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Supplementary Material Available: Description of experimental procedures and spectroscopic data for **1**–**3** and listings of the details of the data collection, final positional and equivalent isotropic parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters for **1** and **2** (19 pages); listings of observed and calculated structure factors for **1** and **2** (33 pages). Ordering information is given on any current masthead page.

A Novel Mode of Coordination for Phosphorus

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The transition-metal coordination chemistry of ADPnO[1] systems containing 3-coordinate, 10-electron pnictogen centers (10-Pn-3,[2] Pn = P, As, or Sb) proved to be valuable in understanding the nature of bonding in these systems.[3-8] Previous work on these molecules shows that they behave differently depending on the pnictogen. The heavier analogues, ADAsO and ADSbO are capable of donating either one or both lone pairs on the pnictogen to transition-metal fragments while maintaining their planar, 10-Pn-3, form.[4-7] However, ADPO adopts a folded, 8-P-3 form upon coordination to metal centers.[3,5-8] This special behavior of ADPO toward transition-metal Lewis acids has its origins in a configuration mixing that transfers σ-electron density to the π-systems at phosphorus.[6,8,9] In this way planar 10-P-3 ADPO is stabilized by ~14 kcal/mol over its folded 8-P-3 form.[9] Thus far, the complexes of ADPO which have been investigated have employed metals (Cr, W,[10] Mn,[7] Fe,[8] Ru,[6] Pt[3]) which have sufficiently high P→M bond strengths to disturb the 8-P-3 vs 10-P-3 ADPO balance. Silver(I) species have been demonstrated to have low P→Ag bond strengths with activation energies for dissociation less than 11 kcal/mol.[11] Thus, silver(I) should have less of a perturbing effect on the planar 10-P-3 ADPO ring system.

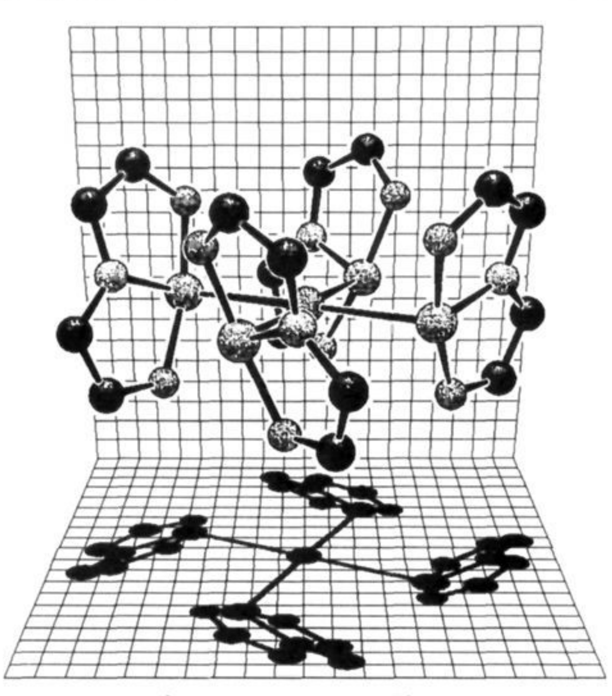
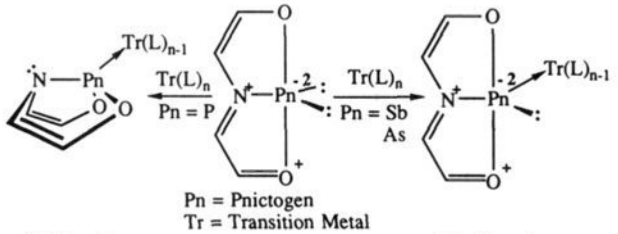


Figure 1. KANVAS[18] drawing of $[(ADPO)_4Ag]^+$. Hydrogens and *tert*-butyls have been omitted for clarity.

