ordered. It is noted that the sum of the two occupancies at the sites of W(6) and (W(8) is nearly 1.00, suggesting that one water molecule is perhaps trapped in a canal and is occupying the two positions statistically. When the water occupies the site W(6), it is coordinated to the sodium ion, and when it is at site W(8), it is hydrogen bonded to W(5) and perhaps also to W(7). It is also interesting that the sum of the occupancies of the water molecules W(7) on the twofold axis and W(4) and W′(4) related by this twofold axis is approximately 2.0. This indicates that two water molecules occupy these three sites.

A striking feature of the crystal packing is that there are alternating layers of nucleotides and water channels in which the sodium ions are embedded. Interestingly, the atomic groups that are capable of taking part in hydrogen-bond formation are all either pointing toward the water layer or are coordinated to the sodium ion. The crystal density indicates the presence of eight water molecules in the asymmetric unit, while only a total of about six have been located. In the final difference electron density map, there is a diffuse region of density 0.6 e/Å^3 in the region centered on (0.20, 0.05, 0.20). This position occurs in the "hole" in the structure in the region surrounded by the hydrogen bonds forming a pentagon. It is the region of the disordered water molecules (Figure 2). Therefore, it appears likely that the "volatile" water molecules that have escaped were loosely bound in this "hole" region of the lattice.

Many of the programs used in this work were written by S. T. R. for use with the UNIVAC 1107 and 1108 computers on the Case Western Reserve University campus. The full-matrix least-squares program of Busing, Martin, and Levy[10] was adapted for the UNIVAC computers.

Acknowledgments. We wish to thank Mr. Douglas Rohrer for the collection of data and Dr. R. Parthasarathy of the Roswell Park Memorial Institute, Buffalo, N. Y., for kindly performing the block-diagonal least-squares refinement in the early stages of the structure analysis.

Communications to the Editor

Structural Interconversions and Ligand-Exchange Reactions of Phosphine Adducts to Platinum(II) Complexes

Sir:

Recently several five-coordinate platinum(II) complexes have been reported.[1–4] While these compounds might be expected to undergo stereochemical rearrangements[5] with relative ease, the ligand structure permitting, no conclusive evidence has been reported for such behavior. Eaton[6] observed that the inability to find the tin nuclear magnetic resonance in $Pt(SnCl_3)_5^{3-}$ might be attributed "to the effects of a rapid exchange reaction." In this communication we report *direct evidence for both ligand exchange and molecular rearrangement* by studies of the temperature-dependent proton magnetic resonance (pmr) spectra of methyldiphenylphosphine adducts of platinum(II) dithiolates.

Earlier[4] we reported the isolation of crystalline methyldiphenylphosphinebis(p-dithiocumato)platinum (II) (Ia, X = H; Y = i-C_3H_7). In addition, methyldiphenylphosphinebis(3,4,5-trimethoxydithiobenzoato)platinum(II) (Ib, X = Y = OCH_3) has been prepared. The pmr spectra of these complexes were observed in $CHCl_3$. With increasing temperature, the ^{195}Pt coupling ($J_{Pt-P-CH_3}$ = 39 cps) on the methyldiphenylphosphine is relaxed (Figure 1), but J_{P-CH_3} remains at −10.8 cps. Since the J_{P-CH_3} coupling constant in uncoordinated methyldiphenylphosphine[7] is +3.4 cps, more than 95% of the phosphine must be present as the coordinated species.

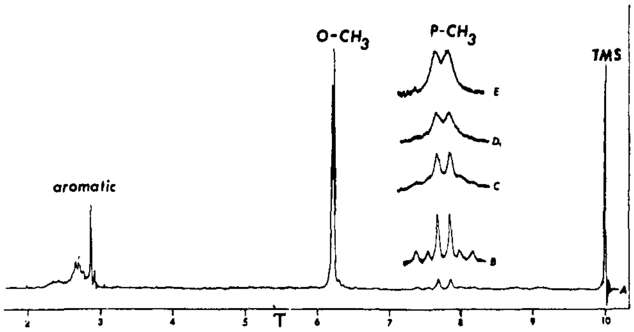

Figure 1. Nmr spectrum of bis(3,4,5-trimethoxydithiobenzoato)platinum(π)methyldiphenylphosphine (Ib) in $CDCl_3$: A, complete spectrum at 33°; B, increased spectrum amplitude of trace A; C, 46°; D, 54°; E, 61°.

The temperature-dependent lifetime, τ, for the phosphine complex was calculated[8] from a computer output line-shape analysis (Figure 2) based on the adiabatic approximation.[9] Plots of log $1/\tau$ *vs.* $1/T$ yielded activation energies (E_a) of 4.2 and 19.7 kcal/mole for Ia and Ib, respectively. Values of τ at a given temperature decrease when (1) triphenylphosphine is added, (2) the concentration of complex is increased, or (3) the complex is dissolved in CS_2 instead of $CHCl_3$.

