Contribution from the Department of Chemistry,
University of New Mexico, Albuquerque, New Mexico 87131

Formation of a Formal Diphosphine Monocation and Dication from (Methylamino)bis(difluorophosphine)[1]

R. W. LIGHT, R. T. PAINE,* and D. E. MAIER

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The reactions of (methylamino)bis(difluorophosphine), $CH_3N(PF_2)_2$, with the strong transition-metal nucleophile $NaMo(\pi\text{-}C_5H_5)(CO)_3$ in 1:1 and 1:2 mole ratios in THF solution produce new species with compositions described by the formulas $F_2PN(CH_3)PFMoCp(CO)_3$ and $F_2PN(CH_3)PMo_2Cp_2(CO)_4$, respectively. The new compounds have been characterized by chemical analyses, solution conductance, and mass, infrared, and ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectrometric techniques. The data show that the diphosphine ligand in each compound contains a unique phosphorus atom in a highly deshielded electronic environment: P′ in $F_2PN(CH_3)P'Mo_2Cp_2(CO)_4$ has the lowest ^{31}P shift yet reported in a phosphine ligand. Structures for the new compounds containing formal cationic diphosphine ligands are proposed.

Introduction

Aminohalophosphines $(R_2N)_yPX_{3-y}$ may be classified as multifunctional ligands since they are capable of combining with electrophilic and nucleophilic reagents at several different sites on the ligand backbone. For example, aminohalophosphines form a variety of well-known coordination complexes with classical Lewis acceptors by using either the phosphorus or the nitrogen atom lone pairs.[2] The chemistry of the ligands is not, however, limited to lone-pair coordination modes. For instance, it was recently observed that in the presence of strong halide ion acceptors, the phosphorus–halogen bond in several simple aminohalophosphines underwent cleavage with the resultant formation of dicoordinate aminophosphine cations.[3-7] Subsequently, it was found that metathesis reactions between a cyclic aminofluorophosphine, $CH_3NCH_2CH_2N(CH_3)PF$, and the sodium salts of transition-metal nucleophiles $Mo(\pi\text{-}C_5H_5)(CO)_3^-$, $Fe(\pi\text{-}C_5H_5)(CO)_2^-$, and $Fe(CO)_4^{2-}$ produce unique organometallic phosphine complexes containing the cyclic phosphine cations $[CH_3NCH_2CH_2N(CH_3)P^+]$ and $[CH_3NCH_2CH_2N(CH_3)P\text{–}PN(CH_3)CH_2CH_2N(CH_3)^{2+}]$.[8]

The classical coordination chemistry of diphosphine ligands has been vigorously studied; however, the existence of cationic diphosphine species has only been briefly mentioned.[6] Since the initial reports on the formation and properties of cationic monophosphines have generated further interest in these species and since there is additional diversity available in diphosphine systems, we have chosen to examine the potential cation-forming chemistry of these ligands. In particular, (methylamino)bis(difluorophosphine), $CH_3N(PF_2)_2$,[9] has been observed to form mono(borane(3)) and bis(borane(3)) classical coordination complexes,[10] a five-membered heteroatom ring complex with B_2H_4,[11] and monodentate and bidentate complexes with low-valent transition metals.[12,13] In each complex the coordinate bond involves overlap of an acceptor orbital and the phosphorus atom lone pair. In no prior case has P–F bond scission been observed. We report here on the first such reaction from the interaction of the transition-metal nucleophile $NaMoCp(CO)_3$ with $CH_3N(PF_2)_2$ in 1:1 and 2:1 mole ratios. The resulting metathesis reactions produce NaF and novel organomolybdenum–phosphorus complexes **1** and **2**, which may be considered to contain the formal cationic ligands $CH_3N(PF_2)PF^+$ and $CH_3N(PF_2)P^{2+}$.

Experimental Section

General Information. Standard high-vacuum and inert-atmosphere synthetic techniques were used for the manipulations of all reagents and reaction products. Conductance measurements were performed with a Barnstead Model PM-70CD conductance bridge and a commercial dip-type micro conductance cell. Mass spectra were recorded on a Du Pont Model 21-491 spectrometer operating at 70 eV with an inlet temperature of 30 °C and a source temperature of 100 °C. Samples were introduced through a heated-solids probe. Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrometer. The samples were prepared on KBr windows or as KBr pellets. The spectra were calibrated with polystyrene film absorptions. The NMR spectra were recorded on a Varian XL-100 NMR spectrometer operating at 25.2 MHz (^{13}C), 40.5 MHz (^{31}P), 94.1 MHz (^{19}F), and 100 MHz (^1H). The data were collected in the pulse mode by using a Nicolet TT-100 data system. Samples were contained in sealed 5-mm tubes rigidly placed in a 12-mm tube containing a deuterated-lock solvent. Spectral standards were $(CH_3)_4Si$ (^{13}C, ^1H), 85% H_3PO_4 (^{31}P), and $CFCl_3$ (^{19}F).

Materials. The $CH_3N(PF_2)_2$ was prepared by literature methods.[9] The $[CpMo(CO)_3]_2$ was purchased from Strem Chemicals, and the $NaMoCp(CO)_3$ was prepared in dry THF by reduction of the dimer with sodium amalgam. Each solvent was rigorously dried and degassed over an appropriate drying agent. All solvent transfers were accomplished by vacuum distillation.