Table I. Selected Bond Distances and Angles for $[(ADPO)_4Ag]^+SbF_6^-$ and ADPO[a]

property	$[(ADPO)_4Ag]^+$	ADPO
P–Ag	261.2 (1)	
P–O	179.2 (3), 181.5 (3)	179.2 (2), 183.5 (2)
P–N	172.0 (4)	170.3 (2)
$C-C_{ring}$	134.1 (6), 134.6 (6)	134.2 (4), 133.7 (4)
C–N	137.6 (5), 138.3 (5)	137.5 (3), 138.2 (3)
C–O	134.0 (5), 131.8 (5)	133.1 (4), 132.8 (4)
O–P–O	167.6 (2)	167.7 (1)
N–P–O	84.4 (2), 83.7 (2)	84.2 (1), 83.5 (1)
P–Ag–P	90.00 (1), 179.00 (1)	
Ag–P–N	113.3 (1)	

[a] Bond distances in pm and angles in deg.



8-Pn-4 complex **10-Pn-3 ADPnO** **10-Pn-4 complex**

We now report the synthesis and structure of $[(ADPO)_4Ag]^+SbF_6^-$, which represents the first example of a transition-metal complex containing a ψ-tbp 10-P-4 phosphorus center. The reaction (eq 1) of $[Ag(NCCH_3)_4]^+SbF_6^-$ with 4 equiv of ADPO in CH_2Cl_2 gave yellow crystalline $[(ADPO)_4Ag]^+SbF_6^-$ in 67% isolated yield.[12]

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[1] The ADPnO acronym has been previously described and is used for simplicity in place of the name of the ring system it represents: 5-*a*za-2,8-*d*ioxa-1-*pn*ictabicyclo[3.3.0]octa-2,4,6-triene. See ref 5, footnote 1d for details.

[2] The *N*-X-*L* nomenclature system has been previously described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Algeria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753). *N* valence electrons about a central atom X, with *L* ligands.

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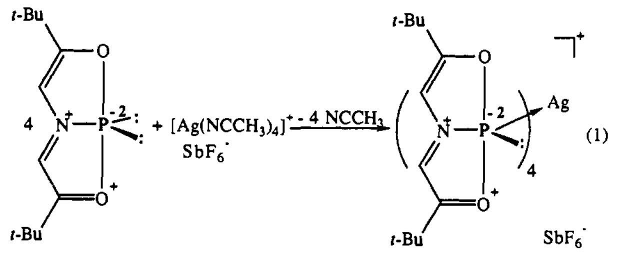

10-P-3 ADPO $[(ADPO)_4Ag]^+SbF_6^-$

The solid-state structure[13] of $[(ADPO)_4Ag]^+$ is illustrated in Figure 1. Silver (with an unusual square-planar geometry for an 18e, silver cation) is located on a 4-fold symmetry axis. This may be due to the unique steric requirement of accommodating 4 ADPO units, with each having ψ-tbp phosphorus centers. The Ag-P distance of 261.2 (1) pm is slightly shorter than the Ag-P distances seen for tetrahedral $Ag(PPh_3)_4^+$ (range 261.5→274.6 pm).[14-16] The ADPO ligand is essentially planar (largest deviation is 6.2 pm for one of the t-Bu bearing carbons) and has very similar structural parameters to those of uncomplexed 10-P-3 ADPO[5,17] (Table I). The N-P-Ag angle of 113.3 (1)° clearly indicates the stereochemical activity of a lone pair of phosphorus.

The multinuclear NMR and elemental analysis data are consistent with the above structure. Lability of the ADPO ligands in $(ADPO)_4Ag^+$ is evident from the ^1H NMR data. An averaged chemical shift and coupling constant were observed when excess ADPO was added to a CD_2Cl_2 solution of $[(ADPO)_4Ag]^+SbF_6^-$. However, the downfield shift in the ^1H NMR for ring protons is consistent with the planar, oxidized form of the ligand backbone. The increase in $^3J_{PH}$ (9.6→14.3 Hz) is consistent with trends observed for increased phosphorus coordination number is smaller than in previous examples (~26 Hz).[3,6-8] The ^{15}N NMR chemical shift (δ -124.5, $^1J_{PN}$ = 64.4 Hz) is close to uncomplexed ADPO (δ -126.3, $^1J_{PN}$ = 80.0 Hz). The reduction of P-N coupling constant follows the expected trend.[5] The ^{31}P NMR spectrum consists of a broad singlet at δ 166 ppm. The absence of Ag-P coupling down to -95 °C in CD_2Cl_2 reflects the high lability of ADPO ligands. The NMR data suggest that the ligand exchange rate in $[(ADPO)_4Ag]^+SbF_6^-$ is even faster than the rates observed for $Ag[P(C_6H_4CH_3)_3]_4^+$ or $Ag[P(OC_2H_5)_3]_4^+$.[11]

Supplementary Material Available: A complete description of the X-ray crystallographic structure determination on $[(ADPO)_4Ag]^+SbF_6^-$ including experimental procedures, tables of data, and ORTEP structure drawing (7 pages). Ordering information is given on any current masthead page.

