with $a = 3.57$ Å, $b = 16.34$ Å, and $c = 3.91$ Å (Figure 2A).[11] Notably, ablation of orthorhombic $SrCuO_2$ targets using a KrF excimer laser (248 nm) and deposition of the ablated material onto <100> oriented $SrTiO_3$ substrates at 500 °C yields a new structural phase with a 1:1 Sr:Cu stoichiometry.[12] X-ray diffraction patterns (θ–2θ scans) of the new $SrCuO_2$ films can be indexed as a tetragonal $SrCuO_2$ layered phase with the c-axis oriented perpendicular to the substrate surface (Figure 2B). The c-axis lattice parameter calculated from these experimental data is 3.35 Å. To support our structural assignment of the product, we have simulated the diffraction pattern for tetragonal $SrCuO_2$ (Figure 2C). The excellent agreement between the experimental and simulated patterns shows that the product obtained by PLD is the infinite layer phase. Small impurity peaks that can be indexed as the (111) and (061) peaks of the orthorhombic phase are also observed in the experimental diffraction scans at $2\theta = 34.4°$ and 40.3°. Since this impurity represents <10% of the product, we conclude that the major phase produced in our low-temperature PLD studies is tetragonal $SrCuO_2$.

The tetragonal phase of $SrCuO_2$ represents the parent structure of the layered copper oxide superconducting materials and has thus been an important synthetic target of solid-state chemists. The tetragonal phase is, however, inaccessible to conventional high-temperature approaches, except for the specific stoichiometry $Sr_{0.14}Ca_{0.86}CuO_2$.[13,14] Unfortunately, the subtle ionic size effects that stabilize the tetragonal phase for this compound preclude systematic investigations of doping. Several groups have also reported that tetragonal $SrCuO_2$ can be prepared at high temperatures by applying very high pressures (20–65 kbar) during reaction.[16,17] These studies offer a general approach to the tetragonal phase (as does PLD), although the instrumentation needed to achieve ultrahigh pressure is available in relatively few laboratories compared to laser deposition systems. The highly-oriented crystalline samples obtained by PLD are also ideal for detailed physical measurements, in contrast to ceramic samples obtained from high-pressure syntheses.

We have carried out a number of studies to elucidate the factors that control the growth of the layered phase. First, we find that as the $SrCuO_2$ growth temperature is increased from 500 to 700 °C, there is a decrease in the degree of c-axis orientation of the tetragonal phase, and there is an increase in the percentage of orthorhombic phase formed. In addition, PLD of the thermodynamically stable tetragonal compound $Sr_{0.14}Ca_{0.86}CuO_2$ between 500 and 700 °C yields only tetragonal-phase product.[14,15] These results strongly indicate that low-temperature growth (accessible by PLD) kinetically traps the metastable tetragonal phase of $SrCuO_2$. We also find that there are a decrease in the degree of c-axis orientation of the tetragonal phase and an increase in the percentage of orthorhombic impurity phase for films grown on MgO ($a = 4.2$ Å) versus $SrTiO_3$ ($a = 3.905$ Å). Since the a-axis lattice parameter of tetragonal $SrCuO_2$ ($a = 3.92$ Å) is better matched for epitaxial growth on $SrTiO_3$, we suggest that

the substrate also helps to stabilize the desired tetragonal phase.

In summary, we have utilized the unique characteristics of PLD to prepare highly oriented films of tetragonal $SrCuO_2$. The ready accessibility of high-quality crystalline samples of this material offers an outstanding opportunity to study electronic and magnetic consequences of doping in this model system[18] and suggests in general the potential of PLD for new materials synthesis.

Supplementary Material Available: Experimental X-ray diffraction patterns for a tetragonal $Sr_{0.14}Ca_{0.86}CuO_2$ ceramic target and a 5000-Å $Sr_{0.14}Ca_{0.86}CuO_2$ film prepared by PLD and a simulated diffraction pattern for c-axis oriented tetragonal $Sr_{0.14}Ca_{0.86}CuO_2$ (1 page). Ordering information is given on any current masthead page.

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(18) Niu, C. M.; Lieber, C. M. In preparation.

