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Heavier Main-group Atoms as Ligands to Transition-metal Centers

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Introduction

Heavy main-group elements of the third and lower rows are distinguished from their lighter congeners by the presence of filled p-orbitals in their cores. The greater radial extension of heavy element np vs. ns valence orbitals results in greater p character for σ bonds formed by them compared to σ bonds formed by the $n = 2$ elements. Consequently, second-row elements exhibit striking differences in their chemistry when compared to the heavier members of their families. This is well known for simple inorganic and organo main-group compounds, and the results summarized below serve to illustrate this fact for main-group transition-metal chemistry.

Results and Discussion

Compounds of the type $M(O)(OR)_4$, where M = Mo or W and R = a variety of alkyl groups, have been known for over 25 years (3,5). Recent work has shown that they undergo comproportionation reactions with $M_2(OR)_6$ species containing a metal-metal triple bond, forming triangular clusters of the type $M_3(\mu_3\text{-O})\ (\mu_3\text{-OR})\ (\mu\text{-OR})_3(OR)_6$ (4). The electrochemistry and UV-visible spectra of these latter compounds have been correlated with their electronic structure based on Fenske-Hall molecular orbital calculations (2). In order to compare differences in physical properties caused by small perturbations in the ligand environment surrounding these metal clusters, it was of interest to synthesize the analogous sulfido-capped metal triangles.

The compounds $W(S)(OR)_4$, where R = tert-butyl or isopropyl, are made by adding $WSCl_4$ to the appropiate lithium alkoxide (4 equiv) in ether at −78°. ^{1}H NMR spectroscopic data revealed only one type of alkoxide ligand for each compound, suggesting that both are monomeric in solution. An X-ray crystal structure determination confirmed this for the solid-state structure of $W(S)(OBu^t)_4$ (Figure 1). However, all attempts at comproportionation reactions between these compounds and $W_2(OR)_6$ (R = Bu^t, Pr^i, or CH_2Bu^t) species failed to yield any evidence for the desired $W_3(\mu_3\text{-S})(\mu_3\text{-OR})(\mu\text{-OR})_3(OR)_6$ product. Space-filling diagrams of the $M_3(\mu_3\text{-O})$ species suggest that the pocket for the μ_3-E ligand formed by the surrounding alkoxides is simply too small to accommodate a sulfur atom with its van der Waals radius *ca.* 0.45 Å larger than that of oxygen, the difference in radii being attributable to the ten core electrons of sulfur.

In 1982 Schrock *et al.* reported the preparation of $[(Bu^tO)_3W{\equiv}N]_x$ by metathesis of $W_2(OBu^t)_6$ with acetonitrile or benzonitrile (8). Alkoxide-for-halide ligand exchange on $Mo(N)Cl_3$ gives the corresponding molybdenum compound (1). X-ray crystal structure determinations revealed that both nitrido compounds exist in the solid state as linear polymers of trigonal pyramidal $(RO)_3M{\equiv}N$ units bound head-to-tail via weak M---N bonds. While many other transition-metal compounds with terminal nitrido ligands are known, there are as yet no structurally-characterized examples of terminal phosphides. With this in mind, we investigated the reactivity of P_4 with $M_2(OR)_6$ (M = Mo, W; R = Bu^t, Pr^i, CH_2Bu^t) species.

The reaction between $W_2(OCH_2Bu^t)_6(HNMe_2)_2$ and P_4 in toluene at 75° for four hours gives two products. The product formed in 75% yield has two types of neopentoxide ligands in a 2:1 ratio and contains no phosphorus according to elemental analysis

