Volume 25
Number 22
October 22, 1986

Inorganic Chemistry

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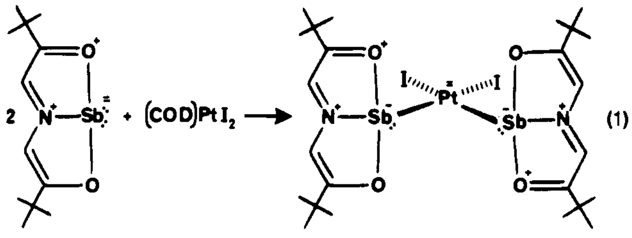
Communications

A New Class of Pnictogen–Transition Metal Adducts: A Stereoactive Lone Pair at a 10-Sb-4 Antimony Center[1]

Sir:

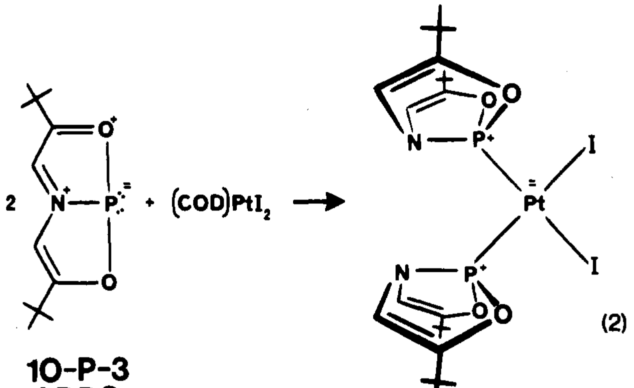
We now report the synthesis and characterization of the first 10-Sb-4 center of an antimony-platinum complex, derived from the 10-Sb-3 3,7-di-*tert*-butyl-5-aza-2,7-dioxa-1-stibabicyclo-[3.3.0]octa-2,4,6-triene (ADSbO)[2] system.



10-Sb-3
ADSbO

1

Recently, we reported the synthesis and characterization of the first phosphorus–platinum complex containing an 8-P-4 center,[3] which is formally derived from the 8-P-3 electromorph[4] of 3,7-di-*tert*-butyl-5-aza-2,7-dioxa-1-phosphabicyclo[3.3.0]octa-2,4,6-triene (ADPO). The two systems differ in that the lighter pnictogen, phosphorus, rehybridizes upon complexation to the platinum center to become an 8-P-4 adduct (eq 2). In the present example (eq 1) there is no rehybridization at the heavier pnictogen upon complexation to the platinum. The antimony maintains its full complement of 10 electrons.



10-P-3
ADPO

2

The reaction of 2 equiv of ADSbO with (1,5-cyclooctadiene)platinum(II) diiodide in toluene provides **1** in good yield (80%) (eq 1). Compound **1** is a black flaky solid with a melting point of 166 °C.[5] The downfield shift in the ^{1}H NMR (δ 8.38)

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(1) The *N*-X-*L* nomenclature system has previously been described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753): *N* valence electrons about a central atom X, with *L* ligands. The terms "pnictogen" and "pnictide" have been used to refer to the main group 5 (group 15) elements (N, P, As, Sb, Bi). These terms are derived from the Greek word *pniktos* (suffocate—the origin of the prefix "pnicto"). See: Brown, R. W. *Composition of Scientific Words*; George W. King Printing Co.: Baltimore, MD, 1954; p 620. The terms "pnigogen" and "pnicogen" have also been used to identify this family of elements (Suchow, L. *Inorg. Chem.* **1978**, *17*, 2041). The latter two terms are somewhat inappropriate since *pnigo* (the source of pnigogen) means "choke" rather than "suffocate" and "pnicogen" does not reflect the proper etymology (the "t" should not be omitted). For the spoken words, the terms "pnictogen" and "pnictide" are clearly and easily enunciated. Thus we prefer the terms derived from "pnicto" (pnictogen and pnictide).

(2) Stewart, C. A.; Harlow, R. L.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1985**, *107*, 5543.

(3) Arduengo, A. J., III; Stewart, C. A.; Davidson, F. *J. Am. Chem. Soc.* **1986**, *108*, 322.

(4) Culley, S. A.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1984**, *106*, 1164.

(5) We have obtained the following NMR data on **1** in CD_2Cl_2: ^{1}H NMR δ 1.24 (s, 18 H), 8.38 (s, 2 H); $^{13}C\{^1H\}$ δ 28.2 (CH_3), 41.1 ($C(CH_3)_3$), 123.3 (CH), 195.2 (CO); ^{195}Pt (ref K_2PtCl_4/D_2O) δ −3405. Anal. ($C_{24}H_{40}N_2O_4Sb_2PtI_2$): C, H, N.