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(12) ADPO (500 mg, 2.07 mmol) was dissolved in CH_2Cl_2 (15 mL) and solid $[Ag(NCCH_3)_4]^+SbF_6^-$ (262 mg, 0.517 mmol) was added at room temperature. The resulting yellow-green solution was stirred for 15 min and the volatiles were removed under vacuum. The residue was extracted into CH_2Cl_2, filtered through Celite, and concentrated under reduced pressure. The addition of hexane followed by cooling to -25 °C gave yellow crystals of $[(ADPO)_4Ag]^+SbF_6^-$ (453 mg) in 67% yield, mp 173-174 °C dec. NMR data in CD_2Cl_2: ^1H δ 1.24 (s, 18 H), 7.70 (d, $^3J_{PH}$ = 14.4 Hz, 2 H); $^{13}C\{^1H\}$ δ 27.9 (CH_3), 34.5 ($C(CH_3)_3$), 113.3 (d, J_{PC} = 2.8 Hz, NC), 171.6 (CO); ^{31}P δ 166; ^{15}N δ -124.5 (d, $^1J_{PN}$ = 64.4 Hz) (reference $NH_4{}^{15}NO_3$). Anal. ($C_{48}H_{80}AgF_6N_4O_8P_4Sb$): C, H, N.

(13) Crystal data for $[(ADPO)_4Ag]^+SbF_6^-$ at 203 K with Mo Kα radiation: a = 1619.2 (2) Å, c = 2385.6 (2) pm, tetragonal, $P4/ncc$, Z = 4, 1219 unique reflections with $I > 3\sigma(I)$. The final R factors were R = 0.028, R_w = 0.026. The largest residual density in the final difference Fourier map was 0.03 e/Å^3. Further details of the crystal structure are available in the supplementary material.

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(18) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL by E. Keller (Kristallographisches Institute der Universitat Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE), to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.

A Novel Iron-Sulfur Center in Nitrile Hydratase from *Brevibacterium* sp.[1]

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We report that nitrile hydratase from *Brevibacterium* sp. contains a ferric ion in a biologically novel coordination environment. Nitrile hydratases are bacterial enzymes that catalyze the hydration of nitriles to amides.[3] The best characterized is from *Brevibacterium* sp., strain R312, and is probably an $\alpha_2\beta_2$ tetramer of 94 000 Da.[4,5] The EPR spectrum of this protein (g_1 = 2.27, g_2 = 2.12, g_3 = 1.97) is consistent with a rhombically distorted octahedral, low-spin ferric complex.[6,7] We present resonance Raman and EXAFS spectra that suggest that the iron exists in a ligand field of sulfur and nitrogen or oxygen donor atoms.

The iron k-edge X-ray absorption spectrum[8] (Figure 1a) of nitrile hydratase[9] shows a shoulder at 7116 eV[10] associated with sulfur coordination.[11] The shoulder at 7112 eV, assigned to the

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(9) The enzyme was purified from an amidase-deficient mutant of *Brevibacterium* sp., strain R312, according to a modification of the published procedure.[4] The enzyme solutions used had specific activities ranging from 400 to 600 μmol methacrylonitrile hydrated min^{-1} mg^{-1}, which corresponds to 900-1200 units/mg as measured by hydration of propionitrile.[4] Our preparations contain approximately 1.7 equiv of iron/protein; EPR integrations routinely show 1 ± 0.1 spin/iron. Samples were prepared in 0.01 M HEPES buffer, pH 7.8 (at 4 C), containing 40 mM sodium butyrate as a stabilizing agent.[4]

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