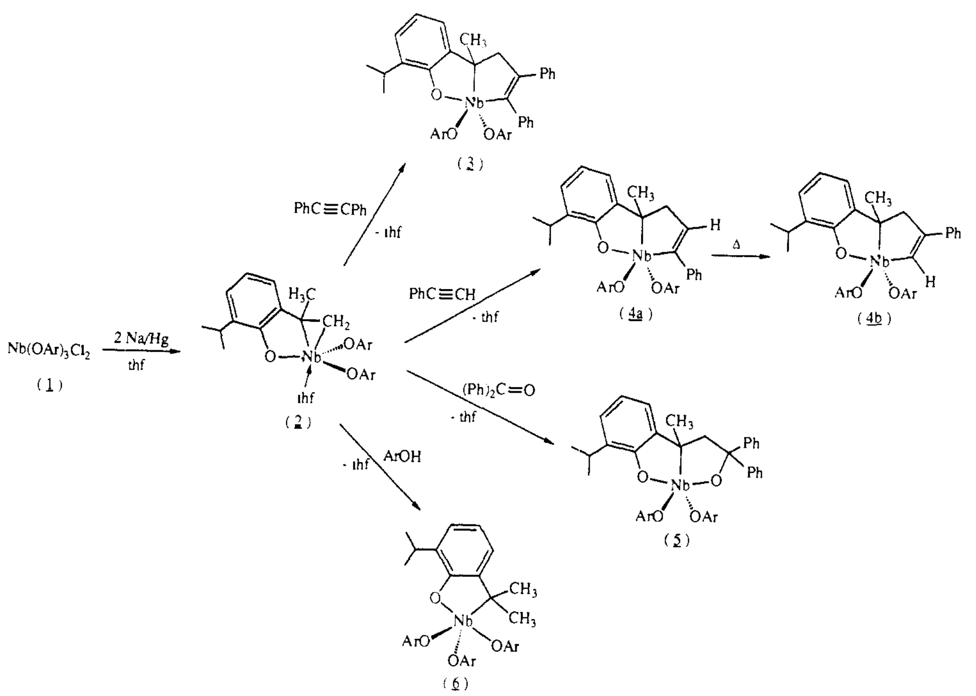
Scheme I[a]



[a] OAr = 2,6-diisopropylphenoxide; thf = tetrahydrofuran.

description of the bonding rather than as a niobium(III) olefin complex.[10]

The metallacyclopropane ring in **2** will undergo coupling (ring expansion) with a number of unsaturated molecules with displacement of the coordinated thf (Scheme I). Reaction with PhC≡CPh takes place to yield the metallacyclopentene complex $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2(OC_6H_3Pr^iCMeCH_2CPh{=}CPh)]$ (**3**) in almost quantitative yields.[8] In **3** the $OC_6H_3Pr^iCMeCH_2C(Ph){=}C(Ph)$ methylene protons appear as a well-resolved AB pattern in the ^1H NMR spectrum. A single-crystal X-ray diffraction analysis of **3** (Figure 2) shows the metallacyclopentene ring to be essentially planar. The coordination to the metal via the aryl oxide oxygen atom results in the formation of two five-membered metallacycle rings which appear to be readily accommodated with little strain being evident (Figure 2). The reaction of **2** with the nonsymmetric alkyne PhC≡CH initially leads to the formation of a metallacyclopentene (**4a**) in which the phenyl substituent is adjacent to the metal center. This kinetic product slowly isomerizes at room temperature in solution to the thermodynamically more stable isomer (**4b**) in which the phenyl substituent is present at the 3-position of the ring (Scheme I). Thermolysis of solutions of **4a** at 100 °C for minutes yields **4b** with no evidence in the ^1H NMR spectra for any residual **4a**. Reaction of the metallacyclopropane compound **2** with $Ph_2C{=}O$ leads to the oxametallacyclopentane compound $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2(OC_6H_3Pr^iCMeCH_2CPh_2O)]$ (**5**) (Scheme I).

