Organometallics **2007,** *26,* 4354−4356

Trimethylsilylated Allyl Complexes of the Heavy Alkali Metals, $\mathrm{M[1,3\text{-}(SiMe_3)_2C_3H_3](thf)}_n$ (M = K, Cs)

Keith T. Quisenberry,[†] Cameron K. Gren,[†] Rosemary E. White,[†] Timothy P. Hanusa,[*,†] and William W. Brennessel[§]

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and X-ray Crystallographic Laboratory, Chemistry Department, University of Minnesota, Minneapolis, Minnesota 55455

Received April 27, 2007

Summary: Reaction of elemental cesium with 1,3-bis(trimethylsilyl)propene produces the corresponding substituted allyl derivative. The complex and its previously prepared potassium counterpart form the THF solvates $\mathrm{K[1,3\text{-}(SiMe_3)_2C_3H_3](thf)_{3/2}}$ *and* $\mathrm{Cs[1,3\text{-}(SiMe_3)_2C_3H_3](thf)}$*, respectively, which crystallize as coordination polymers in the solid state. In the case of the cesium complex, the packing is polymeric in two dimensions. As was previously found for the potassium complex, the cesium compound is an initiator for methyl methacrylate polymerization.*

Introduction

Heterometallic lanthanide/alkali metal allyl complexes have recently been shown to be useful polymerization initiators.[1,2] Interestingly, however, the potassium derivative of the bulky 1,3-bis(trimethylsilyl)allyl anion polymerizes methyl methacrylate more effectively when used as the sole catalyst rather than as part of a mixed metal species.[3] Such activity naturally makes the allyl complexes of the heavy alkali metals (K−Cs) of interest, but compared to allyllithium complexes[4,5] they are less well-known species. There are only two reports of structurally characterized potassium allyl complexes,[2,3] for example, and none for rubidium and cesium. The latter two have been characterized in solution[6] and with computational studies.[7] In this note, the synthesis and characterization of a cesium complex containing the trimethylsilyl-substituted allyl ligand $[1,3\text{-}\mathrm{(SiMe_3)_2C_3H_3}]^-$ $[\mathrm{A'}]^-$ is described, as are the solid-state structures of THF solvates of the cesium allyl and its potassium counterpart.[2,3]

Results and Discussion

Synthesis of Allyl Complexes. An allyl complex of cesium was synthesized by direct reaction of the trimethylsilyl-substituted propene with the alkali metal in THF (eq 1).

$$1,3\text{-}(\mathrm{SiMe_3})_2\mathrm{C_3H_4} + \mathrm{Cs} \xrightarrow{\mathrm{THF}} \mathrm{Cs[A'](thf)}_x + 1/2\ \mathrm{H_2} \tag{1}$$

Although the reaction was initially conducted at low temperature (−78 °C) during the addition of the propene hydrocarbon to discourage formation of the coupled allyl dimer $[1,3\text{-}\mathrm{(SiMe_3)_2C_3H_3}]_2$,[8] it was found that warming the reaction above the melting points of the metal (28 °C) improved the modest yield without producing the dimer. The direct reaction route avoids the use of mercury derivatives that have previously been employed in the preparation of alkali metal derivatives of the unsubstituted allyls.[6,9,10]

The proton NMR spectrum of the cesium allyl product displays a singlet, doublet, triplet pattern that is typical for π-bound allyls with *syn*, *syn* trimethylsilyl arrangements.[3,11] One THF is present per allyl anion, but elemental analysis of the solvated allylcesium species provided low carbon and hydrogen values. This probably reflects the lability of THF on the cesium center. Heating the cesium complex under vacuum completely removes the THF, and the resulting sample analyzes appropriately for 1:1 cesium:allyl.

Solid-State Structures. Organometallic species of the heavy alkali metals often form coordination polymers,[12] and both $\mathrm{K[A'](thf)_{3/2}}$ and $\mathrm{Cs[A'](thf)}$ do also. In both structures, the C−C−C angles of the allyl anions are similar to the 130.3° angle calculated for the free $[\mathrm{A'}]^-$ anion,[13] and the $\mathrm{SiMe_3}$ groups are arranged in *syn*, *syn* configurations. As is generally found

---

[*] Corresponding author. E-mail: t.hanusa@vanderbilt.edu.