Preparation of $[CH_3N(PF_2)PF][MoCp(CO)_3]$, 1. A mixture of 2.0 mmol of $CH_3N(PF_2)_2$, approximately 2.0 mmol of $NaMoCp(CO)_3$, and 50 mL of THF was stirred at 23 °C for 12 h in a previously evacuated 150-mL Schlenk flask. The contents of the flask were then frozen at −196 °C, and the evolved CO was collected and measured with a Toepler pump system. Typically less than 20% of the CO present in the starting metal–carbonyl anion was recovered. NMR spectra show a corresponding formation of **2** in about 10% yield via a competing reaction. The reaction mixture was then warmed to 23 °C and filtered under nitrogen, and the THF was vacuum evaporated. The red-yellow oil formed in 80% yield corresponds to $[CH_3N(PF_2)(PF)][MoCp(CO)_3]$, **1**. The oil is air and moisture sensitive, and it is soluble in THF and benzene. Extensive vacuum pumping on the oil results in the formation of a glass. Attempts to purify **1** using solvent extraction procedures resulted in significant decomposition. Anal. Calcd for $C_9H_8MoNO_3P_2F_3$: C, 27.50; H, 2.04; N, 3.56. Found: C, 27.51; H 2.19; N, 3.69. Mass spectrum [*m/e* (assignment, relative intensity)]: 365 ($Mo(C_5H_5)(CO)_2P_2F_3NCH_3^+$, 1), 337 ($Mo(C_5H_5)(CO)P_2F_3NCH_3^+$, <1), 310 ($Mo(C_5H_5)(CO)_3PFCH_3^+$, 2), 242 ($Mo(C_5H_5)PFNCH_3^+$, 5), 182 ($Mo(C_5H_5)F^+$, 7), 99 ($OPF_2CH_2^+$, 41), 98 ($OPF_2CH^+$, 35), 88 ($PF_3^+$, 18), 80 ($OPFCH_2^+$, 47), 79 ($OPFCH^+$, 5), 78 ($OPFC^+$, 20), 69 ($PF_2^+$, 100), 60 ($PNCH_3^+$, 40), 46 ($PCH_3^+$, 6). Infrared spectrum (cm^{-1}) (mull; from the carbonyl region): 1990 and 1930. Equivalent conductance (THF, 0.04 M): $\Lambda = 0.08$ cm^2. Phosphorus-31 NMR (THF, 32 °C): δ 136.6 ($^1J_{P1F1} = 1306$ Hz, $^1J_{P1F2} = 1243$ Hz, $^2J_{P1P2} = 32$ Hz, $^3J_{P1F3} = 4$ Hz), 275.2 ($^1J_{P2F3} = 1057$ Hz, $^2J_{P2P1} = 32$ Hz). Fluorine-19 NMR (THF, 32 °C): δ −27.6, −30.9 ($^1J_{F2P1} = 1243$ Hz, $^1J_{P1F1} = 1306$ Hz), −146.4 ($^1J_{F3P2} = 1057$ Hz). Carbon-13 NMR (THF, 32 °C): δ 93.28, 37.87. Proton NMR (benzene, 32 °C): δ 4.04, 2.03.

Preparation of $[CH_3N(PF_2)P][Mo_2Cp_2(CO)_4]$, 2. A mixture of 2.0 mmol of $CH_3N(PF_2)_2$, 4.0 mmol of $NaMoCp(CO)_3$, and 50 mL of THF was stirred at 23 °C for 12 h in a previously evacuated 150-mL Schlenk flask. The contents of the flask were then frozen at −196 °C, and the evolved CO was collected and measured by using a Toepler pump system: 3.3 mmol recovered, 83% yield based upon starting materials, 98% yield based upon ligand consumed. The reaction

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mixture was warmed to 23 °C and filtered under nitrogen, and the THF was vacuum evaporated. The yellow oil remaining was isolated with 84% yield, and it corresponds to $[CH_3N(PF_2)P][Mo_2Cp_2(CO)_4]$, **2**. The oil is extremely sensitive to air, moisture, and solvent extraction procedures which has hampered analyses. The compound retains THF even upon pumping, and it is soluble in THF and benzene. Extensive pumping on the oil results in the formation of a sticky solid. Anal. Calcd for $C_{15}H_{13}Mo_2NO_4P_2F_2$: C, 31.99; H, 2.33; N, 2.49; Mo, 34.07. Found: C, 33.90; H, 2.89; N, 2.40; Mo, 34.14. Mass spectrum [*m/e* (assignment, relative intensity)]: 567 ($Mo_2(CO)_4(C_5H_5)_2PNCH_3PF_2^+$, 3), 483 ($Mo_2(CO)(C_5H_5)_2PNCH_3PF_2^+$, 7), 455 ($Mo_2(C_5H_5)_2PNCH_3PF_2^+$, 14), 390 ($Mo_2(C_5H_5)PNCH_3PF_2$, 4), 228 ($Mo(C_5H_5)_2^+$, 6), 182 ($Mo(CO)_3^+$, 9), 73 ($C_4H_9O^+$, 37), 72 ($C_4H_8O^+$, 75), 71 ($C_4H_7O^+$, 97), 69 ($PF_2^+$, 100), 60 ($PNCH_3^+$, 55), 57 ($PNC^+$, 80). Infrared spectrum (cm^{-1}) (mull; from the carbonyl region): 1995, 1940, 1895, 1747, and 1710 cm^{-1}. Equivalent conductance (THF, 0.07 M): $\Lambda = 0.05\ cm^2$. Phosphorus-31 NMR (THF, 32 °C): δ 154.8 ($^1J_{P1F} = 1257$ Hz, $^2J_{P1P2} = 54$ Hz), 404.1 ($^2J_{P2P1} = 54$ Hz, $^3J_{P2F} = 10$ Hz). Fluorine-19 NMR (THF, 32 °C): δ_{F2} −46.2 ($J_{FP1} = 1251$ Hz, $^2J_{F1F2} = 54$ Hz, $^3J_{FP2} = 10$ Hz). Carbon-13 NMR (THF, 32 °C): δ 93.60, 91.62, 35.94. Proton NMR (THF, 32 °C): δ 5.71, 5.83.

