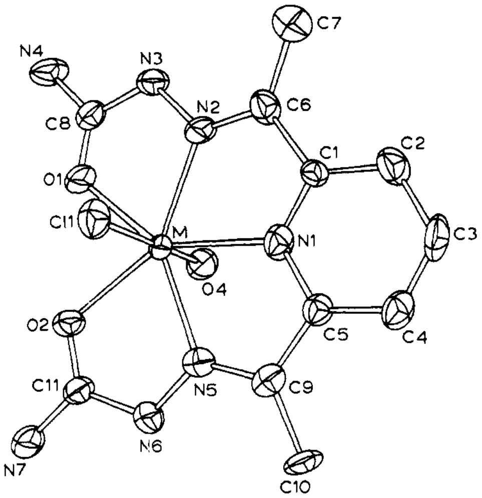

Figure 1. An ORTEP drawing of the chloroaqua(2,6-diacetylpyridinebissemicarbazone)metal(II) cation, where the metal is Fe(II), Co(II), and Zn(II). The atoms N1, N2, N5, O1, and O2 form an approximately planar pentagonal arrangement around the metal ion with Cl1 and O4 in the axial positions. The angles in the Co(II) complexes are N1-Co-N2, 70.3°; N1-Co-N5, 70.4°; N2-Co-O1, 71.9°; N5-Co-O2, 71.4°; and O1-Co-O2, 76.4° (all ±0.2°) and illustrate the approximately planar pentagonal coordination about the Co(II) atom.

The axial metal–chlorine bonds of 2.506, 2.479, and 2.433 Å and the metal–water bonds of 2.153, 2.141, and 2.121 Å, for the Fe, Co, and Zn cases, respectively, both decrease going from Fe to Zn. This change is opposite to that expected on electronic grounds or on the basis of the radius of the metal ion. However, all the in-plane distances are larger in the Zn complex compared with the Fe complex, which suggests that the axial M–Cl and M–OH_2 distances are determined by nonbonded contacts. The importance of intramolecular contacts in copper chloride[10] and gallium chloride[11] complexes has also been noted.

An important conclusion which can be drawn from our studies concerns the possibility of utilizing planar pentadentate ligands to explore pentagonal bipyramidal coordination in other elements. Planar pentadentate ligands have been ignored, apparently, because the pentagonal bipyramidal geometry is relatively rare in coordination complexes. Our results suggest that DAPSC or other planar pentadentate ligands can produce pentagonal bipyramidal complexes in other elements and that the possibilities are virtually limitless. Other studies along these lines are in progress. Finally, as has been demonstrated in other cases,[12] the final stereochemistry of a metal complex appears to be determined by the constraints on the ligand, and unusual geometries may be limited mainly by synthetic difficulties.[13]

Acknowledgments. We are grateful for a grant of computer time from the University of Florida Computing Center (G. J. P.), a Graduate School Fellowship (D. W.), and financial support from the National Cancer Institute of the U. S. Public Health Service (Grant CA-12390).

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[10] M. Mathew and G. J. Palenik, *Inorg. Chim. Acta*, **5**, 573 (1971).

[11] K. Dymock and G. J. Palenik, unpublished results.

[12] (a) E. Larsen, G. N. LaMar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, **11**, 2652 (1972); (b) S. C. Jackels and N. J. Rose, *ibid.*, **12**, 1232 (1973).

[13] R. A. D. Wentworth, *Coord. Chem. Rev.*, **9**, 171 (1973) has reviewed this point with respect to the problem of trigonal prismatic *vs.* octahedral coordination.

Stereochemical Dependence of Lone Pair Interactions in the Photoelectron Spectra of Nitrogen–Phosphorus Compounds

Sir:

The discovery[1] of a planar nitrogen geometry in $(CH_3)_2NPF_2$ prompted a surge of interest in the structures[2] and stereochemistry[3] of aminophosphines. The stereochemistry of the corresponding aminophosphoranes has also received attention;[4] however, no structural data have been published for this class of compounds.

The purpose of the present communication is to report studies of the pes (photoelectron spectra) of various nitrogen–phosphorus compounds that suggest interesting conclusions concerning their structures and the effects of lone pair interactions in them.