Compound **2** will also undergo reactions with protic reagents. Treatment of green **2** with 1 equiv of $HOC_6H_3Pr^i_2\text{-}2,6$ results in the formation over minutes of the new metallacycle compound $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^iCMe_2)]$ (**6**) along with 1 equiv of thf (Scheme I). The formulation of **6** as containing a five-membered metallacycle ring is based upon NMR spectroscopic data as well as preliminary X-ray data.[12] Further studies into the mechanism and possible generality of the dehydrogenation reaction are currently underway.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research.

Supplementary Material Available: Details of the analytical and spectroscopic data as well as of the crystallographic studies, tables of positional parameters, general temperature factors, and bond distances and angles for **2** and **3** (34 pages); tables of observed and calculated structure factors for **2** and **3** (33 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of $[(W(CO)_3)_6(Te_2)_4]^{2-}$: A 14-Membered Cluster with a Novel Shape

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Historically, the chemistry of transition-metal selenides and tellurides has not been well developed, but recently it has come under increased investigation. This is because their chemistry is substantially different from that of the sulfides,[1] and also because they are finding use as convenient precursors to solid materials.[1b,2] We have been investigating the reactions of soluble polyselenide and polytelluride anions with various classes of metal complexes.[3] One class of compounds that has an exceptionally rich chemistry

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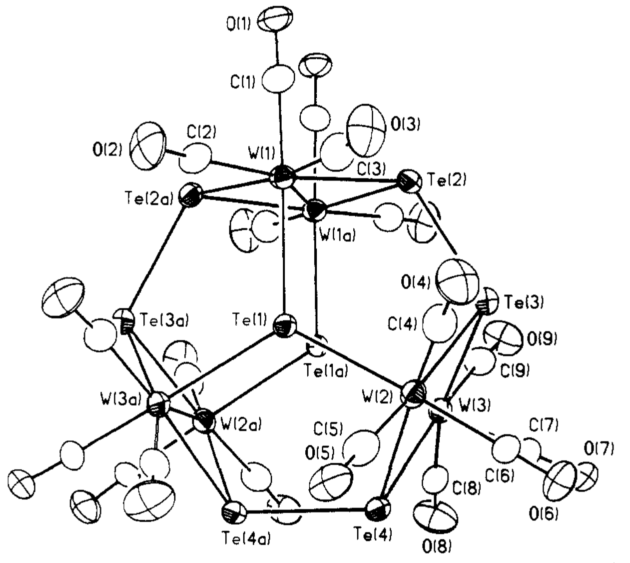

Figure 1. Thermal ellipsoid plot of molecule I, $[(W(CO)_3)_6(Te_2)_4]^{2-}$ (50% probability). Some significant distances in angstroms are as follows: W1-Te1 2.825 (2), W1-Te2 2.713 (2), W1-Te2A 2.706 (2), W2-Te1 2.882 (2), W2-Te3 2.728 (2), W2-Te4 2.719 (2), W3-Te3 2.722 (2), W3-Te4 2.722 (2), W3-Te1A 2.842 (2), W1-W1A 3.099 (2), W2-W3 2.083 (2), Te1-Te1A 2.855 (2), Te2-Te3 2.852 (2), Te4-Te4A 2.850 (2). Some significant angles in degrees are as follows: W1-Te1-W2 119.2 (0), W1-Te1-W3A 119.8 (0), W2-Te1-W3A 120.6 (0), W1-Te2-W1A 69.8 (0), W2-Te3-W3 68.9 (0), W2-Te4-W3 69.0 (0).

is the metal carbonyls. For example, polyselenides react with $Mo(CO)_6$ and $W(CO)_6$ to completely decarbonylate the metal center and oxidize it to MSe_4^{2-} in excellent yield.[4]

