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Steven C. Avanzino, William L. Jolly*

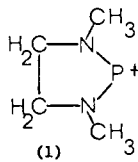
Department of Chemistry, University of California
and the Materials and Molecular Research Division
Lawrence Berkeley Laboratory, Berkeley, California 94720

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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 coworkers¹ 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, PF₅ or BF₃, a cyclic cation (**1**) could be



produced. Subsequently, Parry and coworkers²⁻⁴ reported that several acyclic aminochlorophosphines form cationic species in the presence of a chloride ion acceptor such as AlCl₃. In particular, the complexes [((CH₃)₂N)₂PCl]₂AlCl₃ (**2**),³ [((CH₃)₂N)₂PCl]AlCl₃ (**3**),³ [((CH₃)₂N)₂PCl][((CH₃)₂N)₃P]AlCl₃ (**4**),³ (CH₃)₂NPCl₂·AlCl₃ (**5**),⁴ and [((CH₃)₂N)₃P]AlCl₃ (**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 F₃PAICl₃ which does contain an 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, [((CH₃)₂N)₂P⁺ or (CH₃)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 R₃P-PR₂⁺. Compounds **3**⁴ and **5**⁴ apparently contain the isolated cationic species (Me₂N)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**

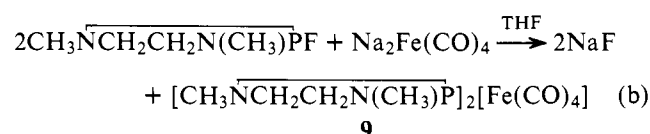
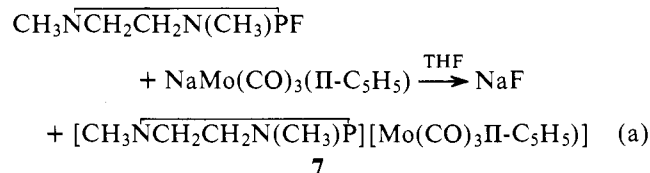
toward several strong nucleophilic transition metal reagents. Typically, the cyclic ligand CH₃NCH₂CH₂N(CH₃)PF⁺ and the sodium salt of Mo(II-C₅H₅)(CO)₃⁻, Fe(II-C₅H₅)(CO)₂⁻, or Fe(CO)₄²⁻ are combined on an equivalence basis in dry THF at -78 °C under an atmosphere of dry nitrogen. The solution is then 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 [CH₃NCH₂CH₂N(CH₃)P⁺][(II-C₅H₅)Mo(CO)₃]⁻ (**7**), [CH₃NCH₂CH₂N(CH₃)P⁺][(II-C₅H₅)Fe(CO)₂]⁻ (**8**), and [CH₃NCH₂CH₂N(CH₃)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 C₁₂H₁₅MoN₂O₃P: 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 (PN₂C₄H₁₀Mo(CO)₂(C₅H₅)⁺, 4), 278 (PMo(CO)₃(C₅H₅)⁺, 4), 249 (N₂C₄H₁₀Mo(C₅H₅)⁺, 4), 247 (Mo(CO)₃(C₅H₅)⁺, 5), 221 (N₂C₂H₆Mo(C₅H₅)⁺, 4), 222 (PMo(CO)(C₅H₅)⁺, 6), 206 (NC₃H₇Mo(C₅H₅)⁺, 7), 191 (Mo(CO)(C₅H₅)⁺, 15), 163 (Mo(C₅H₅)⁺, 37), 137 (MoC₃H₃⁺, 24), 117 (PN₂C₄H₁₀⁺, 100), 98 (Mo⁺, 20), 74 (C₂H₅NP⁺, 84), 60 (NPCH₃⁺, 86), 44 (NC₂H₆⁺, 100), 42 (NC₂H₄⁺, 63). The mass spectrum of **9** does show a weak parent ion: 402 ((PN₂C₄H₁₀)₂Fe(CO)₄⁺, <1), 374 ((PN₂C₄H₁₀)₂Fe(CO)₃⁺, <1), 285 (PN₂C₄H₁₀Fe(CO)₄⁺, <1), 257 (PN₂C₄H₁₀Fe(CO)₃⁺, <1), 229 (PN₂C₄H₁₀Fe(CO)₂⁺, 1), 201 (PN₂C₄H₁₀Fe(CO)⁺, 2), 173 (PN₂C₄H₁₀Fe⁺, 4), 140 (Fe(CO)₃⁺, 4), 117 (PN₂C₄H₁₀⁺, 100), 87 (FeP⁺, 15), 84 (Fe(CO)⁺, 11), 74 (C₂H₅NP⁺, 11), 60 (CH₃NP⁺, 12), 56 (Fe⁺, 24), 44 (NC₂H₆⁺, 96), 42 (NC₂H₄⁺, 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(C₅H₅), 1880 (m), 1687; Na₂Fe(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.

