ee). With (–)-MnTIB as the starting reagent, (*R*)-(–)-*tert*-butyl methyl sulfoxide (49% ee) was ultimately obtained.

The degree of asymmetric induction at sulfur in 2 appears to be largely regulated by steric effects and, in the case of benzyl methyl sulfide, was almost nonexistent. However, even when induction is low, the separation of the *major* diastereomer from CH_2Cl_2/Et_2O appears to be general, and sulfoxides of high optical purity can be prepared (Table II). We note that Johnson and his co-workers previously synthesized [(–)-menthyloxy]benzyl-*p*-tolylsulfonium fluoroborate by the sequential treatment of benzyl *p*-tolyl sulfide with 1-chlorobenzotriazole, (–)-menthol, and silver fluoroborate.[12] Recrystallization of the sulfonium salt from benzene/Et_2O and hydrolysis gave (–)-benzyl *p*-tolyl sulfoxide with an optical purity of 87%.[12]

The method described herein for the synthesis of (menthyloxy)sulfonium tosylates has been applied to other chiral alcohols. For example, ligand exchange of MTIB with (1*R*)-*endo*-(+)-fenchyl alcohol, (1*S*)-*endo*-(–)-borneol, and (–)-cholesterol followed by the addition of methyl *p*-tolyl sulfide gave the alkoxysulfonium tosylates 3 (89%), 4 (93%), and 5 (13%), all with low diastereoselectivities (0.6–5% de).[13]
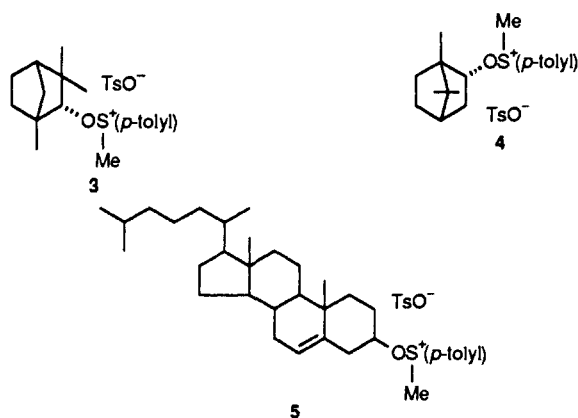
(12) Johnson, C. R.; Bacon, C. C.; Kingsbury, W. D. *Tetrahedron Lett.* 1972, 501.
(13) The elemental analyses (C, H) of 3 and 4 are consistent with $^1/_2$-molar hydrates [4 slightly off (+0.49%) on carbon] while the elemental composition of 5 indicates that it is the unhydrated sulfonium salt.

Gas-Phase Reactivity of Metal Alloy Clusters

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Study of the production and reactivity of gas-phase mixed-metal clusters in a well-characterized flow reactor offers a unique opportunity to investigate the complex and interesting properties that often accompany the corresponding heterogeneous alloys. Determining the reactivity trends of small metal alloy particles provides a promising way not only of investigating the evolution of bulk behavior but also of elucidating the electronic and geometric makeup of metallic entities of finite dimensions. These latter aspects are currently the focus of intense experimental and theoretical activity.

