Communications to the Editor

η^6-Arene Complexation to a Phosphenium Cation

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Discovery of the fascinating sandwich structure of ferrocene[3] initiated the development of vast series of compounds involving the now classical π-complexation. Most elements have been observed to engage in π-complexation with unsaturated hydrocarbons[4] and in some cases with other nonmetal ligands.[5] Cyclopentadienide derivatives are perhaps the most widely encountered π-ligands, including extensive use with a number of p-block elements,[6] which are observed to adopt variable hapticity in the solid state.[7] Examples of η^6-arene complexation with select p-block elements have been known for 30 years,[8] and a more general series of compounds has recently been developed for the p-block metals and metalloid elements.[9] Nevertheless, arene π-complexation to the nonmetallic p elements remains a rarity. Here we describe the first examples of benzenoid π-complexation to phosphorus in iminophosphenium salts and illustrate the intimate role of the anion in the properties of these species.

Our interest in the synthetic potential of small highly reactive nonmetal systems led us to examine the (2,4,6-tri-*tert*-butylphenyl)iminophosphenium (Mes*NP$^+$) cation, which was recently reported by Niecke as the toluene solvated tetrachloroaluminate salt [Mes*NP][$AlCl_4$]$\cdot C_7H_8$ (**1**).[10] Using a similar approach, we have performed the reaction of Mes*NPCl with equimolar solutions of $GaCl_3$ in toluene and in benzene, as well as reactions with excess $GaCl_3$ in the same solvents. ^{31}P NMR examinations of the reaction mixtures indicate quantitative formation of a single product in each case; these products have been isolated and characterized[11] as the salts [Mes*NPC_7H_8][$GaCl_4$] (**2**), [Mes*NPC_6H_6][$GaCl_4$] (**3**), [Mes*NPC_7H_8][Ga_2Cl_7] (**4**), and [Mes*NPC_6H_6][Ga_2Cl_7] (**5**), respectively.

Salts **2** and **3** are isostructural to **1**, and, consistent with the previous report,[10] three close cation–anion contacts are evident between the phosphorus center and the chlorine centers of two anions. However, we note that the arene molecule is also involved in the coordination sphere of the phosphorus center, resulting in a distorted trigonal bipyramidal geometry, as illustrated for salt **3** in Figure 1 [axial, Cl(3)a and Cl(2)b; equatorial, Cl(1)a, N(1), and arene]. Salts **4** and **5** contain the larger digallate anion, which affords one less contact to the phosphorus center, giving a distorted tetrahedral coordination geometry at phosphorus, as shown for salt **4** in Figure 2. Therefore, all salts (**2**–**5** and, presumably, **1**[10]) contain "half-sandwich" π-complexation of an arene molecule to the phosphorus center. The P–arene$_{\mathrm{centroid}}$ distances [**2**, 3.02(1) Å; **3**, 3.001(7) Å; **4**, 2.727(7) Å; **5**, 2.745(4) Å] are obviously shorter than the nearest P···Cl cation–anion contacts [**2**, P(1)···Cl(1) 3.237(8) Å, P(1)···Cl(2) 3.139(9) Å, P(1)···Cl(4)b 3.474(8) Å; **3**, P(1)···Cl(1) 3.083(4) Å, P(1)···Cl(2)b 3.389(4) Å, P(1)···Cl(3) 3.429(3) Å; **4**, P(1)···Cl(3) 3.487(4) Å, P(1)···Cl(5) 3.584(4) Å; **5**, P(1)···Cl(1) 3.395(3) Å, P(1)···Cl(7) 3.570(3) Å] and are comparable to those observed for other p-block π-arene complexes.[9]

The structural data indicate a stronger P–π-arene interaction in the digallate salts **4** and **5** than in the gallate salts **2** and **3**, and

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[1] Author for correspondence regarding chemistry.