Results and Discussion

In the reports on the existence of cationic phosphines,[3-6,8] ionic structure assignments have been deduced from the nature of the preparative metathesis reaction, conductivity measurements, the absence of ligand phosphorus–halogen infrared vibrations, and unusually low-field ^{31}P chemical shifts. In only one recently reported example, $[(i\text{-}Pr_2N)_2P^+][AlCl_4^-]$,[7] has an unambiguous molecular structure been determined, and this structure reveals an isolated cation having approximate trigonal-planar geometry about the dicoordinate phosphorus atom. Parry and co-workers[4] in their first description of the formation of the noncyclic cations $(Me_2N)_2P^+$ and Me_2NPCl^+ noted that the coordinatively unsaturated cationic phosphines should be capable of functioning as both weak σ electron donors and σ or π electron acceptors. Such bifunctionality is a consequence of the availability of a lone pair, an empty molecular orbital, and a formal positive charge all localized on the central phosphorus atom. Systems which demonstrate this bifunctionality have now been reported. Parry and co-workers[5] have prepared a classical neutral coordination complex $CH_3NCH_2CH_2N(CH_3)P(F)Fe(CO)_4$, and a crystal structure determination showed that the molecule has the expected trigonal-bypyramidal geometry about the iron atom with the neutral phosphine ligand axially bound through its lone pair.[14] This complex, when combined with PF_5, produces an ionic product $[CH_3NCH_2CH_2N(CH_3)PFe(CO)_4^+][PF_6^-]$ in which the phosphorus lone-pair coordination mode is presumably retained.[5] In contrast, the combination of the same ligand with $NaMoCp(CO)_3$ produces a compound formally represented as $[CH_3NCH_2CH_2N(CH_3)P^+][MoCp(CO)_3^-]$ which cannot employ phosphorus lone-pair coordination to the metal center without violating effective atomic number tenets.[8] Acceptor behavior by the phosphorus atom is implied.

In the present study the combinations of the potentially tridentate ligand $CH_3N(PF_2)_2$ with the metal nucleophile $NaMoCp(CO)_3$ in 1:1 and 1:2 mole ratios in THF solution have been explored in an effort to further delineate the scope of this intriguing cation chemistry. The 1:1 mole ratio produces formal metathesis products, NaF and $[CH_3N(PF_2)PF^+][MoCp(CO)_3^-]$ (**1**), as summarized by eq 1. The

$$CH_3N(PF_2)_2 + NaMoCp(CO)_3 \xrightarrow[23\ °C,\ 12\ h]{THF} NaF + \underset{\mathbf{1}}{[CH_3N(PF_2)(PF)^+][MoCp(CO)_3^-]} \quad (1)$$

primary reaction occurs without displacement of CO, and the THF-soluble red-yellow product **1** is an air- and moisture-sensitive oil. The combination of $CH_3N(PF_2)_2$ with $NaMoCp(CO)_3$ in a 1:2 mole ratio in THF also results in a formal metathesis reaction which is summarized by eq 2. This

$$CH_3N(PF_2)_2 + 2NaMoCp(CO)_3 \xrightarrow[23\ °C,\ 12\ h]{THF} 2NaF + 2CO + \underset{\mathbf{2}}{[CH_3N(PF_2)P^{2+}][Mo_2Cp_2(CO)_4^{2-}]} \quad (2)$$

reaction is accompanied by CO evolution in a ratio of 2 mol of CO liberated to 1 mol of ligand consumed. The yellow, air-sensitive product **2** is soluble in THF and benzene, and it solvates tenaciously with THF. This reaction is responsible for the generation of small variable amounts of CO in the 1:1 reaction condition. Due to difficulties in achieving exact stoichiometric mixtures of starting reagents, reaction 2 accompanies reaction 1 when excess metal nucleophile is present. Chemical analyses and mass spectra provide evidence in support of the general composition assignments for **1** and **2**. The mass spectrum of **1** shows a fragmentation pattern typical of an aminophosphine–metal carbonyl complex; the highest mass ion observed corresponds to the parent-minus-CO ion $[CH_3N(PF_2)PFMoCp(CO)_2]^+$, *m/e* = 365.[15] The mass spectrum of **2** also shows a typical fragmentation pattern, and the parent ion $[CH_3N(PF_2)PMo_2Cp_2(CO)_4]^+$ is detected at a low relative intensity.

The structural assignments for **1** and **2** are of interest with relation to the structures of other complexes which are known or proposed to contain a tervalent phosphine cation. Although **1** and **2** have been schematically presented in eq 1 and 2 as formal separated ion complexes, structures involving ion-pair or covalent phosphorus–molybdenum interactions must also be evaluated in the light of the characterization data which follow.

Table I. Equivalent Conductance Data

compd	equiv conduct[a]	concn, M	solvent
1, $F_2PN(CH_3)PF^+MoCp(CO)_3^-$	0.06	0.04	THF
2, $F_2PN(CH_3)P^{2+}[MoCp(CO)_2]_2$	0.037	0.07	THF
3, $(Ph_3P)_2N^+Cl^-$	2.7	0.004	THF
4, $CH_3NCH_2CH_2N(CH_3)P^+NbF_6^-$	42	0.28	CH_3NO_2
5, $CH_3NCH_2CH_2N(CH_3)P^+MoCp(CO)_3$	0.15	0.03	THF
6, $(CH_3)_2NP^+AlCl_4^-$	1.1[b]	0.01	CH_2Cl_2
7, $NaMoCp(CO)_3$	1.7	0.04	THF
8, $[MoCp(CO)_3]_2$	0.006	0.01	THF
9, NaF	nil	nil	THF
10, NaI	0.19	0.04	THF

[a] All measurements were recorded at 23 °C except $NaMoCp(CO)_3$ (25 °C), and the conductances are corrected for solvent ionization. [b] Reference 4.