(6) The following NMR data have been obtained for **3** in CD_2Cl_2: ^{1}H NMR δ −0.74 (t, $^3J_{PH} = 6.6$ Hz, 3 H), 1.43 (s, 18 H), 7.41 (m, 30 H), 8.72 (s, 2 H); $^{13}C\{^1H\}$ δ 3.4 ($PtCH_3$, dd), 27.9 (CH_3, s), 41.1 ($C(CH_3)_3$, s), 123.9 (CH, s), 128 (Ph, m), 131 (Ph, m), 134 (Ph, m), 195.6 (CO, s); $^{31}P\{^1H\}$ δ 19.4 (apparent dt due to ^{195}Pt satellites, $^2J_{PP} = 15.5$ Hz, $^1J_{PtP} = 2066$ Hz), 37.3 (apparent dt due to ^{195}Pt satellites, $^2J_{PPt} = 15.5$ Hz, $^1J_{PtP} = 3041$ Hz); ^{195}Pt δ −3174 (ref K_2PtCl_4/D_2O) dd, $^1J_{PPt} = 3041$ Hz, $^1J_{PtP} = 2066$ Hz).

(7) One equivalent of 10-Sb-3 ADSbO in ether was added to a suspension of $(CH_3)_2CO{\cdot}PtCH_3(trans\text{-}(Ph_3P)_2)^+SbF_6^-$ in ether. The reaction was allowed to stir for 12 h at room temperature. The volatiles were removed in vacuo, and the dark red solid was recrystallized from CH_2Cl_2/hexamethyldisiloxane. The crystal data (23 °C) were as follows: $C_{49}H_{53}NO_2SbP_2PtSbF_6{\cdot}{}^1/_2C_6H_{18}Si_2O$, monoclinic, space group $P2_1/c'$ $a = 1246.6$ (3) pm, $b = 1752.9$ (4) pm, $c = 2749.3$ (5) pm, $\beta = 92.64$ (2)°, $Z = 4$, $D_c = 1.49$ g/cm^3, crystal size 0.20 × 0.20 × 0.40 mm. Only the 4337 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The structure was solved by the Patterson method to locate the Pt atom. The remaining atoms were located in succeeding difference Fourier syntheses. The final *R* factors were $R = 0.065$ and $R_w = 0.090$.

(8) This perspective drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut 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 with the lighting source at infinity so the shadow sizes are meaningful.

(9) ^{1}H NMR data for $ADPO{\cdot}PtCH_3(trans\text{-}p\text{-}Tol_3P)_2)^+SbF_6^-$ in CD_2Cl_2: δ 0.1 (m, CH_3, 3 H), 0.9 (s, 18 H), 2.4 (s, Tol CH_3, 18 H), 4.91 (d, ligand ring protons, $J_{PH} = 30.0$ Hz, 2 H), 7.39 (m, 24 H).

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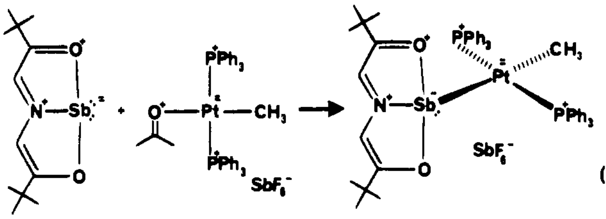
Table I. Bond Lengths and Angles in 3

bond lengths, pm		bond angles, deg	
Sb–O	216.1 (9), 219.2 (10)	O–Sb–O	146.2 (4)
Sb–N	210.3 (12)	N–Sb–O	73.2 (4), 73.3 (4)
C–O	130.0 (2), 128.0 (2)	N–Sb–Pt	118.5 (3)
C–C$_{ring}$	138.0 (2), 137.0 (2)	Sb–Pt–P	89.8 (1), 97.7 (1)
C–N	136.0 (2), 138.0 (2)	P–Pt–C	83.6 (4), 88.8 (4)
Sb–Pt	264.1 (1)	Sb–O–C	115.7 (9), 114.0 (1)
Pt–C	208.0 (2)	C–N–Sb	118.0 (1), 118.0 (1)
Pt–P	230.7 (4), 231.0 (4)	C–C–N	113.0 (1), 112.0 (2)
		C–C–O	118.0 (1), 121.0 (2)

for the ring proton is consistent with the high degree of positive charge in the ligand backbone (as also observed in the spectrum of initial ADSbO). The ^{13}C resonances also exhibit downfield shifts associated with this positive charge still retained in the tridentate ligand on antimony. This is in contrast to what has previously been observed in the metal complexes of ADPO (eq 2).

The reaction of 1 equiv of ADSbO with $(CH_3)_2CO{\cdot}PtCH_3(\textit{trans}\text{-}(Ph_3P)_2)^+SbF_6^-$ in ether affords 3 in 30% yield. Complex 3 is a dark red crystalline solid melting at 221 °C with decomposition.[6] The asymmetry of the molecule is consistent with the nonequivalency of the triphenylphosphines in the ^{31}P{^{1}H} NMR resonances at δ 19.4 (apparent dt due to ^{195}Pt satellites, $^2J_{PP}$ = 15.5 Hz, $^1J_{PPt}$ = 2066 Hz) and 37.3 (apparent dt due to ^{195}Pt satellites, $^2J_{PP}$ = 15.5 Hz, $^1J_{PPt}$ = 3041 Hz). The ligand backbone in free ADSbO bears considerable positive charge, as evidenced from multinuclear magnetic resonance spectra.[2] Coordination of the antimony of ADSbO to the platinum cation in 3 further increases the electron demand on the ADSbO backbone and results in a considerable downfield shift in the resonances of the ring protons of the ADSbO moiety in 3 (δ 8.72). These data require the presence of a stereoactive lone pair at the antimony center.



