

solvated analogue), which, in the absence of other reactants, recombines with CO or dimerizes via very rapid reactions. In the presence of added PPh₃, ethylene, or dihydrogen, adducts of I are formed. Rates of addition of the former two are quite rapid while dihydrogen addition occurs with a rate significantly slower. In all cases, however, the initial adducts formed react eventually with the photolabilized CO to reform the more stable starting complex RhCl(CO)(PPh₃)₂. These observations are consistent with a previous continuous photolysis investigation which reported no net photochemistry of this species in the absence of oxygen.¹¹ Preliminary flash photolysis studies¹² of the iridium analogue Vaska's complex IrCl(CO)(PPh₃)₂ demonstrate the formation of a transient analogous to I although the subsequent reactions display significant differences.

Acknowledgment. This research was sponsored by the National Science Foundation. The rhodium used in these studies was provided on loan by Johnson Matthey, Inc.

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Seven-Coordinate Aluminum in [AlCl₂-benzo-15-crown-5][AlCl₂Et]

Simon G. Bott, Hosny Elgamal, and Jerry L. Atwood*

Department of Chemistry, University of Alabama
University, Alabama 35486

Received July 30, 1984

Crown ethers have been utilized as multidentate ligands to form unusual or unique coordination states for numerous metals.¹ One particularly fruitful area has been the reaction between crown ethers and ML₂ species, resulting in a number of modes of complexation involving both direct M-O interaction and L...O hydrogen bonding.²⁻¹¹ A general condition for the former to occur, as reported by Christensen et al.,¹² is that the ratio (*R*) of the metal ion diameter to the crown cavity diameter be between 0.75 and 0.90.¹³ Within this range, however, two types of complex can exist—those in which the metal and oxygens are coplanar, resulting in a bipyramidal structure having L axial, and those in which cis sites are occupied by L, leaving the metal lying out of the plane of the oxygens. Which mode occurs is again largely dependent on *R*, lower values leading to the "included" metal (e.g., Ca(NCS)₂-benzo-15-crown-5-S (S = H₂O, CH₃OH)⁶ has the calcium

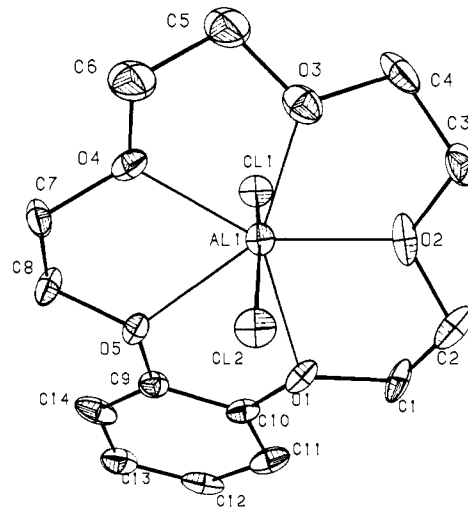


Figure 1. [AlCl₂-benzo-15-crown-5]⁺ cation. The Cl-Al-Cl angle is 169° and the lengths involving Al(1) are Al(1)-O(1) = 2.28 (1), Al(1)-O(2) = 2.03 (1), Al(1)-O(3) = 2.06 (1), Al(1)-O(4) = 2.08 (1), Al(1)-O(5) = 2.30 (1), Al(1)-Cl(1) = 2.202 (5), and Al(1)-Cl(2) = 2.197 (7) Å.

lying 1.22 Å out of plane, *R* = 1.01-1.31, whereas Ca(NCS)₂-18-crown-6³ contains the calcium coplanar with the oxygens, *R* = 0.70-0.86).

Reaction of EtAlCl₂ with 12-crown-4 and 18-crown-6 produces cationic complexes of aluminum coordinated to four oxygens and two cis chlorines. The diameter of Al³⁺ is 1.34 Å, and this gives a value for *R* of 0.90-1.10 for these complexes.¹⁴ Thus by analogy with the calcium series, reaction of EtAlCl₂ with benzo-15-crown-5 (*R* = 0.61-0.79) produces the title compound, corresponding to the 2:1 complex of AlCl₃ with the same crown.¹⁵ The X-ray investigation revealed that the cation consists of the first structurally characterized seven-coordinate aluminum,^{16,17} the coordination polyhedron being a pentagonal bipyramid with five equatorial oxygens and two axial chlorines (Figure 1).

The aluminum is coplanar with the oxygens and is displaced away from the aromatic group. Thus the Al-O distances for O(2), O(3), and O(4) are much shorter than those for the two oxygens adjacent to the benzo group. The latter two distances are among the longest Al-O lengths so far reported,¹⁸ but justification for referring to them as bonds arises from both the near ideality of the pentagonal-bipyramidal geometry¹⁹ combined with the definite bonding distances to the other three oxygens and the elongated Al-Cl distances (2.200 (3) Å compared to 2.143 (6) Å in the anion).

(14) *R* for 12-crown-4 is 0.91-1.10, while *R* for 18-crown-6 is 0.42-0.51. However, with a ratio as low as the latter, the aluminum atom opts for an octahedral configuration like that of the 12-crown-4 derivative (Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E.; Atwood, J. L., unpublished results).

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(16) Single crystals of the title compound were obtained by the slow cooling of a toluene solution. Space group *Pbca*; cell constants *a* = 21.306 (9) Å, *b* = 17.747 (4) Å, *c* = 13.267 (3) Å, with eight formula units per unit cell and *D*_c = 1.40 g cm⁻³. Least-squares refinement based on 1667 observed reflections led to a final *R* = Σ(|F_o| - |F_c|) / Σ|F_o| = 0.100. The rather high *R* value is due to disorder in the anion. This has the effect of smearing the contribution of the ethyl group over at least four positions. The details of data collection and refinement are as given in Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* 1979, 45. Anisotropic thermal parameters were used for all atoms except those of the ethyl group of the anion. Hydrogen atoms were not located.