Conductivity data for **1**, **2**, and several related compounds in nonaqueous solution are summarized in Table I. The data indicate that **1** and **2** are not extensively ionized in THF.[16] Tetrahydrofuran is known to stabilize ion-pair formation in certain salts with a concomitant reduction of solution conductivity. In particular, $NaCo(CO)_4$,[17] $NaMn(CO)_5$,[18] $Na_2Fe(CO)_4$,[19] $Mg[FeCp(CO)_2]$,[20] $NaFeCp(CO)_2$,[21] and $NaMoCp(CO)_2P(OPh)_3$[21] have been found to ion-pair strongly in ethereal solvents. Pannell and Jackson[21] have specifically shown that $NaMoCp(CO)_2P(OPh)_3$ forms both a solvent-separated ion pair and a sodium–isocarbonyl-bound tight ion pair in THF while $NaFeCp(CO)_2$ displays both of these binding modes and a direct sodium–iron-bound tight ion-pair interaction. Extensive conductance and infrared studies of $NaMn(CO)_5$ and several phosphine substitution derivatives[22] as well as bis(triphenylphosphin)iminium salts of $Co(CO)_4^-$,

$HFe(CO)_4^-$, $V(CO)_6^-$, and $(\mu\text{-H})[Cr(CO)_5^-]_2$[23] in THF have verified the presence of complex ion-pair binding in these complexes. With reasoning parallel to that developed for the above systems, it also may be reasonable to ascribe the low conductance of THF solutions of **1**, **2**, **5**, and **6** to tight ion-pair binding between a phosphine cation and transition-metal anion. Of course, covalent interactions between the formal phosphine cation and the metal anion also could account for the small observed degrees of ionization.

Infrared spectra provide additional structural information. Two carbonyl bands are expected for a free $CpMo(CO)_3^-$ species having local C_{3v} symmetry;[24] however, one or more additional bands may be expected as the symmetry of the species is lowered. Compound **1** displays carbonyl absorptions, which are medium dependent, at 1990 (s) and 1930 (s) cm^{-1} from a mull sample, 1992 (s), 1934 (s), 1913 (sh), 1895 (sh), 1872 (m), and 1835 (m) cm^{-1} from a cyclohexane solution, and 1994 (s), 1919 (s), 1895 (sh), and 1844 (m) cm^{-1} from a KBr pellet.[25] The infrared spectrum of **2** from a KBr pellet shows three carbonyl bands at 1987, 1914, and 1835 cm^{-1} while a spectrum from a THF solution shows bands at 1992, 1927, 1899, and 1857 cm^{-1}. The number and positions of these bands are consistent with their assignment as terminal stretching modes. Comparisons of these data with frequencies obtained from other complexes containing the $CpMo(CO)_3^-$ moiety are possible, but they must be made with some caution. The infrared spectra of $NaMoCp(CO)_3$ in THF and pyridine[26] show absorptions at 1897 (s), 1793 (s), and 1742 (s) and at 1893 (s), 1775 (s), and 1749 (m) cm^{-1}, respectively. Further, $(en)_3Cd[MoCp(CO)_3]_2$ (mull) shows carbonyl bands at 1888 (s), 1778 (s), and 1744 (s) cm^{-1} [27] while a CH_2Cl_2 solution of $Cd[MoCp(CO)_3]_2$ shows bands at 1990 (sh), 1968 (vs), 1892, and 1867 (vs) cm^{-1}.[27] The structures of the solution species and the insoluble cadmium derivative are not known with certainity; however, it has been suggested that ionic or ion-pair interactions are present in the first three compounds, and a Cd–Mo metal–metal interaction is suggested for the last complex.[26,27] Several related compounds are known to contain ion-pair interactions utilizing metal–isocarbonyl linkages: $(THF)_4MgMoCp(CO)_3$ (mull),[20] 1908 (s), 1810 (s), 1674 (s) cm^{-1}; $(THF)_4MgMoCp(CO)_3$ (benzene),[20] 1925 (s), 1825 (s), 1668 (s) cm^{-1}; $Mg(py)_4[MoCp(CO)_3]_2$ (mull),[27] 1918, 1828, 1667 cm^{-1}; $Mg(py)_4[MoCp(CO)_3]_2$ (pyridine),[26] 1915, 1819, 1664 cm^{-1}. The carbonyl bands in the region 1675–1650 cm^{-1} in these complexes are diagnostic of the isocarbonyl structural feature.[28] Clearly, in **1** and **2** an isocarbonyl ion-pair interaction is eliminated from consideration since a vibration in this region is not observed. Although medium effects are present in the above data, there appears to be a correspondence between the three terminal carbonyl bonds in $NaMoCp(CO)_3$ and $(en)_3Cd[MoCp(CO)_3]_2$ and three of the carbonyl bands in **1** and **2**. However, each of the primary carbonyl bands in **1** and **2** appears shifted by approximately 100 cm^{-1} to *higher* frequency from the corresponding bands in the sodium- and base-coordinated cadmium analogues. The shift is similar in magnitude to that observed upon comparison of $NaMoCp(CO)_3$ with $Cd[MoCp(CO)_3]_2$ and $CH_3MoCp(CO)_3$.[29] The shifts in **1** and **2** appear consistent with the phosphine cations acting to some degree as electron acceptors toward the respective molybdenum atom centers. The data are inconsistent with the cations acting as strong electron-pair donors or with the presence of solvent-separated ion pairs. In the absence of a precedent case, it is not clear that a direct ion-pair interaction can be eliminated on the basis of this data.

