on the complexes of the $B_2H_4{\cdot}2P(CH_3)_3$ ligand involving other metals in oxidation state zero and their reaction chemistry is in progress, and the results will be reported elsewhere at a later date.

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Registry No. $Ni(CO)_2[B_2H_4{\cdot}2P(CH_3)_3]$, 94890-80-9; $Ni(CO)_4$, 13463-39-3; $BH_3{\cdot}P(CH_3)_3$, 1898-77-7; $BH_2Cl{\cdot}P(CH_3)_3$, 64160-46-9; $Ni(CO)_2(PF_3)_2$, 13859-78-4; $Ni(CO)_2[P(C_6H_5)_3]_2$, 13007-90-4; $Ni(CO)_2(PH_3)_2$, 83365-30-4.

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An Imido-Capped Tungsten Cluster: $W_3(\mu_3\text{-NH})(O\text{-}i\text{-Pr})_{10}$

Sir:

A variety of triangular molybdenum and tungsten clusters have been discovered within the past few years.[1,2] These are either bicapped or hemicapped by groups such as O, S, and CR and have M_3X_{17}, M_3X_{16}, M_3X_{13}, M_3X_{11}, and M_3X_{10} skeletons. We report here our preparation and characterization of the first example of an imido-capped triangulo tungsten cluster, $W_3(\mu_3\text{-NH})(O\text{-}i\text{-Pr})_{10}$.

Following our discovery of the comproportionation of d^0 tungsten–oxo and –alkylidyne alkoxides with M≡M bonds in $M_2(OR)_6$ compounds (M = Mo, W) to give, respectively, oxo-[3] and alkylidyne-capped[4] trinuclear compounds, $M_2W(\mu_3\text{-O})(OR)_{10}$ and $M_2W(\mu_3\text{-CR}')(OR)_9$, where R = *i*-Pr and CH_2-*t*-Bu and R′ = Me, Et and Ph, we sought to prepare a nitrido cluster. The attempted one-pot synthesis failed to yield the desired nitride but provided instead the imido cluster, $W_3(\mu_3\text{-NH})(O\text{-}i\text{-Pr})_{10}$, as blue crystals in ca. 30% yield, according to eq 1.[5]

$$W_2(O\text{-}i\text{-Pr})_6(py)_2 + (t\text{-BuO})_3W{\equiv}N \xrightarrow[\text{hexane}/i\text{-PrOH}]{22\ ^\circ\text{C}} W_3(\mu\text{-NH})(O\text{-}i\text{-Pr})_{10} + 3\,t\text{-BuOH} + 2\text{py} \quad (1)$$

The reaction pathway leading to the formation of the imido-capped cluster in (1) is presently not known. Of particular interest is whether or not the imido group is formed prior to or subsequent to the assembly of the trinuclear unit.

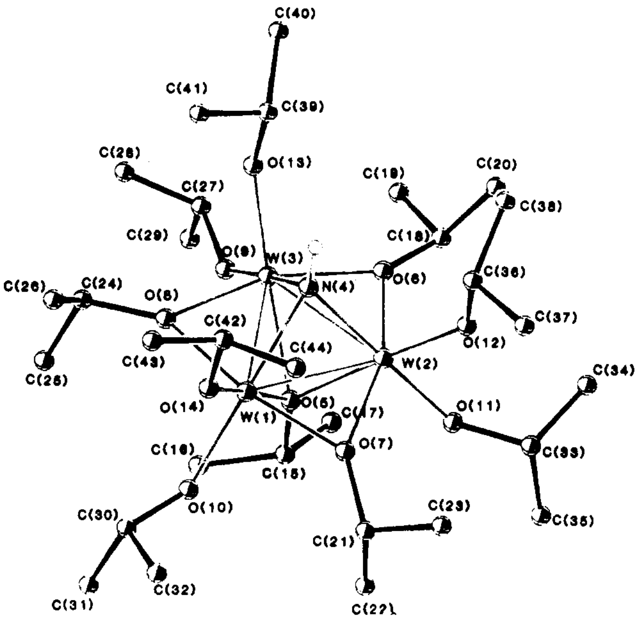

Figure 1. Ball and stick drawing of the $W_3(\mu_3\text{-NH})(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_6$ molecule. The hydrogen atom on N(4) was not located crystallographically but is drawn in its calculated position to show its influence on the neighboring oxygen atoms O(12), O(13), and O(14) (see text).

