H, 5.4; N, 16.0; Cl 10.1. Found: C, 25.9; H, 5.5; N, 15.0; Cl, 9.5.

The compound $[(C_8H_{16}N_4H_3)_2Te_2O_2]Cl_2 \cdot 4CHCl_3 \cdot 2CH_3OH$ forms monoclinic crystals: space group $P2_1/c$; $a = 10.430$ (3) Å, $b = 15.633$ (9) Å, $c = 15.407$ (6) Å, $\beta = 107.76$ (3)°; $V = 2392.4$ (18) Å^3; $Z = 2$, $d_{calcd} = 1.724$ g/cm^3. Least-squares refinement using the 1943 observed reflections revealed the structure depicted in Figure 2 ($R = 0.080$ and $R_w = 0.098$). The hydrogen atoms could not be unambiguously located. Oxidation state and bond distance considerations suggest the presence of hydrogen atoms on N1, N4, and N10 but not on N7 or the bridging oxygen atoms. The two tellurium atoms in the $[(C_8H_{16}N_4H_3)_2Te_2O_2]^{2+}$ cation are not within bonding distance (Te–Te = 3.107 (2) Å) and are bridged by two μ-oxygen atoms in a manner similar to that in the binuclear tellurate(VI) anion $Te_2O_6(OH)_4^{4-}$.[11]

The most interesting feature of this structure is the tellurium coordination polyhedron. The relevant bond distances and angles are summarized in Table I. This tellurium coordination polyhedron may be viewed as a pentagonal pyramid with O1, O1′, N4, N1, and N10 in the basal plane and the deprotonated nitrogen atom N7 in the apical position. The standard deviation of the five basal atoms from planarity is 0.18 Å, and the atoms Te and N7 are displaced on opposite sides of the best plane of the five basal atoms by 0.20 and 1.78 Å, respectively. The average of the five apical–basal angles, i.e. those involving N7, (Table I) is slightly acute (84.7°), indicating that the lone pair in the axial position of the original pentagonal bipyramid is slightly more sterically demanding than the N7 in the other axial position. The five adjacent basal–basal angles (Table I) range from 67.7 to 77.3° as compared with the 72° expected for a regular pentagon base. This deviation from ideal 5-fold symmetry is rather small considering the constraints imposed by the four fused five-membered chelate rings formed by the coordinated macrocylic tetraamine. These constraints also make one of the distances from the central Te to the basal nitrogens (i.e., N1) significantly longer (2.703 (18) Å) than the distances to the other two basal nitrogens (N4 and N10) suggesting that the Te–N1 bond is appreciably weaker than the Te–N4 and Te–N10 bonds so that the pentagonal-pyramidal coordination can be described as "incipient".

This preliminary result suggests that the structures of crystalline products from reactions of tellurium(IV) derivatives with macrocyclic poly(secondary amines) might be a fertile source of unusual coordination polyhedra derived from larger underlying polyhedra with stereochemically active lone pairs and that such products merit more detailed attention.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant CHE-82-12166.

Supplementary Material Available: Tables II–V, listing crystal data, positional parameters, anisotropic thermal parameters, and bond angles and distances for $TeCl_7O_2N_4C_{11}H_{25}$, and an ORTEP diagram of the $[(C_8H_{16}N_4H_3)_2Te_2O_2]^{2+}$ cation showing the four $CHCl_3$ molecules of crystallization (5 pages); tables of calculated and observed structure factors (45 pages). Ordering information is given on any current masthead page.

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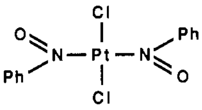
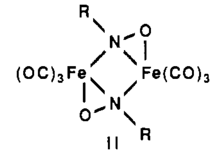
Molecular Structure of (μ-η^1-Nitrosobenzene-*N*)(μ-η^2-nitrosobenzene-*N,O*)(η^1-nitrosobenzene-*N*)tris(trimethylphosphine)diplatinum(II), a Complex Containing Three Linkage Isomers of Nitrosobenzene

Sir:

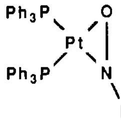
Aliphatic and aromatic nitro compounds may be reduced to amines with metal hydrides,[1,2] with hydrogen in the presence of a transition-metal catalyst,[3] or by catalytic hydrogenation.[4] These reductions may proceed through an intermediate nitroso compound, although such intermediates have never been structurally characterized. Several examples of transition-metal nitroso compounds exist.[5-13] The nitroso group may be bound η^1 to the metal through nitrogen as a σ base (I)[5-7] or may bridge two metal centers in an η^1 or η^2 fashion (II).[8-10] The reaction between $Pt(C_2H_4)(PPh_3)_2$ and nitrosobenzene results in side on η^2 coordination of the N–O group (III).[11] This complex inserts substrates into the Pt–N bond to give nitrones (IV).[12] Some studies suggest that nitroso groups may coordinate to a metal through the oxygen atom,[13] though this has never been established crystallographically.



