exhibits absorptions at 273 (14,200) and 219 (9210) [λ_{max} (ϵ)].

The thermal decomposition of the azo-coupled species to produce the diazonium-substituted borane product was found to proceed more rapidly and with fewer complications in the case of the 2,4,6-tribromophenyl arylazo system than the other substituted phenyl derivatives examined. In addition, the polarity of the solvent correlated with the rate of product formation. Polar solvents, such as acetonitrile, gave a faster reaction than less polar solvents such as ethyl acetate and diglyme. These observations suggest that the reaction proceeds *via* ionic intermediates rather than by a concerted transfer of the hydrogen from nitrogen to carbon. The unprotonated ion, $1\text{-}(1\text{-Br-}4\text{-}N_2Ph)B_{10}H_9{}^{2-}$, was stable toward thermal decomposition and did not form the $B\text{-}N_2{}^+$ function. This observation demands that a proton be present to effect an electrophilic attack at azo carbon. Further work is in progress and will be reported elsewhere.

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Observation by ESCA of Inequivalent Fluorines in ClF_3, SF_4, and PF_5

Sir:

X-Ray photoelectron spectroscopy (ESCA) is rapidly developing as a method for studying how valence electrons redistribute themselves when atoms are formed into molecules. Recent studies[1,2] have shown that charges on atoms in molecules can be extracted from core-level binding energy shifts and that these charges are in good agreement with both theoretical expectations and with other kinds of chemical evidence. We report here the application of this technique to the molecules ClF_3, SF_4, and PF_5. Of particular interest is the result that the inequivalent fluorines in these molecules can be distinguished in the photoelectron spectra. For SF_4 and ClF_3 the lines due to the two kinds of fluorines are clearly resolved. For PF_5 the lines are not resolved, but the asymmetry of the photoelectron peak clearly indicates the inequivalence of the two kinds of fluorine. We believe this to be the first demonstration that ESCA can be used to distinguish between atoms that differ only in their geometric orientation with respect to the same central atom.

Each of these molecules has the structure of a trigonal bipyramid with each having two axial fluorines. For PF_5 there are three equatorial fluorines; for SF_4, two equatorial fluorines and one equatorial lone pair; for ClF_3, one equatorial fluorine and two equatorial lone pairs. In each case the bond length for the axial fluorines is longer than that for the equatorial fluorines. The axial bonds are thought to be three-center bonds and more ionic than the equatorial bonds.[3] The axial fluorines are expected, therefore, to have higher negative charges than the equatorial ones and, consequently, lower binding energies for their core electrons.

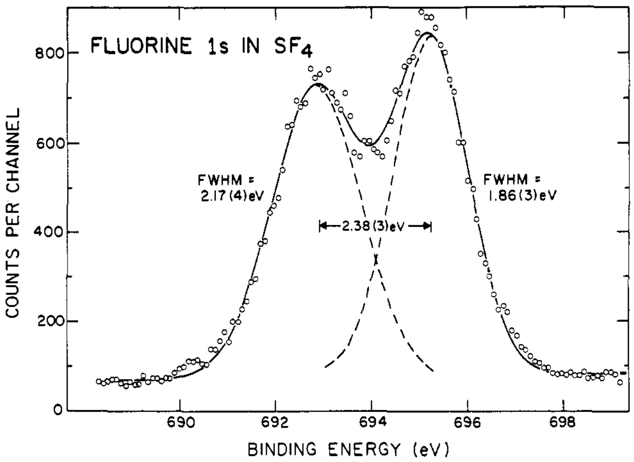

Figure 1. X-Ray photoelectron spectrum of fluorine 1s electrons in SF_4, Al Kα radiation.