Since the tetratellurometalates (MTe_4^{2-}) are not known, we attempted to gain entry to these systems using polytellurides to oxidize metal carbonyls. Reaction of equimolar amounts of Te_4^{2-} with $M(CO)_6$ only results in disubstitution of CO forming a cis complex $(CO)_4MTe_4^{2-}$.[5] However, it was found that use of an excess of metal carbonyl with various amorphous alkali-metal polytellurides, such as K_2Te_2, results in a variety of new molecules with different stoichiometries, such as $[W_4Te_2(CO)_{18}]^{2-}$ and $[Cr_4Te_3(CO)_{20}]^{2-}$.[6] This is of particular interest in materials synthesis, since it has been shown that use of clusters containing different ratios of tellurium to metal leads to formation of different materials.[1b,2b]

The products are considerably different when highly crystalline polytellurides with quaternary organic cations are combined with metal carbonyls. The reaction of $W(CO)_6$ with pure $[(C_6H_5)_4]_2[Te_4]$ generates a new cluster $[(W(CO)_3)_6(Te_2)_4]^{2-}$, which has an extremely unusual structure. In this paper we describe the preparation and structure of this molecule, which may be the first in a large class of transition-metal main-group cages.

The title molecule can be prepared by the reaction in DMF solvent as shown in eq 1.[7] A slightly impure product can be isolated in reasonable yield, but analytically pure material can be obtained in 6% yield upon repeated recrystallization from CH_2Cl_2/ether. The dark brown product is moderately air sensitive in the solid state and very air sensitive in solution.

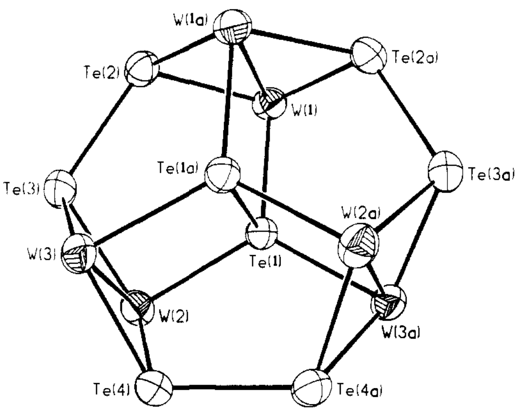

Figure 2. Thermal ellipsoid plot of I with CO ligands removed, highlighting the shape of the cluster.

$$[(C_6H_5)_4P]_2[Te_4] + 3W(CO)_6 \xrightarrow{100\ °C} [(C_6H_5)_4P]_2[(W(CO)_3)_6(Te_2)_4] \quad (1)$$

The molecule was characterized by IR studies, elemental analysis, and single-crystal X-ray diffraction.[8] It contains a central ditelluride which is side-bound to three ditungsten dimers creating a three-membered paddle wheel with the Te_2 as the axis. Each of the paddles is joined by another Te_2 group, creating a very unusually shaped cluster. Each tungsten vertex is coordinated by three carbonyls which are arranged in pyramidal fashion and are essentially undistorted, with an average W–C–O angle of 176 (2)° (See Figure 1). The tungsten atoms are also ligated by three tellurium atoms and are seven-coordinate if the W–W bonds are considered. The environment can best be viewed as a distorted *fac* octahedron with the W–W bond passing through one edge. The cluster has molecular D_{3h} symmetry, but the presence of the counterions restricts it to crystallographic 2-fold symmetry.

The central Te_2 group has a Te–Te distance of 2.855 (2) Å, which can be considered within bonding distance. (The Te–Te distance in elemental Te is 2.84 Å.[9]) The three ditungsten dimers are also bonded with an average distance of 3.088 (9) Å. The similarity of the bonding distances makes the coordination environment around each central tellurium almost planar. (Atom Te(1) lies 0.12 Å out of the plane of the three tungsten atoms, as opposed to the 0.94 Å expected for an ideal tetrahedron.) The three equatorial detellurides are also bonded to each other [2.851 (2) Å average].

