Figure 1. Degrees of freedom investigated for planar triplet trimethylenemethane.

Table I. Distortions of Triplet Trimethylenemethane from Its D_{3h} Equilibrium Geometry, Given in the Text. Energies Are Given in Kilocalories/Mole Relative to That of the Equilibrium Structure, -154.82948 hartrees. Here the CH Distance and HCH Angle Were Kept at Their Predicted Equilibrium Values

$\Delta\theta$(CCC), deg	Δr_1(CC), Å	Δr_2(CC), Å	ΔE, kcal
0	0	0	0.00
−10	−0.025	+0.025	+5.36
−10	−0.050	+0.025	+7.84
−10	−0.025	+0.050	+6.21
−10	−0.050	+0.050	+8.45
0	−0.025	+0.025	+0.61
0	−0.050	+0.025	+2.48
0	−0.025	+0.050	+1.13
0	−0.050	+0.050	+2.83
0	+0.025	−0.025	+0.52
−10	+0.025	−0.025	+3.72
0	0	+0.025	+0.27
−10	0	+0.025	+4.48
0	−0.025	0	+0.57
−10	−0.025	0	+5.06
−20	−0.025	+0.025	+21.14
−20	−0.050	+0.025	+24.97
−20	−0.025	+0.050	+22.08
−20	−0.050	+0.050	+25.78
+10	0	0	+3.36
−10	0	0	+3.96
−10	+0.050	−0.050	+4.21
−10	+0.025	+0.025	+4.94
−10	0	+0.050	+5.41
−5	+0.025	−0.025	+1.13
−15	+0.025	−0.025	+8.73

prediction of hydrocarbon (even for severely strained hydrocarbons) equilibrium geometries. The coordinate system adopted is seen in Figure 1. The predicted equilibrium geometry lies in the D_{3h} point group, as expected: θ(CCC) = 120°; ϕ(CH) = 117.6°; r_1(CC) = r_2(CC) = 1.413 Å; r_3(CH) = 1.073 Å. The most interesting structural feature is that the carbon–carbon bond distance is somewhat closer to that of a double (1.34 Å) than a single (1.54 Å) bond. The HCH angle is similar to that (116.6°) in ethylene,[10] and the CH distance is a bit smaller than in ethylene (1.076 Å).

Given the predicted equilibrium geometries, a number of excursions were considered to examine the possibility of a secondary minimum. Initially the E' direction (θ decreased, r_2 increased) was considered, but other C_{2v} possibilities were evaluated as well. Our results are summarized in Table I, where it is seen that there is no adjacent triplet secondary minimum for planar $C(CH_2)_3$. Thus it appears that an alternative explanation of the ESR spectrum is required.[11]

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(6) In ref 3, Hehre, Salem, and Willcott imply that a geometry optimization was carried out for the triplet state, but no details are given.
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(11) Another possibility suggested by Dowd and Chow[1] is that the "second state" is the orthogonal or 0°, 0°, 90° twisted form of triplet trimethylenemethane. We concur with their apparent feeling that this geometry is firmly ruled out by prior theoretical studies.[2-5] which place the orthogonal triplet at least 10 kcal above the D_{3h} equilibrium geometry.

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A Simple Method for Obtaining X-Ray Photoelectron Spectra of Species in Liquid Solution

Sir:

In x-ray photoelectron spectroscopy, it is important to prevent sample vapors from interfering with the flight path of the photoelectrons in the electron energy analyzer chamber. The study of liquid samples by XPS is usually ruled out because most liquids have vapor pressures which are too high. Even if the vapor pressure of a liquid is low enough to avoid interference in the electron analyzer, the vapor pressure directly over the liquid is generally so high that photoelectrons from the liquid are masked and the observed XPS spectrum corresponds to that of the vapor, not the liquid. Using a "liquid beam" technique, Siegbahn et al. obtained XPS spectra of formamide, ethylene glycol, benzyl alcohol, and a solution of potassium iodide in formamide.[1-3] Later, a liquid-coated moving wire system was developed by the same group to study ethylene glycol.[4] Recently Delahay et al.[5] have obtained ultraviolet photoelectron spectra of various liquids using an apparatus in which the liquid is carried into the irradiation zone by a rotating disk which is partially immersed in a refrigerated bath of the liquid. All these methods require complicated experimental apparatus and are therefore unlikely to be widely applied.