The X-ray photoelectron spectra of the fluorine 1s levels in these compounds in the gas phase were measured in our cylindrical mirror electron spectrometer[4] using aluminum Kα X-rays. Pressures in the gas cell were approximately 0.1 Torr. The materials were purchased commercially and were used without further purification. According to the manufacturers the purities were ClF_3, 98%; SF_4, 90–94%; PF_5, 99%. Because of the reactivity of these compounds it is important to establish that the peaks appearing in the spectra are not due to reaction products. Our experience over the months previous to these experiments with xenon fluorides and interhalogens indicates that such reactive materials quickly consume the substances in the spectrometer that they are likely to react with. After the first few minutes of running, the spectrum is that of the pure compound. In each case we have also examined the region of the 2p or 2s electrons for the central atom and have found no evidence for contamination with impurities.

The photoelectron spectrum for the fluorine 1s electrons in SF_4 is shown in Figure 1. We see the clear resolution of the two peaks arising from the two kinds of fluorines. We have analyzed these results by fitting two gaussian peaks to the data. First we note that the area ratio of the fitted peaks is 1 to within about 2%, in agreement with expectations. The peak corresponding to the higher binding energy electrons has the narrower width, in accord with chemical effects on line widths that have been reported by us[5] and by others.[6] The splitting between the two peaks is 2.38 ± 0.03 eV. Because there are equal numbers of the two kinds of fluo-

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(1) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Amer. Chem. Soc.*, **94**, 6565 (1972).

(2) G. D. Stucky, D. A. Matthews, J. Hedman, M. Klasson, and C. Nordling, *ibid.*, **94**, 8009 (1972).

(3) R. E. Rundle, *Rec. Chem. Progr.*, **23**, 195 (1962).

(4) P. H. Citrin, R. W. Shaw, Jr., and T. D. Thomas in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 105.

(5) R. W. Shaw, Jr., and T. D. Thomas, *Phys. Rev. Lett.*, **29**, 689 (1972).

(6) R. M. Friedman, J. Hudis, and M. L. Perlman, *ibid.*, **29**, 692 (1972).

rines we cannot assign the peaks to particular fluorines on the basis of intensities.

We have not yet analyzed the data for the other two compounds in such detail. The ClF_3 spectrum shows two resolved peaks in a ratio of about 2:1. The larger peak, due to the axial fluorines, is at the lower binding energy, in agreement with the idea that the axial fluorines are more negative than the equatorial ones. The PF_5 spectrum is not clearly resolved, but consists of one asymmetric peak, whose shape is consistent with the two axial fluorines being more negatively charged than the three equatorial ones.

In addition to the results reported above, we have observed evidence for the nonequivalent fluorines in BrF_3, BrF_5, and IF_5. We are preparing a more complete analysis of all these results.

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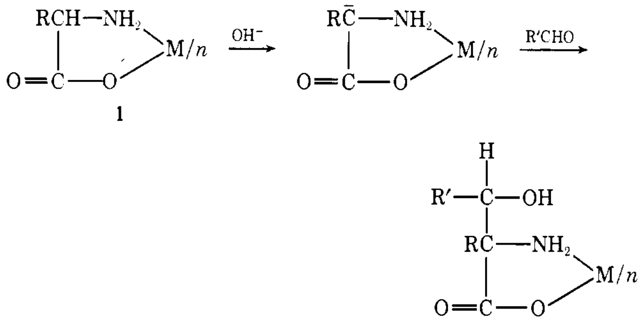
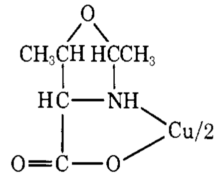
Nature of the Copper(II) Complex Formed in the Reaction of Formaldehyde with Bis((*S*)-serinato)copper(II)

Sir:

The reaction of (α-amino acidato)metal complexes, **1**, with aldehydes under alkaline conditions has been considered to occur as follows (*n* = oxidation state of metal; R = H, CH_3, etc.).[1–8]