The monoamines **1** and **4** exhibit single pes peaks at 10.35 and 9.58 eV, respectively (Table I). These peaks can be assigned unambiguously to ionization of the N(2p) lone pair electrons, both on the basis of their line

Table I. Pes Ionization Potentials[a] for N(2p) and P(3p) Lone Pair Orbitals in Nitrogen–Phosphorus Compounds

Compound	No.	N(2p)	P(3p)
$(CH_3)_2NPF_4$	**1**	10.35	
$[(CH_3)_2N]_2PF_3$	**2**	8.84, 9.95	
$[(CH_3)_2N]_3PF_2$	**3**	8.04, 9.03, 9.31	
$(CH_3)_2NPF_2$	**4**	9.58	10.48
$[(CH_3)_2N]_2PF$	**5**	8.18, 9.14	10.40
$[(CH_3)_2N]_3P$	**6**	7.61, 7.89, 8.86	9.98

[a] Vertical ionization potentials in electron volts.

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[1] E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

[2] (a) L. V. Vilkov, L. S. Khaikin, and V. V. Evdokimov, *Zh. Strukt. Khim.*, **10**, 1101 (1969); (b) G. C. Holywell, D. W. K. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. A*, 785 (1971); (c) A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, **93**, 6772 (1971); (d) J. R. Durig and J. M. Casper, *J. Cryst. Mol. Struct.*, **2**, 1 (1972); (e) P. Forti, D. Damiami, and P. G. Favero, *J. Amer. Chem. Soc.*, **95**, 756 (1973).

[3] M. P. Simmonin, J. J. Basselier, and C. Charrier, *Bull. Soc. Chim. Fr.*, 3544 (1967); A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, **90**, 4185 (1968); D. Imbery and H. Friebolin, *Z. Naturforsch. B*, 236, 759 (1968); H. Goldwhite and D. G. Rowsell, *Chem. Commun.*, 713 (1969); A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 1085, 5206 (1970); M. P. Simmonin, C. Charrier, and R. Burgada, *Org. Magn. Resonance*, **4**, 113 (1972); M. P. Simmonin, R. M. Lequan, and F. W. Wehrli, *J. Chem. Soc., Chem. Commun.*, 1204 (1972); I. G. Czismadia, L. M. Tel, A. H. Cowley, M. W. Taylor, and S. Wolfe, *ibid.*, 1147 (1972); S. DiStefano, H. Goldwhite, and E. Mazzola, *Org. Magn. Resonance*, in press.

[4] (a) M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zh. Strukt. Khim.*, **8**, 1097 (1967); (b) V. V. Sheluchenko, M. A. Sokalskii, M. A. Landau, G. I. Drozd, and S. S. Dubov, *ibid.*, **10**, 142 (1969); (c) M. A. Sokalskii, G. I. Drozd, M. A. Landau, and S. S. Dubov, *ibid.*, **10**, 1113 (1969); (d) J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, **10**, 1538 (1971); (e) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (f) F. N. Tebbe and E. L. Muetterties, *ibid.*, 7, 172 (1968); (g) E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 5674 (1972); (h) A. H. Cowley and J. R. Schweiger, *J. Chem. Soc., Chem. Commun.*, 560 (1972).

