$\mathrm{Pb[N(SiMe_3)_2]_2}$ in 5 mL of n-$\mathrm{C_6H_{14}}$ at 20 °C gave a red precipitate. The mixture was stirred at this temperature for 2 h. Filtration afforded the red, analytically pure, air-sensitive $\mathrm{Pb(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_2}$.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with lattice constants $a = 13.853$ (5), $b = 14.289$ (5), $c = 14.830$ (6) Å; $\beta = 92.90$ (4)°; and $\rho_{\text{calcd}} = 1.16$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 1681 observed reflections led to a final R value of 0.060. The tin analogue **2** is isostructural and possesses unit cell parameters $a = 13.882$ (3), $b = 14.164$ (4), $c = 15.064$ (4) Å; $\beta = 93.95$ (2)°; and $\rho_{\text{calcd}} = 1.25$ g cm^{-3}. The final R value was 0.040 for 3262 observed reflections. For both structures hydrogen atoms were included and all nonhydrogen atoms were refined with anisotropic thermal parameters.

Scrutiny of Table II reveals that there are only two significant differences between the $\mathrm{M(OAr')_2}$ structures. The shorter Ge–O bond apparently causes an increase in ligand–ligand repulsion which in turn produces a larger O–Ge–O bond angle, 92.0 (4)°, compared with the O–Sn–O angle, 88.7 (2)°. There are no crystal structures of two-coordinate $\mathrm{M^{II}}$ (M = Ge, Sn) complexes in the literature, but the M–O distances in **1** and **2** are near the short end of the reported range for other Ge–O or Sn–O bonds: 1.730 (1) Å for M = Ge[12] in $\mathrm{[(PhCH_2)_3M]_2O}$ and 1.919 (1) Å for the Sn analogue.[12]

Acknowledgment. We are grateful to the National Science Foundation for partial support (to J.L.A.).

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β-Elimination from 6-Alkylmercaptopurine Ribonucleosides

Sir:

In a nonenzymatic process that could serve as a model for the biogenesis of thiolated bases in tRNA, 6-chloropurine ribonucleoside reacts with glutathione to yield a thioether, from which 6-mercaptopurine ribonucleoside is generated by treatment with alkali.[1] Recent evidence from this laboratory seemed to support a hydrolytic mechanism for the second step, offering an apparent method for converting cysteine into serine residues in glutathione and other peptides.[2] Further analysis shows that this evidence was misleading.

Thioethers derived from glutathione and N-acetylcysteine, after alkaline degradation as described earlier[2] followed by mild acid hydrolysis (2 M HCl, 100 °C, 2 h), yielded ~0.4 equiv of dehydroalanine as determined by the procedure of Patchornik et al.[3,4] The thioether derived from glutathione, after acid hydrolysis (6 M HCl, 155 °C, 20 min) and analysis with a Technicon single-column analyzer, was found to contain equimolar amounts of glycine and glutamic acid, with no trace of serine or cysteine. Ethanol, detected in earlier experiments in which 6-ethylmercaptopurine ribonucleoside was treated with alkali, was found to have resulted from traces of ethanol in the commercial alcohol dehydrogenase that had been used for analysis. Changes in ultraviolet spectrum, associated with the slow alkaline decomposition of 6-ethylmercaptopurine ribonucleoside,[2] are found to have been the result of degradation of the purine ring.

We conclude that sulfur transfer from glutathione to purine ribonucleoside, in alkaline solution, does not occur by hydrolysis. Instead, thioethers of 6-mercaptopurine ribonucleoside undergo β-elimination to yield 6-mercaptopurine ribonucleoside and an olefin, at a rate that is strongly dependent on the nature of the thioether.[2] In cases where elimination is slow, degradation of the purine ring system becomes significant as a competing reaction.

