Organoberyllium Chemistry

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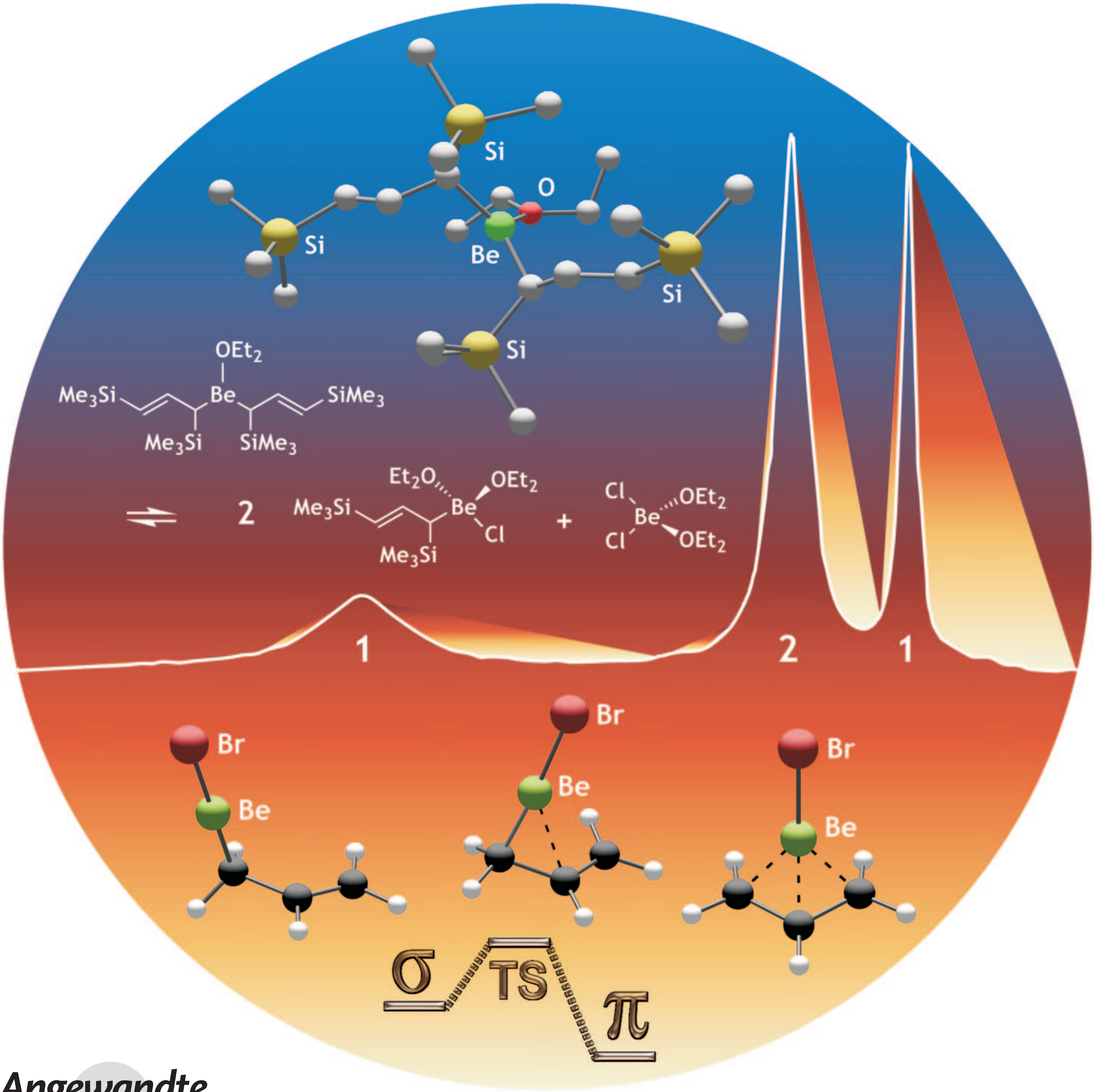
Bis(1,3-trimethylsilylallyl)beryllium**

Stephen C. Chmely, Timothy P. Hanusa, and William W. Brennessel*



Despite its being a member of the highly electropositive s-block elements, the large charge/radius ratio of beryllium insures that its compounds have considerable covalency.[1] A wide variety of ligand types has been incorporated into beryllium complexes, including alkyls,[2] alkynyls,[3] aryls,[4] amides,[5] thiolates,[5] arsenides,[6] carbenes,[7] trimethylsilyls,[8] tris(pyrazolyl)hydroborates,[9] and various types of substituted cyclopentadienyl ligands.[10] Di(allyl)beryllium and several adducts were reported by Wiegand and Thiele,[11] who prepared the parent compound from the reaction of diethylberyllium and tri(allyl)boron. The unsolvated product is virtually insoluble in hydrocarbon solvents, melts above 200 °C, and is presumably polymeric, although its structure has not been determined. It dissolves in THF, from which a disolvate $[Be(C_3H_5)_2(thf)_2]$, whose structure is also unknown, can be isolated.