The pmr studies of Ia and Ib show that phosphine

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[1] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc* 170 (1961).

[2] A. D. Westland, *J. Chem. Soc.*, 3060 (1965).

[3] R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

[4] J. P. Fackler, Jr., W. C. Seidel, and J. A. Fetchin, *ibid.*, **90**, 2707 (1968).

[5] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1966, p 132.

[6] D. R. Eaton, *J. Am. Chem. Soc.*, **90**, 4272 (1968).

[7] J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *ibid.*, in press.

[8] Dr. M. J. Weeks is acknowledged for this contribution.

[9] C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 36 (1965).

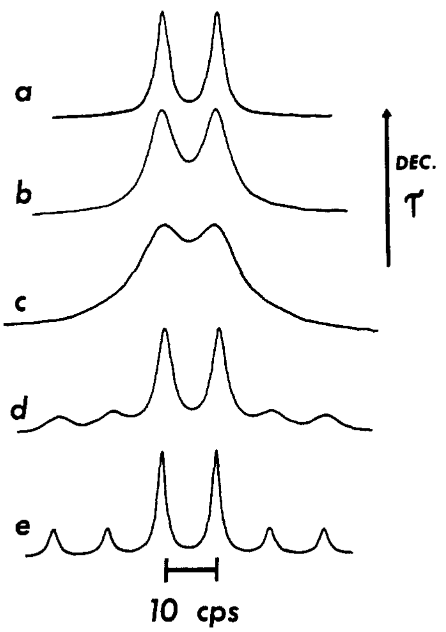

Figure 2. Calculated temperature-dependent methyl proton magnetic resonance of methyldiphenylphosphine coordinated to platinum(II) (values of τ (sec)): (a) 0.00075, (b) 0.0025, (c) 0.01, (d) 0.075, (e) 10.0.

exchange occurs even in the absence of excess phosphine, at room temperature and above. While the exchange reaction clearly is dependent on the phosphine concentration, detailed mechanistic studies are incomplete at present.

Bis(O,O′-diethyl dithiophosphato)platinum(II)methyldiphenylphosphine (II) was prepared by mixing the base with an equivalent amount of the dithiophosphate complex in carbon disulfide.[4] The room-temperature pmr spectrum of the CS_2 solution shows platinum-methyl coupling ($J_{\mathrm{Pt-P-CH_3}}$ = 39 cps, $J_{\mathrm{P-CH_3}}$ = 11 cps) indicative of phosphine coordination[4] to the metal (Figure 2e). This pattern does not change as the temperature is lowered.

The unusual feature in the pmr spectrum of II is the observation of a single sharp triplet (J = 7 cps) for the $-CH_3$ protons of the four ligand ethyl groups at temperatures above $-5°$. As the temperature is lowered, the single triplet pattern collapses until at $-46°$ two sharp triplets (J = 7 cps) separated by about 12 cps are observed. This temperature dependence is reversible and the pmr line shapes of the adduct are independent of concentration. The pmr behavior[4] of methyldiphenylphosphinebis(N,N - diethyldithiocarbamato)platinum(II) (III) on the other hand is essentially independent of temperature from room temperature[10] to $-70°$ in CS_2.

Excess phosphine causes a collapse of the $\mathrm{Pt-PCH_3}$ coupling with all of these complexes, indicating phosphine exchange; however, with II and III some additional reactions also occur.[4,11]

The pmr spectrum of II has been analyzed according to the method of Grunwald, *et al.*,[12,13] assuming exchange between equally populated, chemically distinct sites. Linearity of log $1/\tau$ *vs.* $1/T$ from -5 to $-46°$ indicates E_a is $\sim$15.4 kcal/mole. Assuming a unimolecular process produces the observed change in the lifetime for II as a function of temperature, a $\Delta H^{\ddagger}$ of $\sim$15 kcal/mole and a $\Delta S^{\ddagger}$ of $\sim$9 eu are calculated.[14]

One explanation of the observed pmr behavior for II suggests that an equilibrium exists between a square-planar, open chelate ring complex and a trigonal-bipyramidal, five-coordinate species (reaction 1). The low-temperature spectrum could correspond to the "frozen-out" species (A). However, if such a mechanism were important generally with these 1,1-dithiolate adducts, the ethyl groups in III should not be magnetically equivalent at $-70°$. Also, platinum-phosphorus bond breaking appears to be more facile than expected if the phosphorus atom actually occupied a coordination position in the square-planar species.[15]