(3)

10-Sb-3
ADSbO

3

The structure of 3 has been verified by single-crystal X-ray structure determination.[7] The solid-state structure of the complex is illustrated in Figure 1, and pertinent bond distances and angles are given in Table I. There are some slight distortions of the ADSbO moiety upon complexation. The Sb–O bonds increase by about 3 pm, the O–Sb–O angle decreases from 149.6° in free ADSbO to 146.2° in the complex, and finally the Sb–N bond increases about 4 pm in the complex. These changes in bond angles and lengths can be attributed to steric congestion at the platinum center due to the two trans triphenylphosphine ligands although electronic factors may also play a role. It is noteworthy that in spite of the steric congestion the ADSbO system maintains its 10-electron count and planar ligand backbone. ADPO readily forms an adduct with $(CH_3)_2CO{\cdot}PtCH_3(\textit{trans}\text{-}(p\text{-}Tol_3P)_2)^+SbF_6^-$ to afford a system in which the phosphorus of the ADPO has rehybridized to an 8-P-4 center resulting in a folded ring system similar to the case of complex 2.[9]

The structures of these 10-Sb-4 systems are in contrast to that of the ADPO systems, in which the phosphorus switches from a 10-electron center to an 8-electron center upon complexation to the metal. The antimony maintains a high electron count, using one lone pair of electrons for coordination to the metal while the other lone pair remains at the pnictogen and is stereoactive. By contrast, the lighter pnictogen (P) must rehybridize to place a lone pair of electrons in a more directional sp^3 orbital. The (approximate) sp^2 orbitals that contain the lone pairs at heavier pnictogen centers (antimony) achieve sufficient overlap with the orbitals of the metals that there is no need to rehybridize. We are currently studying systems that will utilize both lone pairs of electrons at the heavier pnictogen to bridge transition metals.

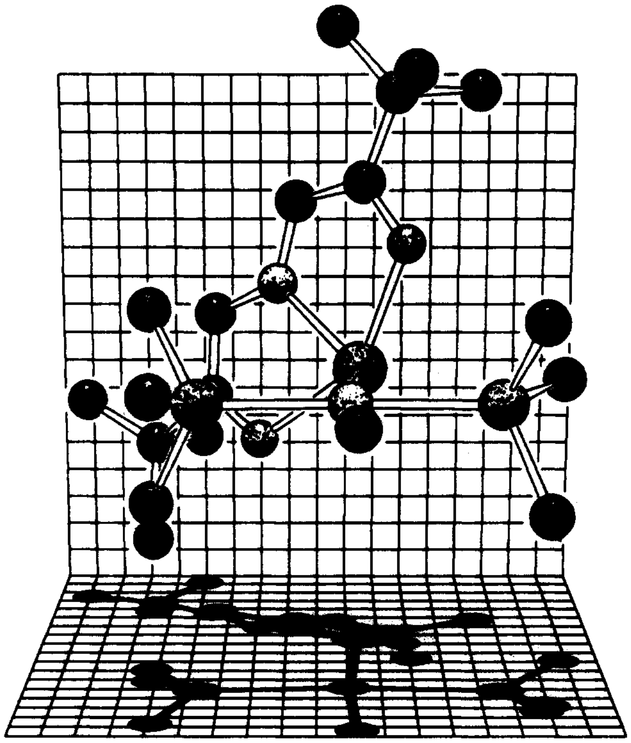


Figure 1. KANVAS[8] drawing of 3. The hydrogens and all but the *ipso*-carbons of the phenyl rings have been omitted for clarity.

Acknowledgment is made to Dr. David Thorn for helpful discussions and a supply of the bis(triphenylphosphine)methylplatinum and bis(tri-*p*-tolylphosphine)methylplatinum cations.

Registry No. 1, 104130-26-9; 3, 104130-28-1; (COD)PtI$_2$, 12266-72-7; PtCH$_3$(*trans*-(Ph$_3$P)$_2$)$^+$SbF$_6^-$, 104130-30-5.

Supplementary Material Available: A view of 3, complete description of the X-ray crystallographic structure determination of 3, and tables of experimental details, positional and thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

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Received March 23, 1986

Synthesis and Structure of the Nickel(II) Complex of 1,1,1-Tris(((2-(methylthio)ethyl)thio)methyl)ethane, an All-Sulfur Ligand That Promotes Hexakis(thioether) Coordination

Sir:

Prompted by the potential analogy of thioethers to phosphines and by the occurrence of thioether coordination in blue copper proteins,[1] we[2-6] and others[7,8] have recently been investigating the

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(1) *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*, Karlin, K. D., Zubieta, J., eds.; Adenine: Guilderland, NY, 1983.

(2) Hintsa, E. J.; Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 3738-9.

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