If each ditelluride unit is considered a dianion, each tungsten has a formal oxidation state of 1+. This would account for the observed W–W bonding distance. Each tellurium atom donates a lone pair of electrons to each metal center, completing the 18-electron count around each metal. The equatorial Te atoms clearly contain a stereochemically active lone pair of electrons in approximate sp^3 hybridization (W–Te–W angles ca. 70°). However, the central tellurium atoms donate three lone pairs in a trigonal-planar environment. So, while this structure once again illustrates the willingness of tellurium to adopt nonclassical coordination environments,[10,11] the cluster is valence-precise.

The overall shape of the cluster is unusual (see Figure 2). The outer shell is similar to the outer shell of the hcp fragment in

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(7) Under an argon atmosphere, 0.444 g of $W(CO)_6$ (1.26 mmol) and 0.500 g of $(Ph_4P)_2(Te_4)$ (0.420 mmol) were dissolved in 8 mL of dry deaerated DMF, and the mixture was stirred at 100 °C for 12 h. The resultant brown solution was layered with 10 mL of diethyl ether and stirred overnight at 4 °C. The resulting tan powder was filtered off, and the solvents were removed by filtration. The solid was redissolved in 5 mL of CH_2Cl_2, filtered, layered with 5 mL of diethyl ether, and stored overnight at 4 °C. The pale brown solid was filtered and the solution layered with a further 5-mL aliquot of ether and stored overnight at 4 °C. This process was repeated (usually twice) until suitable black crystals were obtained, which were isolated by filtration and washed with ether. Yield: 45 mg [6% based on $W(CO)_6$]. Anal. Calcd for $C_{68}H_{44}Cl_4O_{18}Te_8W_6$: C, 23.49; H, 1.27. Found: C, 23.06; H, 1.33. IR (Nujol mull): ν_{CO} 1946 (s), 1945 (m), 1919 (m), 1870 (s) cm^{-1}.

(8) Crystal structure data for $[(C_6H_5)_4P]_2[(W(CO)_3)_6(Te_2)_4]\cdot CH_2Cl_2$: space group, monoclinic, $C2/c$, $a = 21.651$ (13) Å, $b = 15.554$ (7) Å, $c = 25.150$ (12) Å, $\beta = 91.18$ (5)°, $V = 8464$ (7) Å^3, $Z = 4$, $D_{calcd} = 2.73$ g cm^{-3}, μ Mo Kα = 112.30 cm^{-1} (transmission factors: 0.28–1.00), $T = 21$ °C. Measured 13 353 reflections ($3.5° \leq 2\theta \leq 45°$) of which 5589 were unique ($R_{int} = 0.042$); refinement used 3388 reflections with $F_o^2 > 3\sigma(F_o^2)$ and resulted in residuals of $R = 0.0351$ and $R_w = 0.0413$ (479 parameters).

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Rh$_{13}$(CO$_{24}$)$^{5-}$.[12] However, instead of an interstitial metal atom, the title molecule contains a ditelluride group holding it together. Fourteen-vertex clusters are quite rare. One 14-vertex cluster has been reported which does not have a shape related to that of molecule 1.[13] In addition, there is the enormous class of Chevrel type clusters which have the same elemental composition but are face-capped octahedra.[14]

Acknowledgment. We are grateful to the National Science Foundation for support (Grant No. CHE-8802217).

Supplementary Material Available: Tables of complete structural data, positional parameters, complete distances and angles, thermal parameters, and hydrogen atom coordinates for the title molecule (6 pages); table of observed and calculated structure factors for the title molecule (20 pages). Ordering information is given on any current masthead page.