The cumulative pmr data for these phosphine adducts of 1,1-dithiolates are best explained by assuming a room-temperature stereochemical rearrangement between a solvated square-pyramidal five-coordinate adduct and a five-coordinate trigonal-bipyramidal species (reaction 2). Square-pyramidal to trigonal-bipyramidal rearrangements are generally expected to be rapid.[6,16] This is particularly true for d^8 systems since no energy level reordering occurs in the process.[17]

In the dithiophosphate complex II, the phenyl groups in the phosphine ligand diamagnetically shield two of the ethyl groups more effectively than the remaining two in the "frozen-out," low-temperature, square-pyramidal structure. For III, this configuration produces symmetry-equivalent ethyl groups, as

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(10) (a) Alkyl esters of dithiocarbamates show broad α pmr spectra at room temperature: C. E. Holloway and M. H. Gitlitz, *Can. J. Chem.*, **45**, 2659 (1967). At $-40°$ resolved signals were observed indicating that the barrier to rotation about the $\mathrm{C\overset{\cdots}{-}N}$ bond is fairly high. These compounds display thioureide C–N stretching frequencies near 1490 $\mathrm{cm^{-1}}$ indicative of substantial $\mathrm{C\overset{\cdots}{-}N}$ double-bond character: J. P. Fackler, Jr., and D. Coucouvanis, *Inorg. Chem.*, 7, 181 (1968). The nickel(II) and platinum(II) complexes of the diethyl dithiocarbamate show C–N stretches at 1511 and 1530 $\mathrm{cm^{-1}}$, respectively, while this band is found at $\sim$1520 $\mathrm{cm^{-1}}$ in III. The infrared data suggest that rotation about the $\mathrm{C\overset{\cdots}{-}N}$ bond in these metal complexes should be more restricted than with the alkylated dithiocarbamates. (b) B. F. G. Johnson and K. H. Al-Obaidi, *Chem. Commun.*, 876 (1968), reported the presence of pmr nonequivalent R groups in $\mathrm{Mo(S_2CNR_2)_3NO}$ where the $\mathrm{C\overset{\cdots}{-}N}$ stretch appears at $\sim$1510–1530 $\mathrm{cm^{-1}}$.

(11) J. P. Fackler, Jr., and W. C. Seidel, submitted for publication.

(12) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, 27, 630 (1957).

(13) Armed Services Technical Information Agency, AD 213032, Technical Note No. 2, Contract No. AF 61(052)-03, The Weizmann Institute of Science, Rehovot, Israel.

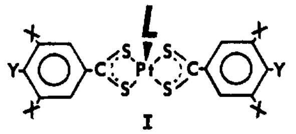
(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 101. $\Delta S^{\ddagger}$ varies somewhat with a choice of T_2. The above value, calculated assuming $1/T_2$ as the half-width at half-height of the exchange averaged spectrum, is probably low. $\Delta S^{\ddagger}$ is clearly positive.

(15) L. Cattalini, R. Ugo, and A. Orio, *J. Am. Chem. Soc.*, **90**, 4800 (1968), recently presented kinetic evidence that the formation of a five-coordinate species in a rhodium(I) system is fast. The intermediate then slowly expels a ligand to produce the four-coordinate product.

(16) M. Mahler and E. Muetterties, *Inorg. Chem.*, 4, 1520 (1965).

(17) Eaton[6] ingeniously has applied "Woodward–Hoffmann rules" to molecular rearrangements of transition metal complexes assuming a *crystal-field description* of the energy levels. The results appear quite satisfactory for the trigonal-bipyramid–square-pyramid rearrangements with low-spin d^8 complexes. However, with the "thermally allowed" d^8 planar–tetrahedral rearrangement, the result is less meaningful. A molecular orbital description of the bonding in planar d^8 systems generally places the $\sigma^*[d_{x^2-y^2}]$ orbital (d_{xy} in Eaton's Figure 2) as the lowest empty antibonding function. This function may be only 50–60% metal in character in these "covalent" low-spin complexes. In the tetrahedral geometry the lowest partly filled function is $t_2^*(d_{xz}, d_{yz}, d_{xy})$, an essentially nonbonding or weakly antibonding function. It is nearly entirely metal atom in character. Thus, *a sizable charge redistribution must occur during the planar–tetrahedral rearrangement in low-spin d^8 complexes.* Photochemical "charge transfer" may produce this more readily than thermal processes.

observed. In II, rearrangement through a trigonal-bipyramidal structure equilibrates the ethyl groups. A weakly associated solvent molecule could be liberated in this process to account for the positive $\Delta S^{\pm}$ The ability of phosphine to catalyze phosphine exchange and the observation of what may be six-coordinate species precipitating from solution when excess Ph_2PCH_3 is added to Ia and Ib further support the hypothesis that the low-energy configuration in these complexes is a solvated PtS_4L square pyramid.