Bulky allyl ligands[12] and those with pendant groups[13] have been used to suppress oligomerization and enhance solubility in a wide range of metal complexes. The chance to use such ligands in organoberyllium chemistry is appealing, especially as the reactivity of alkyl and aryl beryllium chlorides may depend on their state of aggregation in solution.[14] Herein we report the synthesis, solution behavior, and crystal structure of a base adduct of bis(1,3-trimethylsilylallyl)beryllium. We also describe computational investigations of the preferred bonding mode of allyl ligands to beryllium (that is, σ-bound (η^1) or π-bound (η^3)).

The colorless complex $[BeA'_2(Et_2O)]$ ($A' = [1,3\text{-}(SiMe_3)_2C_3H_3]^-$) was synthesized by the salt metathesis reaction of $BeCl_2$ and KA′ in Et_2O [Eq. (1)]. The product is highly air- and moisture-sensitive, and is extremely soluble in a wide range of solvents, from ethers to alkanes.

$$2\,KA' + BeCl_2 \xrightarrow[25\,^{\circ}C]{Et_2O} [BeA'_2(Et_2O)] + 2\,KCl \qquad (1)$$

Complexes of the type BeR_2 are good Lewis acids and form stable etherates,[15] and unlike the related magnesium complex $[MgA'_2(Et_2O)]$,[16] $[BeA'_2(Et_2O)]$ does not desolvate under vacuum. An attempt to use the azeotropic "toluene reflux" method[17] to remove the coordinated ether (8 h total time) was also unsuccessful. An effort was made to form an adduct with 2,2′-bipyridine by treating a suspension in ether of the colorless $[BeCl_2(bipy)]$[18] with KA′; the mixture immediately turned deep red, which is similar to the result from the reaction of bipy with $[Be(C_3H_5)_2(thf)_2]$.[11] Attempted removal of the solvent generated an insoluble brown solid and a deep green oil, the latter possibly containing $[Be(bipy)_2]$.[19]

Single crystals of $[BeA'_2(Et_2O)]$ were grown from hexane, and the complex was found to be monomeric in the solid state (Figure 1).[20] Each beryllium center is surrounded by two σ-coordinated allyl moieties and the oxygen of a diethyl ether molecule in a distorted, but nearly perfectly flat, trigonal planar environment (sum of angles around metal = 359.9°). This crystal structure is the first of an allyl beryllium complex.

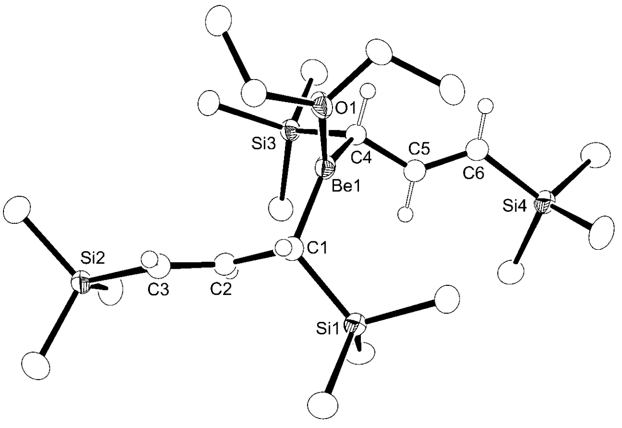


Figure 1. ORTEP of $[BeA'_2(Et_2O)]$. Thermal ellipsoids set at 50%; hydrogen atoms not on the C_3 framework of the allyl groups omitted for clarity. Selected bond distances [Å] and angles [°]: Be–C1 1.752(5), C1–C2 1.479(4), C2–C3 1.343(4), Be–C4 1.756(4), C4–C5 1.484(3), C5–C6 1.336(4), Be–O 1.661(4); C1-Be-C4 137.65(16), O-Be-C1 109.38(14), O-Be-C4 112.91(14).