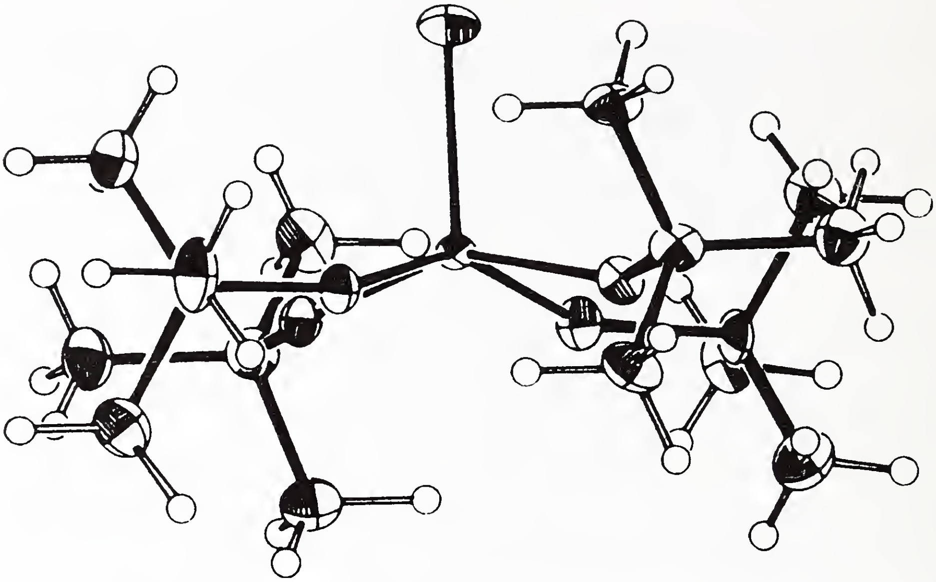

FIGURE 1. ORTEP diagram of $W(S)(OBu^t)_4$. Pertinent interatomic distances (Å) and angles (°) are: W-S, 2.1396(13); W-O, 1.886(3); S-W-O, 105.09(10); W-O-C, 142.47(27); O-W-O(cis), 86.13(13); O-W-O-(trans), 149.83(13).

and ^{31}P NMR spectroscopy. It is the subject of continuing study. The other product, formed in 25% yield, has only one type of neopentoxide ligand and displays a ^{31}P NMR resonance upfield at -205.2 ppm vs. 85% H_3PO_4 with a small coupling to ^{183}W of 16 Hz. An X-ray crystal structure determination revealed it to be $(\eta^3\text{-}P_3)W(OCH_2Bu^t)_3(HNMe_2)$ (Figure 2). This represents the first member in a class of

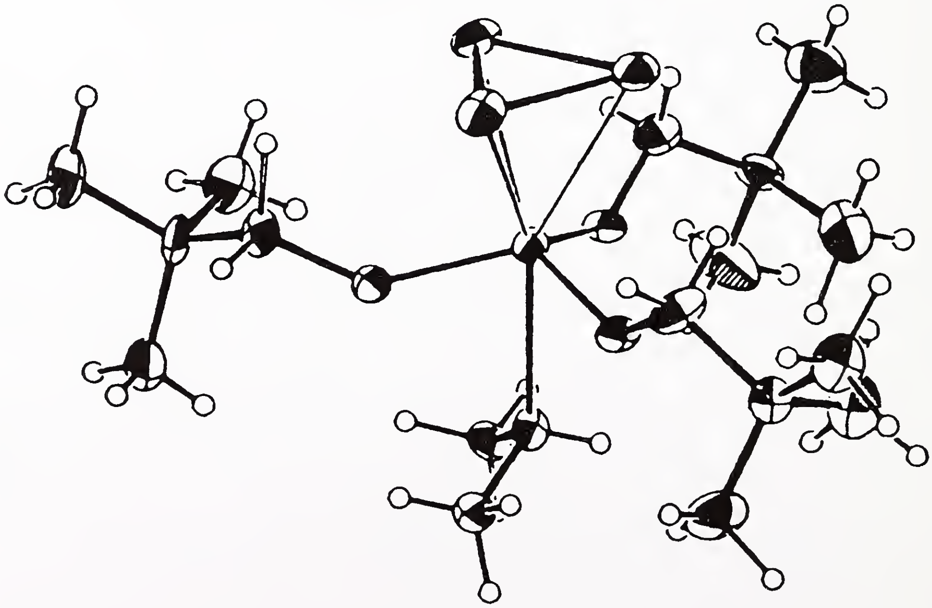

FIGURE 2. ORTEP diagram of $(\eta^3\text{-}P_3)W(OCH_2Bu^t)_3(HNMe_2)$. Pertinent interatomic distances (Å) and angles (°) are: W-P, 2.4930(25); W-O, 1.908(5); W-N, 2.315(7); P-P, 2.155(4); P-W-P, 51.23(9); P-W-O(proximal), 88.34(17); P-W-O(distal), 134.15(17); W-O-C, 136.6(5); P-W-N, 150.03(18); O-W-O, 114.17(24); O-W-N, 75.80(24); W-P-P, 64.39(9).