The jellium model,[1] which treats the nuclei (and core electrons) of the constituent atoms as smeared out in a specified potential
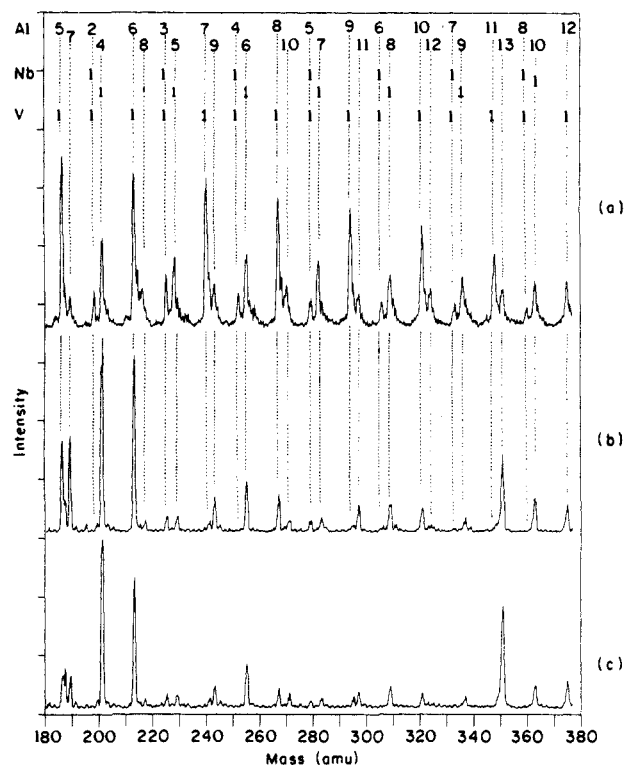
(1) (a) Knight, W. D.; Clemenger, K.; de Heer, W.; Saunders, W.; Chou, M.; Cohen, M. *Phys. Rev. Lett.* 1984, *52*, 2141. (b) Chou, M.; Cleland, A.; Cohen, M. *Solid State Commun.* 1984, *52*, 645. (c) Chou, M.; Cohen, M. *Phys. Lett. A* 1986, *113*, 420.

Figure 1. Reaction of metal clusters with O_2: (a) 0.0 sccm of O_2, (b) 30.6 sccm of O_2, and (c) 60.0 sccm of O_2. Intensity scales are arbitrary.

well and allows all of the valence electrons of the cluster to fill electronic shells (as in the hydrogen atom), has been a useful model[2] in accounting for special abundances of small alkali clusters in terms of their electronic structure. In addition, recent results[3] on the thermal reactivity (etching action) of bare aluminum cluster anions with oxygen showed Al_{13}^- and Al_{23}^- as products, species that are also predicted shell closinings of the spherical jellium model.[1] However, the jellium model has failed to account for the trends in aluminum cluster polarizabilities[4] and in some of their reactivity behavior.[5] Moreover, magic numbers have been seen for cobalt clusters pointing to icosahedral structures,[6] but none have been seen that can be attributed to the electronic structure of transition-metal clusters, raising questions about the general validity of the model.

One particularly useful way of investigating the importance of the electronic contribution to stability is by examining the influence of substituting one or more atoms in the cluster with one of differing valence.[7] The present report deals with the reaction (etching action) of oxygen on aluminum clusters containing niobium and/or vanadium. Niobium and vanadium have five valence electrons each ($4d^4 5s^1$ and $3d^3 4s^2$, respectively), and aluminum has three ($3s^2 3p^1$). Determination of the trends in reactivity with cluster size, the produced magic number alloy clusters, and comparison of the results with the bare aluminum results sheds light on the jellium model, the importance of electronic effects, and the free electrons involved.

The details of the apparatus have been reported previously.[8] The metal clusters are produced in a laser vaporization source

(2) Saito, Y.; Minami, K.; Ishida, T.; Noda, T. *Z. Phys. D.* 1989, *11*, 87.
(3) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W.; Jr. *J. Chem. Phys.* 1989, *91*, 2753.
(4) de Heer, W.; Milani, P.; Châtelain, A. *Phys. Rev. Lett.* 1989, *63*, 2834.
(5) (a) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W., Jr. Aluminum Cluster Reactions, submitted. (b) Cox, D. M.; Trevor, D. J.; Whetten, R. L.; Kaldor, A. *J. Phys. Chem.* 1988, *92*, 421.
(6) Klots, T. D.; Winter, B. J.; Parks, E. K.; Riley, S. J. *J. Chem. Phys.* 1990, *92*, 2110.
(7) Kappes, M. M. *Chem. Rev.* 1988, *88*, 382.
(8) (a) Castleman, A. W., Weil, K. G.; Sigsworth, S. W.; Leuchtner, R. E.; Keesee, R. G. *J. Chem. Phys.* 1987, *86*, 3829 (b) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W., Jr. Metal Cluster Cation Reactions: Carbon Monoxide Association to Cu_n^+ Ions. *J. Chem. Phys.*, in press.