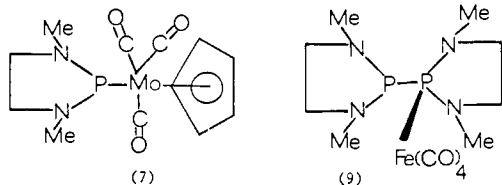
The ³¹P NMR spectra (H₃PO₄ standard) of **7** in THF at 32 °C consists of a singlet at 271 ppm (downfield) while that of **9** in THF at 32 °C consists of an AB multiplet centered at 161.2 ppm with *J* = 357 Hz and |ν_A - ν_B| = 2396 Hz. The ³¹P chemical shifts of aminophosphines have been used to assign 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 ³¹P 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, Me₄Si external standard) shows a methyl doublet at 1.77 ppm (*J*_{H_CN_P} = 11.5 Hz) (rel intensity 6), a methylene doublet at 1.97 ppm

($J_{\text{HCNP}} = 5.5$ Hz) (rel intensity 4), and a cyclopentadienyl proton singlet at 4.57 ppm (rel intensity 5). Compound **9** shows ^1H resonances centered at 2.04 ppm with overlapping multiplet structure which has not been fully resolved. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (THF, 32 °C, Me_4Si external standard) of **7** shows a methyl doublet at 33.55 ppm (downfield) ($J_{\text{CNP}} = 9.0$ Hz), a methylene doublet at 57.70 ppm ($J_{\text{CPN}} = 4.0$ Hz), a Cp ring singlet at 87.73 ppm, and a carbonyl singlet at 215.22 ppm. The spectrum of **9** shows a methyl multiplet (unresolved) at 35.67 ppm, a methylene multiplet at 53.85 ppm, and a carbonyl singlet at 214.75 ppm.

The compositions of **7**, **8**, and **9** are established by elemental analyses and/or mass spectra. Furthermore, the reaction stoichiometry and characterization data are consistent only with the following equations



The structures of these unusual coordination complexes are now of central interest and the NMR and infrared data outlined here are consistent with the schematic arrangements shown here. We propose the structure of **7** in analogy to the



proposed structure of the mononuclear bis(pentafluorophenyl)phosphine-metal carbonyl complexes reported by Green and coworkers.¹² The structural possibilities for **9** are most interesting. The second-order ^{31}P NMR pattern and the coupling constant and chemical-shift parameters suggest that the iron center is asymmetrically positioned between the two phosphorus coordination sites of the condensed diphosphine, but it is not yet clear if the iron atom is primarily associated with only one phosphorus atom as schematically shown here. X-ray crystal structure analyses of these compounds are in progress, and their structures and photochemistry will be presented separately.

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References and Notes

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R. W. Light, R. T. Paine*

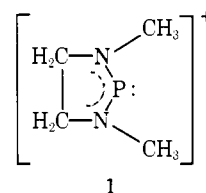
Department of Chemistry, University of New Mexico
Albuquerque, New Mexico 87131

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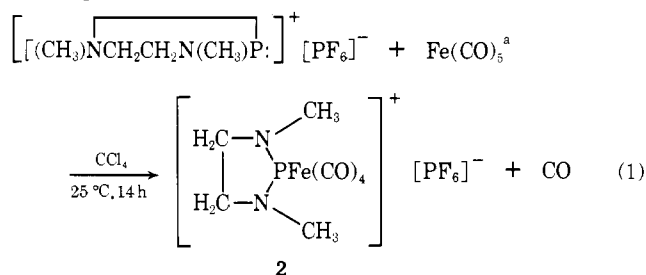
Iron Carbonyl Complexes Containing Positively Charged Phosphorus Ligands

Sir:

A 1972 paper by Fleming, Lupton, and Jekot¹ described a cyclic cationic phosphorus species **1**. A more recent paper from

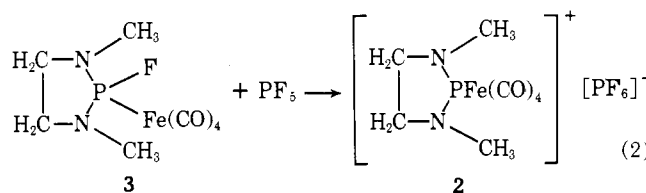


this laboratory² described the related noncyclic cations, $[[(\text{CH}_3)_2\text{N}]_2\text{P}]^+$ and $[(\text{CH}_3)_2\text{NPCI}]^+$. It was recognized in very early studies of these systems that the presence on phosphorus of (1) a free-electron pair, (2) a positive charge, and (3) a vacant p orbital should make ligands of this type effective π -type Lewis acids as well as weak σ -type Lewis bases. These arguments are supported by the observation that the cyclic cation (**1**) will slowly displace CO from $\text{Fe}(\text{CO})_5$ in accordance with eq 1.



^a $\text{Fe}_2(\text{CO})_9$ can also be used.

An alternative procedure for generating **2** involves the preparation of the easily characterized, stable compound, **3**. Fluoride can be removed from this species by a Lewis acid such as PF_5 to give **2**. The appropriate reaction is given in eq 2. The



process is equally effective for preparing the analogous noncyclic³ cationic species $[[(\text{CH}_3)_2\text{N}]_2\text{PFe}(\text{CO})_4]^+$ (**4**). A recent x-ray study of **3** in this laboratory⁴ has shown unambiguously that the molecule has trigonal-bipyramidal geometry and that the phosphine is in the axial position around Fe. The structure