The Be–C bonds of about 1.75 Å in length are similar to those observed in the three-coordinate *m*-terphenyl complexes $Ar^*BeX(OEt)_2$ ($Ar^* = 2,6\text{-}Mes_2C_6H_3$; $Mes = 2,4,6\text{-}Me_3C_6H_2$) of 1.740(6) Å (X = Cl) and 1.749(7) Å (X = Br), and in $BePh_2(OBu_2)$ (1.734(2) Å).[7b] The C1–C2/C2–C3 and C4–C5/C5–C6 bond lengths differ by 0.14 Å, and are strongly localized into single and double bonds. The Be–O bond (1.661(4) Å) is within the normal range for Be–O bonds (1.60–1.70 Å), and is comparable to that in $Mes_2Be(OEt_2)$ (1.638(5) Å)[4a] and $Ph_2Be(OBu_2)$ (1.647(2) Å).[7b]

As is the case for the σ-bonded complexes $[MgA'_2(Et_2O)]$[16] and $[GaA'_3]$,[21] the ^1H NMR spectrum of $[BeA'_2(Et_2O)]$ at room temperature presents a simple "π-like" pattern of an apparent singlet (from $SiMe_3$), a doublet, and a triplet (Figure 2). The compound is clearly fluxional in solution, however, and on cooling, the doublet from the terminal protons shifts downfield and eventually broadens into a singlet (by −50 °C); by −70 °C it almost disappears into the baseline, whereas the triplet from the central proton simply broadens and the $SiMe_3$ signal shifts but remains unsplit, suggesting that the exchange process involving σ/π fluxionality is of low energy.

Evidence for the persistence of a σ-bonded structure in solution is provided by IR and beryllium NMR spectroscopy

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[*] S. C. Chmely, Prof. T. P. Hanusa
Department of Chemistry, Vanderbilt University
Nashville, TN 37235 (USA)
Fax: (+1) 615-343-1234
E-mail: t.hanusa@vanderbilt.edu
Homepage: http://www.vanderbilt.edu/AnS/Chemistry/faculty/bio.php?ID=19
Dr. W. W. Brennessel
X-ray Crystallographic Facility, B51 Hutchison Hall
Department of Chemistry, University of Rochester
Rochester, NY 14627 (USA)

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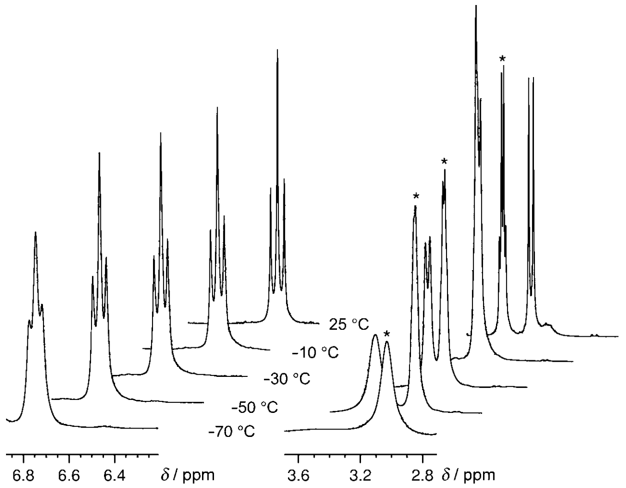
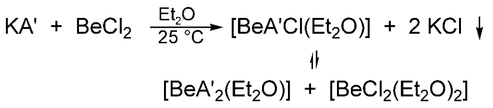


Figure 2. Variable-temperature ^{1}H NMR spectrum of the allyl protons of [BeA′$_2$(Et$_2$O)] in [D$_8$]toluene. An asterisk (*) marks the methylene resonance of the diethyl ether ligand. The vertical heights of the two regions are not to scale. For the complete spectra, see the Supporting Information.

measurements. A broad absorption at 1568 cm^{-1} is observed in an Et$_2$O solution for [BeA′$_2$(Et$_2$O)]; this value is close those of the double-bond stretching frequencies reported for σ-bonded diallyl magnesium and allyl magnesium bromide (1577 and 1588 cm^{-1}, respectively).[22] John and co-workers have tabulated ^{9}Be NMR chemical shift values that are diagnostic for coordination numbers in solution.[23] Typically, organoberyllium complexes with low formal coordination numbers, such as the diethyl etherate of dimethylberyllium (coordination number 3, $\delta = 20.8$ ppm in Et$_2$O), are observed well downfield of 0 ppm. [BeA′$_2$(Et$_2$O)] has a ^{9}Be chemical shift of $\delta = 18.2$ ppm, which is consistent with a three-coordinate geometry in solution. DFT investigations were used to predict the ^{9}Be chemical shift value of [BeA′$_2$(Et$_2$O)] with the method described by John (B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d)).[23] It was calculated at $\delta = 20.4$ ppm, which is in good agreement with the observed value.