[†] Vanderbilt University.

[§] University of Minnesota.

(1) Maiwald, S.; Weissenborn, H.; Sommer, C.; Müller, G.; Taube, R. *J. Organomet. Chem.* **2001**, *640*, 1−9. Woodman, T. J.; Sarazin, Y.; Garratt, S.; Fink, G.; Bochmann, M. *J. Mol. Catal. A: Chem.* **2005**, *235*, 88−97. Woodman, T. J.; Schormann, M.; Bochmann, M. *Organometallics* **2003**, *22*, 2938−2943.

(2) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 3028−3030.

(3) Simpson, C. K.; White, R. E.; Carlson, C. N.; Wrobleski, D. A.; Kuehl, C. J.; Croce, T. A.; Steele, I. M.; Scott, B. L.; Hanusa, T. P.; Sattelberger, A. P.; John, K. D. *Organometallics* **2005**, *24*, 3685−3691.

(4) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Liu, D.-S.; Mak, T. C. W.; Wang, Z.-X. *J. Chem. Soc., Dalton Trans.* **1999**, 1257−1262. Hitchcock, P. B.; Lappert, M. F.; Wang, Z.-X. *Chem. Commun.* **1996**, 1647−1648. Schuemann, U.; Weiss, E.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1987**, *322*, 299−307. Praesang, C.; Sahin, Y.; Hofmann, M.; Geiseler, G.; Massa, W.; Berndt, A. *Eur. J. Inorg. Chem.* **2004**, 3063−3073. Marr, F.; Fröhlich, R.; Hoppe, D. *Tetrahedron: Asymmetry* **2002**, *13*, 2587−2592.

(5) Boche, G.; Fraenkel, G.; Cabral, J.; Harms, K.; van Eikema Hommes, N. J. R.; Lohrenz, J.; Marsch, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 1562−1565.

(6) Brownstein, S.; Bywater, S.; Worsfold, D. J. *J. Organomet. Chem.* **1980**, *199*, 1−8.

(7) Hommes, N. v. E.; Bühl, M.; Schleyer, P. v. R.; Wu, Y.-D. *J. Organomet. Chem.* **1991**, *409*, 307−320.

(8) Quisenberry, K. T.; Smith, J. D.; Voehler, M.; Stec, D. F.; Hanusa, T. P.; Brennessel, W. W. *J. Am. Chem. Soc.* **2005**, *127*, 4376−4387.

(9) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459−5464.

(10) A similar reaction was conducted with rubidium metal. Only a small amount (ca. 10% yield) of a product whose NMR spectra were consistent with the formula $\mathrm{Rb[A'](thf)}$ could be isolated, however. The product could not be obtained in a form suitable for single-crystal X-ray diffraction and was not further studied.

(11) Carlson, C. N.; Hanusa, T. P.; Brennessel, W. W. *J. Am. Chem. Soc.* **2004**, *126*, 10550−10551.

(12) Smith, J. D. *Adv. Organomet. Chem.* **1998**, *43*, 267−348. Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855−3858. Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem.* **1987**, *99*, 563−4.

(13) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *Angew. Chem., Int. Ed.* **1999**, *38*, 217−219.