We have found that high quality x-ray photoelectron spectra can be readily obtained for compounds dissolved in glycerin[6] and that aqueous solutions can be converted into glycerin solutions which give good XPS spectra of the solutes. This technique is adaptable to most commercial x-ray photoelectron spectrometers, with little instrument modification.

Glycerin has a very low vapor pressure (2×10^{-4} Torr) at room temperature.[7] Many ionic compounds can be dissolved in glycerin in high concentrations. These factors make glycerin

Table I. Core Binding Energies and Line Widths of Nitrogen Compounds Dissolved in Glycerin

Compd	E_B(N 1s), eV	E_B(Na 1s) or E_B(K 2p$_{3/2}$, 2p$_{1/2}$), eV
NH$_4$*N*O$_3$	407.32 (1.6)[a]	
NaNO$_2$	403.4 (1.3)	1072.2 (1.9)[a]
NaN*N*N	403.34 (1.4)	1072.2 (1.9)
*N*H$_4$NO$_3$	402.07 (1.9)	
NaNN*N*	399.02 (1.8)	
KOCN	398.0 (1.8)	293.4 (1.7), 296.0 (1.6)
K$_3$Fe(CN)$_6$	398.0 (1.6)	293.1 (1.4), 296.1 (1.0)

[a] Parenthesized values are fwhm values in electronvolts; the uncertainties in these values are ±0.1–0.2 eV.

Figure 1. X-ray photoelectron spectra of salts in glycerin: A, the computer-fitted nitrogen 1s spectrum of NH$_4$NO$_3$; B, the computer-fitted nitrogen 1s spectrum of NaN$_3$; C, the sulfur 2p spectrum of Na$_2$S$_2$O$_3$. The broadened, misshapen peaks are due to sample decomposition under the x-ray flux.

an excellent solvent for XPS studies. We chose to study the N 1s spectra of a series of nitrogen-containings salts (Table I) covering a wide range of nitrogen oxidation states. Most of these salts have previously been examined as solids;[8,9] hence it is possible to compare the results obtained in the different phases. We also obtained the S 2p spectrum of a solution of sodium thiosulfate.

In most cases the salts were dissolved at a concentration of 1–2 *m* in glycerin by vigorously stirring the finely powdered salts with hot anhydrous glycerin and then cooling. The salts were reagent grade materials; the glycerin was from a freshly opened bottle of J. T. Baker "Photrex" reagent and was used without purification.

The following method was used for converting aqueous solutions into glycerin solutions. The aqueous salt solution and glycerin, in a 1:2 volume ratio, were thoroughly mixed in a round-bottomed flask. The water was removed at 65 °C, using a high vacuum rotary evaporator. During the vacuum removal of the water, which took ~24 h, a significant amount of glycerin distilled from the bottom of the flask, condensed on the walls, and collected in an annular trap in the upper part of the flask.

A Du Pont 650 electron spectrometer equipped with a multichannel analyzer was used. To prevent the sample temperature from rising above room temperature during the run, we used a bored-out sample probe through which ice–water was circulated. A thin film of the glycerin solution was spread completely over the flat, sand-blasted surface of the probe tip. The only sample which showed evidence of radiation damage was the solution of Na$_2$S$_2$O$_3$, which decomposed to elemental sulfur and a high oxidation state sulfur species. The core electron binding energies of the compounds in Table I were referenced against the C 1s line of the hydrocarbon contaminant present in the spectrometer, assuming E_B(C 1s) = 285.0 eV. Most of the reported values are averages of independent measurements which differed by no more than 0.1 eV. In the case of NH$_4$NO$_3$ and NaN$_3$, the binding energies are given to 0.01 eV because the *relative* values of each pair of binding energies (NH$_4^+$/NO$_3^-$ and N*N*N$^-$/NN*N*$^-$) were reproducible to better than 0.05 eV. With suitable referencing, this technique can yield very accurate chemical shift values for dissolved species. The effects of sample charging were minimized by alternating runs of the sample core levels with runs of the carbon reference line. The raw spectral data were fit to Gaussian lineshapes using the least-squares curve fitting program GAMET.[10]