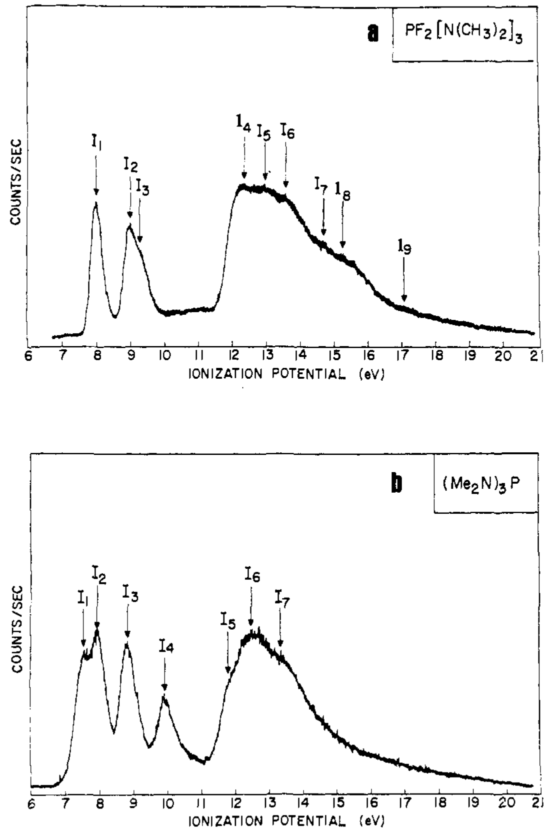

Figure 1. Photoelectron spectra of (a) $[(CH_3)_2N]_3PF_2$ and (b) $[(CH_3)_2N]_3P$.

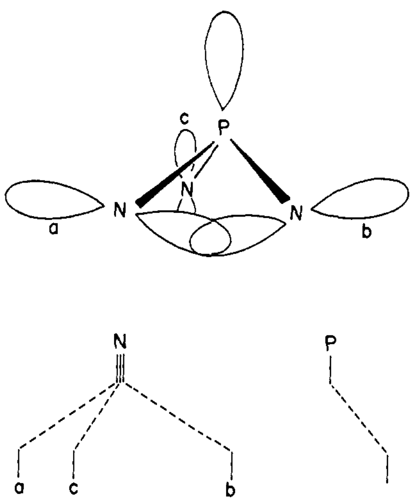

Figure 2. Interaction of nitrogen and phosphorus lone pair orbitals in $[(CH_3)_2N]_3P$.

widths[5] and from considerations of inductive effects. Employing the same arguments it is evident that the diamines **2** and **5** exhibit two N(2p) ionizations (Table I) while three such ionizations, I_1, I_2, and I_3 (Figure 1), are observed in the pes of the triamines **3** and **6**.

The N(2p) levels in the diamines and triamines are split by interactions between the nitrogen lone pairs. If, as is commonly assumed, the triamines have threefold symmetry (*e.g.*, D_{3h} or C_{3v}), the interactions between the nitrogen lone pairs give rise to one combination of A-type symmetry and two degenerate combinations of E-type symmetry.[6] If the overlap is predominantly of σ type, the E levels lie lower in energy while the reverse is true if the overlap is predominantly of π type. In either case ionization from the E level should give rise to two pes bands, the degeneracy being removed by Jahn–Teller distortion of the ion.[7]

The pes of **3** follows this pattern (Figure 1a). Since the split E level gives rise to a band of higher IP than the A level, the E combinations must be the lower in energy and the nitrogen lone pair interactions consequently of σ type. While the structure of **3** is not known, low-temperature nmr studies of aminophosphoranes[4] and alkylthiophosphoranes[8] imply that the nitrogen lone pairs are orthogonal to the axial PF bonds.[9] If the same is true in **3**, the N(2p) lone pair atomic orbitals (AO's) lie in the equatorial plane and so overlap in σ fashion.

This interpretation is supported by a comparison of the pes of **3** with that of tris(dimethylamino)borane,[10] $B[N(CH_3)_2]_3$. The two low-energy bands are similar in shape but inverted, the N(2p) overlap in $B[N(CH_3)_2]_3$ being of π type. The Jahn–Teller splitting of the E levels is similar in both cases.

The pes of **6** seems at first sight to resemble that of **3** but with the A and E levels inverted. This would imply π-type overlap of the N(2p) lone pairs. However, an electron diffraction study[2a] of **6** indicated that if it has the assumed C_{3v} symmetry, then the dihedral angle between the nitrogen and phosphorus lone pairs is 60°, implying that the nitrogen–phosphorus lone pair interactions are more nearly of σ type than π type. It is therefore extremely difficult to believe that the order of the A and E levels in **6** could be inverted.

It seems more likely that the difference between **3** and **6** arises from the latter *not* having threefold symmetry, due to repulsive interactions between the nitrogen and phosphorus lone pairs. Thus if the N(2p) AO's lie in a plane there will be *three* strong repulsions between them while if they are all parallel to the phosphorus lone pair there will be *three* strong N–P repulsions. If, however, two are orthogonal to the phosphorus and one parallel, there will be *one* N–N repulsion and *one* N–P repulsion, *i.e.*, a total of two repulsions instead of three. The resulting orbital diagram is shown in Figure 2. Two of the nitrogen lone pairs are symmetrically split (a,b) through interaction with each other while the other is raised (c) in energy by interaction with the phosphorus lone pair. The resulting orbital energies clearly correspond to the observed pes.