10.1021/om700410a CCC: $37.00

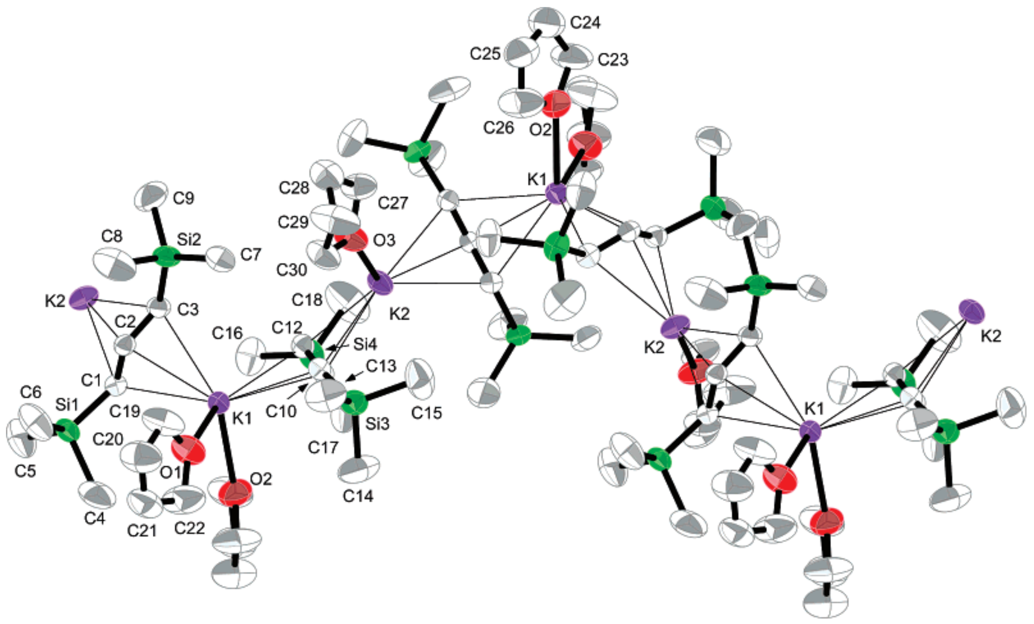

Figure 1. Diagram of the polymeric $\{K[A'](thf)_{3/2}\}_\infty$ structure. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms have been omitted for clarity. Oxygen atoms are in red, potassium in violet, and silicon in green.

for such substituents,[3,11] the silicon atoms lie near their respective C_3 planes. Beyond such similarities are distinctive differences in the coordination environments for each compound, as described below.

$\{K[A'](thf)_{3/2}\}_\infty$. Crystals of $\{K[A'](thf)_{3/2}\}_\infty$ were grown from THF solution at room temperature.[14] Unlike the monomeric lithium species Li[A′](tmeda),[5] but like the related dme solvate $\{K[A'](dme)\}_\infty$,[3] the structure of $\{K[A'](thf)_{3/2}\}_\infty$ is a one-dimensional coordination polymer, with $K(1)(A')(thf)_2$ units alternating with K(2)(A′)(thf) units, running parallel to the *c* axis (Figure 1). Two of the trimethylsilyl groups are disordered over two positions, and all three of the THF molecules are disordered over two positions.

The existence of two different coordination environments around the potassium centers in $\{K[A'](thf)_{3/2}\}_\infty$ generates distinctive structural features. For example, roughly linear K(1)−K(2)−K(1)′ sections (170.2°) alternate with strongly bent K(2)−K(1)−K(2)′ sequences (103.3°), whereas in $\{K[A'](dme)\}_\infty$, the corresponding K(1)−K(2)−K(1) and K(2)−K(1)−K(2) angles are more comparable, at 153.3° and 141.9°, respectively.[2,3] The range of K−C distances in $\{K[A'](thf)_{3/2}\}_\infty$ (2.93−3.12 Å) is slightly larger than in $\{K[A'](dme)\}_\infty$ (2.98−3.10 Å), and the average distance to the formally six-coordinate K(1) (3.05 Å) is marginally larger than the average to the five-coordinate K(2) (3.01 Å). In general, however, the distances are similar to those for potassium cyclopentadienides (cf. 2.99 to 3.08 Å in $[K(C_5(SiMe_3)H_4)]_\infty$ and 2.93 to 3.10 Å in $[K(C_5(SiMe_3)_3H_2)]_\infty$[15]), an indication of the comparably ionic bonding in the complexes.

$\{Cs[A'](thf)\}_\infty$.[16] The immediate environment around the cesium in $\{Cs[A'](thf)\}_\infty$ consists of a (disordered) THF ligand and two π-bound allyl ligands, so that a coordination polymer is formed along the crystallographic *a* axis (Figure 2). The Cs−Cs′−Cs″ angle is exactly 180°, and although there is considerable spread in Cs−C contacts (3.331(6)−3.509(7) Å), the distances to the two allyl ligands are roughly equivalent (Cs−(C1,C3) = 3.48 Å (av), Cs−C2 = 3.33 Å; Cs′−(C1,C3) = 3.45 Å (av), Cs′−C2 = 3.28 Å). The longer of these distances is comparable to the average Cs−C contacts in the polymeric cesium azaallyl complex $\{Cs[N(CHPh)_2](thf)\}_\infty$ (3.50 Å),[17] although the center Cs−N bonds of the azaallyl fragments are considerably shorter (3.11, 3.21 Å).