$W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$. A Polynuclear Polyhydride Supported Exclusively by Alkoxide Ligands

Malcolm H. Chisholm,* Keith S. Kramer, and William E. Streib

Department of Chemistry and Molecular Structure Center Indiana University, Bloomington, Indiana 47405

Complexes of transition metals with metal–hydrogen bonds are of critical importance in many stoichiometric and catalytic reactions.[1,2] Since the initial discovery of $HCo(CO)_4$ and $H_2Fe(CO)_3$ in the 1930s, the chemistry of metal hydrides and metal polyhydrides has been developed with the now classical ligands of organometallic chemistry, namely, carbon monoxide, tertiary phosphines, cyclopentadienes, and related soft π-acceptor ligands. It has been our belief that hard π-donor ligands such as alkoxides (siloxides and aryloxides) should also support an extensive organometallic chemistry for the early transition metals in their higher oxidation states where there are vacant d_π orbitals.[3] Within this field a potentially important class of compounds are metal hydrides supported by alkoxide ligands, $M_x(H)_y(OR)_z$. The first well-characterized member of this series was $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$[4] followed by related $W_2(H)(OR)_7L$[5] and $NaW_2(H)(OR)_8$[6] complexes. For tantalum, Wolczanski and co-workers[7] reported the synthesis of $[(silox)_2Ta(H)_2]_2$, where silox = $(t\text{-}Bu)_3SiO$, and its reactions with carbon monoxide. More recently, Rothwell and co-workers[8] have characterized a novel stereochemically rigid seven-coordinated tantalum(V) trihydride supported by attendant aryloxide ligands: $TaH_3(OAr')_2L_2$, where L = PMe_2Ph and Ar' = $2,6\text{-}R_2C_6H_3$, and found that these and related niobium complexes provide catalysts for the cis-hydrogenation of fused aromatic rings.[8] Hoffman et al.[9] reported the reversible formation of

(11) Teske, V. C. L.; Muller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1970,** *379,* 234.

(12) The ablation was carried out with a laser power density of 1–2 J/cm² and a repetition rate of 5 Hz. The oxygen pressure during deposition was 10 mTorr. The Sr:Cu ratio determined by electron microprobe analysis (Cameca MBX) was 1:1 for films prepared under these conditions.

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(14) We have also prepared films of $Sr_{0.14}Ca_{0.86}CuO_2$ compound by PLD. Diffraction analyses (supplementary material) show that the thermodynamically stable tetragonal layered phase is obtained as c-axis oriented films for growth temperatures between 500 and 700 °C. The $Sr_{0.14}Ca_{0.86}CuO_2$ film c-axis (3.28 Å) is smaller than that observed for $SrCuO_2$ (3.35 Å), as expected.[13,15] The similarity of the diffraction results obtained for the $SrCuO_2$ and $Sr_{0.14}Ca_{0.86}CuO_2$ PLD products further supports our structural assignment for $SrCuO_2$.