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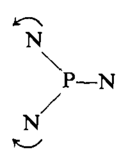
(5) In all the trivalent phosphorus–nitrogen pes which we have recorded thus far the P(3p) lone pair ionizations have been broader than the N(2p) lone pair ionizations.

(6) A. D. Walsh, *J. Chem. Soc.*, 2301 (1953).

(7) It is easily seen that bending of the PN bonds



raises the energy of one of the E-type MO's and lowers that of the other.

(8) S. C. Peake and R. Schmutzler, *Chem. Commun.*, 1662 (1968); *J. Chem. Soc. A*, 1048 (1970).

(9) For a discussion of the relative importance of lone pair–bond pair repulsions and P(3d) orbital effects in phosphoranes, see R. Hoffmann, J. M. Howell, and E. L. Muetteriles, *J. Amer. Chem. Soc.*, **94**, 3047 (1972). However, it is not necessary to invoke P(3d) orbital participation in order to explain the present results.

(10) H. Bock and W. Fuss, *Chem. Ber.*, **104**, 1687 (1971).

These arguments suggest strongly that $[(CH_3)_2N]_3P$ does not have C_{3v} symmetry and that its structure should be reinvestigated.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant No. GP 38027X), the Air Force Office of Scientific Research (Contract F44620-71-C-0119), and the Robert A. Welch Foundation for generous financial support.

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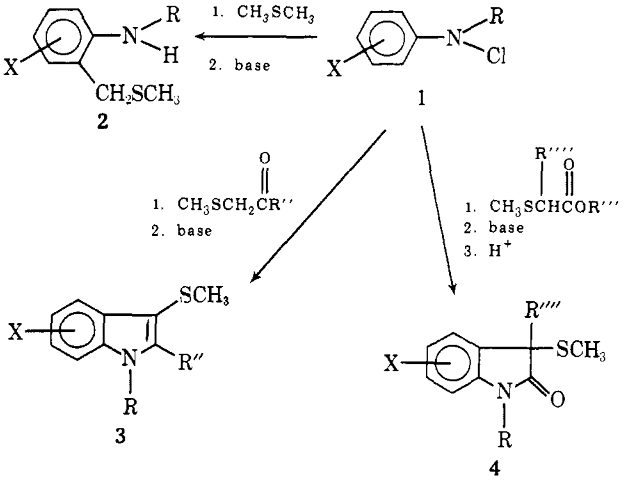
Received June 25, 1973

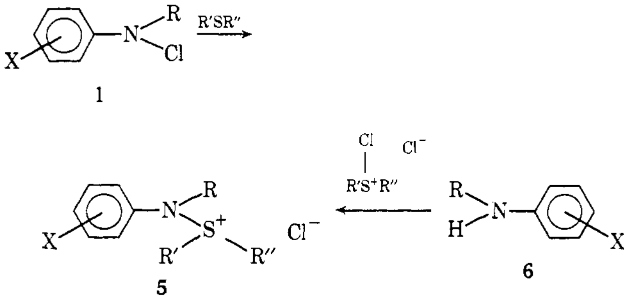
Use of Halogen–Sulfide Complexes in the Synthesis of Indoles, Oxindoles, and Alkylated Aromatic Amines

Sir:

Recently, we reported on the reactions of *N*-chloroanilines (**1**) with dialkyl sulfides, β-keto sulfides, and α-carboalkoxy sulfides to yield intermediate azasulfonium salts, which on treatment with base produced methylthiomethylanilines (**2**),[1] 3-methylthioindoles (**3**),[2] and 3-methylthiooxindoles (**4**)[3] in good to excellent yields. Raney-nickel desulfurization of these products gave *o*-alkylanilines, indoles, and oxindoles, respectively. A major limitation of this surprisingly general synthetic process was associated with the instability of the *N*-chloroaniline when X was a cation stabilizing group such as *p*-methoxy. As we have previously shown, *N*-chloro-*p*-anisidines are extremely reactive,[4] even at temperatures as low as −78°. Thus, our original procedures[1-3] were not readily applicable to the synthesis of 4-methoxyanilines, 5-methoxyindoles, or 5-methoxyoxindoles. In view of the importance of methoxylated natural products related to the desulfurized versions of **2**, **3**, and **4**, we now wish to report a major modification of our original synthetic concept which permits the preparation of the desired methoxylated compounds.



