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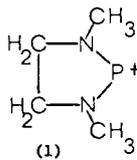
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### Interaction of the Dicoordinate Phosphorus Cation 1,3-Dimethyl-1,3,2-diazaphospholidide with Transition Metal Nucleophiles

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<sup>1</sup> 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<sub>5</sub> or BF<sub>3</sub>, a cyclic cation (**1**) could be



produced. Subsequently, Parry and coworkers<sup>2-4</sup> reported that several acyclic aminochlorophosphines form cationic species in the presence of a chloride ion acceptor such as AlCl<sub>3</sub>. In particular, the complexes [((CH<sub>3</sub>)<sub>2</sub>N)<sub>2</sub>PCl]<sub>2</sub>AlCl<sub>3</sub> (**2**),<sup>3</sup> [((CH<sub>3</sub>)<sub>2</sub>N)<sub>2</sub>PCl]AlCl<sub>3</sub> (**3**),<sup>3</sup> [((CH<sub>3</sub>)<sub>2</sub>N)<sub>2</sub>PCl][((CH<sub>3</sub>)<sub>2</sub>N)<sub>3</sub>P]AlCl<sub>3</sub> (**4**),<sup>3</sup> (CH<sub>3</sub>)<sub>2</sub>NPCl<sub>2</sub>·AlCl<sub>3</sub> (**5**),<sup>4</sup> and [((CH<sub>3</sub>)<sub>2</sub>N)<sub>3</sub>P]AlCl<sub>3</sub> (**6**)<sup>3</sup> do not form molecular addition compounds with Al-N or Al-P coordinate bonds. This is in contrast with the known addition complex F<sub>3</sub>PAICl<sub>3</sub> which does contain an Al-P coordinate bond.<sup>5</sup> Instead, each of the aminochlorophosphines forms an ionic complex in which the cation is considered to contain a dicoordinate Lewis acid species, [((CH<sub>3</sub>)<sub>2</sub>N)<sub>2</sub>P]<sup>+</sup> or (CH<sub>3</sub>)<sub>2</sub>NPCl<sup>+</sup>. In compounds **2**,<sup>3</sup> **4**,<sup>3</sup> and **6**<sup>3</sup> the dicoordinate phosphorus is observed to coordinate 1 mol of phosphine base resulting in the formation of diphosphine cations of the general type R<sub>3</sub>P-PR<sub>2</sub><sup>+</sup>. Compounds **3**<sup>4</sup> and **5**<sup>4</sup> apparently contain the isolated cationic species (Me<sub>2</sub>N)<sub>2</sub>P<sup>+</sup> and MeNPCl<sup>+</sup>.

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,<sup>4,6</sup> 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<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)PF<sup>+</sup> and the sodium salt of Mo(Π-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub><sup>-</sup>, Fe(Π-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub><sup>-</sup>, or Fe(CO)<sub>4</sub><sup>2-</sup> 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<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)P<sup>+</sup>][(Π-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sup>-</sup> (**7**), [CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)P<sup>+</sup>][(Π-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sup>-</sup> (**8**), and [CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)P<sup>+</sup>]<sub>2</sub>[Fe(CO)<sub>4</sub>]<sup>2-</sup> (**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<sub>12</sub>H<sub>15</sub>MoN<sub>2</sub>O<sub>3</sub>P: 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.<sup>7</sup>

