case an approximately 50 cm^{-1} decrease is observed. We attribute this decrease to an intramolecular donor/acceptor interaction between an endocyclic nitrogen lone pair of electrons and the electropositive carbon center in the carbonyl group. Similar intramolecular nitrogen/carbonyl effects have been observed in the infrared spectra of cyclic amino ketones.[15] If one considers the phosphazene ring to have three-center (PNP) π molecular orbitals with nodes at the phosphorus atoms,[16] then this perturbation will affect only one of the three such regions in a cyclotriphosphazene. The loss of the ability of the nitrogen lone pair to interact with phosphorus centers will weaken the phosphorus–nitrogen bond in this region.[17] Therefore, one observes a strong phosphorus–nitrogen stretching vibration in the normal region (1270 cm^{-1}) and a significantly lower value associated with the phosphorus–nitrogen bonds deprived of the nitrogen lone pair interaction. Furthermore the phenyl multiplet in the ^{1}H NMR of I does not show significant separation between the ortho, meta and para protons indicating a decrease in the positive nature of the carbonyl carbon.

The prominent peaks in the mass spectra of I and II are dominated by ligand fragmentation processes. In both cases the $P_3N_3F_5OH^+$ ion is prominent. One can envision the formation of this ion via the elimination of the appropriately substituted acetylene, i.e., elimination of phenylacetylene from the molecular ion of I. The ion derived from the acetylene is observed in each case. It is also of interest to note the large $C_6H_5CN^+$ ion in the mass spectrum of I.

The stability of I and II is in marked contrast to that of carboxylic acid derivatives of phosphazenes. The interaction of the benzoate anion with $P_3N_3Cl_6$ yields the trimetaphosphate anion and benzonitrile.[5,18] The mechanism for this reaction is believed to proceed through ring nitrogen lone pair attack on the carbonyl carbon followed by rearrangement to the phosphonyl function and N-substituted phosphazane (see below). While we observe evidence for nitrogen lone pair–carbonyl interaction in I and II, we do not observe the facile rearrangement which occurs in the benzoate reaction.

Registry No. I, 63915-14-0; II, 63915-13-9; $P_3N_3F_6$, 15599-91-4; acetophenone, 98-86-2; cyclohexanone, 108-94-1.

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(9) Chemical shifts in ppm; coupling constants in Hz; all J(PF) values are based on a first-order approximation; R = C_8H_7O, R′ = C_6H_9O.

(10) In cm^{-1}.

(11) Only high-intensity peaks are reported. Several low-intensity, high-mass fragments are in the spectrum of I. Several high-intensity, low-mass fragments due to the organic groups of both I and II are also omitted.

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Synthesis and Characterization of Mixed-Halide, Partially Oxidized Potassium Tetracyanoplatinates

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The detailed understanding of the metallic state of highly conducting one-dimensional (1-D) inorganic complexes has been thwarted by the paucity of materials available for study.[1-4] This has been especially true for the study of systematic variations due to disorder,[5] metal, ligands, Fermi energy, etc.[1,2] For this reason it seemed appropriate to synthesize $K_2Pt(CN)_4X_{0.3}{\cdot}3H_2O$ (X = Cl, Br),[1] **1**, with a variable mixture of chloride and bromide in the tetragonal lattice and study the ramifications of such a structural modification on the physical properties. Herein we report on the synthesis of $K_2Pt(CN)_4Br_{\sim 0.16}Cl_{\sim 0.16}{\cdot}xH_2O$, **2**, by slow evaporation of an aqueous solution of 440 mg of $K_2Pt(CN)_4$, 59.7 mg of $K_2Pt(CN)_4Br_2$, and 49.8 mg of $K_2Pt(CN)_4Cl_2$.