The N 1s binding energies in Table I closely parallel those measured for the same compounds in the solid state.[8] Figures 1A and 1B show the fitted XPS spectra of solutions of NH$_4$NO$_3$ and NaN$_3$, respectively. Within the statistical uncertainty, the areas of the nitrate and ammonium peaks are equal and the peak assigned to the middle nitrogen atom of N$_3^-$ is one-half as intense as that due to the two terminal nitrogen atoms of N$_3^-$. The NH$_4^+$ line is ~20% broader than the
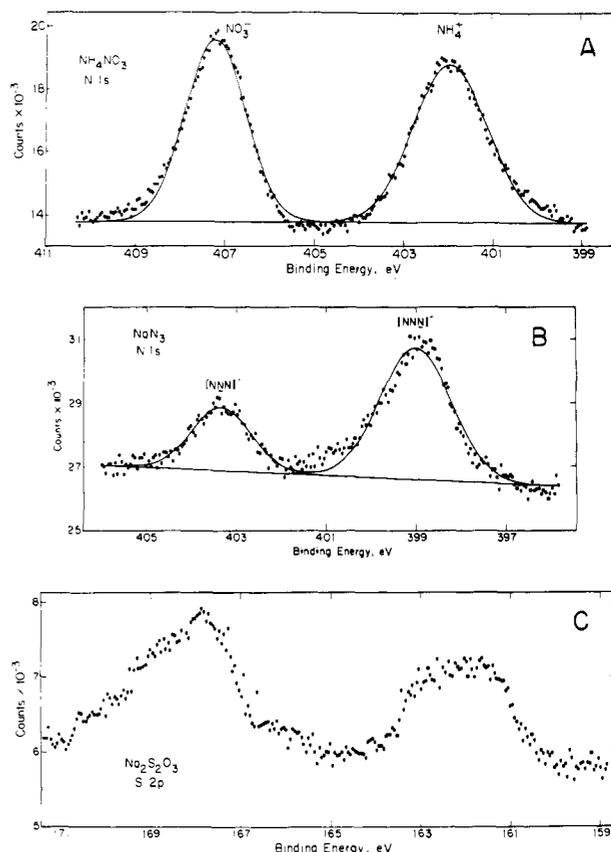
NO$_3^-$ line; this feature has been previously observed[11,12] and has been explained in terms of vibrational broadening related to the much greater negative charge of the nitrogen atom in NH$_4^+$.[13] The width of the line due to the terminal atoms of N$_3^-$ is ~30% greater than the width of the line due to the middle atom. This greater line width is also probably due to vibrational broadening, but in this case is probably caused by marked changes in bond order accompanying the core ionization of a terminal atom.[13]

The S 2p spectrum of the Na$_2$S$_2$O$_3$ solution is shown in Figure 1C. The two bands separated by ~6 eV correspond to the presence of two types of sulfur atoms having very different charges. Although this result is consistent with the known structure of the thiosulfate ion, the irregular shape and great width of these bands and the evident decomposition of the sample lead us to believe that at least four different sulfur species contributed to the peaks. Therefore no attempt was made to curve fit the data.