The following characterization data for **7** and **9** provide unequivocal composition analysis and tentative structural assignments.<sup>8</sup> The mass spectrum (70 eV) of **7** shows a characteristic fragmentation pattern, but the parent ion is too weak to observe<sup>9,10</sup> (*m/e* (assignment, rel intensity)): 336 (PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub>Mo(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 4), 278 (PMo(CO)<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 4), 249 (N<sub>2</sub>C<sub>4</sub>H<sub>10</sub>Mo(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 4), 247 (Mo(CO)<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 5), 221 (N<sub>2</sub>C<sub>2</sub>H<sub>6</sub>Mo(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 4), 222 (PMo(CO)(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 6), 206 (NC<sub>3</sub>H<sub>7</sub>Mo(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 7), 191 (Mo(CO)(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 15), 163 (Mo(C<sub>5</sub>H<sub>5</sub>)<sup>+</sup>, 37), 137 (MoC<sub>3</sub>H<sub>3</sub><sup>+</sup>, 24), 117 (PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub><sup>+</sup>, 100), 98 (Mo<sup>+</sup>, 20), 74 (C<sub>2</sub>H<sub>5</sub>NP<sup>+</sup>, 84), 60 (NPCH<sub>3</sub><sup>+</sup>, 86), 44 (NC<sub>2</sub>H<sub>6</sub><sup>+</sup>, 100), 42 (NC<sub>2</sub>H<sub>4</sub><sup>+</sup>, 63). The mass spectrum of **9** does show a weak parent ion: 402 ((PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub>)<sub>2</sub>Fe(CO)<sub>4</sub><sup>+</sup>, <1), 374 ((PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub>)<sub>2</sub>Fe(CO)<sub>3</sub><sup>+</sup>, <1), 285 (PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub>Fe(CO)<sub>4</sub><sup>+</sup>, <1), 257 (PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub>Fe(CO)<sub>3</sub><sup>+</sup>, <1), 229 (PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub>Fe(CO)<sub>2</sub><sup>+</sup>, 1), 201 (PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub>Fe(CO)<sup>+</sup>, 2), 173 (PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub>Fe<sup>+</sup>, 4), 140 (Fe(CO)<sub>3</sub><sup>+</sup>, 4), 117 (PN<sub>2</sub>C<sub>4</sub>H<sub>10</sub><sup>+</sup>, 100), 87 (FeP<sup>+</sup>, 15), 84 (Fe(CO)<sup>+</sup>, 11), 74 (C<sub>2</sub>H<sub>5</sub>NP<sup>+</sup>, 11), 60 (CH<sub>3</sub>NP<sup>+</sup>, 12), 56 (Fe<sup>+</sup>, 24), 44 (NC<sub>2</sub>H<sub>6</sub><sup>+</sup>, 96), 42 (NC<sub>2</sub>H<sub>4</sub><sup>+</sup>, 40). The infrared spectra are similar for each compound in the carbonyl stretching region (Nujol mull, cm<sup>-1</sup>): **7**, 1894 and 1815; **9**, 2037 and 1929. These data show a distinct shift to higher frequency from the sodium salts: NaMo(CO)<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>), 1880 (m), 1687; Na<sub>2</sub>Fe(CO)<sub>4</sub>, 1891, 1759. This shift is expected if the phosphorus cation is acting as an electron-withdrawing group on the transition metal base.<sup>11</sup> Shifts of this order have been observed for related bis(pentafluorophenyl)phosphine-metal carbonyl complexes.<sup>12</sup> 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 <sup>31</sup>P NMR spectra (H<sub>3</sub>PO<sub>4</sub> 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<sub>A</sub> - ν<sub>B</sub>| = 2396 Hz. The <sup>31</sup>P chemical shifts of aminophosphines have been used to assign coordination numbers.<sup>13</sup> The AB pattern of **9** is similar to the spectrum obtained for **4**<sup>3</sup> and the chemical shift is intermediate between the values expected for coordination numbers three and four. Although the <sup>31</sup>P chemical shift for **7** falls within the chemical shift range of dicoordinate aminophosphines (260 ± 20 ppm),<sup>4</sup> the volatility and carbonyl stretching frequencies suggest that the cation has a strong interaction with the metal anion. The <sup>1</sup>H NMR spectrum (benzene, 25 °C, Me<sub>4</sub>Si external standard) shows a methyl doublet at 1.77 ppm (*J*<sub>H<sub>C</sub>N<sub>P</sub></sub> = 11.5 Hz) (rel intensity 6), a methylene doublet at 1.97 ppm