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[11] (a) General procedure: in an evacuated, moisture-free vessel, $GaCl_3$ (1 or 2 mmol) in arene (20 mL) was added to a solution of Mes*NPCl (1 mmol) in arene (20 mL). ^{31}P NMR spectrum of the reaction mixtures contained a single signal (70–95 ppm). Solvent was removed *in vacuo*, giving a yellow powder or oil, recrystallized as described below. (b) Characterization data for salt **2** ([Mes*NPC_7H_8][$GaCl_4$]): recrystallized from toluene, approximate isolated yield 50%; dp 157–160 °C; releases arene under vacuum (f), analysis not obtained; NMR (CD_2Cl_2), ^{31}P 76 ppm; ^{1}H Mes* 7.36 (s, 2H), 1.45 and (s, 18H), and 1.28 ppm (s, 9H), toluene 7.56–7.47 (m, 5H) and 2.48 ppm (s, 3H); ^{13}C Mes* 123.7, 30.6, and 29.4 ppm, toluene 132.4, 131.4, 128.1, and 22.0 ppm, quaternary carbon nuclei not observed; IR (Nujol mull, CsI plates) 1594 (w), 1267 (m), 1243 (w), 1133 (m), 886 (m), 762 (w), 722 (m), 699 (m), 674 (w), 400 (s), 368 (s), and 266 (s) cm^{-1}. Crystal data: $C_{25}H_{37}Cl_4GaNP$, MW = 594.08, $F(000) = 2464$, space group = *Pbca*, $a = 25.006(9)$ Å, $b = 20.358(8)$ Å, $c = 12.126(5)$ Å, $V = 6173(8)$ Å^3, $Z = 8$, $d_c = 1.278$ g cm^{-3}, reflections with $I > 3\sigma I = 1136$, parameters = 289, $R = 0.0760$, $R_w = 0.0760$, G0F = 2.17. (c) Characterization data for salt **3** ([Mes*NPC_6H_6][$GaCl_4$]): recrystallized from benzene, approximate isolated yield 40%; releases arene under vacuum (f), analysis not obtained; dp ~90 °C; NMR (CD_2Cl_2), ^{31}P 76 ppm (in benzene reaction mixture, 71 ppm); ^{1}H Mes* 7.47 (d, $^5J_{PH} = 2$ Hz, 2H), 1.56 (s, 18H), and 1.33 (s, 9H) ppm, benzene 7.38 ppm (s, 6H); ^{13}C Mes* 123.8 (d, $^4J_{PC} = 3$ Hz), 30.9 (s), and 30.1 ppm (d, $^5J_{PC} = 2$Hz), benzene 128.7 ppm (s), quaternary carbon nuclei not observed; IR (Nujol mull, CsI plates) 1979 (w), 1842 (w), 1597 (s), 1267 (m), 1245 (m), 1134 (m), 1066 (m), 1033 (m), 927 (w), 886 (s), 764 (m), 699 (s), 674 (s), 393 (s), 361 (s), and 263 (m) cm^{-1}. Crystal data: $C_{24}H_{35}Cl_4GaNP$, MW = 580.05, $F(000) = 2400$, space group = *Pbca*, $a = 24.948(4)$ Å, $b = 20.195(4)$ Å, $c = 11.953(3)$ Å, $V = 6022(4)$ Å^3, $Z = 8$, $d_c = 1.279$ g cm^{-3}, reflections with $I > 3\sigma_I = 1463$, parameters = 280, $R = 0.0419$, $R_w = 0.0419$, GOF = 3.278. (d) Characterization data for salt **4** ([Mes*NPC_7H_8][Ga_2Cl_7]): recrystallized