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Nitrogen-15-Labeled Deoxynucleosides. 3. Synthesis of [3-^{15}N]-2′-Deoxyadenosine

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The purine N3 atom is not involved in either the Watson–Crick H bonding normally present in DNA or the Hoogsteen pairing which has recently been implicated in three- and four-stranded structures.[1-7] It is therefore generally available as a minor groove DNA binding site for the hundreds of small molecules known to bind to DNA and to act as antibiotic, antiviral, and antineoplastic agents.[8] For example, two-dimensional NMR studies and single-crystal X-ray diffraction analysis of complexes between small DNA fragments and the drugs netropsin[9,10] and distamycin[11-13] have shown that amide NH atoms of each drug form H bonds involving the adenine N3, in addition to other H bonds and van der Waals contacts. Although the very high binding affinity of netropsin has been shown to be overwhelmingly enthalpy driven,[14] it has been proposed that the base specificity is due mainly to the close van der Waals contacts rather than to hydrogen bonding.[9] By using [3-^{15}N]-labeled DNA fragments it may be possible to elucidate both the existence and the strength of the H bonds to these and other molecules which bind in the minor groove.

The synthesis of [3-^{15}N]-labeled adenine has been reported by several groups.[15-17] Each of these syntheses followed essentially the same route, in which the ^{15}N is introduced by nitration of 4-bromoimidazole under forcing conditions using [^{15}N]-HNO$_3$. We have devised an alternate route which uses an azo coupling reaction for introduction of the ^{15}N and proceeds through the intermediacy of [5-^{15}N]-labeled 5-aminoimidazole-4-carboxamide (AICA). An unrelated route to the [5-^{15}N]-labeled 5-aminoimidazole ribonucleoside (AIRs) was recently reported.[18] AICA is a versatile precursor, which is most commonly used for entry into the guanine or isoguanine families,[19,20] although it is usually used as the AICA-riboside rather than the heterocycle itself.[21,22] We have found that AICA also can be used for the adenine family by cyclization to hypoxanthine using diethoxymethyl acetate in DMF at reflux. Although these conditions are more vigorous than those required for cyclization of 4,5-diaminopyrimidines using this reagent,[23,24] the reaction works well. In addition, we report high-yield enzymatic conversion of [3-^{15}N]-adenine to [3-^{15}N]-2′-deoxyadenosine.

Early studies directed toward purine synthesis found that the 2-methyl- and 2-phenylimidazole-4,5-dicarboxylic acids coupled with aryldiazonium ions to give the corresponding 5-arylazo 4-carboxylic acids.[25] The unsubstituted imidazole-4,5-dicarboxylic acid, however, gave largely the 2-arylazo derivative. We reasoned that it might be possible to use a 2-bromo substituent as a protecting group to force the coupling back to the 5-position. The bromine then could be removed concomitantly with reduction of the azo linkage. Thus (Scheme I), commercially available imidazole-4,5-dicarboxylic acid (**1a**) was first esterified to **1b** and then brominated with *N*-bromosuccinimide (NBS) to give **2a**. Direct bromination of the diacid gave a complex mixture, while in contrast the diester reacted cleanly. After hydrolysis to **2b**, coupling with the [β-^{15}N]-4-bromobenzenediazonium ion (**3**), generated in situ by diazotization of 4-bromoaniline using [^{15}N]-NaNO$_2$, gave the 5-azo derivative **4** in 85% yield. The preparation of [5-^{15}N]-AICA (**6**) proved to be most successfully accomplished by conversion to the 4-carboxamide at this stage, rather than after the reduction. Reaction of **4** with cold ethyl chloroformate followed by treatment with ammonia in THF gave crystalline **5** in quantitative yield.

Removal of the 2-bromo group and cleavage of the azo group were then effected under 8 psi of H$_2$ for 5 h in a mixture of methanol, KOH, and 5% Pd/C. The [5-^{15}N]-AICA (**6**) obtained from this reaction has a faint purple color and is contaminated with small amounts of KOH and KBr. Nevertheless, these salts do not interfere with conversion of **6** to [3-^{15}N]-hypoxanthine (**7**)

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