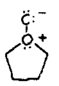
sonably decent yield from **7** or **8** is surprising.

It is highly unlikely that the net elimination of a carbon atom from most strained allenes or carbenes in solution results in a *free* carbon atom. Such processes would be highly endothermic as seen by the following rough estimates for singlet states in the gas phase:[15] $CH_2 \rightarrow$ C atom + H_2, $\Delta H = +93$ kcal/mol; **1** → C atom + benzene, $\Delta H = +130$ kcal/mol; **15** → C atom + benzene, $\Delta H = +36$ kcal/mol; **16** → C atom + benzene, $\Delta H = +58$ kcal/mol. The conclusion would not be grossly different for the triplet states. Ring strain would raise the energy of the starting material and would lower the ΔH of reaction. In fact, black deposits were observed from **15** when it was generated in the vapor phase.[11]

In solution, it is much more likely that the carbon atom is transferred to a nucleophilic atom or bond in the solvent. It was reported that 15 reacts with THF to give CO and ethylene.[11] In the thermolysis or photolysis of **7**, the infrared spectra of the evolved gases showed CO (bands centered at 2110 and 2170 cm^{-1}) and ethylene (bands centered at 3110 and 3035 cm^{-1}).[18] Our MNDO calculations indicate the direct transfer of the carbon atom to the oxygen atom of THF (producing **17**) would lower the above ΔH values by about 25 kcal/mol.

The thermolysis of **7** in Me_2SO gave **10** and Me_2S. Deoxygenation of Me_2SO by carbenes has also been reported to give ketones,[18] but the ketone **6** was not observed in the present work.

We can only speculate on the identity of the intermediate which gives up the carbon atom. 1-Triptycylmethylene and 2-triptycylmethylene, which are related to **3** by carbene–allene rearrangements,[8] were shown not to be involved since their separate generation from their tosylhydrazone salts gave a large number of normal products but no **10**.[19] Rearrangement of **3** to the norcaradienylidene **18** or the norbornadienylidene **19** might be followed by the loss of a carbon atom. A recent report has considered the involvement of norcaradienylidenes and norbornadienylidenes in rearrangements.[8b] The formation of **14** by hydrogen abstraction might implicate the triplet version of **4** in some of these reactions. Work concerned with these intermediates and designed to test for the necessity of a through-space interaction with the benzo rings is in progress.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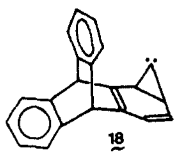
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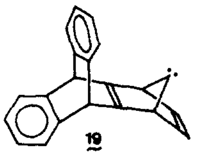
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Acknowledgment. This work was supported by the Monts-NSF project ISP-8011449, a Murdock Charitable Trust Grant of Research Corporation, and donors of the Petroleum Research Fund, administered by the American Chemical Society. University of Montana Faculty Research Grants were also used in this research. MONTS funds were also used in the purchase of the 270-MHz NMR spectrometer used in this work. A 360-MHz proton NMR spectrum was also obtained at the Colorado State University Regional NMR Center (NSF CHE-8208821). The assistance of Dr. P. W. Jennings, Dr. K. Emerson, L. J. Sears, and R. Larsen (Montana State University) in obtaining high-resolution mass spectrometric and X-ray crystallographic information is sincerely appreciated.

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(15) The heats of formation used in these estimates came from Waali (Waali, E. E., unpublished singlet MNO results), for CH_2 (107 kcasl/mol), **15** (186 kcal/mol), **16** (163 kcal/mol), and **17** (119 kcal/mol); Ref. 4d for **1** (91 kcal/mol); Dewar and Thiel (Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99. 4970) for benzene (21.2 kcal/mol); and *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2, 83 for the singlet carbon atom (200 kcal/mol).

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(18) Birge, R. R.; Haney, J. L.; Ricco, E. "Vapor Phase Spectra for Air Pollution Studies"; Report AFCEC-TR-75-15, Air Force Civil Engineering Center, Tyndall AFB, FL, 1975.

