to low-temperature column chromatography on silica (−20°C, hexane/diethyl ether 99/1). The eluents were concentrated to dryness in vacuo, and the residues crystallized from pentane at −20°C. **5**: Pale yellow crystals, yield 0.18 g (51%), m.p. 128°C (decomp). **8**: Pale yellow crystals, yield 0.25 g (81%), m.p. 89°C (decomp).

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[14] Selected MS data (pos. CI, NH_3, 70 eV, ^{184}W): **5**: *m/z* (%): 761 (100) [$(M+NH_4)^+$]; **8** : *m/z* (%): 632 (42) [M^+]; correct C,H elemental analyses for **5** and **8**.

[15] Crystal structure analyses: The crystals (**5:** 0.70 × 0.50 × 0.30 mm; **8:** 0.58 × 0.48 × 0.40 mm) were mounted in inert oil at −100°C on a Siemens P4 diffractometer. Intensities were registered by using ω scans in the 2θ region 6–50°. Absorption corrections were based on Ψ scans). The structures were solved by direct methods (SHELXS-86) and refined against F^2 using SHELXL-93 (G. M. Sheldrick, Universität Göttingen). Hydrogen atoms were refined by using a riding model, with the exception of methyl H (rigid groups) and the nitrogen-bonded H0 in **5** (freely refined). **5**: $C_{24}H_{18}NO_{13}PW$, $M_r = 743.21$, monoclinic, space group C2/c, $a = 2513.1(3)$, $b = 1455.1(2)$, $c = 1552.6(2)$ pm, $\beta = 108.941(10)°$, $V = 5.3699(10)$ nm^3, $Z = 8$, $\rho_{calcd} = 1.839$ Mg m^{-3}, $\lambda = 0.71073$ pm, $T = 173$ K. Of a total of 9431 reflections, 4720 were independent ($R_{int} = 0.0497$). Final $wR2 = 0.0620$ for all data, conventional $R(F)$ ($R1$) = 0.0307, for 369 parameters and 265 restraints; max. $\Delta\rho$ −798 and 913 e nm^{-3}. **8**: $C_{21}H_{21}O_9PW$, $M_r = 632.20$, triclinic, space group $P\bar{1}$, $a = 966.5(2)$, $b = 985.2(2)$, $c = 1322.9(3)$ pm, $\alpha = 111.29(2)$, $\beta = 91.12(2)$, $\gamma = 92.00(2)°$, $V = 1.1722(4)$ nm^3; $Z = 2$, $\rho_{calcd} = 1.791$ Mg m^{-3}, $\lambda = 0.71073$ pm, $T = 173$ K. Of a total of 6336 reflections, 3989 were independent ($R_{int} = 0.0101$). Final $wR2 = 0.0428$ for all data, conventional $R1 = 0.0165$, for 296 parameters and 217 restraints; max. $\Delta\rho$ −890 and 660 e nm^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Canbridge Crystallographic Data Centre as supplementary publication nos. CCDC-102463 and CCDC-102464. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Synthesis and Crystal Structure of the Bis(allyl)calcium Complex $[Ca\{C_3(SiMe_3)_2H_3\}_2 \cdot (thf)_2]$**

Melanie J. Harvey, Timothy P. Hanusa,* and
Victor G. Young, Jr.

The cyclopentadienyl ring and its substituted derivatives are the most frequently encountered ligands in organocalcium, -strontium, and -barium chemistry.[1, 2] Alkaline-earth metal complexes containing other carbanionic groups (e.g., alkyls,[3, 4] indenyl,[5] pentadienyl,[6] or fluorenyl[7]) are described, but as a class have received far less attention. The allyl anion represents the simplest π-delocalized ligand, and although some allylbarium compounds are known,[8, 9] the allyl–(Ca,Sr,Ba) bond has never been structurally authenticated. By applying the methods of steric stabilization that allowed the isolation of a bis(pentadienyl)calcium compound,[6] we now describe the synthesis of the first crystallographically characterized bis(allyl)calcium complex.