with continuous helium flow and thereafter introduced into a high-pressure flow-tube apparatus (ca. 0.5 Torr). The target rod is aluminum, and when the laser vaporization source is impregnated with niobium and vanadium, a distribution of bare aluminum and mixed-metal clusters is observed. The clusters are well thermalized before reacting with a neutral reagent (oxygen). Reactants and products are mass filtered and detected downstream with a quadrupole mass spectrometer and pulse counting techniques. Gases such as N_2 have been introduced without changing the original anion distribution, confirming the expected absence of collision induced dissociation processes in the flow-tube apparatus.

A portion of a typical spectrum is shown in Figure 1a. Several series of ions are seen, including the bare aluminum clusters Al_n^- (n = 7–13) and the mixed-metal clusters VAl_n^- (n = 5–12), $NbAl_n^-$ (n = 4–10), and $VNbAl_n^-$ (n = 2–8). The relative amounts of the mixed clusters compared with the bare aluminum clusters can be altered by changing the laser focus, and under certain conditions an additional series $V_2NbAl_n^-$ (n = 0–6) is also obtained in this mass range.

In Figure 1b, a spectrum covering the same mass range shows the results of the addition of 30.6 sccm of oxygen through the reactant gas inlet. The spectrum shows that nearly one-half of the peaks from the previous spectrum have reacted away. The reactivity pattern at this intermediate reaction condition evidently results from odd–even electron alternation and its concomitant influence on reactivity. With the exception of VAl_5^-, each of the remaining species in Figure 1b has an even number of electrons, indicating that the pairing of electrons increases the stability of the ions, or at least decreases their reactivities.

After the addition of 60.0 sccm of oxygen, three peaks dominate the spectrum. As can be seen in Figure 1c, these are Al_{13}^-, $NbAl_4^-$, and VAl_6^-. Al_{13}^- has been shown[3] to be a stable product from the reaction of bare aluminum clusters with oxygen. In the current experiment the $NbAl_n^-$ clusters react to produce $NbAl_4^-$, and the VAl_n^- clusters react to product VAl_6^-.

An important question to which the present findings provide insight concerns the counting of the d electrons of transition metals in terms of the free-electron model. In one version where the d orbitals are considered to hybridize with the other orbitals in the cluster, all the valence electrons would participate in governing the electronic structure. In this case both vanadium and niobium would contribute five electrons to the cluster. Otherwise, the d electrons would be considered as core electrons which would have V and Nb contribute two electrons and one electron, respectively.[9] The observed odd–even alternation in reactivity is a clear indication that both atoms donate an odd number of electrons. The jellium model accounts for the special stability of Al_{13}^- (and Al_{23}^-), and the stability of $NbAl_4^-$ can also be explained by its electronic structure if all five electrons are available; this compound has 18 valence electrons, which is a jellium shell closing, and also has special stabilities in coordination compounds (18-electron rule). If every valence electron is counted as in the previous examples, VAl_6^- has 24 electrons, which is not a predicted shell closing. (Note, however, if one of vanadium's electrons is promoted by hybridization, providing one free s electron, the species then becomes a 20-electron system, and its lack of reactivity would be in accord with the jellium model.)

In conclusion, the jellium model is a good guide to the reactivity patterns and related electronic structure of metal alloy clusters, but by no means provides a compendious concept. The interaction of the electronic orbitals of aluminum with those of the transition metals may be sufficiently strong to enable all of the electrons to contribute to reactivity behavior, as evidenced by the lack of differences for systems containing $4s^2$ and $5s^1$ electrons and by the general observation that odd–even electron number accounts for the reactivity of these alloy systems. Finally, it is interesting to speculate whether a structural form of VAl_5^- might not involve

electron hybridization and hence would behave as an 18-electron system; this may account for the lack of reactivity of this species.