(19) Pang, D.; Tivakornpannarai, S., University of Montana, unpublished results.

Molybdenum–Tungsten Mixed-Metal Trinuclear Clusters, $[Mo_2W(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ and $[MoW_2(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$

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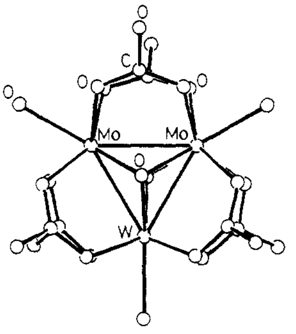
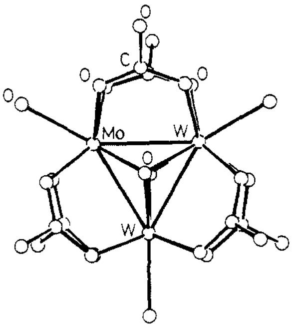
A number of metal–metal bonded mixed-metal compounds are known for carbonyl clusters[2] but only a few for noncarbonyl clusters with no strong σ-donor and π-acceptor ligand.[3] The latter clusters would show a more fundamental aspect of the metal–metal bond, since the metal ions in carbonyl clusters are electronically perturbed by carbonyl ligands. We wish to report here two new mixed molybdenum(IV)–tungsten(IV) trinuclear clusters, orange red $[Mo_2W(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ (abbreviated as Mo_2W) and orange $[MoW_2(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ (MoW_2). Since the corresponding red trimolybdenum(IV)[4] (Mo_3) and yellow tritungsten(IV)[5] (W_3) clusters are known,[6] a whole series of four complexes, Mo_3, Mo_2W, MoW_2, and W_3, are now available. To our knowledge, this is the first complete series of trinuclear metal–metal bonded non-carbonyl clusters involving two metal ions.[7,8]



Mo_2W



MoW_2

Sodium tungstate dihydrate (5 g; 0.015 mol) and 10 g of zinc dust in 300-cm^3 acetic anhydride was refluxed for 15 min. After addition of 5 g (0.021 mol) of sodium molybdate dihydrate and 10 g of zinc dust the reflux was continued for further 24 h. The precipitate (ca. 18 g) was dissolved in 1 dm^3 of 0.4 M HBr and

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(1) On leave from Department of Chemistry, Inner Mongolia Pedagogical University, Huhhot, People's Republic of China.

(2) See: Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 4th ed.; Wiley: New York, 1980; pp 1062, 1094. Also, for recent examples: (a) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 1759–1760. (b) Bogan, L. E., Jr.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 3843–3850. (c) Arndt, L. W.; Darensbourg, M. Y.; Fackler, J. P., Jr.; Lusk, R. J.; Marler, D. O.; Youngdahl, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 7218–7219. (d) Doyle, G.; Eriksen, K. A.; Van Engen, D. *J. Am. Chem. Soc.* **1985**, *107*, 7914–7920.

(3) Some examples. (a) $[CrMoCl_9]^{3-}$: Matson, M. S.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1974**, *96*, 7837–7839. (b) $MoW((CH_3)_3CCOO)_4$: Katovic, V.; Templeton, J. L.; Hoxmeier, R. J.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 5300–5302. Katovic, V.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 5586–5587. (c) $CrMo(CH_3COO)_4$: Garner, C. D.; Senior, R. G.; King, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 3526–3529.

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(5) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Kuppers, H.; Miller, M.; Sektowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245–3253.

(6) Cotton, F. A. *Polyhedron* **1986**, *5*, 3–14.

(7) Whole series of $[M_2M'(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ is known for iron(III)–chromium(III), in which the metal–metal bond is absent (Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291–362). See also: Straughan, B. P.; Lam, O. M. *Inorg. Chim. Acta* **1985**, *98*, 7–10.