In order to improve the solubility and crystallinity of the final compound, we selected 1,3-bis(trimethylsilyl)propene as the ligand precursor. This was converted into its lithium salt,[10] and then transmetalated with KO*t*Bu in hexane at room temperature to yield $K[C_3(SiMe_3)_2H_3]$ in quantitative yield. Reaction of slightly more than two equivalents of $K[C_3(SiMe_3)_2H_3]$ with CaI_2 in THF at −78°C produces the colorless complex $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$ in high yield. It has good solubility in THF and aromatic hydrocarbons. The ^1H NMR spectrum of the complex in [D$_8$]THF contains a singlet for the trimethylsilyl protons, a doublet at $\delta = 2.98$ ($^3J = 16$ Hz) corresponding to the protons on the carbon atoms adjacent to the $SiMe_3$ groups, and a triplet at $\delta = 6.87$ from the unique hydrogen atom on the center carbon atom. The spectrum is invariant from room temperature to

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[*] Prof. T. P. Hanusa, M. J. Harvey
Department of Chemistry
Vanderbilt University
Nashville, TN 37235 (USA)
Fax: (+1)615-322-4936
E-mail: t.hanusa@vanderbilt.edu

Dr. V. G. Young, Jr.
Department of Chemistry
University of Minnesota
Minneapolis, MN 55455 (USA)

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172(2) K, which suggests that the molecule is either nonfluxional or the rearrangements are of extremely low energy. Note that the C1 and C3 carbon atoms of [1,3-bis(trimethylsilyl)allyl]lithium are also magnetically equivalent to 170 K.[10] Below this temperature, some inequivalence appears in their ^{13}C NMR shifts, but isotopic perturbation experiments suggest this is the result of unsymmetrical solvation of the lithium cation, rather than asymmetric Li−C_3 bridging.

The solid-state structure of the bis(allyl)calcium compound was obtained on a colorless crystal slowly grown from a saturated THF/toluene solution.[11] The complex crystallizes as the disolvate $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$, with a crystallographically imposed C_2 axis through the calcium atom; only half the molecule is unique (Figure 1). Disorder that was found in one thf molecule was successfully resolved with a two-site model. The two allyl ligands are in an *anti* configuration, and the angle between the C_3 planes is 115.5°. The C−C bonds in the allyl ligand are essentially the same length at 1.402(4) Å (C1−C2) and 1.387(4) Å (C1−C3).

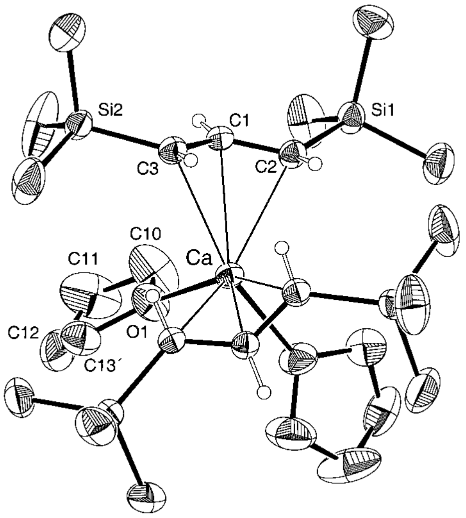

Figure 1. ORTEP plot of $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$. For clarity, the hydrogen atoms not directly bonded to the C_3 allyl fragment are not shown, and only one of the conformations of the thf ligands is depicted. Selected bond lengths [Å] and angles [°]: Ca−C2 2.648(3), Ca−C1 2.652(3), Ca−C3 2.662(3), Ca−O1 2.353(2), C1−C3 1.387(4), C1−C2 1.402(4); O1-Ca-O1′ 80.44(13), C3-C1-C2 129.8(3).