from hexane/toluene at −20 °C, isolated yield 25%; mp 75–78 °C. Anal. Calcd for **4**: C, 38.99; H, 4.84; N, 1.82. Found: C, 38.36; H, 5.31; N, 2.02. NMR (CD_2Cl_2) ^{31}P 95 ppm, (in toluene 91 ppm, reaction mixture 91 ppm); ^{1}H Mes* 7.42 (s, 2H), 1.50 (s, 18H), and 1.31 ppm (s, 9H), toluene 7.76–7.66 (m, 5H) and 2.56 ppm (s, 3H); ^{13}C Mes* 124.0, 30.6, and 29.4 ppm; toluene 134.2, 133.1, 130.0, and 22.3 ppm, quaternary carbon nuclei not observed; IR (Nujol mull, CsI plates) 1971 (w), 1892 (w), 1842 (w), 1787 (w), 1594 (m), 1266 (s), 1244 (m), 1134 (m), 1067 (m), 887 (s), 764 (m), 419 (s), 401 (s), 362 (s), and 263 (s) cm^{-1}. Crystal data: $C_{25}H_{37}Cl_7Ga_2NP$, MW = 770.16, $F(000) = 780$, space group = $P\bar{1}$, $a = 11.571(4)$ Å, $b = 16.335(5)$ Å, $c = 11.326(3)$ Å, $\alpha = 91.47(4)°$, $\beta = 117.87(2)°$, $\gamma = 105.34(3)°$, $V = 1797(1)$ Å^3, $Z = 2$, $d_c = 1.423$ g cm^{-3}, reflections with $I > 3\sigma I = 2416$, parameters = 391, $R = 0.0464$, $R_w = 0.0464$, GOF = 2.114. (e) Characterization data for salt **5** ([Mes*NPC_6H_6][Ga_2Cl_7]): recrystallized from a benzene/hexane, isolated yield 82%; mp 78–81 °C. Anal. Calcd for **5**: C, 38.12; H, 4.67; N, 1.85. Found: C, 37.97; H, 4.47; N, 1.89. NMR (CD_2Cl_2): ^{31}P 93 ppm; ^{1}H Mes* 7.40 (s, 2H), 1.48 (s, 18H), and 1.30 ppm (s, 9H), benzene 7.80 ppm (s, 6H); ^{13}C Mes* [124.0, 30.6, and 29.3 ppm, benzene 132.6 ppm, quarternary carbon nuclei not observed; IR (Nujol mull, CsI plates) 1981 (w), 1849 (w), 1597 (m), 1268 (m), 1135 (m), 1068 (m), 1025 (w), 986 (w), 929 (w), 887 (m), 763 (w), 700 (s), 400 (s), 367 (s), and 265 (s) cm^{-1}. Crystal data: $C_{24}H_{35}Cl_7Ga_2NP$, MW = 756.13, $F(000) = 764$, space group = $P\bar{1}$, $a = 11.579(2)$ Å, $b = 16.350(3)$ Å, $c = 11.085(3)$ Å, $\alpha = 90.74(2)°$, $\beta = 118.00(2)°$, $\gamma = 73.53(2)°$, $V = 1758.9(8)$ Å^3, $Z = 2$, $d_c = 1.428$ g cm^{-3}, reflections with $I > 3\sigma I = 3338$, parameters = 377, $R = 0.0386$, $R_w = 0.0336$, GOF = 1.314. (f) Under dynamic vacuum for 24 h, compounds **2** and **3** lose arene to leave a pale yellow powder characterized as follows. Anal. Calcd [Mes*NP][$GalCl_4$] for **3**: C, 43.07; H, 5.82; N, 2.79. Found: C, 43.02; H, 5.79; N, 2.97. IR (Nujol mull, CsI plates): 1594 (s), 1266 (w), 1243 (w), 1134 (w), 1066 (w), 927 (w), 885 (m), 763 (m), 693 (m), 373 (s), 360 (s), and 261 (m) cm^{-1}.