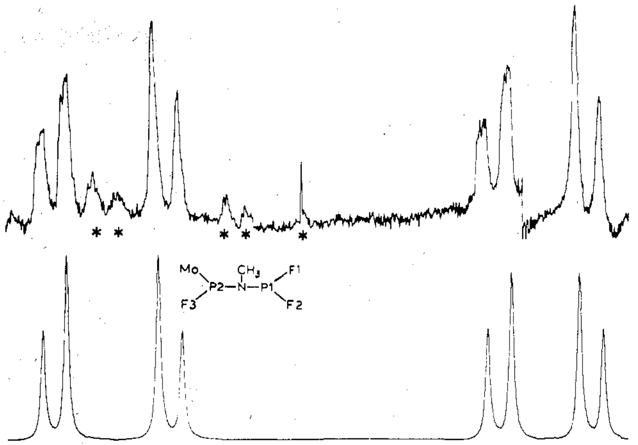


Figure 1. 94.1-MHz ^{19}F NMR spectrum and simulation of $[F_2PN(CH_3)PF^+][MoCp(CO)_3^-]$ in THF at 32 °C (downfield half). The asterisk indicates impurity resonance.

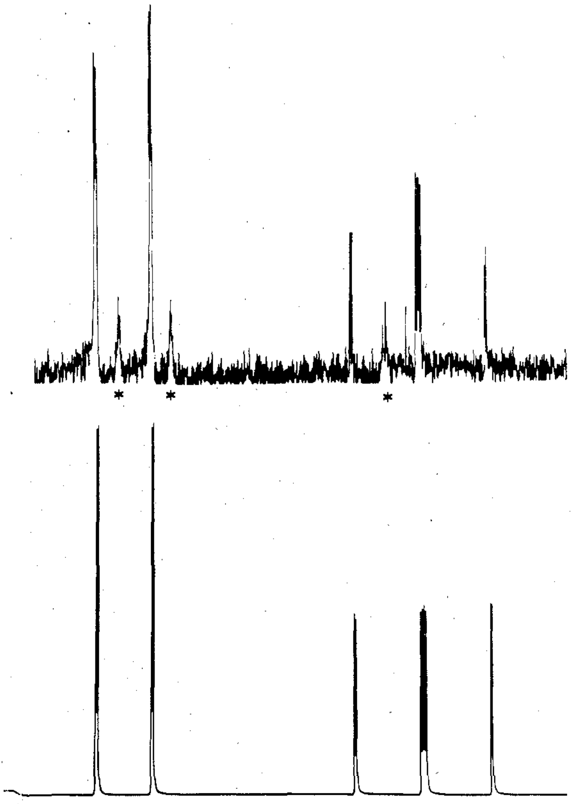


Figure 2. 40.5-MHz $^{31}P\{^1H\}$ NMR spectrum and simulation of $[F_2PN(CH_3)PF^+][MoCp(CO)_3^-]$ in THF at 32 °C. The asterisk indicates impurity resonance.

The NMR spectra of **1** and **2** are complex but structurally informative. The ^1H NMR spectrum of **1** shows a Cp proton singlet at 4.04 ppm and a methyl multiplet centered at 2.03 ppm. These absorptions compare favorably with absorptions found for $NaCpMo(CO)_3$[30] and the free ligand.[31] The $^{13}C\{^1H\}$ NMR spectrum shows a singlet at 93.28 ppm which may be assigned to equivalent carbon atoms in the Cp ring and a complex multiplet centered at 37.87 ppm arising from the methyl carbon coupled to inequivalent phosphorus and fluorine atoms. The downfield portion of the ^{19}F NMR spectrum of **1** is shown in Figure 1 along with a spectrum simulation.[32] The spectrum consists of two multiplets centered at −27.6 and −30.9 ppm (upfield of $CFCl_3$) which form an ABX pattern (F1 = A, F2 = B, P1 = X) with $^1J_{F1P1} = 1306$ Hz, $^1J_{F2P1} = 1243$ Hz, and $^2J_{F1F2} = 71$ Hz. The upfield portion of the ^{19}F NMR spectrum shows a doublet pattern centered at −146.4 ppm with $^1J_{F3P2} = 1057$ Hz. The $^{31}P\{^1H\}$ NMR spectrum of **1** contains two multiplets centered at 136.6 and 275.2 ppm (downfield of H_3PO_4); the spectrum and a simulation are shown in Figure

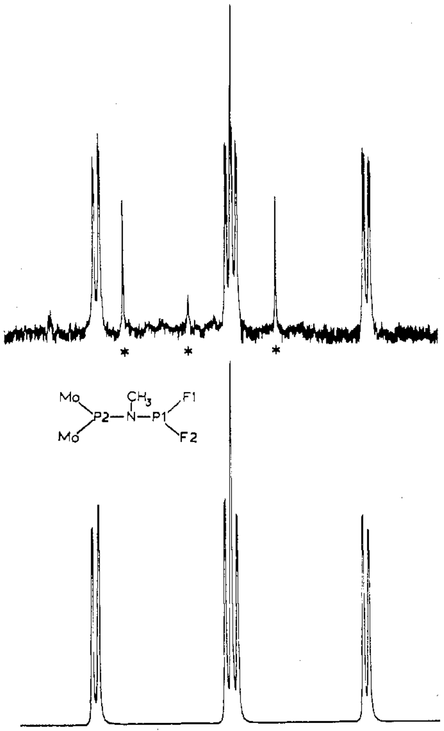


Figure 3. 94.1-MHz ^{19}F NMR spectrum and simulation of $[F_2PN(CH)_3P^{2+}][Cp(CO)_2MoMoCp(CO)_2{}^{2-}]$ in THF at 32 °C.