There is evidence for a Schlenk-type equilibrium in the ^{9}Be NMR spectrum of the reaction between equimolar amounts of KA′ and BeCl$_2$ (Scheme 1). After the reaction is allowed to proceed for 1 h, three peaks are observed in the ^{9}Be NMR spectrum of the filtered reaction mixture; their shifts and assignments are listed in Table 1. The signal at $\delta = 18.4$ ppm almost matches that for [BeA′$_2$(Et$_2$O)] alone, and the signal assigned to [BeCl$_2$(Et$_2$O)$_2$] is close to the value reported for the isolated complex measured in Et$_2$O ($\delta = 3.1$ ppm).[24] It also has the narrowest width of the three resonances, a feature associated with four-coordinate beryllium structures of high symmetry.[23] To our knowledge, this is the first time a Schlenk equilibrium in organoberyllium compounds has been directly observed with ^{9}Be NMR spectroscopy.[25] The relative signal heights indicate that a statistical distribution of species exists, unlike the case with RBeX compounds containing less bulky R groups (such as Me, Ph), where the equilibrium lies toward the RBeX side.[2b]



Scheme 1. Schlenk equilibrium involving [BeA′$_2$(Et$_2$O)] and [BeCl$_2$(Et$_2$O)$_2$].

Table 1: NMR parameters for the products from the equimolar reaction of KA′ and BeCl$_2$ in Et$_2$O.

Compound	δ_{exp}[a]	Relative area	$w_{1/2}$ [Hz]
[BeCl$_2$(Et$_2$O)$_2$]	4.7	1	14.2
[A′BeCl(Et$_2$O)$_2$]	7.6	2	27.4
[BeA′$_2$(Et$_2$O)]	18.4	1	91.9

[a] Shifts in ppm from 1.0 M BeCl$_2$(aq).

We recently found that the almost universally observed σ-bonding in magnesium allyl compounds[13a] may be a consequence of the isolation of the compounds with coordinated ethers; in the absence of such bases, a π-bonded mode for the complexes is energetically favorable.[16] Whether the same situation applies to beryllium allyl compounds is not entirely clear, but π bonding would not normally be expected.[26] Wu et al., for example, determined that the minimum energy structure of [(C$_3$H$_5$)BeBr] at the MP2//HF level of theory contains a σ-bound allyl ligand.[27] However, John and co-workers computationally modeled the allyl ligand in the compound [(η^3-C$_3$H$_5$)BeAs(*t*-Bu)$_2$], and found that a π-bonded allyl group on beryllium was reasonable.[23]

We investigated this question for [(C$_3$H$_5$)BeH] at the BB1K/aug-cc-pVTZ level of theory,[28] and found that both σ- and π-bonded modes were minima ($N_{\text{imag}} = 0$) on the potential energy surface, with the π-bonded species 3.3 kcal mol^{-1} ($\Delta G°$) below the energy of the σ-bonded form (Figure 3). The major change in moving to the transition state is a rotation of the BeH unit over the center of the allyl unit. The activation barrier to the transition geometry ($\nu_{\text{imag}} = -71.5$ cm^{-1}) is only 0.84 kcal mol^{-1} above the σ-bonded form, which is consistent with facile $\eta^1 \rightleftarrows \eta^3$ equilibria in solution. The same pattern is found for [(C$_3$H$_5$)BeBr] using DFT methods, but the higher electronegativity of bromine