Complex **1** (X = Cl, Br) can be synthesized by a variety of techniques including electrochemical oxidation[6] in the presence of KX or effectively partially oxidizing[1,7] $K_2Pt(CN)_4$ with X_2 (X = Cl, Br) in aqueous solution. The former method, however, cannot be utilized to prepare **2** since even in the presence of excess bromide, **1** (X = Cl) will preferentially form.[8]

Complex **2** was obtained in 66% yield from $Pt^{II}(CN)_4{}^{2-}$, *trans*-$Pt^{IV}(CN)_4Cl_2{}^{2-}$, **3**, and *trans*-$Pt^{IV}(CN)_4Br_2{}^{2-}$, **4**, via eq 1. The microanalytical data of **2** support the mixed-halogen

$$50K^+ + 21Pt^{II}(CN)_4{}^{2-} + 2\,trans\text{-}Pt^{IV}(CN)_4Br_2{}^{2-} + 2\,trans\text{-}Pt^{IV}(CN)_4Cl_2{}^{2-} \xrightarrow{H_2O} 25K_2Pt(CN)_4Br_{\sim 0.16}Cl_{\sim 0.16}{\cdot}xH_2O \qquad (1)$$

$K_2Pt(CN)_4Br_{\sim 0.16}Cl_{\sim 0.16}{\cdot}xH_2O$[9] formulation. Powder x-ray diffraction data of **2** clearly show that **2** is neither a simple mixture of **1** (X = Cl and Br) nor an ordered system with alternating unit cells containing chloride and bromide (as well as the vacant site typically associated with **1**) as neither doublets indexed[11] to the *P*4*mm* space group of **1**[12] nor a unique new power diffraction pattern was observed. This was confirmed from analysis and refinement of the lattice constants taken from single-crystal x-ray data.[13] The derived unit cell parameters for **2** are a = 9.851 (2) Å, c = 5.766 (1) Å, and V = 559.6 (2) Å^3.[13] The c axis lies approximately halfway between the values reported by Williams et al. for **1** (X = Br)[12b] and **1** (X = Cl)[12a] which suggest an intermediate oxidation between $K_2Pt(CN)_4Br_{0.30}$ and $K_2Pt(CN)_4Cl_{0.33}$.[14] Reflections for **1** (X = Cl or Br) were not observed.

These lustrous metallic gold appearing needle crystals exhibit ν_{CN} at 2148 cm^{-1} (Nujol) and no evidence for ν_{PtX}. This is consistent with the structure of **1**, where only disordered ionic halides are observed,[1,12] and the infrared spectra in the ν_{CN} region for **1** (X = Br,[1,15] Cl[1,15b]) and $M_{1.75}Pt(CN)_4{\cdot}xH_2O$ (M = K, Cs).[15b] Thus, **2** is best described by the tetragonal *P*4*mm* structure of **1** except that the ~60% occupied halogen sites

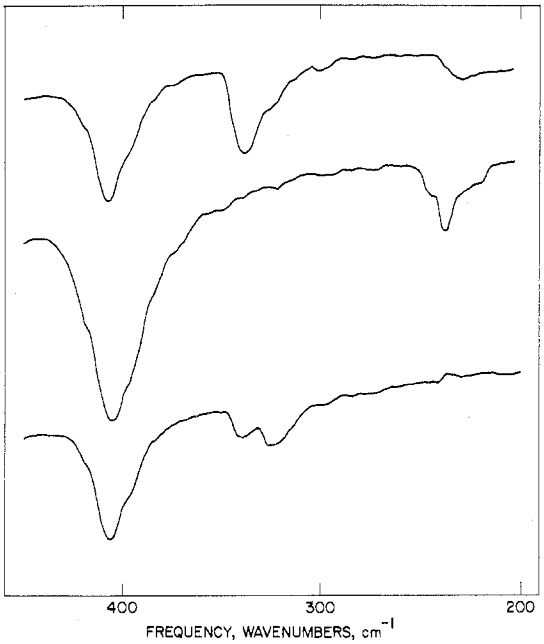

Figure 1. Far-infrared spectra of *trans*-$K_2Pt(CN)_4Cl_2$ (top trace), *trans*-$K_2Pt(CN)_4Br_2$ (middle trace), and *trans*-$K_2Pt(CN)_4BrCl$ (bottom trace).