1

The metal-containing product of the reaction has rarely been isolated[7,8] since the reaction mixtures are normally treated under acid conditions, *e.g.*, with H_2S, to give the corresponding metal-free α-hydroxymethyl-substituted amino acid. Recently,[9] it has been shown that reaction of glycine with acetaldehyde in alkaline solution in the presence of basic copper(II) carbonate gives the bis(oxazolidine)copper(II) complex shown schematically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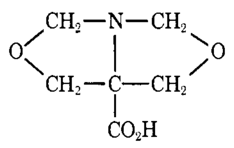
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as **2**. Threonine is obtained when **2** is treated with H_2S. Formation of **2** indicates that the amino group is attacked by the aldehyde to form the *N*-hydroxymethyl derivative. Attack by the aldehyde on the carbanion species formed under the basic conditions also occurs and the oxazolidine is subsequently formed by cyclization. The ready formation of the carbanion is indicated by proton magnetic resonance studies on glycinato–Co(III) complexes in D_2O. The exchange of the hydrogens on the α carbon with deuterium is extremely rapid.[10] Rate studies in the presence of hydroxide ion of the exchange of the α-carbon hydrogen in several other coordinated α-amino acids also indicate carbanion formation.[11] We wish to report a novel metal ion-assisted reaction of bis((*S*)-serinato)copper(II) (**1**, R = $-CH_2OH$, M = Cu, *n* = 2) with excess formaldehyde at pH 7–9 which results in the formation of the bis(amino acidato)copper(II) complex of **3**.[12] The results of an X-ray structure analysis of the deep blue crystals are also reported. The complex, isolated in 80% yield, is optically inactive, but an intermediate[13] corresponding to **4** which can be isolated in the initial stages of the reaction is optically active. The intermediate slowly loses activity at 40° in the presence of formaldehyde at pH 7–9. This behavior supports the formation of the mono-*N*-hydroxymethyl species as the first step in the reaction rather than the removal of the hydrogen on the α-carbon atom to form a carbanion. Cyclization of the hydroxymethyl groups occurs followed by addition of hydroxymethyl groups on the α-carbon atom (this step leads to loss of optical activity) and the secondary nitrogen. Cyclization again occurs to give the copper(II) complex of **3**. The importance of the copper(II) ion in this reaction is shown by the fact that no detectable reaction occurs in the absence of metal ion over a period of at least 1 week. Catalytic hydrogenation of the copper(II) complex in water or treatment with H_2S gives high yields of α-hydroxymethylserine, indicating that the cyclic structure is readily ruptured under such conditions. Treatment of the complex with sodium borohydride in aqueous solution, however, followed by esterification gives the ester, **5** (R = CH_3, C_2H_5). The latter method appears to have general application as a method for the synthesis of analogs of **3** having a variety of substituents in both rings. This aspect will be reported in detail at a later date.

Tabular crystals of the deep blue reaction product are monoclinic and have space group $P2_1/c$. The unit-

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 633.

[2] M. Sato, K. Okawa, and S. Akabori, *Bull. Chem. Soc. Jap.*, **30**, 937 (1957).

[3] S. Akabori, T. T. Otani, R. Marshall, M. Winitz, and J. P. Greenstein, *Arch. Biochem. Biophys.*, **83**, 1 (1959).

[4] T. T. Otani and M. Winitz, *ibid.*, **90**, 254 (1960).

[5] Y. Ikutani, T. Okuda, M. Sato, and S. Akabori, *Bull. Chem. Soc. Jap.*, **32**, 203 (1959).

[6] M. Murakami and K. Takahashi, *ibid.*, **32**, 308 (1959).

[7] T. Ichikawa, S. Maeda, Y. Araki, and Y. Ishido, *J. Amer. Chem. Soc.*, **92**, 5514 (1970).

[8] T. Ichikawa, S. Maeda, T. Okamoto, Y. Araki, and Y. Ishido, *Bull. Chem. Soc. Jap.*, **44**, 2779 (1971).

[9] J. P. Aune, P. Maldonado, G. Larcheres, and M. Pierrot, *Chem. Commun.*, 1351 (1970).

[10] D. H. Williams and D. H. Busch, *J. Amer. Chem. Soc.*, **87**, 4644 (1965).

[11] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 5133 (1967).

[12] The systematic name for **3** is dihydro-1*H*,3*H*,5*H*-oxazolo[3,4-*c*]oxazole-7a-carboxylic acid.

[13] All new compounds gave satisfactory analyses.