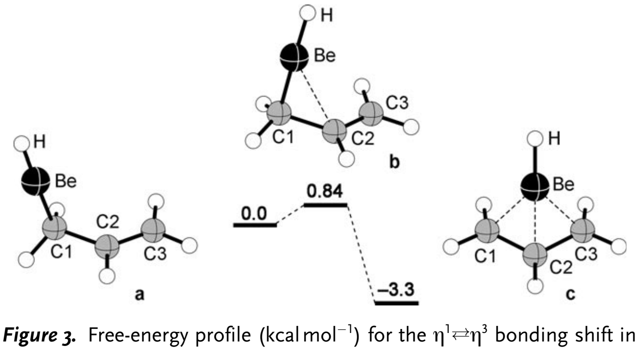


Figure 3. Free-energy profile (kcal mol^{-1}) for the $\eta^1 \rightleftarrows \eta^3$ bonding shift in [(C$_3$H$_5$)BeH]. Selected bond lengths [Å] and angles [°]: a) Be–C1 1.681, C1–C2 1.484, C2–C3 1.323; Be-C1-C2 107.5; b) Be–C1 1.677, Be⋯C2 2.311, C1–C2 1.482; C2–C3 1.328; Be-C1-C2 93.8; c) (C_s) Be–C1 1.839, Be–C2 1.821, C1–C2 1.390, Be-C1-C2 67.0.

favors the σ-bonded form to a greater extent, so that the π-bonded form is only 1.2 kcal mol^{-1} ($\Delta G°$) more stable. The activation barrier to the transition geometry ($\nu_{imag} = -97.5$ cm^{-1}) is 1.7 kcal mol^{-1} above the σ-bonded form.

Additional DFT investigations were performed on a set of allyl complexes related to [BeA$'_2$(Et$_2$O)]. Silyl substitution has been shown to be a good compromise between unsubstituted and bis(trimethylsilylated) allyl compounds in terms of computational time and accuracy,[16] and was employed for geometry optimizations with the B3PW91 functional and the aug-cc-pVDZ basis set for all atoms. The optimized geometries of these molecules are shown in Figure 4.

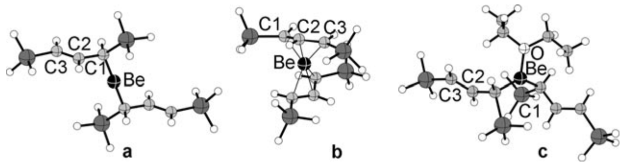


Figure 4. The optimized geometries of [Be(1,3-(SiH$_3$)$_2$C$_3$H$_3$)$_2$] showing both σ- (a) and π-type (b) bonding of the allyl moieties, and the effect of adding a single molecule of Et$_2$O (c). Selected bond lengths [Å]: a) (C_i) Be–C1 1.684, C1–C2 1.496, C2–C3 1.349; b) (C_2) Be–C1 1.858, Be–C2 1.828, Be–C3 1.985, C1–C2 1.429, C2–C3 1.401; c) Be–O 1.698, Be–C1 1.757, C1–C2 1.485, C2–C3 1.335.

Unlike the case with the magnesium counterpart,[16] but like the [(C$_3$H$_5$)BeX] species studied above, both σ- (with C_i symmetry, Figure 3 a) and π-bound (with C_2 symmetry, Figure 3 b) structures of [Be(1,3-(SiH$_3$)$_2$C$_3$H$_3$)$_2$] are local minima on the potential energy surface; $\Delta G°$ is lower for the π-bound structure by 4.0 kcal mol^{-1}. The σ-bound structure has distinctly localized C−C/C=C bonds, but the C1−C2 and C2−C3 bonds (1.429 and 1.401 Å, respectively) in the C_2 structure indicate that considerable delocalization of the π electrons has occurred. The Be−C1 and Be−C2 bonds (1.858 Å and 1.828 Å, respectively) are within bonding distance (cf. the average Be−C distance in the π-bound ring of beryllocene of 1.92 Å[11b]); Be−C3 is slightly longer (1.985 Å). As with the case of [Mg(π-C$_3$H$_5$)$_2$], it is probably appropriate to view the bonding as being "slipped-π".[16]

DFT methods were also used to model the effect of solvation on [Be(1,3-(SiH$_3$)$_2$C$_3$H$_3$)$_2$]. Successive addition of THF molecules to the calculated π-bound allyl magnesium structure causes slipping of first one and then both of the allyl moieties to a σ-bound form.[16] In contrast, addition of a single Et$_2$O to the π-bound structure of [Be(1,3-(SiH$_3$)$_2$C$_3$H$_3$)$_2$] causes a simultaneous slip of both allyl moieties to a σ-bonding mode (Figure 4 c), which is consistent with the solid-state structure of [BeA$'_2$(Et$_2$O)]. Although this shift may be partially driven by steric effects, we find the same effect with the calculated structure of the less-crowded compound [Be(σ-C$_3$H$_5$)$_2$(Me$_2$O)], so that electronic influences of the coordinated bases are likely to be involved as well.