P_3-containing monomeric compounds that is supported by π-donating ligands, all of which used P_4 as the source of the P_3 fragment. Notable by their absence are any transition-metal compounds containing a terminal phosphide ligand or an η-N_3 ligand. This can be attributed to the comparable radial extensions of the 2s and 2p orbitals, and the greater radial extension of the 3p vs. the 3s orbital (6). In the η^3-N_3 case the similar orbital radii would facilitate sp hybridization which, together with the large N_2 bond strength, would cause ligand disproportionation to a terminal $M \equiv N$ species and N_2. In the $M \equiv P$ case the phosphorus 3p π orbitals would be rather diffuse and oriented orthogonally to the metal-phosphorus vector, thus giving poor M-P π overlap and consequently weak M-P π bonds, while the M-P σ bond would be expected to have little phosphorus s character. In a Fenske-Hall molecular orbital calculation on the model compound $(\eta^3\text{-}P_3)W(OH)_3(NH_3)$ both the σ and π components of the W-to-P_3 bond are predicted to arise from phosphorus 3p orbitals oriented parallel to the metal-phosphorus vector. This results in much greater metal-phosphorus overlap and thus a much stronger bond. The phosphorus 3s orbitals remain essentially unhybridized and are used to form P-P σ bonds.

The amide ligand is pervasive in inorganic and organometallic chemistry. The synthesis, chemical, and physical properties of compounds containing it have been exhaustively reviewed (7). However, its heavier group 15 analogues are comparatively scarce. Since arsenic forms weaker bonds to transition metals and carbon than does nitrogen, prospects for novel chemistry of the arsenide ligand looked promising.

Reaction of $1,2\text{-}M_2Cl_2(NMe_2)_4$ (M = Mo, W) with 2 equivalents of $LiAsBu^t_2$ in ether at -78° in the dark yields $1,2\text{-}M_2(AsBu^t_2)_2(NMe_2)_4$. X-ray crystal structure determinations revealed that both compounds crystallized in the anti rotameric form and are isostructural (Figure 3). In comparing the amide and arsenide ligands, the former's short bond lengths to the metal atoms and their planarity argue strongly for sp^2 hybridization of the nitrogen atoms with a consequently large amount of N → M π donation. In contrast, the long M-As distances, which are comparable to what one would expect based

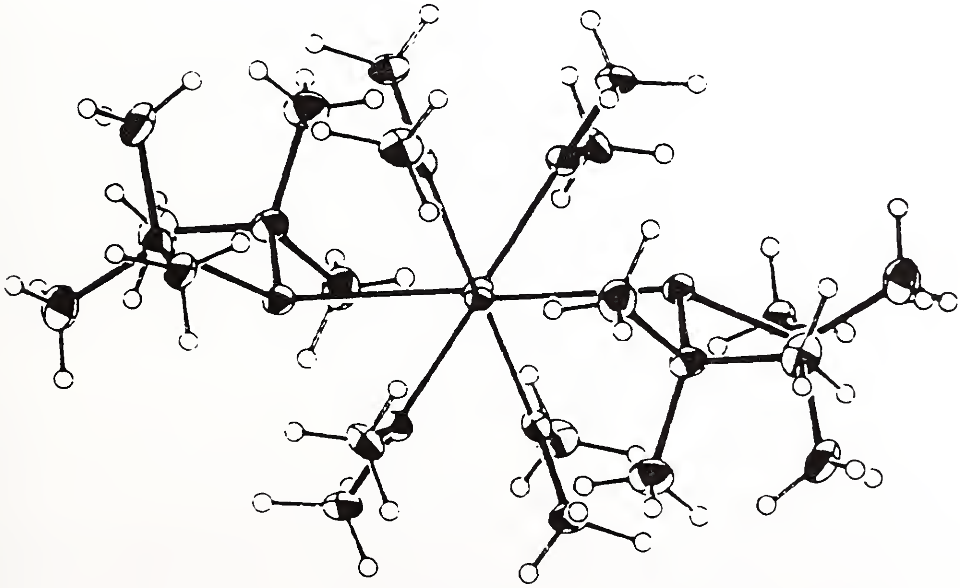

FIGURE 3. ORTEP diagram of $1,2\text{-}Mo_2(AsBu^t_2)_2(NMe_2)_4$ viewed down the metal-metal vector. Pertinent interatomic distances (Å) are: Mo-Mo, 2.2159(12); Mo-N, 1.972(6); Mo-As, 2.6161(11). For the tungsten analogue: W-W, 2.3001(11); W-N, 1.955(9); W-As, 2.5949(15).