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Interaction of the Dicoordinate Phosphorus Cation 1,3-Dimethyl-1,3,2-diazaphospholidide with Transition Metal Nucleophiles

Sir:

Synthetic routes to dicoordinate phosphorus cations have recently attracted attention due in part to the intriguing structures and coordination properties which these species display. One class of trivalent, tricoordinate phosphines, the aminophosphines, has proved to be an abundant source of dicoordinate cationic species. Fleming and coworkers[1] prepared the cyclic ligand 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine, and they found that, in the presence of strong fluoride ion acceptors, PF_5 or BF_3, a cyclic cation (**1**) could be

(1)
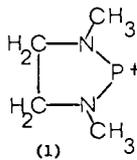
produced. Subsequently, Parry and coworkers[2-4] reported that several acyclic aminochlorophosphines form cationic species in the presence of a chloride ion acceptor such as $AlCl_3$. In particular, the complexes $[[(CH_3)_2N]_2PCl]_2AlCl_3$ (**2**),[3] $[[(CH_3)_2N]_2PCl]AlCl_3$ (**3**),[3] $[[(CH_3)_2N]_2PCl][[(CH_3)_2N]_3P]AlCl_3$ (**4**),[3] $(CH_3)_2NPCl_2 \cdot AlCl_3$ (**5**),[4] and $[[(CH_3)_2N]_3P]AlCl_3$ (**6**)[3] do not form molecular addition compounds with Al–N or Al–P coordinate bonds. This is in contrast with the known addition complex F_3PAlCl_3 which does contain a Al–P coordinate bond.[5] Instead, each of the aminochlorophosphines forms an ionic complex in which the cation is considered to contain a dicoordinate Lewis acid species, $[(CH_3)_2N]_2P^+$ or $(CH_3)_2NPCl^+$. In compounds **2**,[3] **4**,[3] and **6**[3] the dicoordinate phosphorus is observed to coordinate 1 mol of phosphine *base* resulting in the formation of diphosphine cations of the general type $R_3P-PR_2^+$. Compounds **3**[4] and **5**[4] apparently contain the isolated cationic species $(Me_2N)_2P^+$ and $MeNPCl^+$.

It should be expected that these dicoordinate cations may act not only as strong Lewis acids toward 1 mol of phosphine base, but also they might act as Lewis acids toward other nucleophiles. The behavior of dicoordinate phosphine ions has only been partially explored,[4,6] and this prompts us to report our investigations of the interaction of the cyclic cation **1**

toward several strong nucleophilic transition metal reagents. Typically, the cyclic ligand $CH_3NCH_2CH_2N(CH_3)PF^1$ and the sodium salt of Mo $(\Pi\text{-}C_5H_5)(CO)_3{}^-$, $Fe(\Pi\text{-}C_5H_5)(CO)_2{}^-$, or $Fe(CO)_4{}^{2-}$ are combined on an equivalence basis in dry THF at -78 °C under an atmosphere of dry nitrogen. The solution is then warmed to room temperature with rapid stirring and the stirring is continued for 24 h. The solution is filtered under nitrogen, the solvent stripped from the filtrate, and the product collected in a nitrogen-filled dry bag. The resulting products $[CH_3NCH_2CH_2N(CH_3)P^+][(\Pi\text{-}C_5H_5)Mo(CO)_3{}^-]$ (**7**), $[CH_3NCH_2CH_2N(CH_3)P^+][(\Pi\text{-}C_5H_5)Fe(CO)_2{}^-]$ (**8**), and $[CH_3NCH_2CH_2N(CH_3)P^+]_2[Fe(CO)_4{}^{2-}]$ (**9**) are purified by extraction, recrystallization, and sublimation: **7** and **8**, benzene extraction, benzene/pentane recrystallization, yellow crystals (130 °C sublimation) and red crystals (95 °C sublimation with some decomposition), respectively; **9**, cyclohexane extraction, cyclohexane recrystallization, yellow crystals (35 °C sublimation); yields >80%. Anal. Calcd for $C_{12}H_{15}MoN_2O_3P$: C, 39.79; H, 4.18; Mo, 26.59; N, 7.74; P, 8.55. Found: C, 39.42; H, 4.41; Mo, 26.84; N, 7.90; P, 8.89.[7]