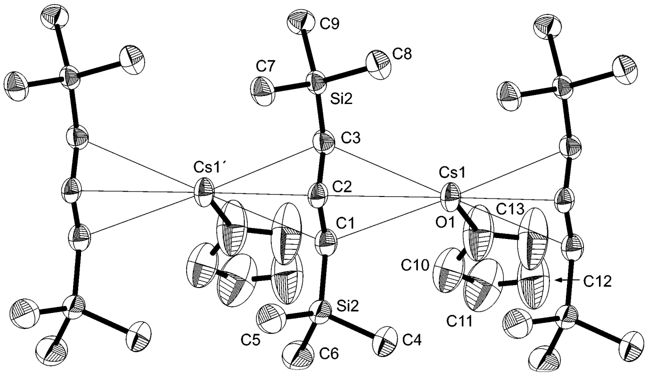

Figure 2. Diagram of the non-hydrogen atoms of $\{Cs[A'](thf)\}_\infty$, illustrating the numbering scheme used in the text. Thermal ellipsoids are drawn at the 50% level, and only one orientation of the disordered THF ligand is shown.

The linear ordering of cesium ions and allyl anions is part of a two-dimensional packing arrangement parallel to the *ab* plane (see Figure 3). For each polymeric layer, there are two rows (side by side in the *c* direction) of Cs−allyl repeat units parallel to the *a* axis and staggered with respect to each other. The plane of each allyl anion is perpendicular to the *a* axis. Hence each cesium atom has a coordination sphere containing two allyl groups, two methyl groups (at distances of 3.67 and 3.95 Å), one THF solvent molecule, and a final site that is blocked by

---

[14] Crystals of $K[A'](thf)_{3/2}$ are orthorhombic, space group $Pna2_1$, with a = 23.151(2) Å, b = 11.0862(9) Å, c = 16.9491(14) Å, V = 4350.1(6) Å^3, Z = 4, and ρ_{calc} = 1.016 g cm^{-3} for fw = 665.39. Refinement of 7483 reflections collected at 173 K with Mo Kα radiation led to residuals of $R(F^2)$ = 0.0559 and $R_w(F^2)$ = 0.1054 (all data).

[15] Harvey, M. J.; Hanusa, T. P.; Pink, M. *J. Chem. Soc., Dalton Trans.* **2001**, 1128−1130.

[16] Crystals of Cs[A′](thf) are monoclinic, space group $P2_1/n$, with a = 6.4496(8) Å, b = 10.1112(13) Å, c = 30.041(4) Å, β = 90.587(2)°, V = 1959.0(4) Å^3, Z = 4, and ρ_{calc} = 1.324 g cm^{-3} for fw = 390.45. Refinement of 3461 reflections collected at 173 K with Mo Kα radiation led to residuals of $R(F^2)$ = 0.0672 and $R_w(F^2)$ = 0.1198 (all data).

[17] Pauls, J.; Chitsaz, S.; Neumüller, B. *Organometallics* **2002**, *21*, 1515−1517.