(8) Trinuclear mixed-metal molybdenum–tungsten complexes, $Mo_2W(\mu_3\text{-}O)(\mu_3\text{-}O\text{-}i\text{-}Pr)(\mu\text{-}O\text{-}i\text{-}Pr)_6(O\text{-}i\text{-}Pr)_3$ (Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kober, E. M. *Inorg. Chem.* **1985**, *24*, 241–245) and $Mo_2W(\mu_3\text{-}CCH_3)(\mu_3\text{-}O\text{-}i\text{-}Pr)(\mu\text{-}O\text{-}i\text{-}Pr)_6(O\text{-}i\text{-}Pr)_3$ (Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234–1241), were reported, but their MoW_2 counterparts were only poorly characterized or not known.

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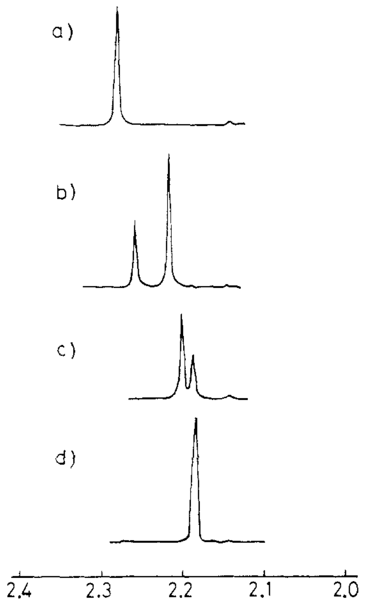

Figure 1. ^1H NMR spectra, 400 MHz, in aqueous solution of the bromide salt of (a) $[W_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$, (b) $[MoW_2O_2(CH_3COO)_6(H_2O)_3]^{2+}$, (c) $[Mo_2WO_2(CH_3COO)_6(H_2O)_3]^{2+}$, and (d) $[Mo_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$.

allowed to stand for 2 days. A mixture of the trinuclear clusters was separated into each component by SP-Sephadex C-25 cation exchange column chromatography (successive three columns of 4 cm in diameter and 140 cm in length). It took nearly a month for complete separation. Three components, orange red, orange, and yellow in elution order, were obtained with 0.1 M HBr as eluent (elution rate was ca. 1 dm^3 per day). These were eventually found to be Mo_2W, MoW_2, and W_3 clusters, respectively. Slow evaporation under reduced pressure at room temperature gave crystals of ca. 1 g of the bromide of each component, $[M_2M'(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2{\cdot}H_2O$. Analysis of C, H, Br, Mo, and W were consistent with the formula indicated. The Mo and W contents were determined by an ICP method.

The 400-MHz ^1H NMR spectra in D_2O (Figure 1) provide the most convincing evidence that the orange red and the orange crystals are mixed-metal clusters and not a mixture of the two homonuclear trimers. One sharp methyl singlet is observed at 2.188 and at 2.285 ppm (vs. $((CH_3)_3Si)_2O$ internal standard) for the Mo_3 and the W_3 cluster, respectively. On the other hand, each of two mixed-metal complexes shows two methyl singlets with integrated intensity ratio of 2:1. The Mo_2W complex gives signals at 2.189 and 2.204 ppm (1:2 ratio) and the MoW_2 complex at 2.218 and 2.260 ppm (2:1 ratio). Electronic absorption spectra (Figure 2) of these complexes in aqueous solution show two peaks in the visible region except for the Mo_2W complex which exhibits one broad band with a distinct shoulder at lower energy side. There is a systematic trend among the W_3, MoW_2, and Mo_3 complexes that corresponding transitions shift to shorter wavelengths with an increase in intensity as molybdenum is replaced by tungsten.