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(9) Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989,** *111,* 1531.
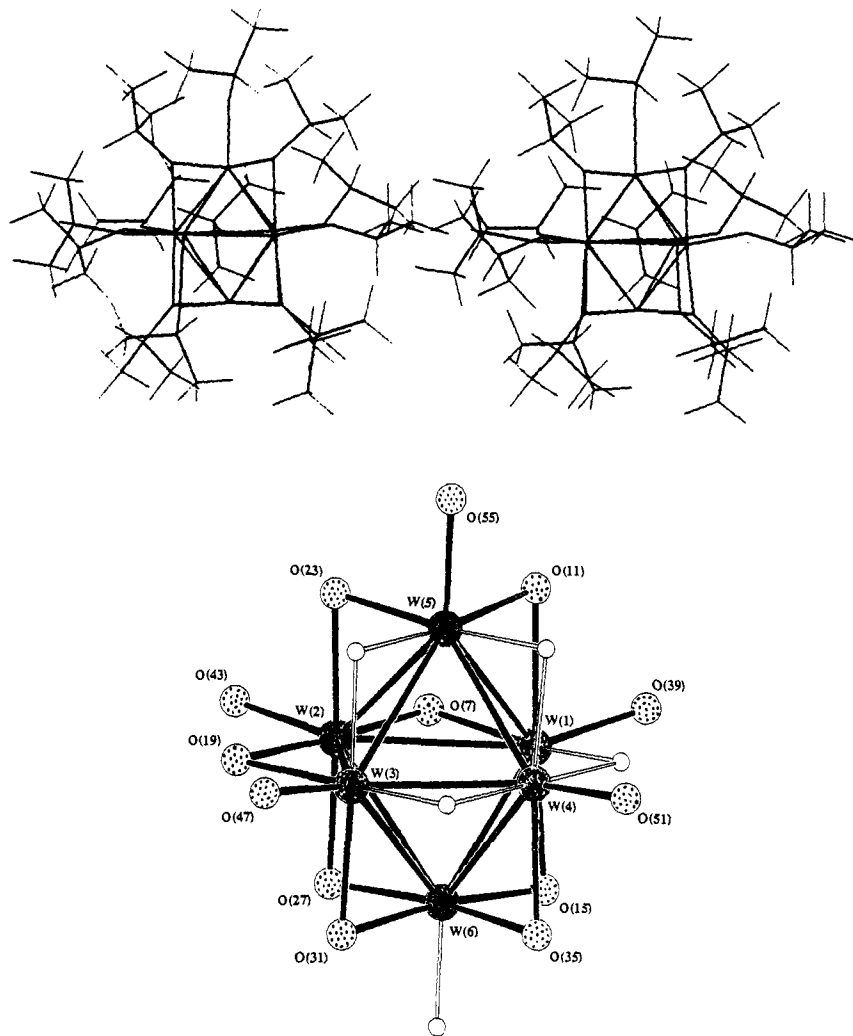
Figure 1. A stereoview of the $W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$ molecule showing the octahedron of W atoms and the attendant alkoxide ligands. The central W_6O_{13} core is shown below, and the atom number scheme is given. The proposed location of the hydride ligands is shown in this drawing. Bond distances and angles are given in the supplementary material.

$Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_5(H)$ and acetone from $Re_3(\mu\text{-}O\text{-}i\text{-}Pr)_3$-$(O\text{-}i\text{-}Pr)_6$.

For some time we have known that $1,2\text{-}M_2R_2(OR')_4$ compounds[10] react in hydrocarbon solvents with molecular hydrogen, but we have not until now been able to characterize the metal-containing products. We report here on a reaction that generates a novel hexanuclear polyhydride, $W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$, which we believe is the first member of a group of complexes of formula $M_6(H)_n(OR)_{18-n}$.

The compound $W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$, I, is formed when $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$[10b] is exposed to H_2 (3 atm) in a hydrocarbon solvent.[11] Compound I is the major tungsten-containing product formed in this reaction and is isolated as black crystals in ca. 40% yield based on W. Compound I is air sensitive and hydrocarbon soluble. Though we do not know how I is formed in the hydrogenolysis reaction, we do know that isobutane is eliminated. So, by either a σ-bond metathesis or a H_2 oxidative addition/reductive elimination sequence, a reactive species $W_2(H)_2(O\text{-}i\text{-}Pr)_4$ could be involved. The oligomerization[12] of three $W_2(H)_2(O\text{-}i\text{-}Pr)_4$ fragments would yield $W_6(H)_6(O\text{-}i\text{-}Pr)_{12}$. Compound I contains

one less hydride and one more alkoxide ligand than this seemingly logical product, and at the present time we can but speculate how this has come about.

A single-crystal X-ray study revealed[13] a distorted octahedron of W atoms with 13 attendant $O\text{-}i\text{-}Pr$ ligands. See Figure 1. Eight of the 12 edges of the W_6 octahedron are bridged by $O\text{-}i\text{-}Pr$ ligands, and five of the apices of the octahedron have terminal $O\text{-}i\text{-}Pr$ ligands. The W–W distances span the range 2.58–2.85 Å and the W–O distances 1.95–2.21 Å with the distances associated with the bridging groups being roughly 0.1 Å longer than those of the terminal. There is no structural evidence for the existence of a coordinated $i\text{-}PrOH$ ligand; the data are consistent with the presence of 13 alkoxide ligands.