are further disordered by the random occupancy with chloride (~32%) and bromide (~32%). Through variation of the ratios of **3** and **4** in eq 1, **2** can be synthesized with variable halogen stoichiometries, i.e., $K_2Pt(CN)_4Cl_xBr_{0.3-x}\cdot 3H_2O$. Furthermore, the ramifications of the introduced additional disorder associated with **2** (with respect to **1**) can be studied.

As part of the study of **2** the aqueous equimolar reaction product of **3** and **4** was reevaluated to determine if it was a simple mixture of **3** and **4** or *trans*-$Pt^{IV}(CN)_4BrCl^{2-}$, **5**. The mixed-halogen complex **5** was prepared from a minimum amount of warm water[16] and has been a postulated intermediate in the halide-assisted anation of Pt(IV) complexes.[17] The infrared spectra (in a polyethylene pellet) of **3**–**5** in the ν_{CN} and ν_{Pt-X} regions were obtained. In the ν_{CN} region sharp singlets at 2172, 2162, and 2169 cm^{-1} were observed for **3**–**5**, respectively. In contrast to the ν_{Pt-Cl} and ν_{Pt-Br} absorption frequencies at 338 and 258 cm^{-1} for **3** and **4**, respectively, **5** lacked these absorptions and exhibited ν_{Pt-X} at 324 and 340 cm^{-1}, Figure 1. Furthermore, the x-ray powder diffraction pattern of **5** cannot be decomposed into the powder patterns of **3** and **4**. Thus, **5**[18] is a unique phase.

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Registry No. *trans*-$K_2Pt(CN)_4Cl_2$, 12072-77-4; *trans*-$K_2Pt(CN)_4Br_2$, 12072-67-2; *trans*-$K_2Pt(CN)_4BrCl$, 63765-22-0; $K_2Pt(CN)_4$, 562-76-5; bromine, 7726-95-6; chlorine, 7782-50-5.

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o-Diphenylphosphinophenol and Its Coordination Compounds

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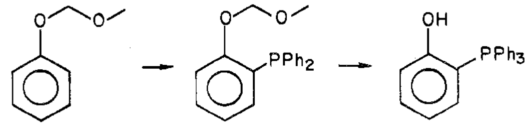
Transition metal complexes of phosphinoanisoles have been recently reported with attention to their lability,[1] oxidative additions,[2] and *o*-dealkylation.[3] The latter study also describes metal complexes formally derived from the previously unknown class of ligands, *o*-diorganophosphinophenols. Herein we describe a convenient synthesis for *o*-diphenylphosphinophenol from phenol itself; furthermore we describe several of its metal complexes.

Results and Discussion

o-Diphenylphosphinophenol is prepared from phenol in three steps: first the phenol is protected and activated, next the diphenylphosphino group is attached, and finally the hydroxyl group is deprotected. Methoxymethyl phenyl ether is easily prepared on a large scale by the reaction of phenol with sodium hydride followed by treatment with chloromethyl methyl ether. The metalation of methoxymethyl phenyl ether[4,5] by butyllithium yields the *o*-lithio derivative which, when reacted in situ with chlorodiphenylphosphine, yields **1**. Similar orthometalations have been used by us to prepare other phosphorus chelates.[1] **1** exhibits the chemical and spectroscopic characteristics expected for a tertiary arylphosphine. Acid catalyzed methanolysis of **1** cleanly gives the desired phenol (**2**), PPhOH, in 42% overall yield. **2** is easily sublimable, shows



1 2

a broad absorption in the infrared at 3400 cm^{-1}, and has a proton resonance absorption at δ 6.15 which disappears upon