Both the compounds, Mo_2W and MoW_2, crystallize in well-formed hexagonal columns. The single crystals of Mo_2W and MoW_2 consist of the rhombohedral lattice with very similar lattice constants: for Mo_2W, $a = b = c = 11.809$ (5) Å, $\alpha = \beta = \gamma = 106.37$ (4)°, and $V = 1394.5$ (12) $Å^3$ and for MoW_2, $a = b = c = 11.812$ (4) Å, $\alpha = \beta = \gamma = 106.34$ (3)°, and $V = 1396.5$ (10) $Å^3$. These lattice parameters are again similar to those reported for Mo_3.[9] Crystal densities of Mo_2W and MoW_2 were found to be 2.33 and 2.54 g cm^{-3}, respectively, by a floatation method (acetic anhydride/$CHBr_3$), which are consistent with calculated values (2.35 for Mo_2W and 2.57 g cm^{-3} for MoW_2 based on $Z = 2$).

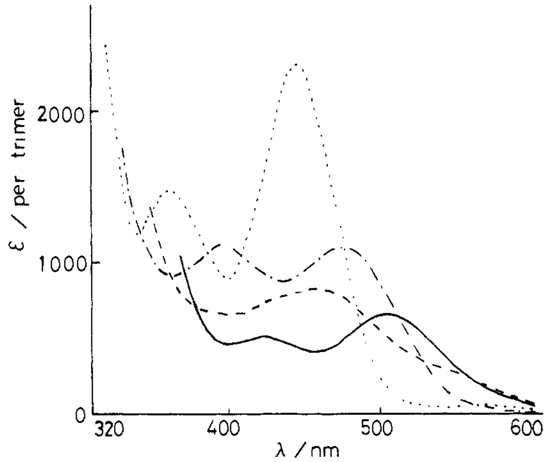

Figure 2. Electronic absorption spectra in 1 M $HClO_4$ of $[Mo_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$ (—), $[Mo_2WO_2(CH_3COO)_6(H_2O)_3]^{2+}$ (---), $[MoW_2O_2(CH_3COO)_6(H_2O)_3]^{2+}$ (-··-), and $[W_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$ (····).

The results of the X-ray study indicate that, in the crystal lattice of Mo_2W or MoW_2, molybdenum and tungsten are statistically disordered, giving apparently the same crystal symmetry to Mo_2W and MoW_2 as that of Mo_3. This is not surprising, since reported bond lengths and angles about Mo in $[Mo_3O_2(CH_3COO)_6(H_2O)_3]Br_2{\cdot}H_2O$[9] are very similar to corresponding values about W in $[W_3O_2(CH_3COO)_6(H_2O)_3](CF_3SO_3)_2$.[10]

Acknowledgment. We are grateful to M. Ebihara for the measurement of ^1H NMR spectra, Professor F. Takei (Research Institute for Iron, Steel and Other Metals, Tohoku University) for the ICP analysis, and to Takeda Science Foundation for partial financial support. Useful discussions and constant encouragement by Professor K. Saito (Coordination Chemistry Laboratories, Institute for Molecular Science) are gratefully acknowledged.

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Intramolecular Generation and [2,3]-Sigmatropic Rearrangement of Oxonium Ylides

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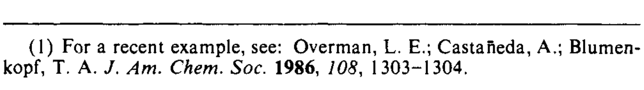
The controlled generation and utilization of reactive intermediates in the construction of organic compounds is a cornerstone of organic synthesis. However, the development of methodology utilizing oxygen-based reactive intermediates[1] has lagged far behind those based on carbon, nitrogen, phosphorous, and sulfur. We report here our preliminary results on the intramolecular generation of allylic oxonium ylides and their subsequent [2,3]-sigmatropic rearrangement to give five-, six-, and eight-membered oxygen heterocycles.



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[1] For a recent example, see: Overman, L. E.; Castañeda, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 1303-1304.