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Synthesis and Molecular Structure of $\mathrm{Pd_4[P(C_6H_5)_2(CH_3)]_4(CO)_5}$: A New Tetranuclear Carbonyl Cluster

Sir:

We are systematically investigating the reactions of the nitrite ligand with carbon monoxide. Square planar $\mathrm{Ni(NO_2)_2}$ complexes of tertiary phosphines have previously been shown to react with CO forming $\{\mathrm{NiNO}\}^{10}$ complexes and $\mathrm{CO_2}$ nearly quantitatively.[1-4] Reaction 1 proceeds by formation of a five-coordinate carbon monoxide complex followed by transfer of an oxygen atom from an adjacent $-\mathrm{NO_2}$ ligand to produce carbon dioxide and the nickel nitrosyl complex. To assess the role of the metal in the oxidation of CO by $-\mathrm{NO_2}$, we have now examined the reaction of CO with $-\mathrm{NO_2}$ complexes of Pd(II). In contrast to reaction 1, carbon monoxide reacts with $\mathrm{Pd(NO_2)_2L_2}$ to form the previously unknown tetranuclear palladium(0) clusters, $\mathrm{Pd_4(CO)_5L_4}$ (reaction 2). The molecular structure of one of these palladium clusters has been determined and is the subject of this report.

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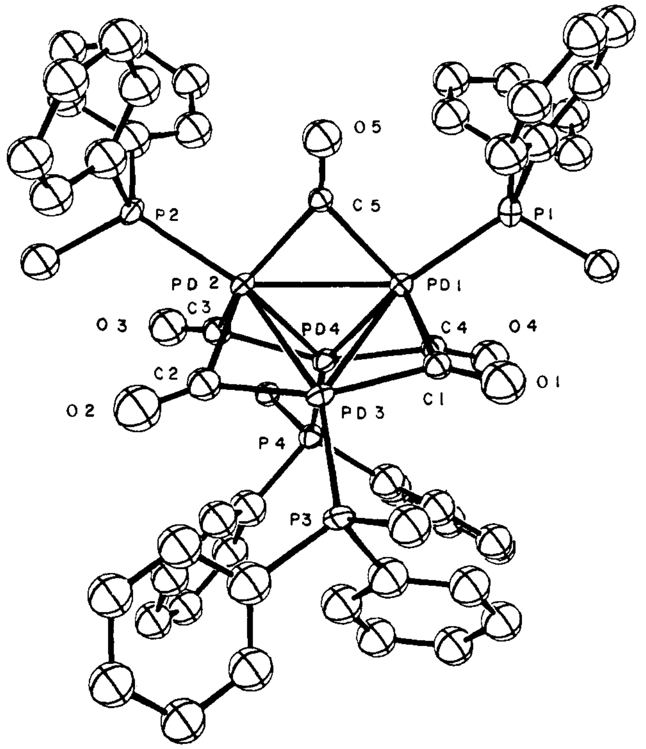

Figure 1. A view of the molecular structure of $Pd_4[P(CH_3)(C_6H_5)_2]_4(CO)_5$ showing the numbering scheme for the cluster atoms. The hydrogen atoms and numbering of the noncluster atoms have been deleted for clarity. The thermal ellipsoids are 50% probability envelopes.

$$Ni(NO_2)_2L_2 + CO \rightarrow Ni(NO)(NO_2)L_2 + CO_2 \quad (1)$$

$$Pd(NO_2)_2L_2 + CO \rightarrow Pd_4(CO)_5L_4 + 2CO_2 + N_2O + \text{other products} \quad (2)$$

The reaction of CO with $Pd(NO_2)_2L_2$ (L = PPh_3, PPh_2Me, and $PPhMe_2$) was examined in dichloromethane. While each complex reacts with CO, *trans*-$Pd(NO_2)_2(PPh_2Me)_2$ provided the most tractable products. Thus the reaction of *trans*-$Pd(NO_2)_2(PPh_2Me)_2$ with excess carbon monoxide (1 atm) in dichloromethane for a period of 12 h resulted in the formation of a dark red solution, N_2O and CO_2. Examination of the gases evolved from this reaction by IR spectroscopy and gas chromatography gave a ratio of CO_2:N_2O:$Pd(NO_2)_2(PMePh_2)_2$, of 2.0:1.0:1.0. Addition of N_2-saturated *n*-hexane to the red solution resulted in well-formed dark red crystals. These air-sensitive crystals were isolated and stored under nitrogen. The infrared spectrum (KBr) of the red product consisted of a single band in the bridging carbonyl region at 1840 cm^{-1} with a shoulder at 1820 cm^{-1}, while no bands attributable to Pd-H were observed. The ^1H NMR spectrum consisted of singlets at 1.85 and 2.06 ppm and a complex multiplet near 7.50 ppm due to the methyl and phenyl groups, respectively, of the tertiary phosphine ligand. The compound was analyzed for C, H, and O.[5] Although the elemental analyses were in excellent agreement with the formulation of the compound as the $Pd_4(PMePh_2)_4(CO)_5$ tetramer,[6] it was too air sensitive and nonvolatile to obtain a reliable molecular weight. Consequently, a single-crystal X-ray structure determination was initiated to determine the nuclearity and molecular geometry of this novel compound.