The following characterization data for **7** and **9** provide unequivocal composition analysis and tentative structural assignments.[8] The mass spectrum (70 eV) of **7** shows a characteristic fragmentation pattern, but the parent ion is too weak to observe[9,10] (m/e (assignment, rel intensity)): 336 ($PN_2C_4H_{10}Mo(CO)_2(C_5H_5)^+$, 4), 278 ($PMo(CO)_3(C_5H_5)^+$, 4), 249 ($N_2C_4H_{10}Mo(C_5H_5)^+$, 4), 247 ($Mo(CO)_3(C_5H_5)^+$, 5), 221 ($N_2C_2H_6Mo(C_5H_5)^+$, 4), 222 ($PMo(CO)(C_5H_5)^+$, 6), 206 ($NC_3H_7Mo(C_5H_5)^+$, 7), 191 ($Mo(CO)(C_5H_5)^+$, 15), 163 ($Mo(C_5H_5)^+$, 37), 137 ($MoC_3H_3^+$, 24), 117 ($PN_2C_4H_{10}^+$, 100), 98 ($Mo^+$, 20), 74 ($C_2H_5NP^+$, 84), 60 ($NPCH_3^+$, 86), 44 ($NC_2H_6^+$, 100), 42 ($NC_2H_4^+$, 63). The mass spectrum of **9** does show a weak parent ion: 402 $((PN_2C_4H_{10})_2Fe(CO)_4^+$, <1), 374 $((PN_2C_4H_{10})_2Fe(CO)_3^+$, <1), 285 $(PN_2C_4H_{10}Fe(CO)_4^+$, <1), 257 $(PN_2C_4H_{10}Fe(CO)_3^+$, <1), 229 $(PN_2C_4H_{10}Fe(CO)_2^+$, 1), 201 $(PN_2C_4H_{10}Fe(CO)^+$, 2), 173 $(PN_2C_4H_{10}Fe^+$, 4), 140 $(Fe(CO)_3^+$, 4), 117 $(PN_2C_4H_{10}^+$, 100), 87 $(FeP^+$, 15), 84 $(Fe(CO)^+$, 11), 74 $(C_2H_5NP^+$, 11), 60 $(CH_3NP^+$, 12), 56 $(Fe^+$, 24), 44 $(NC_2H_6^+$, 96), 42 $(NC_2H_4^+$ 40). The infrared spectra are similar for each compound in the carbonyl stretching region (Nujol mull, cm^{-1}): **7**, 1894 and 1815; **9**, 2037 and 1929. These data show a distinct shift to higher frequency from the sodium salts: $NaMo(CO)_3(C_5H_5)$, 1880 (m), 1687; $Na_2Fe(CO)_4$, 1891, 1759. This shift is expected if the phosphorus cation is acting as an electron-withdrawing group on the transition metal base.[11] Shifts of this order have been observed for related bis(pentafluorophenyl)phosphine–metal carbonyl complexes.[12] Other infrared peaks are observed which are characteristic of the skeletal vibrations of the cation and anion fragments; however, a lack of complete assignments, particularly for the cation, prohibit further structural conclusions at this time.

The ^{31}P NMR spectra (H_3PO_4 standard) of **7** in THF at 32 °C consists of a singlet at 271 ppm (downfield) while that of **9** in THF at 32 °C consists of an AB multiplet centered at 161.2 ppm with $J = 357$ Hz and $|\nu_A - \nu_B| = 2396$ Hz. The ^{31}P chemical shifts of aminophosphines have been used to assign coordination numbers.[13] The AB pattern of **9** is similar to the spectrum obtained for **4**[3] and the chemical shift is intermediate between the values expected for coordination numbers three and four. Although the ^{31}P chemical shift for **7** falls within the chemical shift range of dicoordinate aminophosphines (260 ± 20 ppm),[4] the volatility and carbonyl stretching frequencies suggest that the cation has a strong interaction with the metal anion. The ^1H NMR spectrum (benzene, 25 °C, Me_4Si external standard) shows a methyl doublet at 1.77 ppm (J_{HCNP} = 11.5 Hz) (rel intensity 6), a methylene doublet at 1.97 ppm