The new blue crystalline compound isolated from (1) was found[6] to be isomorphous with $W_3(\mu_3\text{-O})(O\text{-}i\text{-Pr})_{10}$, which, like its molybdenum analogue, adopts the M_3X_{11} skeletal geometry as shown in Figure 1. The unit cell dimensions were, however, larger by up to 30σ than those for the oxo capped compound. Also, the W–W distances were longer, 2.556 [2] Å (averaged) vs. 2.541 [3] Å (averaged), by 0.015 Å in the imido-capped compound. The W–N distances 2.08 (2) Å (averaged) were, however, indistinguishable from the W–O(μ_3-oxo) distances. The occupancy factor for the capping group of interest consistently favored N relative to O, but the hydrogen atom was not located crystallographically. Further crystallographic evidence for its presence is available from the relative positions of the *i*-Pr groups in the imido-capped molecule, as they are twisted further away from the capping position, relative to the oxo-capped molecule, in order to accommodate the imido hydrogen atom. Superposition of the three metal atom positions for the two different molecules using a least-squares procedure[6] reveals that the three oxygen positions for these groups (O(12), O(13), and O(14) of Figure 1) lie further from the pseudo-three-fold axis of the molecule by over 0.10 Å compared to corresponding atoms in the oxo-capped species. The oxygen atoms for the remaining *i*-Pr groups are superimposable within experimental error (average Δd = 0.028 Å for the 14 crystallographically independent positions).

Aside from the crystallographic evidence in favor of a capping NH group, there is chemical evidence. (1) The analytical data show the presence of nitrogen in the expected amount. (Anal. Found (calcd) for $W_3O_{10}NC_{30}H_{71}$: C, 30.30 (31.13); H, 6.07 (6.18); N, 1.34 (1.21).) Note crystallography shows that the crystalline samples do not contain solvent molecules of inclusion such as pyridine. (2) The ^{1}H NMR spectrum shows, in addition

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(1) See ref 1–10 in: Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1982**, *104*, 5394.

(2) Muller, A.; Jostes, R.; Cotton, F. A. *Angew Chem.* **1980**, *104*, 5394.

(3) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021. Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kober, E. M. *Inorg. Chem.* **1985**, *24*, 241.

(4) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 3683. Chisholm, M. H.; Conroy, B.; Hoffman, D. M.; Huffman, J. C., results to be submitted for publication.

(5) All reactions were carried out with dry and oxygen-free atmospheres (N_2) and solvents. For the preparations of $W_2(OPr)_6(py)_2$ and $(t\text{-BuO})_3W{\equiv}N$ see: Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

(6) Crystal data for $W_3(NH)(O\text{-}i\text{-Pr})_{10}$: a = 21.478 (10) Å, b = 21.981 (9) Å, c = 10.131 (3) Å, α = 98.57 (2)°, β = 92.50 (2)°, γ = 118.34 (2)°, Z = 4, d_{calcd} = 1.863 g cm^{-3}, space group $P\bar{1}$. Using 9014 reflections having $F > 3.00\sigma(F)$ yielded $R(F)$ = 0.051 and $R_w(F)$ = 0.051. The program BMFIT was described in: Uyen, Pui Sum; Nyburg, S. C. *J. Appl. Crystallogr.* **1978**, *12*, 258. In the present study, with use of Mo Kα radiation (λ = 0.71069 Å) with $6^\circ \leq 2\theta \leq 45^\circ$, the temperature was −158 °C and the dimensions of the crystal were 0.10 × 0.10 × 0.11 mm. The facility, instruments, and programs have been previously described: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(7) ^{1}H NMR data recorded at 360 MHz, 21 °C in benzene-d_6: δ-(OCHMe_2) 1.16 (18 H), 1.39 (6 H), 1.55 (18 H), 1.63 (18 H) (d, J_{HH} = 6 Hz); δ(OCHMe$_2$) 5.35 (3 H), 5.60 (sept, J_{HH} = 6 Hz), 4.37 (4 H) (overlapping septets, J_{HH} = 6 Hz); δ(NH) 9.87 (1 H, br, s).

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to signals associated with four types of O-*i*-Pr ligands, a signal at $\delta = 9.87$ (relative to Me_4Si), of integral intensity 1 H, assignable to the imido proton. (3) The IR spectrum shows a band at 3375 cm^{-1} assignable to ν(N–H). In these respects the new compound is notably different from $W_3(\mu_3\text{-}O)(O\text{-}i\text{-}Pr)_{10}$, and we are confident in our affirmation of this as the first imido-capped triangulo tungsten cluster. This new cluster is an alkoxy analogue of $Fe_3(\mu\text{-}NH)(CO)_{10}$.[8]

Further studies are in progress.

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Note Added in Proof. Synthesis of the ^{15}N-labeled compound $W_3(\mu_3\text{-}^{15}NH)(O\text{-}i\text{-}Pr)_{10}$ has allowed characterization of the imido capping ligand by ^{15}N NMR spectroscopy: $\delta(^{15}NH) = 250.3$ relative to NH_3; $^1J_{^{15}N-^1H} = 79.3$ Hz and $^1J_{^{183}W-^{15}N} = 23.3$ Hz.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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(8) Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1572.

Articles

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Venezia, Venice, Italy, and Christopher Ingold Laboratories, University College London, London WC1H 0AJ, England

Preparation of Chloro-Bridged Dimers and Trans Complexes of Platinum(II) Containing Alkyl Sulfoxides and the Kinetics of the Trans–Cis Isomerization of Dichlorobis(sulfoxide)platinum(II) in Dichloromethane

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Chloro-bridged complexes of the type $[Pt_2L_2(\mu\text{-}Cl)_2Cl_2]$ (L = dimethyl sulfoxide and diethyl sulfoxide) have been prepared and characterized by IR and ^1H NMR spectroscopy. *trans*-$[Pt(L)_2Cl_2]$ complexes have been synthesized by a bridge-splitting reaction of the binuclear complexes with the appropriate sulfoxide. The kinetics of their isomerization to the cis form in dichloromethane is reported and interpreted in terms of an associative mechanism.