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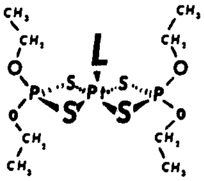

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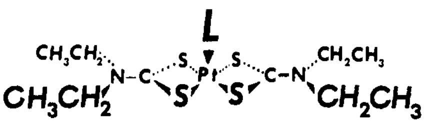

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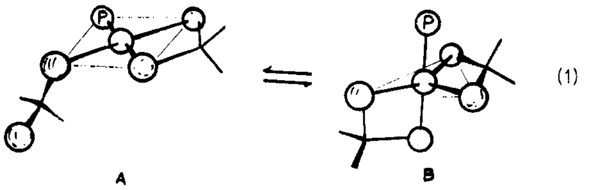

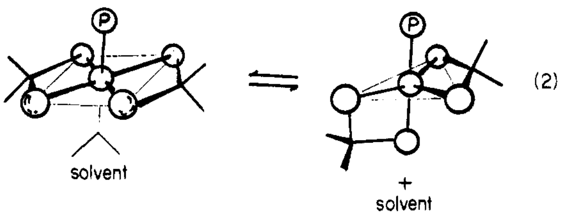

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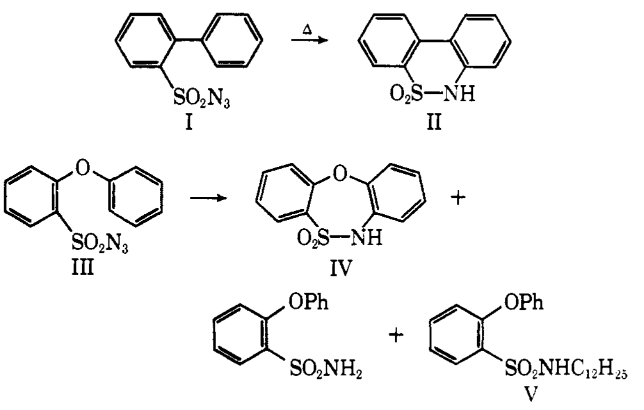
Intramolecular Cyclizations of Sulfonyl Nitrenes

Sir:

Unlike the aryl nitrenes, sulfonyl nitrenes undergo intermolecular aromatic substitution reactions to give sulfonylaniline derivatives.[1] Aryl nitrenes are known to undergo intramolecular ring closures to five- and six-membered heterocycles readily;[1,2] but no reports of the corresponding cyclizations of sulfonyl nitrenes have appeared. We now wish to report examples of such cyclizations, some of which exhibit unusual features.

Thermolysis of biphenyl-2-sulfonyl azide (I),[3] mp 60–61°, in *n*-dodecane or in the absence of solvent at 150° gave 6H-dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide (II), mp 200–202° (lit.[4] mp 196°) (38–70% yield). No biphenyl-2-sulfonamide, mp 121–122°, was detected.



The mechanism of this substitution reaction is under study to determine whether or not it proceeds *via* the formation of an aziridine intermediate.[5]

2-Phenoxybenzenesulfonyl azide (III), mp 79–80°, in *n*-dodecane at 135° for 30 hr gave IV (15%), mp 140–141°. Such a cyclization of a nitrene to a seven-membered ring appears to be unprecedented. 2-Phenoxybenzenesulfonamide (4%), mp 113–114° (hydrogen-abstraction product), and N-dodecyldiphenyl ether 2-sulfonamide (11%; V) (probably an unresolved mixture of positional isomers), bp 208° (0.2 mm) (C–H insertion product), were also formed in the thermolysis. In contrast, no internuclear aromatic cyclization was observed when diphenyl sulfide 2-sulfonyl azide (VI) was heated either alone or in dodecane. Instead, cyclization occurred at divalent sulfur to give VII (10%), mp 191–193°. This, too, appears to be a novel intramolecular cyclization of a nitrene and is understandable in terms of an attack by electrophilic singlet nitrene at the electron-rich sulfur atom resulting in expansion of its valence shell, though a concerted attack by sulfur at the azide and elimination of nitrogen cannot be discounted. Three other products were also formed: VIII (19%), mp 112.5°, IX (5%), as a yellow gum, and X[6] (4%), mp 155–156.6°. That VII was formed and not the desired

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(1) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(2) P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962); P. A. S. Smith, B. B. Brown, R. K. Putney, and R. F. Reinisch, *ibid.*, **75**, 6335 (1953); G. Smolinsky, *ibid.*, **82**, 4717 (1960); **83**, 2489 (1961).

(3) Satisfactory analyses and infrared, nmr, and mass spectral data were obtained for all the new compounds reported.

(4) F. Ullman and C. Grosse, *Ber.*, **43**, 2694 (1910).

(5) R. A. Abramovitch and V. Uma, *Chem. Commun.*, 797 (1968).

(6) Probably formed during the chromatography on alumina; also formed by basic hydrolysis of VII.