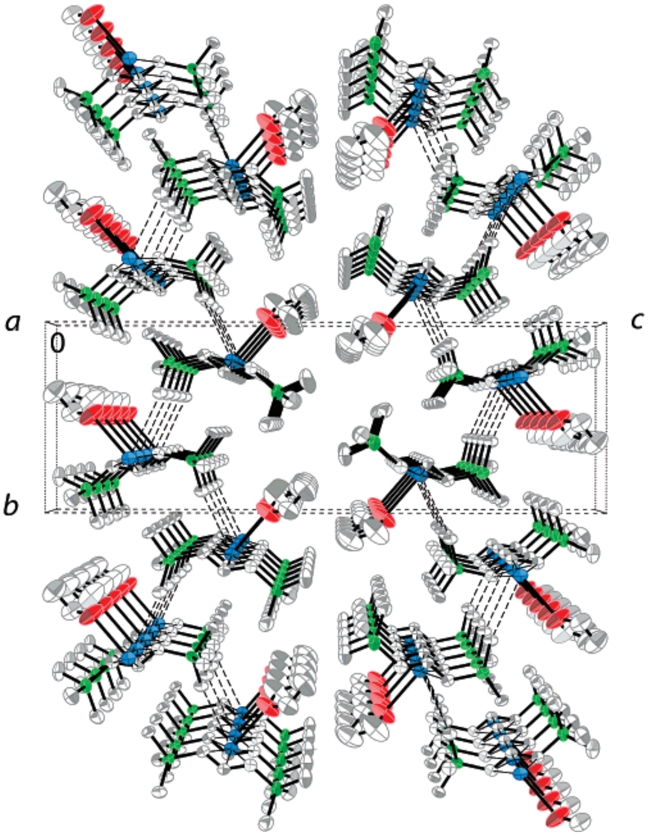

Figure 3. Packing diagram of $\{Cs[A'](thf)\}_\infty$, projected down the crystallographic *a* axis. Oxygen atoms are in red, cesium in blue, and silicon in green. Intermolecular contacts are depicted with dashed lines.

two $SiMe_3$ groups; thus the cesium center may be loosely considered to be seven-coordinate. The disordered THF solvent molecules lie in channels between polymeric layers, and this fact may account for the ease of crystal degradation.The Cs−$C_{(allyl)}$ distances in $\{Cs[A'](thf)\}_\infty$ are similar to Cs−$C_{(Cp)}$ distances found in the six-coordinate $([(C_6H_5)_4P]^+[Cs_2(C_5H_5)_3]^-)$[18] (Cs−$C_{(Cp)}$ = 3.33−3.39 Å), if the values are adjusted for the difference in coordination number of the two complexes. Likewise, the CsO distance in the allylcesium species (2.93(5) Å) is also within the expected range for cesium−THF bonding;[19] it is about 0.1 Å shorter than the distance in the cesium azaallyl $\{Cs[N(CHPh)_2](thf)\}_\infty$ (3.04 Å).[17]

Table 1. Average Bond Distances (Å) and Angles (deg) for $M[A'](thf)_n$[a]

	$\{K[A'](thf)_{3/2}\}_\infty$	$\{Cs[A'](thf)\}_\infty$
	Bond Lengths	
M1−$C_{methylene}$	3.079[6]	3.47[1]
M1−$C_{methine}$	2.974[4]	3.307[8]
M1−O1,O2	2.706(6), 2.695(12)	2.93(5)
M2−O	2.66(2)	
	Bond/Torsion Angles	
C−C−C (allyl)	130.9[4]	131.2(7)
C−C−C-Si[b]	176.4[8]	176.5[6]

[a] Standard deviations of individual bond lengths or angles are given in parentheses. Values in square brackets are the errors of the averages. [b] This value represents the average of the absolute values of the torsion angles.

Initial Polymerization Studies. It has been shown that K[A′] polymerizes methyl methacrylate more effectively when used as the sole catalyst rather than as part of a mixed metal species.[3] In an effort to determine whether group 1 allyl complexes other than K[A′] exhibit similar catalytic activity, methyl methacrylate polymerization reactions were conducted with the Cs[A′](thf) complex. The complex displays conversion rates similar to that of K[A′] (84% and 83%, respectively); however, the allylpotassium species has a much higher TOF (104 000 h^{-1}) than does the allyl cesium species (16 000 h^{-1}). As in the case with K[A′], the polymer produced by the allylcesium initiator is atactic.

In summary, the bulky trimethylsilylated propene HA′ can be used to synthesize an allyl complex of cesium; the THF solvates of the cesium allyl and its previously prepared potassium counterpart form coordination polymers in the solid state. The cesium compound is an initiator for methyl methacrylate polymerization.

Acknowledgment. We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, for support of this research. R.E.W. and K.T.Q. were supported with GAANN Fellowships from the Department of Education.

Supporting Information Available: Additional synthetic and spectroscopic characterization and crystallographic data and files in CIF format for $K[A'](thf)_{3/2}$ and Cs[A′](thf). These are available free of charge via the Internet at http://pubs.acs.org.

OM700410A

---

(18) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 97−99.

(19) Pauer, F.; Stalke, D. *J. Organomet. Chem.* **1991**, *418*, 127−145. Englich, U.; Hassler, K.; Ruhlandt-Senge, K.; Uhlig, F. *Inorg. Chem.* **1998**, *37*, 3532−3537. Pauls, J.; Neumüller, B. Z. *Anorg. Allg. Chem.* **2001**, *627*, 2127−2132.