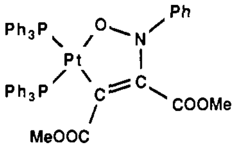
I



II



III



IV

We attempted to catalytically reduce nitrobenzene to aniline with the highly reactive platinum dihydride $PtH_2(PMe_3)_2$ (**1**).[14] When 10 equiv of nitrobenzene was added to a solution of **1** (0.06 M in THF) under a hydrogen atmosphere, the yellow solution became dark brown. No gas evolution was apparent. The reaction solution was paramagnetic, and NMR spectra could not be obtained.[15] Reduction of the solution volume to 1 mL and addition

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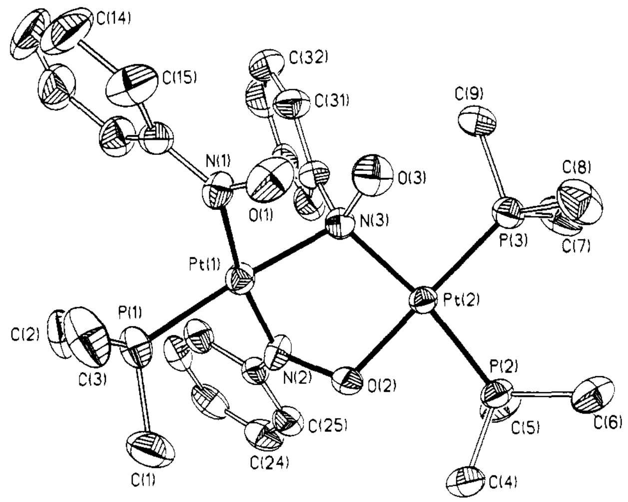
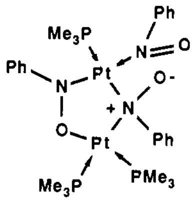


Figure 1. ORTEP diagram of complex **2** showing thermal ellipsoids at 50% probability. Key bond lengths (Å): Pt(1)···Pt(2), 3.502 (1); Pt(1)–N(1), 2.034 (10); Pt(1)–N(2), 1.976 (11); Pt(1)–N(3), 2.112 (11); Pt(1)–P(1), 2.231 (4); Pt(2)–N(3), 2.126 (11); Pt(2)–P(2), 2.243 (4); Pt(2)–P(3), 2.249 (4); Pt(2)–O(2), 2.043 (8); N(2)–O(2), 1.433 (15); N(1)–O(1), 1.296 (14); N(3)–O(3), 1.428 (27). Key bond angles (deg): P(1)–Pt(1)–N(1), 95.9 (3); P(1)–Pt(1)–N(2), 92.5 (3); N(1)–Pt(1)–N(3), 88.5 (4); N(2)–Pt(1)–N(3), 83.0 (4); P(2)–Pt(2)–P(3), 96.0 (1); P(2)–Pt(2)–O(2), 83.5 (3); P(3)–Pt(2)–N(3), 93.2 (3); N(3)–Pt(2)–O(2), 87.2 (4); Pt(1)–N(1)–O(1), 115.9 (8); Pt(1)–N(1)–C(16), 126.8 (7); Pt(1)–N(2)–O(2), 110.4 (7); O(2)–N(2)–C(26), 116.1 (9); Pt(1)–N(2)–C(26), 132.9 (9); O(3)–N(3)–C(36), 106.6 (15); Pt(1)–N(3)–Pt(2), 111.4 (5); Pt(2)–O(2)–N(2), 110.1 (7); O(1)–N(1)–C(16), 117.3 (9).

of 5 mL of Et_2O produced black crystals of a complex with the unusual stoichiometry[16] $Pt_2(PhNO)_3(PMe_3)_3$ (**2**) as the only isolable product (10% yield). This complex is not soluble in common organic solvents. Solid-state magnetic measurements of this compound using a vibrating-sample magnetometer[17] revealed that it is diamagnetic ($\mu_{eff} < 0.1\ \mu_B$). Complex **2** does not form by the direct reaction between PhNO and **1**.