The allyl ligands are bound in a symmetrical η^3 manner to the metal, with an average Ca−C distance of 2.654(5) Å and a spread of only 0.014 Å. Such symmetrical bridging is not observed in allylmagnesium compounds,[12] but is similar to that found for Group 1 allyl complexes.[13] The allyl−Ca distance is indistinguishable from that for cyclopentadienyl rings in formally six-coordinate Ca^{II} centers (e.g., 2.64(2) Å in $[Ca(C_5Me_5)_2]$[14] and 2.67(2) Å in $[\{Ca[C_5(C_3H_7)_4H]I(thf)\}_2]$;[15] it is remarkable that a three-carbon ligand maintains the same separation. It should be noted that in transition metal $[(C_3R_nH_{5-n})MCp]$ complexes, the allyl ligand binds more closely to the metal than does the Cp ring.[16, 17]

The extent of interaction of the allyl group with the Ca^{II} center can be evaluated by several structural criteria. The C-C-C angle of 129.8(3)° is equivalent to the 130.3° angle predicted for free $[C_3(SiMe_3)_2H_3]^-$ from ab initio SCF calculations.[18] In contrast, the hydrogen atoms, which were successfully refined, clearly lie out of the plane of the allyl-carbon atoms: the C3-C1-C2-H2 torsion angle is 16.9°, that for C2-C1-C3-H3 is 16.2°, and the central C1−H1 bond is tipped toward the calcium atom, and forms an angle of 12.8° with the C_3 plane (Figure 2).

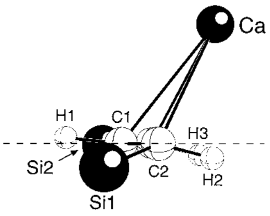

Figure 2. Hydrogen atom displacements in the allyl ligand of $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$. For clarity, the methyl groups have been removed from the silicon atoms, and a dotted line added in the plane of the allyl ligand.

Such hydrogen atom displacements are reminiscent of those calculated or found in other main group and transition metal allyl structures. In the almost completely ionic $[Cs(C_3H_5)]$, for example, the terminal hydrogen atoms are rotated by 24.1° out of the allyl plane, and the central hydrogen atom is tipped toward the cesium atom by 8.0°.[13] The same pattern is observed in the transition metal complex bis(η^3-allyl)nickel.[19] This atomic arrangement has been attributed to the relief of steric interaction between the metal and the allylic hydrogen atoms and to rehybridization of the allyl carbon atoms to improve metal−ligand bonding. Interestingly, the Si1 atom lies 0.38 Å out of the C_3 plane away from the calcium atom; the C3-C1-C2-Si1 torsion angle is 166.4°. The significance of this feature is difficult to interpret, as the Si2 atom is only 0.07 Å from the C_3 plane (C2-C1-C3-Si2 178.1°).

In summary, we have found that the allyl ligand in $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$ displays an intriguing mix of structural features, including a metal−allyl distance that is the same as that found for calcium cyclopentadienyl complexes, but hydrogen atom displacements that are typical of those in other main group and transition metal π-allyl compounds. The presence of the trimethylsilyl groups, although clearly beneficial in stabilizing the compound, limit the reactivity of the allyl anion. The synthesis of other, less sterically hindered, derivatives will be required to study the reactions of heavy Group 2 allyl complexes more fully.

Experimental Section

$[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$: CaI_2 (0.450 g, 1.53 mmol) was suspended in THF (100 mL) under nitrogen at −78 °C. A solution of $K[C_3(SiMe_3)_2H_3]$ (0.772 g, 3.44 mmol) in THF (50 mL) was added dropwise with stirring over 30 min. After being allowed to warm to room temperature overnight, the reaction mixture was stripped to dryness, and the residue extracted with toluene. The extract was filtered, evaporated to dryness, and the crude product recrystallized from toluene/THF. $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$ was obtained as air-sensitive colorless needles (0.78 g, 93 %), m.p. 130−131 °C. Elemental analysis calcd for $C_{26}H_{58}CaO_2Si_4$ (%): C 56.25, H 10.53; found C 54.59, H 10.26. The low value for carbon probably reflects the high air-sensitivity of the compound and/or partial loss of coordinated THF. For comparison the elemental analysis of $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)]$ (%): C 54.70, H, 10.43; ^1H NMR (300 MHz, $[D_8]$THF, 20 °C): $\delta = -0.05$ (s, 36 H, $Si(CH_3)_3$), 2.98 (d, 4 H, C2,C3-allyl-H; $^3J = 16$ Hz), 6.87 (t, 2 H, C1-allyl-H; $^3J = 16$ Hz); ^{13}C NMR (75.5 MHz, $[D_8]$THF, 20 °C): $\delta = 161$ (C2,C3-allyl), 76.8 (C1-allyl), 1.87 ($Si(CH_3)_3$); IR (KBr): $\tilde{\nu} = 2956$ (s, sh), 1595 (w), 1452 (w, br), 1249 (s, sh), 1009 (m, br), 984 (m), 863 (s), 839 (s) cm^{-1}.