2. The coupling constants derived from the spectrum are $^1J_{P1F1}$ = 1306 Hz, $^1J_{P1F2}$ = 1243 Hz, $^2J_{P1P2}$ = 32 Hz, $^3J_{P1F3}$ = 4 Hz, and $^1J_{P2F3}$ = 1057 Hz. The ^{31}P and ^{19}F NMR data are fully consistent with the schematic structural representation of the cation shown in Figure 1. The low-field ABX ^{19}F pattern may be assigned to F1 and F2 while the high-field doublet corresponds to the unique F3 attached to the charge-bearing dicoordinate phosphorus atom. The apparent high-field triplet in the ^{31}P spectrum may be assigned to P1 directly coupled to two slightly inequivalent fluorine atoms. The chemical shift for this phosphorus atom is in the range encountered for tricoordinate, tervalent phosphines.[33] The low-field doublet may be assigned to the unique formal cationic phosphorus atom directly coupled to one fluorine atom. The large downfield shift also is consistent with the dicoordination assignment for this phosphorus atom.[33] The reduction in the ligand P–P coupling constant upon cation formation is dramatic, and this effect is not fully understood.[9]

The ^1H NMR spectrum of **2** shows two resonances in a 1:1 area ratio at 5.71 and 5.83 ppm which may be assigned to the protons on inequivalent Cp rings. The methyl group resonance is obscured by the THF solvent resonance. The $^{13}C\{^1H\}$ NMR spectrum shows two equal-intensity Cp resonances at 93.60 and 91.62 ppm and a methyl multiplet at 35.94 ppm. The area ratio and peak positions are invariant over a temperature range of 30–60 °C. The ^{19}F NMR spectrum of **2** together with a spectrum simulation is shown in Figure 3. The spectrum consists of a slightly second-order set of major doublets with chemical shifts at $\delta_{F1} = -33.4$ and $\delta_{F2} = -46.2$ with $^1J_{FP1}$ = 1251 Hz, $^2J_{F1F2}$ = 54 Hz, and $^3J_{FP2}$ = 10 Hz. The high-field resonance observed in **1** is now absent. The $^{31}P\{^1H\}$ NMR spectrum is shown in Figure 4, and it contains two multiplets centered at 154.8 and 404.1 ppm. The high-field multiplet consists of an apparent triplet ($^1J_{P1F}$ = 1257 Hz) with each member split into a doublet ($^2J_{P1P2}$ = 54 Hz), and this resonance may be assigned to the PF_2 group. The low-field multiplet contains a doublet ($^2J_{P1P2}$ = 54 Hz) with each member split into a triplet ($^3J_{FP2}$ = 10 Hz), and this resonance may be assigned to the formally monocoordinate, dicationic phosphorus atom.[33] The unusually low-field chemical shift of this phosphorus atom δ_{P2} = 404.1 represents the most deshielded phosphorus environment yet reported. In Figure 5, the ^{31}P chemical shifts for $(Me_2N)_3P$ (123 ppm), $(Me_2N)_2P^+$ (264 ppm),[4] $\overline{CH_3NCH_2CH_2N(CH_3)}P^+$ (264 ppm),[3] **1**, and **2** are plotted as a function of phosphorus coordination number. An approximately linear correlation is obtained which lends support to the qualitative application of ^{31}P chemical shift magnitudes as an indicator of formal coordination number on phosphorus in the new complexes.

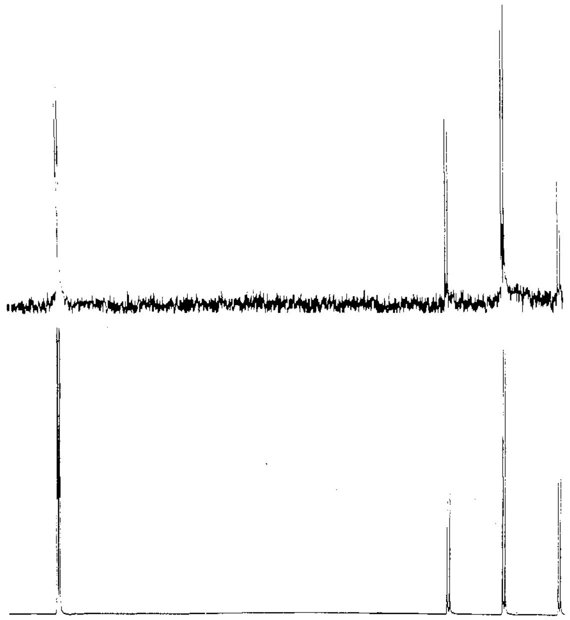


Figure 4. 40.5-MHz $^{31}P\{^1H\}$ spectrum and simulation of $[F_2PN(CH_3)P^{2+}][Cp(CO)_2Mo\text{–}MoCp(CO)_2{}^{2-}]$ in THF at 32 °C.

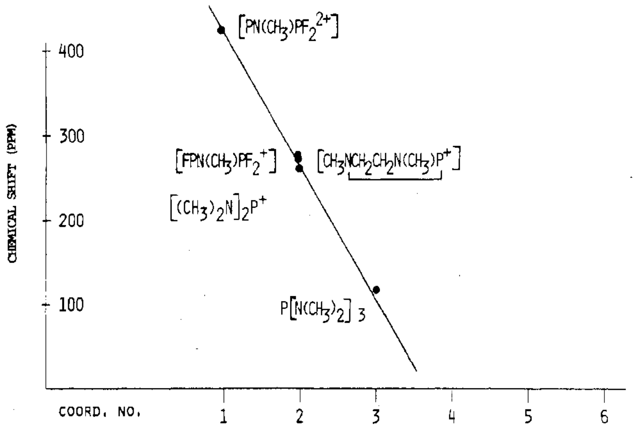
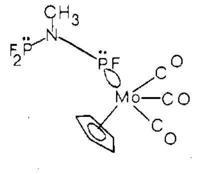
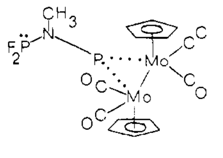


Figure 5. Values for ^{31}P chemical shifts in aminophosphine species as a function of coordination number of the phosphorus atom.