on the sums of covalent radii, and the pyramidality about the arsenic atoms both suggest that the arsenic atoms are only singly bonded to the metal atoms using orbitals that have predominantly p character. Variable-temperature ^{1}H NMR spectroscopy further revealed that, while rotation about the M-N bonds was rapid at room temperature on the NMR time scale, M-As bond rotation and arsenic inversion were also rapid and had lower activation barriers than M-N bond rotation. In fact, while both bond rotation processes were frozen out in the gauche rotamers by -85 °, inversion at arsenic was still rapid. This clearly contradicts the expectation that inversion at heavier group 15 atoms should be much slower than at nitrogen, but is consistent with a transition state having some degree of As $\rightarrow$ M π bonding stabilized by the empty acceptor orbitals on the metal atoms.

Conclusion

The examples given above illustrate the fact that, while heavier main-group elements share common oxidation states with their second row family members, their behavior otherwise can be radically different. This should not be unexpected, however, considering the differences between the 3d and lower transition metals, or between the lanthanides and actinides. Perhaps all this really says is that, although trends can be discerned in the general properties of the elements, each one is still unique and we shouldn't be surprised when they behave as such under closer scrutiny.

Literature Cited

1. Chan, D., M. H. Chisholm, K. Folting, J. C. Huffman and N. S. Marchant, 1986. Trialkoxynitridomolybdenum Compounds: $(RO)_3Mo{\equiv}N$. Preparation, Structures (R = t-Bu and i-Pr), and Comparisons with a Tungsten Analogue (R = t-Bu). *Inorg. Chem. 25*:4170-4174.
2. Chisholm, M. H., F.A. Cotton, A. Fang and E. M. Kober, 1984. Theoretical and Experimental Studies of the Electronic Structure of the $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6$ Type of Triangular Metal Atom Cluster Compound. *Inorg. Chem. 23*:749-754.
3. Chisholm, M. H., K. Folting, J. C. Huffman and C. C. Kirkpatrick, 1984. Reactions of Metal-Metal Multiple Bonds. 10. Reactions of $Mo_2(OR)_6$ (M≡M) and $[Mo(OR)_4]_x$ Compounds with Molecular Oxygen. Preparation and Characterization of Oxo Alkoxides of Molybdenum: $MoO_2(OR)_2$, $MoO_2(OR)_2(bpy)$, $MoO(OR)_4$, $Mo_3O(OR)_{10}$, $Mo_4O_8(OR)_4(py)_4$, and $Mo_6O_{10}(OR)_{12}$. *Inorg. Chem. 23*:1021-1037.
4. Chisholm, M. H., K. Folting, J. C. Huffman and E. M. Kober, 1985. Reactions of Metal-Metal Multiple Bonds. 14. Synthesis and Characterization of *triangulo*-W_3 and -Mo_2W Oxo-Capped Alkoxide Clusters. Comproportionation of M-M Triple Bonds ($\sigma^2\pi^4$) and d° Metal-Oxo Groups: $M{\equiv}M + M{\equiv}O \rightarrow M_3(\mu_3\text{-}O)$. *Inorg. Chem. 24*:241-245.
5. Funk, H., W. Weiss, and G. Mohaupt, 1960. Uber Wolframalkoxide. *Z. anorg. allg. Chem. 304*:238-240.
6. Kutzelnigg, W., 1984. Chemical Bonding in Higher Main Group Elements. *Angew. Chem. Int. Ed. Engl. 23*:272-295.
7. Lappert, M. F., P. P. Power, A. R. Sanger and R. L. Srivastava, 1980. Metal and Metalloid Amides. Horwood, Chichester.
8. Schrock, R. R., M. L. Listemann and L. G. Sturgeoff, 1982. Metathesis of Tungsten-Tungsten Triple Bonds with Acetylenes and Nitriles to Give Alkylidyne and Nitrido Complexes. *J. Am. Chem. Soc. 104*:4291-4293.