The X-ray determination did not locate any hydride ligands, but it did reveal that four edges and one vertex of the W_6 octahedron are potential sites for hydride ligands. We do, indeed, propose that these sites are occupied by hydride ligands and that compound I is $W_6(\mu\text{-}H)_4(\mu\text{-}O\text{-}i\text{-}Pr)_8(H)(O\text{-}i\text{-}Pr)_5$, a new member of a class of clusters having the structural motif of an octahedron of metal atoms with ligands bridging each edge and one ligand

(10) (a) Chisholm, M. H.; Tatz, R. J. *Organometallics* **1986**, *5*, 1590. (b) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Tatz, R. J. *Organometallics* **1986**, *5*, 1599.

(11) All reactions were carried out under a dry and oxygen-free N_2 atmosphere with dried and degassed solvents. Schlenk techniques and drybox facilities were employed in the handling of compounds.

(12) $W_2(Ar)(O\text{-}i\text{-}Pr)_5$ dimerizes to give $W_4(Ar)_2(O\text{-}i\text{-}Pr)_{10}$, for example: Chisholm, M. H.; Folting, K.; Eichhorn, B. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 3146.

(13) Crystal data for I at -170 °C: $a = 12.800$ (3) Å, $b = 20.561$ (5) Å, $c = 11.839$ (3) Å, $\alpha = 103.74$ (1)°, $\beta = 116.61$ (1)°, $\gamma = 88.00$ (1)°, $Z = 2$, $d_{calcd} = 2.31$ g cm^{-3}, space group $P\bar{1}$. Of the 9059 reflections collected (Mo Kα, $6°< 2\theta < 45°$), 7067 were unique and the 5942 having $F > 3\sigma(F)$ were used in the refinement. Final residuals are $R(F)$ 0.048 and $R_w(F) = 0.049$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were included in fixed calculated positions with thermal parameters fixed at one plus the isotropic thermal parameter of the atom to which they were bonded.

Chart I
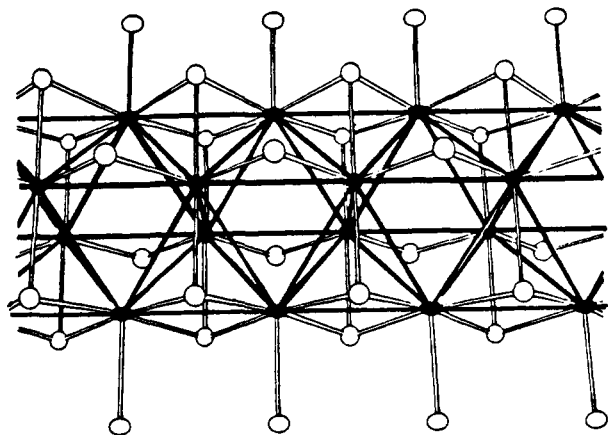
A

at each vertex: $M_6(\mu_2\text{-X})_{12}X_6$.[14]

The ^{1}H NMR spectrum of I recorded in benzene-d_6 at 22 °C, 500 MHz, reveals the presence of 13 O-*i*-Pr groups. Specifically, there are 12 septets (one signal of twice the intensity of the rest due to degeneracy) for the methyne protons. In addition, in the range δ 15–9 there are five signals assignable to hydride ligands. Each resonance shows coupling to ^{183}W ($I = {}^1/_2$, 14.5% natural abundance). From the relative intensities of the satellite spectra, we infer that one hydride is terminal (δ 10.01, $J_{^{183}W^{-1}H} = 130$ Hz) and four are edge bridging. The ^{183}W–^{1}H coupling constants for the bridging hydrides ($J_{W-H} = 88\text{--}104$ Hz) are comparable in magnitude to those observed for $[W_2(\mu\text{-H})(\text{O-}i\text{-Pr})_7]_2$[4b] and $W_2(\mu\text{-H})(\text{O-c-C}_5H_9)_7(\text{HNMe}_2)$.[5] Two of the hydrides show a significant ^{1}H–^{1}H coupling, $J = 10.5$ Hz, and we suggest that those hydride ligands are mutually trans and occupy bridges between W(1)–W(4) and W(3)–W(4). The proposed disposition of μ-H ligands, with three on one face of the W_6 octahedron, generates only one such trans arrangement. By application of the program XHYDEX and the assumed W–H and W–μ-H distances given by Orpen,[15] each of these sites was found to be perfectly acceptable.