Several well-formed crystals were selected and sealed in capillaries using an inert atmosphere box. Intensity data were collected using a Syntex $P2_1$ diffractometer, and the structure was solved by direct methods.[7] The molecule consists of a distorted tetrahedron of palladium atoms. One edge of the tetrahedron is open with a nonbonded Pd-Pd distance of 3.365 (2) Å, giving the molecule a nido structure. The average of the five Pd-Pd bonding distances, 2.750 (2) Å, compares favorably with the 2.742 Å reported for the other Pd(0) cluster which has been structurally characterized,[8] $Pd_3(Bu^t\text{-}NC)_5(SO_2)_2 \cdot 2C_6H_6$. The average of the four terminal Pd-P distances (2.315 (4) Å) lies between the Pd-P distances reported for the other Pd(0) compounds, $Pd(PBu^t{}_2Ph)_2$ (2.285 Å)[9] and $Pd(PPh_3)_2[C_2(CO_2Me)_2]$ (2.326 Å).[10] Each of the five edges of the tetrahedron with a Pd-Pd bond is also bridged by a carbonyl ligand with an average Pd-C distance of 2.085 (16) Å and Pd-C-Pd angle of 82.5 (6)°. A similar Pd-C distance (2.063 Å) was reported for $Pd(PPh_3)_2[C_2(CO_2Me)_2]$. There are no other Pd(0) complexes with bridging carbonyl ligands with which the present structure can be compared. However, the average Pd-C-Pd angle in $Pd_4(PMePh_2)_4(CO)_5$ is typical of those normally found for complexes with bridging carbonyl ligands and metal-metal bonds.[11]

The metal carbonyl framework of $Pd_4(PMePh_2)_4(CO)_5$ is essentially the same as that reported for $Pt_4(PMe_2Ph)_4(CO)_5$ by Vranka et al.[12] Since individual bond distances and angles were not reported for the tetranuclear platinum cluster, a detailed comparison of the palladium and platinum compounds cannot be made. However, the average of the five M-M bonding distances and the one nonbonded distance compare favorably as do the dihedral angles.[13] The nearly indistinguishable bond distances reported for the tetranuclear palladium and platinum clusters are consistent with other structural findings which indicate that the Pd-X and Pt-X distances are nearly the same for isoelectronic and isostructural species.[14]

A second palladium complex is also formed during the reaction between CO and $Pd(NO_2)_2(PMePh_2)_2$. This orange compound has a prominent band at 1740 cm^{-1}. Experiments are in progress to characterize this unusual compound more fully.

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Supplementary Material Available: Fractional coordinates (Table 1) and thermal parameters (Table 2) of $Pd_4(CO)_5[PCH_3(C_6H_5)_2]_4$ (2 pages). Ordering information is given on any current masthead page.

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(7) Intensity data were collected from a crystal of approximate dimensions 0.5 × 0.25 × 0.25 mm using Mo $K\alpha$ radiation. The crystal was triclinic with $a = 11.966$ (1), $b = 12.228$ (3), $c = 21.001$ (3) Å; $\alpha = 103.127$ (9), $\beta = 101.794$ (1), $\gamma = 96.506$ (1)°; space group $P1$; $Z = 2$; $d_{obsd} = 1.56$, $d_{calcd} = 1.57$ g/mL; a total of 10 588 unique data were collected from 4.0 to 50° using θ–2θ scans. The palladium atoms were located by direct methods (MULTAN). Subsequent least-squares refinement and difference Fourier syntheses resulted in the location of all nonhydrogen atoms which were added as fixed contributors. The final conventional unweighted discrepancy factor was 6.8%, with anisotropic thermal parameters for all palladium, and phosphorus atoms and with the rings as rigid groups.
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Conversion of Aryl Azides on Ni Centers into Tetraazadiene–Nickel Complexes [$Ni^0(Ar_2N_4)_2$], [$CpNi^I(Ar_2N_4)$], and [$(RNC)_2Ni^0(Ar_2N_4)$]. Crystal Structure of [$Ni^0\{1,4\text{-}(3,5\text{-}Me_2C_6H_3)_2N_4\}_2$]