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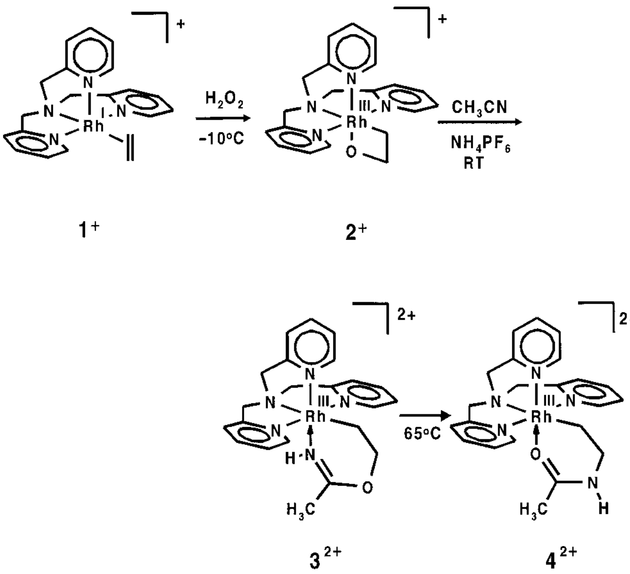
Amidation of $[Rh^I(ethene)]^+$ via a 2-Rhodaoxetane

Bas de Bruin, Mark J. Boerakker, René de Gelder, Jan M. M. Smits, and Anton W. Gal*

The formation of a C–N bond from an olefin and an amine or amide is a very desirable transformation.[1] A catalytic version of this reaction could be a valuable alternative to classical industrial preparations of amines or amides. However, the few catalytic examples reported so far for this reaction are either slow or limited in scope (specific substrate or intramolecular reaction).[2] Therefore, any new approach to formation of C–N bonds from olefins is of great interest. In this context we wish to report the two-step formation of a C–N bond from an olefin, with hydrogen peroxide and a nitrile (as an amide equivalent), via a 2-rhodaoxetane (1-oxa-2-rhodacyclobutane) complex.

Recently, we described the oxidation of $[(tpa)Rh^I(ethene)]^+$, **1**$^+$, (tpa = *N,N,N*-tri(2-pyridylmethyl)amine) with H_2O_2 to the 2-rhodaoxetane **2**$^+$ (Scheme 1).[3] The isolation of **2**$^+$ gave us the unique opportunity to study the reactivity of an unsubstituted 2-metallaoxetane.[4, 5] The 2-rhodaoxetane **2**$^+$ is stable in neat CH_3CN. However, addition of one mole of NH_4PF_6 per mole of **2**$^+$ to a solution of **2**·BPh_4 in CH_3CN at room temperature results in quantitative conversion into the dicationic imino ester **3**$^{2+}$ within four hours (Scheme 1). We



Scheme 1. Step-wise amidation of the Rh^I(ethene) complex **1**$^+$; oxidation with H_2O_2 to 2-rhodaoxetane **2**$^+$, formation of imino ester **3**$^{2+}$ by reaction with NH_4^+/MeCN, and thermal rearrangement to amide **4**$^{2+}$.

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[*] Prof. Dr. A. W. Gal, Dipl.-Chem. B. de Bruin, M. J. Boerakker,
Dr. R. de Gelder, J. M. M. Smits
Department of Inorganic Chemistry
University of Nijmegen
Toernooiveld 1, 6525 ED Nijmegen (Netherlands)
Fax: (+31)24-35534540
E-mail: gal@sci.kun.nl.

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