On the basis of characterization data summarized here, schematic structure assignments may be made. The solution structure data indicate that **1** and **2** are not composed of





separated cation–anion species in THF solution.[35] Instead the interaction between the formal ions in **1** is covalent or direct ion pair in nature. The covalent interaction may involve the *donation* of σ or π electron density from the Mo atom into the empty orbital on the formally dicoordinate phosphorus atom. Apparently this interaction does not effectively shield the phosphorus nucleus, and it is clear from the NMR data and EAN rules that the lone pair on the cationic phosphorus atom is not intimately involved in the bonding to the Mo atom. Hence **1**, like $[CH_3\overline{NCH_2CH_2N(CH_3)P}^+][MoCp(CO)_3^-]$, represents a complex of different kind from $[CH_3\overline{NCH_2CH_2N(CH_3)P}Fe(CO)_4^+][PF_6^-]$.

The product **2** is also unique yet reminiscent of several well-known organometallic phosphido complexes.[36] Ion-pair interactions between the formal ions $[F_2PN(CH_3)P^{2+}]$ and $[Cp(CO)_2Mo–MoCp(CO)_2^{2-}]$ do not satisfy the electron count for the molybdenum atoms; however, electron counting requirements are satisfied if the lone-pair electron density on the formal monocoordinate dication is shared through a bridge interaction to the metal centers. Infrared spectroscopic data suggest that this charge flow is offset by a dominate back-donation of electron density from the Mo atoms to the phosphorus atom. The net result is still a remarkably low-field ^{31}P chemical shift (404.1 ppm) for the formally monocoordinate cation in the associated complex. An unassociated dication $CH_3N(PF_2)P^{2+}$ complex, if prepared, should show a more deshielded monocoordinate ^{31}P environment than that displayed in **2** if this bonding model is accurate. Compound **2**, therefore, differs from the known formally four-coordinate phosphido-bridged metal complexes in which the phosphorus also acts as a two-electron donor[36] and from the three-coordinate phosphinidene complex $(\mu\text{-}C_6H_5)P[Mn(CO)_2Cp]_2$ in which the phosphorus atom acts as a four-electron donor.[37]

One additional novel feature of **2** is worthy of discussion. The ^1H- and $^{13}C\{^1H\}$ NMR data indicate that there are two Cp ring environments in the temperature range 30–60 °C. Equilibration of these two environments has not been observed on the NMR time scale before the compound undergoes thermal decomposition. Stereochemically distinct rings must be a result of a frozen P–N bond conformation in the complex. In the acyclic, ionic monocation complexes studied by Parry[4] and Cowley,[7] temperature-dependent NMR studies have shown that the P–N bonds are subject to hindered rotation such that the alkyl environments on the nitrogen atoms are equivalent at room temperature.[38] That this rotation in **2** is frozen at room temperature is consistent with enhanced $p\pi$–$p\pi$ or $p\pi$–$d\pi$ nitrogen to phosphorus multiple bonding promoted by the large formal positive charge on the monocoordinate phosphorus atom.

The structural analysis presented here, based upon analytical and spectroscopic data, is self-consistent. However, it is not totally unambiguous. In this respect crystal structures of **1** and **2** would be desirable; however, attempts to grow crystals suitable for X-ray diffraction analysis have not yet been successful. Further attempts to grow crystals are in progress on substituent-varied compounds. Although the present absence of crystal structure data leaves some question over the precise nature of the phosphine–metal atom interaction, there is no doubt that these compounds may be considered to contain a formal phosphine monocation in **1** and a dication in **2**. Further, support for this conclusion will be forthcoming in a paper describing related cation chemistry of cyclic phosphetidine ligands.

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Registry No. **1**, 70659-06-2; **2**, 70703-16-1; **3**, 21050-13-5; **4**, 70659-08-4; **5**, 70659-09-5; **7**, 12107-35-6; **8**, 12091-64-4; **10**, 7681-82-5; $CH_3N(PF_2)_2$, 17648-18-9.

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(31) The NMR spectra for the free ligand $CH_3N(PF_2)_2$ provide the following parameters: ^1H, δ 2.40 ($^3J_{HP} = 3.2$ Hz, $^4J_{HF} = 1.4$ Hz); $^{13}C\{^1H\}$, δ 20.71; ^{19}F, δ −74.6 ($^1J_{PF} = 1264$ Hz, $^3J_{PF'} = 47$ Hz, $^4J_{FF} = 11.7$ Hz); $^{31}P\{^1H\}$, δ 141.5 ($J_{PP'} = 437$ Hz). The spin system is $XX'AA'X''X'''$.[9,24]

(32) NMR spectrum simulations were made by using the ITRCAL program provided by Nicolet Technology Corp. with the NIC-80 data processor.