Sir:

In contrast to the versatile coordination chemistry of the α-diimine ligand, RNCHCHNR, which can act as a σ,σ-N,N-chelating,[1a,2a] σ,σ'-N,N-[2b,3] or σ-N,η^2-CN-bridging,[1b] or as a σ-N-monodentate[3]-bonded ligand, only a few metal complexes of the isostructural tetraazadiene ligand, RNNNNR, are known.[4] These are 1:1 complexes with the tetraazadiene ligand σ bonded via the 1,4-nitrogen atoms. The reason for this contrast between α-diimine and tetraazadiene chemistry seems to be the fact that the RN_4R ligand, which apparently does not exist as a free compound, has to be generated directly at the metal center and subsequently stabilized by coordination.

We report here the first example of a bis(tetraazadiene) metal complex, [$Ni^0(ArN_4Ar)_2$], which is the counterpart of the [bis(α-diimine)nickel(0)][5] complexes in α-diimine–metal chemistry. We also describe the stepwise synthesis of [$Ni(ArN_4Ar)_2$] from [Cp_2Ni] via novel [$CpNi^I(ArN_4Ar)$].

Pure [$Ni(ArN_4Ar)_2$] [Ar = 4-MeC_6H_4 (I), 4-$MeOC_6H_4$ (II), 3,5-$Me_2C_6H_3$ (III)][6] was isolated in 20–25% yield from the reaction of [$Ni(COD)_2$] with ArN_3 (1:4 molar ratio) in toluene. The reaction was carried out at room temperature and is exothermic. The dark purple colored solids I–III are diamagnetic as indicated by their ^{1}H NMR solution spectra.[7]

It has been pointed out[8,9] that the tetraazadiene ligand can be bonded in two ways represented by the formal valence structures A and B (Figure 1) which differ with respect to the formal oxidation state of the metal. To obtain information about the bonding in the diamagnetic [$Ni(ArN_4Ar)_2$] complexes, a single-crystal X-ray structure determination of III was carried out.[10] The molecular structure of the monomeric [$(3,5\text{-}Me_2C_6H_3N_4C_6H_3Me_2\text{-}3,5)_2Ni$] units (Figure 2) shows the following important features. There are two independent ArN_4Ar ligands coordinated to the Ni center via the 1,4-nitrogen atoms, so forming two N_4Ni chelate rings. Within each ArN_4Ar ligand both Ar rings and the N_4 unit lie in the same plane while the two N_4Ni chelate rings are mutually perpendicular. Therefore the Ni center has a pseudotetrahedral geometry.

The conjugated arrangement of the double bonds in the N_4 unit of canonical form A is ideally suited for interaction with the aryl π system which would result in multiple bond character in the N_4 unit as well as in the adjacent N–C bonds. These two features are observed in our compound, i.e., almost identical N–N bond distances [1.325 (3) and 1.319 (4) Å] and N–C distances of 1.426 (4) Å. In contrast, in the complex [$(4\text{-}FC_6H_4N_4C_6H_4F\text{-}4)IrCO(PPh_3)_2]BF_4$ the ArN_4Ar ligand contains dissimilar 1,2- and 2,3-N–N distances of 1.400 (16) and 1.270 (16) Å and C–N distances of 1.481 (18) and 1.456 (18) Å, with aryl rings which are noncoplanar with the N_4 unit. This was interpreted as indicative of an ArN_4Ar valence structure of type B and hence an Ir d^6 species.[8] The distinctive structural features of our tetrahedral [$Ni(ArN_4Ar)_2$] complexes support the view that they are best represented by a formal valence structure of type A and thus a Ni^0 d^{10} (18e) electronic configuration.

The complexes I–III are stable in boiling toluene in air, whereas the related [Ni^0(Ar-α-diimine)$_2$] complexes are extremely sensitive to oxidation and thermal decomposition.[5] This difference in stability might be due to a better π-accepting capability of the ArN_4Ar system.