Mechanistically, the reaction of *N*-chloroanilines (**1**) with a disubstituted sulfide initially produces the azasulfonium salt **5**. Base reacts with **5**, removing an α-proton to give a sulfur ylide, which undergoes an intramolecular Sommelet–Hauser type rearrangement with exclusive attack on the aromatic ring ortho to the amino function.[1] Since the instability of methoxylated derivatives of **1** precluded their use in the formation of the key intermediate **5**, we have developed an alternate route to **5** which involves the nucleophilic attack of anilines (**6**) on the long-known[5] complexes, formed from the reaction of halogens with sulfides.



In a typical procedure, 0.044–0.050 mol of sulfide in 10 ml of methylene chloride at −70° was added to a solution of 0.044 mol of chlorine in 120 ml of methylene chloride at *ca.* −70°. On addition, a slight exotherm (*ca.* 5°) was noted. The solution was stirred for 5 min and a solution of 1 equiv of the aniline (**6**) and 1 equiv of triethylamine[6] in 10 ml of methylene chloride at *ca.* −70° was added dropwise. The solution was stirred for 2–4 hr at *ca.* −70° and 0.06 mol of sodium methoxide[7] in 15 ml of absolute methanol was added. The cooling bath was removed and the reaction was allowed to warm to room temperature with stirring over a 12-hr period.[7] Work-up by dilution with water and extraction with methylene chloride gave the crude ortho-substituted aniline. When the sulfide contained a β-keto function, spontaneous cyclization to produce indoles occurred. When the sulfur was β to a carboalkoxy group, acid was added to catalyze cyclization to an oxindole.

Through the general procedure described above, *p*-anisidine (**7**, X = OCH_3) could be converted into 4-methoxy-2-(methylthiomethyl)aniline (**8**, X = OCH_3) in 62% yield. The procedure was quite general. For a series of anilines (**7**, X = CH_3, H, Cl, $CO_2C_2H_5$, and NO_2), reaction with chlorodimethylsulfonium chloride gave the corresponding 2-(methylthiomethyl)anilines in 54, 67, 45, 35, and 31% yields, respectively. The reaction was not restricted to chlorodialkylsulfonium chlorides. When bromodimethylsulfonium bromide was used with aniline, a 69% yield of **8** (X = H) was obtained. Treatment of aniline with halotetramethylenesulfonium halide (**10**, Y = Cl or Br) gave **9** (X = H) in *ca.* 20% yield.

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[1] P. G. Gassman and G. Gruetzmacher, *J. Amer. Chem. Soc.*, **95**, 588 (1973).

[2] P. G. Gassman and T. J. van Bergen, *ibid.*, **95**, 590, 591 (1973).

[3] P. G. Gassman and T. J. van Bergen, *ibid.*, **95**, 2718 (1973).

[4] P. G. Gassman, G. A. Campbell, and R. C. Frederick, *ibid.*, **94**, 3884 (1972); P. G. Gassman and G. A. Campbell, *ibid.*, **94**, 3891 (1972).

[5] For leading references see W. E. Lawson and T. P. Dawson, *ibid.*, **49**, 3119 (1927); F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955); H. Böhme and H. J. Gran, *Justus Liebigs Ann. Chem.*, **581**, 133 (1953); F. Boberg, G. Winter, and G. R. Schultze, *Chem. Ber.*, **89**, 1160 (1956); G. E. Wilson, Jr., and R. Albert, *J. Org. Chem.*, **38**, 2156, 2160 (1973).

[6] The triethylamine was used to neutralize the hydrochloric acid which was generated. In place of the aniline–triethylamine mixture, 2 equiv of the aniline was used in some cases.

[7] In the indole and oxindole syntheses, triethylamine (neat) was used as the base in the ylide generation step, and the reaction mixture was stirred for 15 min at −70° and allowed to warm to room temperature.