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Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611

Pyrolysis and Hydrolysis of 2,2-Dimethyltriazanium Chloride

MILAP A. MATHUR, HARRY H. SISLER,* and LEE N. MORGENTHALER

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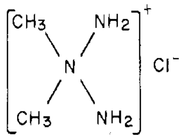
The purification, hydrolysis, and pyrolysis of 2,2-dimethyltriazanium chloride are discussed. The gas chromatography data indicate that the pyrolysis products in a helium atmosphere are NH_4Cl, N_2, $(CH_3)_2NN{=}CH_2$, and small amounts of $(CH_3)_2NNH_2$ and $(CH_3)_2NN{=}NN(CH_3)_2$. Under vacuum, with or without solid NaOH, the products are NH_4Cl, N_2, $(CH_3)_2NN{=}CH_2$, and trace amounts of $(CH_3)_2NN{=}NN(CH_3)_2$ but no $(CH_3)_2NNH_2$. The ultraviolet spectroscopy data for the hydrolysate of $(CH_3)_2N(NH_2)_2Cl$ in 0.5–2.0 N KOH solution indicate that $(CH_3)_2NN{=}CH_2$ is the major product. The value of λ_{max} for $(CH_3)_2NN{=}CH_2$ is pH dependent and shifts toward shorter wavelengths with increased pH. The rate of formation of $(CH_3)_2NN{=}CH_2$ follows approximately first-order kinetics with respect to $(CH_3)_2N(NH_2)_2Cl$. The mechanisms for the formation of various pyrolysis and hydrolysis products of $(CH_3)_2N(NH_2)_2Cl$ are discussed. The melting point of $(CH_3)_2N(NH_2)_2Cl$ has been corrected; the new value is 124 °C with decomposition.

Introduction

One potential process for the synthesis of 1,1-dimethylhydrazine is the liquid-phase[1-3] chloramination of dimethylamine. One of the byproducts of the chloramination is 2,2-dimethyltriazanium chloride,[4-9] $[(CH_3)_2N(NH_2)_2]Cl$. It has been shown that the latter substance is formed by the reaction between the 1,1-dimethylhydrazine and chloramine.[10-13]

Giordano and Sisler[14] have also obtained dimethyltriazanium chloride by the chloramination of trimethylhydrazine. Dimethyltriazanium chloride is reported to be stable in air and in neutral aqueous solutions.[15] It can be recrystallized[10] from boiling ethanol, acetone, diethyl ether, or acetonitrile. In a recent report Giordano, Palenik, and Sisler[16] have shown the structure of 2,2-dimethyltriazanium chloride to be



analogous to the structure of $[N(CH_3)_4]Cl$.

Although 2,2-dimethyltriazanium chloride is among the first known stable alkyl compounds which contain a single bonded chain of more than two nitrogen atoms, it is an undesirable byproduct in the synthesis of unsymmetrical dimethylhydrazine, $(CH_3)_2NNH_2$, by chloramination of dimethylamine. It was, therefore, the object of this study to determine the thermal and hydrolytic stabilities of 2,2-dimethyltriazanium chloride, to determine the various products formed by its pyrolysis and hydrolysis, and to determine the reaction mechanisms for the formation of the various products from the pyrolysis or hydrolysis. This information would be useful in optimizing the yield of unsymmetrical dimethylhydrazine from the chloramination of dimethylamine.

Experimental Section

Materials. The 2,2-dimethyltriazanium chloride used in this study was prepared and purified by procedures described in the literature.[10,11,16] Its ^1H NMR spectrum showed ammonium chloride as an impurity although its melting point agreed with that reported in literature.[10,11] It was, therefore, further purified by dissolving 0.781 g in 30 mL of anhydrous ethanol at room temperature and recrystallizing it by adding an acetone–ether mixture (90 mL of acetone, 300 mL of ether) at −4 °C. The material obtained by this procedure melted at 124 °C (with decomposition) and showed no ammonium chloride impurity in its ^1H NMR spectrum or its infrared spectrum. The dimethylhydrazones of formaldehyde[17] ($(CH_3)_2NN{=}CH_2$) and tetramethyl-2-tetrazene[18] ($(CH_3)_2NN{=}NN(CH_3)_2$) were prepared by methods found in the literature. These compounds were analyzed by gas–liquid chromatography and nuclear magnetic resonance spectroscopy to ascertain that they were free from appreciable amounts of contaminants. Unsymmetrical dimethylhydrazine, $(CH_3)_2NNH_2$, of 95% purity was obtained from the Naval Surface Weapons Center, White Oak Laboratory. It was refluxed and distilled[11] over solid potassium hydroxide in a nitrogen atmosphere before use. The product so obtained invariably contained formaldehyde dimethylhydrazone. The amount of the hydrazone was determined and an appropriate correction was applied when it was necessary. Chloramine was prepared by the reaction of ammonia and chlorine in a nitrogen atmosphere in a gas phase reactor of the type described by Sisler and Mattair.[19] The chloramine content was determined[11] by shaking a measured sample with potassium iodide in 1 N acetic acid solution and titrating the liberated iodine with standard thiosulfate solution. The solvents used were dried and distilled over appropriate drying agents in a nitrogen atmosphere and were stored under dry conditions. The reagents and the buffers were ACS reagent grade and were used as supplied.

Spectra. Ultraviolet spectra were obtained with a Beckman DB spectrophotometer. A hydrogen lamp was used for wavelengths less than 340 nm and a tungsten lamp for the longer wavelengths. The measurements were made in matched quartz cells (with less than 1% of transmittance difference). The infrared spectra of solid samples (in pressed KBr pellets and liquid samples placed between KBr plates) were recorded with a Beckman IR-10 spectrometer. The ^1H NMR spectra of solutions of the samples in $CDCl_3$ or $Me_2SO\text{-}d_6$ were recorded with a Varian Model A-60 A NMR spectrometer using tetramethylsilane as an internal standard.

Analyses. All pH measurements were made with a Corning Model 12 Research pH meter using an Orion Model 91-01-00 pH electrode and Coleman Model 3-711 standard calomel reference electrode. The pH meter was standardized by using ACS grade buffers (pH 10.00 and 6.86) immediately before use. The instrument drift was less than 0.05 pH unit/h. A Perkin-Elmer Model 810 gas chromatograph equipped with twin 12 ft by $^1/_8$ in. E-20 Carbowax KOH 5% columns and a thermal conductivity detector was used for gas–liquid chro-

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