In summary, we have provided the first structural authentication of a σ-bound allyl beryllium complex. The molecule is fluxional in solution, and the rearrangements are facile. Furthermore, the first spectroscopic evidence using ^{9}Be NMR spectroscopy of a Schlenk-type equilibrium for an organoberyllium complex has been obtained. A series of DFT experiments suggest that a beryllium complex that contains π-bound allyl groups is not only possible but energetically favorable in the absence of coordinated bases; π-bonded allyl groups are thus reasonable for the entire set of Group 2 elements, from beryllium to barium.[29]

Experimental Section

The syntheses and manipulations described below were conducted with rigorous exclusion of air and moisture using high vacuum, Schlenk, or glovebox techniques. **CAUTION!** Beryllium salts are extremely toxic and should be handled with appropriate care. [BeA$'_2$(Et$_2$O)]: A solution of KA′ (448.7 mg, 2.0 mmol) in Et$_2$O was added to a stirred solution of BeCl$_2$ (79.9 mg, 1.0 mmol) in Et$_2$O at room temperature. After 2 h of stirring, all volatiles were removed under vacuum and the remaining residue was extracted over a medium porosity frit with hexane. The filtrate was collected, and all volatiles were removed under high vacuum over 18 h to afford a viscous, colorless oil (0.346 g, 77 % yield). Large, colorless, air-sensitive blocks suitable for X-ray diffraction of [BeA$'_2$(Et$_2$O)] were obtained from a concentrated hexane solution of the above at −10 °C. Elemental analysis (%) calcd for C$_{22}$H$_{52}$BeOSi$_4$ (454.01): Be 1.99; found: Be 1.56. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): $\delta = 0.23$ (s, 36 H, Si(CH_3)$_3$), 3.33 (d, 4 H, C1,C3-allyl-H, $^4J = 15$ Hz), 6.53 (t, 2 H, C2-allyl-H, $^3J = 15$ Hz), 0.79 (t, 6 H, (CH_3CH$_2$)$_2$O, $^3J = 7.1$ Hz), 3.40 ppm (q, 4 H, (CH$_3$CH_2)$_2$O, $^3J = 7.0$ Hz). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, 298 K): $\delta = 0.44$ (s, Si(CH$_3$)$_3$), 13.9 (s, (CH$_3$$CH_2$)$_2$O), 31.9 (s, C1,C3-allyl-C), 68.5 (s, (CH$_3$CH$_2$)$_2$O), 153.8 ppm (s, C2-allyl). ^{9}Be NMR (56.2 MHz, C$_6$D$_6$, 298 K): $\delta = 18.2$ ppm. IR (Et$_2$O): 1568 cm^{-1} ($\nu_{C=C}$).

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Keywords: allyl ligands · beryllium · coordination modes · density functional calculations · σ interactions

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[19] The ^{1}H NMR spectrum contains several broad peaks, which is consistent with the paramagnetism of the bipy complex. See Ref. [18].

[20] Crystallographic data for [Be{1,3-(SiMe$_3$)C$_3$H$_3$}$_2$(Et$_2$O)]: C$_{22}$H$_{52}$BeOSi$_4$, $M_r = 454.01$, $T = 100(1)$ K, crystal size $0.34 \times 0.30 \times 0.24$ mm^3, MoKα radiation ($\lambda = 0.71073$ Å), $\mu = 0.204$ mm^{-1}; triclinic, $P\bar{1}$; $a = 9.6404(17)$, $b = 11.642(2)$, $c = 16.030(3)$ Å; $\alpha = 107.290(3)$, $\beta = 107.290(3)$, $\gamma = 107.290(3)°$; $V = 1529.0(5)$ Å^3; $Z = 2$; $\rho_{calcd} = 0.986$ Mg m^{-3}; $2\theta_{max} = 66.28°$; 29095 reflections collected, 11568 independent ($R_{int} = 0.0679$); final $R_1 = 0.0461$, $wR_2 = 0.0868$ ($I > 2\sigma(I)$), GoF = 0.949, $\rho_{max} = 0.467$; $\rho_{min} = -0.442$ e Å^{-3}. CCDC 770345 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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