In conclusion, we have discovered the first of a potentially significant class of tungsten(III) alkoxide clusters, namely, that based on a W_6^{18+} octahedron. The specific presence of five hydrides and 13 alkoxides leads us to believe that other members of the family $W_6(H)_x(OR)_y$ where $x + y = 18$ will be discovered subsequently.

Finally it is worth noting that in many of the ternary oxides of molybdenum and tungsten in their lower oxidation states there are isolated or fused octahedral M_6 cluster units that bear a striking resemblance to the $W_6(H)_5O_{13}$ core found here. For example, a segment of one of the $[Mo_4O_6^-]_\infty$ chains in $NaMo_4O_6$ is shown in A (Chart I), where the dark and unshaded spheres represent Mo and O atoms, respectively.[16]

Further studies are in progress.[17]

Supplementary Material Available: VERSORT drawings, stereoviews, ORTEP drawings, atomic coordinates, anisotropic thermal parameters, complete listing of bond distances and bond angles, and NMR data for I (26 pages); listing of F_o and F_c values (16 pages). Ordering information is given on any current masthead page.

Electron Impact Ionization of Phenylsilane. Evidence for the Formation of Phenylsilyl and Silacycloheptatrienyl Cations

Srihari Murthy, Yatsuhisa Nagano, and J. L. Beauchamp*

Contribution No. 8553
*Arthur Amos Noyes Laboratory of Chemical Physics*
California Institute of Technology
Pasadena, California 91125

Since the original suggestion by Mayerson and co-workers[1] that hydrogen atom loss from the molecular toluene cation results in the formation of the cycloheptatrienyl cation (Ia), a number of studies[2] have attempted to elucidate the structure, energetics, and modes of formation of $C_7H_7^+$ isomers. It is now well understood that electron impact ionization of toluene yields both Ia and IIa. The relative yield of the two isomers is dependent on the internal energy content of the molecular toluene cation.[2a,f,i,j,m,n]

I
a: X = C
b: X = Si

II
a: X = C
b: X = Si
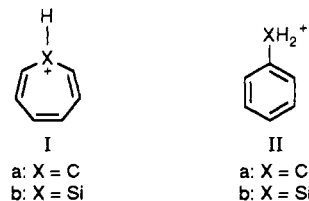
Interestingly, Fourier transform ion cyclotron resonance spectrometric studies[3] in our laboratory of the reactions of $C_6SiH_7^+$ (formed by electron impact ionization of phenylsilane) with the parent neutral indicate that this ion may be formed in two isomeric forms which are noninterconverting at room temperature.[4] As can be seen from Figure 1a, the abundance of $C_6SiH_7^+$ decays initially and then becomes constant at longer times. The initial decay of $C_6SiH_7^+$ is due to reaction process 1. Isolation of

$$C_6SiH_7^+ + C_6H_5SiH_3 \rightarrow C_{12}SiH_{11}^+ + SiH_4 \qquad (1)$$
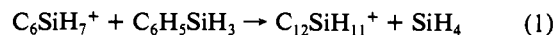
$C_{12}SiH_{11}^+$ in neutral phenylsilane does not yield $C_6SiH_7^+$. Further, isolation of $C_6SiH_7^+$ at long times indicates that it is unreactive. These observations suggest that $C_6SiH_7^+$ consists of a reactive and an unreactive population of ions. In this communication, we provide evidence that suggests that the unreactive and reactive $C_6SiH_7^+$ ions are two structurally distinct forms of the ion: the

(14) This is a common structure for lower valent metal halides of niobium and tantalum: Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; Chapter 19 and references therein. The halides $W_6(X)_{12}X_6$, where X = Cl and Br, have been prepared by halogenation of the $W_6(X)_8X_4$ compounds and are presumably members of this structural family: Lange, U.; Schäfer, H. *Z. Anorg. Allg. Chem.* 1986, *542*, 207.

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(3) (a) The technique of ion cyclotron spectrometry and its chemical applications are discussed in the following: Beauchamp, J. L. *Annu. Rev. Phys. Chem.* 1971, *22*, 527. (b) FT-ICR spectrometry is reviewed in the following: Marshall, A. G. *Acc. Chem. Res.* 1985, *18*, 316.

(4) At least on the order of seconds.