The molecular structure[18] of complex **2**, shown in Figure 1, exhibits three distinct modes of platinum–nitroso bonding. The platinum atoms with two bridging nitroso groups form a puckered five-membered ring. The geometry about each platinum atom is square planar. The bridging η^1-nitroso group exhibits an N(3)–O(3) bond distance of 1.43 (3) Å. This is much longer than the N–O double bond of nitrosocyclohexane (1.27 Å)[5] and suggests a single bond, as does the O(3)–N(3)–C(36) angle of 106.6 (15)°. The bridging η^2-nitroso group also exhibits an N(2)–O(2) single-bond length of 1.43 (1) Å, similar to that of 1.410 (7) Å in $Pt(\eta^2\text{-}ONPh)(PPh_3)_2$.[11] These are among the longest distances recorded for nitrogen–oxygen bonds.[9,10] The third nitroso group replaces one phosphine ligand on Pt(1). The N(1)–O(1) distance of 1.30 (1) Å indicates retention of the N–O double bond and a dative bond of an electron pair on N(1) to Pt(1). The central, five-membered ring is severely puckered at N(2); the other four ring atoms deviate from planarity by 0.05–0.07 Å, whereas N(2) is displaced by 0.85 Å. A bonding scheme for **2** consistent with these results places each platinum atom in a square-planar, 16-electron environment, views each bridging nitrosobenzene as a dianionic ligand, and results in a diamagnetic complex:



Complex **2** is to our knowledge the first example of a compound containing three modes of nitroso–metal bonding. It is also the first structural determination of a μ-η^2-RNO group where the nitrogen and oxygen atoms bridge two metal atoms. In previous examples of bridging η^2-RNO groups, the nitrogen atom binds to both metal centers, while the oxygen atom coordinates to one metal.[8-10] Complex **2** shows no bonding contacts between Pt(2) and N(2). The structure of the η^2-PhNO group thus resembles that found in nitrone complexes IV.[12] These results also support the hypothesis that metal nitrosoarene complexes may be intermediates in the reduction of nitroarene compounds by transition-metal hydrides.

Acknowledgment. This research was supported by the U.S. Army Research Office (Grant DAAG29-85-K-0263). We thank Johnson Matthey for a sample of K_2PtCl_4 under their metal loan program.

Supplementary Material Available: Listings giving the details of the crystallographic data collection, positional and thermal parameters, and interatomic distances and angles (7 pages); a listing of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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(15) Simulations of the EPR spectra of this solution suggest a complex of platinum containing two phosphorus atoms and one nitrogen atom. This species could not be isolated from the solution and may be an impurity present at a small concentration.

(16) Anal. Calcd for $Pt_2P_3N_3O_3C_{27}H_{42}$: C, 34.32; H, 4.86; N, 4.24. Found: C, 34.50; H, 4.51; N, 4.47. IR (Nujol): 1525 (s), 1345 (s), 950 (s), 850 (s), 700 cm^{-1} (s).

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(18) For $C_{27}H_{42}N_3O_3P_3Pt_2$ (293 K): monoclinic, $P2_1/n$, $a = 10.329$ (3) Å, $b = 16.123$ (5) Å, $c = 20.120$ (6) Å, $\beta = 102.62$ (2)°, $V = 3269$ (1) Å^3, $Z = 4$, D(calcd) = 1.909 g cm^{-3}, μ(Mo Kα) = 92.1 cm^{-1}, $\lambda = 0.71073$ Å, T(max)/T(min) = 0.067/0.040. From a black, well-formed crystal (0.28 × 0.28 × 0.30 mm) were collected 6170 reflections ($4° \le 2\theta \le 50°$) (Nicolet R3m), of which 5761 were independent (R(int) = 2.17%) and 3814 with $F_o > 4\sigma(F_o)$ were considered observed and corrected for absorption (XABS). The two Pt atoms were located by direct methods. Rigid-body constraints were applied to the phenyl rings. With all non-hydrogen atoms anisotropic and all hydrogen atoms as idealized isotropic contributions: $R(F) = 4.46\%$, $R_w(F) = 6.04\%$, GOF = 0.975, $\Delta/\sigma = 0.046$, $\Delta(\rho) = 1.18$ e/Å^3, $N_o/N_v = 12.4$. All computations, except XABS, used SHELXTL software (Nicolet Corp., Madison, WI); XABS calculates an empirical absorption tensor from an expression relating F_o and F_c (H. Hope, University of California at Davis).

(19) Presumably two molecules of water and one molecule of trimethylphosphine oxide are formed in this reaction, but they could not be detected in the paramagnetic reaction mixture.

Reactions of Phosgene with Oxide-Containing Species in a Room-Temperature Chloroaluminate Ionic Liquid

Sir:

We wish to report the facile in situ conversion of transition-metal oxide chloride complexes to chloride complexes in a basic room-temperature chloroaluminate ionic liquid and the apparent removal of all traces of oxide-containing species from this solvent with phosgene ($COCl_2$). Familiar examples of room-temperature chloroaluminate ionic liquids include aluminum chloride–1-(1-butyl)pyridinium chloride ($AlCl_3$–BupyCl) and aluminum chloride–1-methyl-3-ethylimidazolium chloride ($AlCl_3$–MeEtimCl).[1]