(17) Reaction of 0.010 mol of benzo-15-crown-5 with 0.020 mol of EtAlCl₂ in toluene produces an immediate two-phase system characteristic of the liquid clathrate effect (Atwood, J. L. In "Inclusion Compounds"; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984). Upon standing, large, colorless, air-sensitive crystals of the title compound are deposited from the lower layer.

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Three structurally similar complexes have been investigated: Mg(NCS)₂-benzo-15-crown-5,⁶ Co(H₂O)₂-benzo-15-crown-5,⁹ and CuCl₂-benzo-15-crown-5-CHCl₃.¹⁰ A comparison of the structural data shows little variation for the conformation of the crown ether (e.g., Mg complex torsion angles vary less than 6% compared with those for the aluminum complex). However, the disparity in the Al-O distances for the title complex is not evident for any of the metal-oxygen lengths in the related complexes. This can be explained by both the increased charge and the smaller diameter of the aluminum cation ($d_{Mg^{2+}} = 1.84 \text{ \AA}$, $d_{Cu^{2+}} = 1.88 \text{ \AA}$, $d_{Co^{2+}} = 1.84 \text{ \AA}$, all values corrected for seven-coordination using the method of Pauling,²⁰ whereas the corrected value for Al³⁺ = 1.44 Å). Thus the lesser donor capability of the "benzo" oxygens reported for [Ti(CH₃)₂-dibenzo-18-crown-6]⁺²¹ becomes more evident for the smaller cation. The bonding system is an extension to that in SF₆ or PF₅, the ability of the oxygens to lie in a plane and the electronegativity of the chlorines combining to stabilize the filling of four bonding and three nonbonding orbitals. As only three of the former are bonding with respect to aluminum and oxygen, a six-electron ten-center pattern is formed, which is in agreement with the "eight-electron" rule and leads to the observed long and irregular bonding distances.²²

Acknowledgment. We are grateful to the National Science Foundation and the Department of Energy (DE-FG22-83PC60780) for support of this research.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Intramolecular Michael Addition of *O*-Carbamates to α,β -Unsaturated Esters. A New Diastereoselective Amination in an Acyclic System^{†1}

Masahiro Hirama,* Takeo Shigemoto, Yutaka Yamazaki, and Shō Itō*

Department of Chemistry, Tohoku University
Sendai 980, Japan

Received October 5, 1984

The synthesis of biologically important amino sugars from noncarbohydrate precursors is currently receiving considerable attention.² A challenging aspect of the effort is the stereocontrolled functionalization of acyclic olefinic systems. Though highly stereoselective oxygenation of double bonds of unsaturated amine derivatives has recently been reported,³ alternative approaches starting from unsaturated alcohols have one obvious

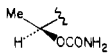
[†]Dedicated to the memory of Professor Kunio Sakan.

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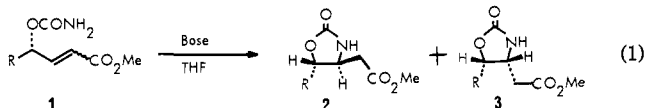
Table I. Diastereoselective Intramolecular Michael Addition of Allylic *O*-Carbamates **1**

entry	substrate		conditions ^a	product	
	R	2,3 double bond		ratio ^b 2:3	% yield ^c
1	1a , Me	<i>E</i>	25 min or 3 s	5:1	66
2	1b , Ph	<i>E</i>	30 min	12:1	85
3	1b , Ph	<i>E</i>	1.5 equiv, 30 min	7:1	68
4	1c , Ph	<i>Z</i>	30 min	>100:1	75
5		<i>E</i>	30 min	>20:1	79

^aCarried out in an anhydrous THF and quenched with saturated aqueous NH₄Cl or pulverized NH₄Cl (1 equiv); 1.0 equiv of KO-*t*-Bu (0 °C) was used, unless otherwise indicated. ^bProduct diastereomer ratio determined by 200-MHz ¹H NMR spectroscopy. ^cYield of isolated mixture of **2** and **3**.

advantage that enantiomerically pure materials are readily accessible.^{4,5} Compared with the two-step procedure, asymmetric epoxidation of allylic alcohols⁵ and subsequent addition of nitrogen nucleophiles,⁶ the direct addition of a nitrogen functionality to an unsaturated alcohol system has not generally been so stereoselective.^{1,7} We disclose here a new aspect of carbamate-mediated functionalization⁸ useful for diastereoselective introduction of a nitrogen functionality directly in the β -position of γ - and δ -hydroxy- α,β -unsaturated esters.

When allylic carbamate esters **1** were stirred with 1.0 equiv of KO-*t*-Bu (THF, 0 °C) under an argon atmosphere, a rapid cyclization via nitrogen occurred¹ producing mainly the *trans*-oxazolidinones **2**, equal to 1,2-*syn* amino alcohols (eq 1, Table



I).^{9,10} The ratio of **2:3** was not affected by changing the reaction time (entry 1), while it was diminished by excess KO-*t*-Bu (entries 2, 3). Other bases such as NaH (1.5 equiv, room temperature) resulted in the similar stereoselectivity with somewhat slower reaction rate. Higher 1,2-asymmetric induction was observed in the compounds with more sterically demanding R groups (entries

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