Introduction

Complexes of sulfoxides with transition-metal ions have received much attention in recent years, especially with respect to their structures and reactivity.[3] These ligands are generally coordinated to platinum(II) and palladium(II) through sulfur, as might be expected from the HSAB principle,[4] the oxygen only activing as donor when the ligands are forced into a sterically crowded environment. Most complexes of the type $[M(L)_2X_2]$ (X = halogen, L = sulfoxide) have the trans configuration when M = Pd, whereas the cis configuration is preferred when M = Pt except with very sterically demanding ligands such as diisoamyl sulfoxide.[5] More recently, *trans*-$[Pt(n\text{-}Pr_2SO)_2Cl_2]$, isolated as an intermediate in the reaction of $[PtCl_4]^{2-}$ with di-*n*-propyl sulfoxide, was shown to isomerize to the cis form in the subsequent reaction. This sequence is consistent with the high trans effect of sulfoxide.[6] Attempts to prepare directly and isolate the *trans*-$[Pt(L)_2Cl_2]$ complexes by the method that was successful for the $n\text{-}Pr_2SO$ complex invariably produced the cis species when L = Me_2SO and Et_2SO as did the method proposed by Braddock and Tobe[7] (reaction between $K_2[PtCl_4]$ and a fivefold excess of Me_2SO, poured into ether to precipitate the trans isomer before it could isomerize to the cis species). Chloroform solutions enriched with the trans isomer have been obtained by photoisomerization of the stable cis species.[8]

In this paper we report the preparation and isolation of the *trans*-$[Pt(Me_2SO)_2Cl_2]$ and *trans*-$[Pt(Et_2SO)_2Cl_2]$ complexes from the new dimers $[Pt_2(Me_2SO)_2Cl_4]$ and $[Pt_2(Et_2SO)_2Cl_4]$ and report the kinetics of their isomerization in dichloromethane.

Experimental Section

Dimethyl sulfoxide, diethyl sulfide, and di-*n*-propyl sulfoxide were purchased from Aldrich Chemical Co., Inc., vacuum distilled, and stored under vacuum over Linde 4A molecular sieves. Diethyl sulfoxide was prepared from Et_2S by the literature method.[9] Dichloromethane was purified by a standard method,[10] and all other chemicals were reagent grade.

Preparations. *cis*-$[Pt(Me_2SO)_2Cl_2]$, *cis*-$[Pt(Et_2SO)_2Cl_2]$, and *trans*-$[Pt(n\text{-}Pr_2SO)_2Cl_2]$ were prepared by published methods[8] and characterized by elemental analyses and infrared spectra.

Bis(μ-chloro)bis[chloro(dimethyl sulfoxide)platinum(II)]. A mixture of *cis*-$[Pt(Me_2SO)_2Cl_2]$ (0.5 g, 1.2 mmol), platinum(II) chloride (0.34 g, 1.3 mmol) and naphthalene (1 g) was finely ground in a mortar and transferred to a boiling tube. The mixture was heated in an oil bath at 165 °C for 30 min with continuous stirring. After the mixture was cooled, it was again ground in a mortar, transferred to a sintered-glass filter, and washed with several 5-cm^3 portions of light petroleum ether (bp 40–70 °C) to remove the naphthalene. The brown-orange residue was dissolved in dichloromethane (200 cm^3), a small amount of charcoal was added, and the solution was filtered through paper. The filtrate was concentrated to 50 cm^3 in a rotary evaporator, and light petroleum ether (50 cm^3) was added to precipitate a fine yellow-orange solid, which was filtered off, washed twice with petroleum ether, and air-dried; yield 60%. Anal. Calcd for $C_4H_{12}Cl_4O_2Pt_2S_2$: C, 6.98; H, 1.76; Cl, 20.6. Found: C, 7.2; H, 1.71; Cl, 20.6.

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(3) For a recent review see: Davies, J. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 115.

(4) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(5) Price, J. H.; Williamson, A. N.; Schramm, R. F.; Wayland, B. B. *Inorg. Chem.* **1972**, *11*, 1280.

(6) Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1974**, *13*, 1991.

(7) Braddock, P. D.; Tobe, M. L., unpublished results, 1972.

(8) Price, J. H.; Birk, J. P.; Wayland, B. B. *Inorg. Chem.* **1978**, *17*, 2245.

(9) Annibale, G.; Cattalini, L.; Canovese, L.; Michelon, G.; Marangoni, G.; Tobe, M. L. *Inorg. Chem.* **1983**, *22*, 975.

(10) Vogel, A. I. "Textbook of Practical Organic Chemistry", 4th ed.; Longmans, Green and Co.: London, 1978.

0020-1669/85/1324-0797$01.50/0