been unsuccessful[3,4] except for one questionable claim.[5] Gordon and Fischer[6] using the INDO molecular orbital method calculated the thermodynamically most stable geometry of carbodiimide and difluorocarbodiimide. The ground state, according to these calculations, is the intuitively favored dissymmetric geometry with the substituents in perpendicular planes which intersect along the N=C=N axis. The calculated energies of activation for thermal racemization of carbodiimide and difluorocarbodiimide are 8 and 22 kcal/mol, respectively. Since the calculations are thought to give barriers which are slightly too high,[6] the barrier in carbodiimide is probably no higher than 8 kcal/mol. Thus, attempts to prepare optically active alkyl- and aryl-substituted carbodiimides will not be possible because of rapid racemization at room temperature. Later *ab initio* SCF calculations by Lehn and Munsch[7] agree with the results of Gordon and Fischer,[6] while recent INDO calculations[8] on dimethylcarbodiimide indicate a minimum energy for a valence angle $CH_3{-}N{=}C$ of 90°.



I

We now report nmr data on the rate of racemization in diisopropylcarbodiimide (I). The methyl groups of either isopropyl are diastereotopic and thus should show different chemical shifts if racemization is slow on the nmr time scale. The 240-MHz[9] proton resonance spectrum of diisopropylcarbodiimide in 1:1 vinyl chloride–dichlorofluoromethane solution shows at −130° and above a doublet (J = 6.5 Hz) for the methyl protons owing to coupling to the adjacent methine proton (Figure 1a). On lowering the temperature the doublet broadens greatly (−140°, Figure 1b) and below −145° (Figure 1c) becomes a 1:2:1 three-

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(1) H. Fischer, "The Chemistry of Alkenes," S. Patai, Ed., John Wiley & Sons, Inc., London, 1964, p 1061.

(2) P. Maitland and W. H. Mills, *J. Chem. Soc.*, 987 (1936).

(3) L. J. Rolls and R. Adams, *J. Amer. Chem. Soc.*, **54**, 2495 (1932).

(4) J. C. Jochims, unpublished results.

(5) K. Schlögl and M. Mechter, *Angew. Chem. Int. Ed. Engl.*, **5**, 596 (1966). These authors report the partial resolution of diferrocenylcarbodiimide. However, since the maximum optical rotation observed, $[\alpha]_D$ −4.8° (c 0.3, benzene), is very small, the possibility that the rotation was due to an impurity must be considered. Unfortunately, the authors did not report any experimental test to show that the carbodiimide itself was optically active. Attempts by Jochims[4] to resolve carbodiimides have sometimes given products with a low rotation, but since the rotations remained after transformation of the carbodiimides into ureas, no actual resolutions had occurred.

(6) M. S. Gordon and H. Fischer, *J. Amer. Chem. Soc.*, **90**, 2471 (1968).

(7) J. M. Lehn and B. Munsch, *Theoret. Chim. Acta.*, **12**, 91 (1968).

(8) D. R. Williams and R. Damrauer, *Chem. Commun.*, 1380 (1969).

(9) Details of the spectrometer, which makes use of a Magnion superconducting solenoid, will be published elsewhere; *cf.* F. A. L. Anet, paper presented at the Tenth Experimental NMR Conference, Pittsburgh, Feb 1969.