Reversible Opening and Closing of Hetero Trimetallic Units in (C5H5)2Y(THF)Re2H7(PMe2Ph)4 and (C5H5)2LuRe2H7(PMe2Ph)4[1]

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Mixed-metal complexes[2] containing two substantially different types of metal have the potential to effect substrate transformations not achievable with either of the individual metallic components. Complexes that can accomplish such bimetallic reactions must contain some ligands that can hold the metals together during the reaction and other ligands that react with substrates. Although suitable bridging ligands have been identified for mixed-metal complexes containing f elements and transition metals,[3] these compounds generally do not contain reactive ligands that can subsequently transfer to substrate. Transition-metal polyhydride phosphine complexes[4] appeared to be an attractive set of starting materials for the synthesis of mixed-transition-metal/f-element species, since the several hydride ligands could provide the desired reactive ligands and also could comprise the necessary linkages to bridge to the lanthanide. Hydride-bridged heterometallic transition-metal complexes are known[5] as well as hydride-bridged polymetallic lanthanide and yttrium complexes including mixed-metal species such as $\{[Cp'_2Y(\mu\text{-H})]_2[Cp'_2Zr(\mu\text{-H})](\mu_3\text{-H})\}$ ($Cp' = C_5H_4Me$).[6] In addition, given parallels in lanthanide and alkali-metal chemistry[7] and the existence of complexes such as $KOsH_3(PMe_2Ph)_3$[8] and $(THF)_2KReH_6(PPh_3)_2$,[9] it seemed likely

(1) Reported in part at the 198th National Meeting of the American Chemical Society, Miami, FL, Sept 1989; paper INOR 340.

(2) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 40 and references therein.

(3) (a) Marianelli, R. S.; Durney, M. T. *J. Organomet. Chem.* **1971**, *32*, C41–C43. (b) Crease, A. E.; Legzdins, P. *J. Chem. Soc., Chem. Commun.* **1973**, 1501–1507. (c) Marks, T. J.; Kristoff, J. S.; Alich, A.; Shriver, D. F. *J. Organomet. Chem.* **1971**, *33*, C35. (d) Onaka, S. *Inorg. Chem.* **1980**, *19*, 2132–2136. (e) Tilley, T. D.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 1772–1774. (f) Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* **1984**, *23*, 432–437. (g) Evans, W. J.; Bloom, I.; Grate, J. W.; Hughes, L. A.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1985**, *24*, 4620–4623. (h) Cotton, F. A.; Davison, A.; Day, V. W.; Fredrich, M. F.; Orvig, C.; Swanson, R. *Inorg. Chem.* **1982**, *21*, 1211–1214. (i) Condorelli, G.; Fragala, I.; Giuffrida, S.; Cassol, A. *Z. Anorg. Chem.* **1975**, *412*, 251–257. (j) Harrison, D. W.; Bunzli, J.-C. G. *Inorg. Chim. Acta* **1985**, *109*, 185–192. (k) Hodgson, D. J.; Michelsen, K.; Pedersen, E. *J. Chem. Soc., Chem. Commun.* **1988**, 1558–1559. (l) Goodgame, D. M. L.; Williams, D. J.; Winpenny, R. E. P. *Polyhedron* **1989**, *8*, 1531–1536. (m) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915–917. (b) Deacon, G. B.; Dietrich, A.; Forsyth, C. M.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1370–1371.

(4) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1–48.

(5) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8310–8312.

(6) (a) Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4454–4460. (b) Evans, W. J.; Sollberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* **1988**, *110*, 439–446.

(7) E.g.: Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292–4297.

(8) Huffman, J. C.; Green, M. A.; Kaiser, S. L.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 5111–5115.

(9) Alvarez, D., Jr.; Lundquist, E. G.; Ziller, J. W.; Evans, W. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 8392–8398.

(9) (a) Ziman, J. M. *Principles of the Theory of Solids*; Cambridge Univ. Press: New York, 1972; p 113. (b) Cox, A. J. *Electronic Structure and Chemistry of Solids*; Oxford Univ. Press: Oxford, 1987; p 68.