The formation of the 18e [$(ArN_4Ar)_2Ni^0$] systems with normal aromatic azides is surprising in view of the report by Stone et al. that pentafluorophenyl azide ($C_6F_5N_3$) reacts with [$Ni(COD)_2$] to yield the monotetraazadiene complex [$(C_6F_5N_4C_6F_5)Ni(COD)$] (IV).[9]

Reactions of I with HCl, CH_2Cl_2, and $CHCl_3$ resulted in formation of as yet unidentified products.[11] Reaction of I with excess t-BuNC in boiling toluene resulted in formation of [$(t\text{-}BuNC)_2Ni(4\text{-}MeC_6H_4N_4C_6H_4Me\text{-}4)$] (V),[12] whereas I failed to react with CO, PPh_3, and bpy, which were likewise expected to result in formation of complexes [$L_2Ni(ArN_4Ar)$]. Since these substitution reactions failed the reaction of I with t-BuNC probably involves attack of an RNC molecule on one of the coordinated ArN_4Ar ligands followed by stabilization of the resulting labile [$(Ar_2N_4)Ni^0$] species by coordination with RNC.

The reaction of [Cp_2Ni] (20e species) with excess 4-$MeC_6H_4N_3$ in boiling toluene is still incomplete after 35 min.[13] Workup of the reaction mixture resulted in the isolation of black microcrystals, [$CpNi\{(4\text{-}MeC_6H_4)_2N_4\}$][14] (VI, 10% yield), in addition to unreacted [Cp_2Ni] (40%) and [$Ni^0\{(4\text{-}MeC_6H_4)_2N_4\}_2$] (5%). Compound VI is paramagnetic and ESR spectra are consistent with the formulation of this compound as a Ni^I species with a monomeric structure[15] and with a σ,σ-N,N-chelate-bonded $(4\text{-}MeC_6H_4)_2N_4$ ligand.[16]

The similarity of the IR spectra in the ligand vibration region of VI and the known monomeric [$CpCo\{(4\text{-}MeC_6H_4)_2N_4\}$] (VII)[14,17,18] strongly indicates that both compounds are isostructural. Accepting that the Cp ring in VI is pentahapto bonded and the ArN_4Ar group acts as a (4e) σ,σ-N,N-chelating ligand (formal valence structure A), [$CpNi\{(4\text{-}MeC_6H_4)_2N_4\}$] must be formulated as a 19e Ni^I species.[19] Using similar arguments, VII, which is diamagnetic, is an 18e Co^I species.

Support for the 19e configuration comes from the observation that reaction of pure VI in boiling toluene (2 h) with 2 equiv of 4-$MeC_6H_4N_3$ gives rise to 18e [$Ni^0\{(4\text{-}MeC_6H_4)_2N_4\}_2$] (52% yield), while reaction of VI with 2 equiv of t-BuNC at room temperature yields [$(t\text{-}BuNC)_2Ni(4\text{-}MeC_6H_4N_4C_6H_4Me\text{-}4)$] (V, 80% yield). In contrast, [$CpCo\{(4\text{-}MeC_6H_4)_2N_4\}$] is unreactive toward excess ArN_3 or t-BuNC.

Considerable interest exists in these ArN_4Ar nitrogen ligands because they can be generated both from aryl azides via metal nitrenes followed by 1,3-dipolar addition reactions[4] or from metal–diazonium intermediates. Such species are postulated in schemes which describe the interaction and conversion of dinitrogen on metal centers.[4] In this respect the formation of I–III and VI is of interest because of the possible involvement of species of the type IX–XIII: [(COD)NiNAr] (IX), [$(COD)NiN_4Ar_2$] (X), [ArNNiNAr] (XI), [$ArNNiN_4Ar_2$] (XII), or [CpNiNAr] (XIII).

Dinitrene species have recently been structurally characterized, i.e., [$Cp_2Mo_2S_2(NR)_2$][20] and *cis*-[$Mo(NC_6H_5)_2DTC_2$].[21] In the [$Ni(COD)_2$]–ArN_3 reactions polymeric material is formed which might be due to polymerization of species of the type XI, since in the bent form the nitrene can readily act as a bridging species. The formation of [Ni^0(Ar-