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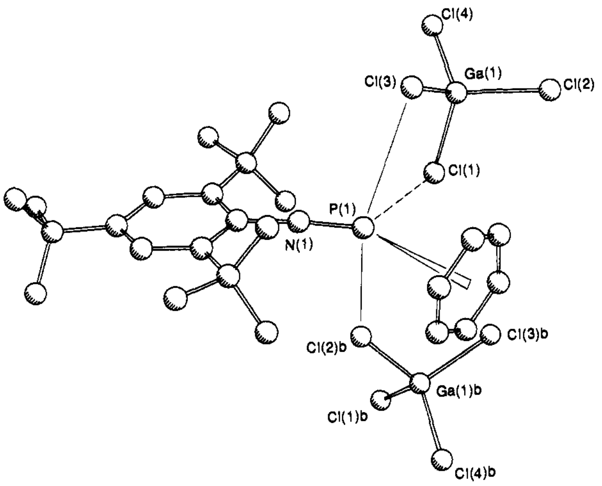

Figure 1. Crystallographic view of [Mes*NPC_6H_6][$GaCl_4$] (**3**) showing the local coordination sphere of the phosphorus center. Selected distances (Å) and angles (deg): P(1)–N(1) 1.484(7), P(1)⋯Cl(1) 3.083(4), P(1)⋯Cl(2)b 3.389(4), P(1)⋯Cl(3) 3.429(4), P(1)⋯$\text{benzene}_{\text{centroid}}$ 3.001(7); P(1)–N(1)–Mes* 175.5(7).

the differences are supported by spectroscopic data. In solution, ^{31}P NMR spectra (**1**, 78 ppm; **2**, 76 ppm; **3**, 76 ppm; **4**, 95 ppm; **5**, 93 ppm) reveal a consistent 15-ppm shift difference between the gallate (aluminate also) and digallate salts. The ^{13}C NMR shifts for the arene unit are deshielded (**2**, C_2 132.4 ppm, C_3 131.4 ppm, C_4 128.1 ppm; **3**, 128.7 ppm; **4**, C_2 134.2 ppm, C_3 133.1 ppm, C_4 130.0 ppm; **5**, 132.6 ppm; $^1J_{PC}$ coupling is not observed) with respect to those in the free benzenoid molecule (toluene, C_2 129.3 ppm, C_3 128.5 ppm, C_4 125.7 ppm; benzene, 128.5 ppm),[12] and the deshielding is more pronounced for the digallate salts than for the gallate salts. Bands corresponding to the complexed arene are evident in the IR spectra for all compounds, and those bands between 2000 and 1700 cm^{-1} are significantly shifted with respect to those of pure arene (toluene, 1943, 1860, 1803, 1735 cm^{-1}; benzene, 1960 and 1815 cm^{-1}).[13]

The relative strengths of the π-complexations are also demonstrated by the loss of arene from the gallate salts *in vacuo*[14], while the digallate salts retain the arene indefinitely under the same conditions (unchanged after pumping overnight), and **4** and **5** have been characterized by chemical analysis. Removal of the benzene from **3** is complete within 2 h at 10^{-3} Torr, as confirmed by chemical analysis.[11] We conclude that the magnitude of the π-complexation is affected by the nature of the anion in the solid state and in solution, assuming that cation–anion interactions are maintained to some degree in solution (intimate ion pair).[15]

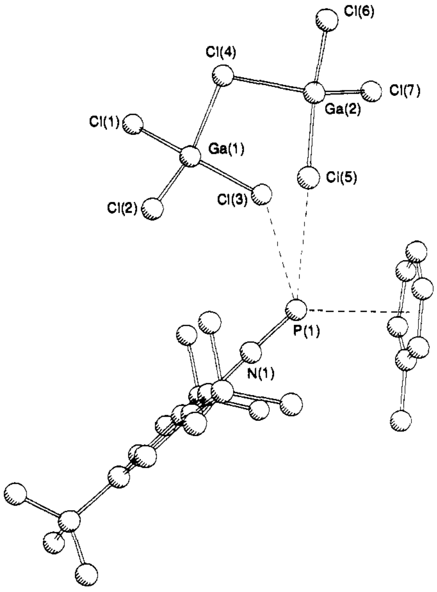

Figure 2. Crystallographic view of [Mes*NPC_7H_8][Ga_2Cl_7] (**4**). Selected distances (Å) and angles (deg): P(1)–N(1) 1.464(9), P(1)⋯Cl(1) 3.487(4), P(1)⋯Cl(5) 3.584(4); P(1)⋯$\text{toluene}_{\text{centroid}}$ 2.745(4); P(1)–N(1)–Mes* 178.7(8).

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Supplementary Material Available: X-ray crystallographic data for [Mes*NPC_7H_8][$GaCl_4$] (**2**), [Mes*NPC_6H_6][$GaCl_4$] (**3**), [Mes*NPC_7H_8][Ga_2Cl_7] (**4**), and [Mes*NPC_6H_6][Ga_2Cl_7] (**5**), including crystal data, atomic positional parameters, anisotropic thermal parameters, and crystallographic views of **2** and **5** (11 pages); listings of observed and calculated structure factors for **2**–**5** (101 pages). Ordering information is given on any current masthead page.

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