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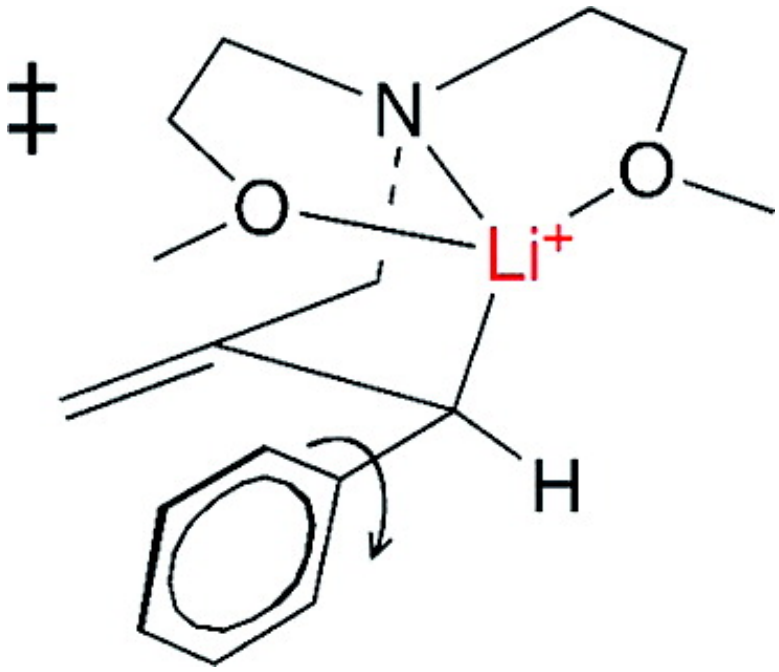

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Arylallylic Lithium Compounds, Internally versus Externally Coordinated: Comparison of Their Structures and Dynamic Behavior via X-ray Crystallography and NMR

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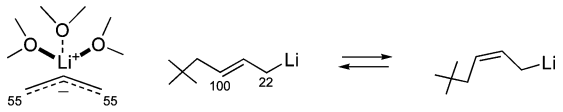
Abstract: A comparison of externally coordinated arylallyllithiums with internally coordinated arylallyllithiums using a combination of X-ray and NMR studies shows that 2-bis(2-methoxyethyl)aminomethyl-1-phenylallyllithium **7**, and 2-bis(2-methoxyethyl)aminomethyl-1,3-diphenylallyllithi um **8**, are indeed fully internally coordinated with all phenyls endo, and lithium is close to one terminal allyl carbon. By contrast, among the externally coordinated analogs 1-phenylallyl-lithium.$(HMPT)_4$ **5**, and 1-phenylallyllithium.(THF) **6**, both phenyls are exo and the proximity of lithium to anion was only detected in compound **6**. Lithium-7 NMR clearly identifies the $Li(HMPT)_4^+$ complex in **5**, whereas a $^7Li\{^1H\}$ HOESY experiment reveals ^7Li to be coordinated to THF in **6** and close to the Ph**C** terminal allyl carbon. Carbon-13 NMR shows that all of the above compounds are fully delocalized despite differences among the sites of lithium and their separations from the anions. Changes in the ^{13}C NMR line shapes show that the diphenyl compound **8** undergoes a very fast 1,3-lithium sigmatropic shift, and all of the phenyls in the above compounds undergo fast rotation around their phenyl $C_{ipso}-C_{allyl}$ bonds. Barriers to rotation, $\Delta H^{\ddagger}$ from NMR line shapes for **5**, **6**, **7**, and **8** respectively, are 19.8, 14.6, 10.2, and 8.9 kcal·mol^{-1}. The decrease in barriers is clearly correlated with a decrease in separation of lithium from an allyl terminal carbon and implies that especially among the latter three, **6**, **7**, and **8**, lithium is involved in the mechanism for phenyl rotation. This question is discussed.

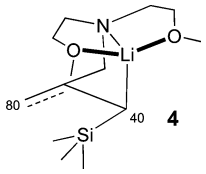
Introduction

As shown via NMR and X-ray crystallography, externally coordinated allylithium, **1**, with selected ^{13}C shifts, is delocalized with coordinated lithium normal to the center of the allyl plane.[1,2]



1 **2** **3**

By contrast *unsolvated* allylic lithium compounds such as **2** ⇄ **3** may be considered to be largely localized because their NMR spectra so closely resemble those of alkenes.[3] Until not long ago, there were no reports of species whose degrees of delocalization lie between those of **1** and the system **2** ⇄ **3**. However, we have since uncovered such species. They are allylic lithium compounds with tethered potential ligands for Li^+, see for example **4**, shown with terminal allyl ^{13}C shifts.



4

NMR and X-ray crystallography confirmed internal coordination of Li^+ and partial delocalization of the allyl moiety. We proposed that the ligand tether is too short to site lithium normal to the center of the allyl plane as in **1**. Instead, it places lithium near normal to the allyl plane at one of the allyl termini. From this aberant site, lithium polarizes the allyl anion to be partly delocalized.[4] It would appear that the *electronic structure* of a nominally delocalized carbanion may be *influenced by the relative orientation of the carbanion with respect to counterion*, which is Li^+ in this case. We call this effect Site Specific Electrostatic Perturbation Of Conjugation, SSEPOC. We have shown how this effect depends on the length of the ligand tether and the ligand structure.[4] One can imagine that alkyl substitution

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might enhance localization, while conjugating substituents would stabilize delocalized carbanionic species. In this work, we report the extent of SSEPOC in the case of internally coordinated arylallyl lithium compounds. Two examples are considered. Results for each will be compared to those for its corresponding externally coordinated analog.

It will be shown that while the externally and internally solvated arylallyllithiums may be regarded as essentially delocalized, internal solvation determines the stereochemistry of phenyl and has profound effects on dynamic behavior of these compounds.

Results and Discussion

Results of our NMR studies of externally coordinated phenylallyllithiums **5** and **6** and internally coordinated species **6** and **7** are conveniently summarized in Table 1.

Compounds **5** and **6** were prepared by metalation of allyl benzene, see **9** → **6** → **5**. Compound **12**, the immediate precursor of **7**, came from the interconversions **10** → **11** → **12**. Compound **16**, the precursor of **8**, was produced by the sequence **13** → **14** → **15** → **16**. Finally, metalation of **12** and **16** produced **7** and **8**, respectively.

Below, we first describe the results of structural studies followed by a comparison of the dynamic rotation behavior among all compounds studied.

The X-ray crystallography of **7** (see the ORTEP plot in Figure 1) establishes that phenyl is endo and lithium is localized near C3 of allyl and is also fully coordinated to both methoxy oxygens and nitrogen of the pendant ligand as well as to oxygen of one THF molecule, see Figure 1 for numbering. Lithium is nearly centered and coplanar with respect to the two methoxy oxygens and C3. The oxygen of THF and nitrogen lie on opposite sides of the latter plane and are nearly colinear with lithium, Figure 2.

The allyl bonds of **7** are of different lengths with C2−C3 at 1.432(2) Å, being significantly longer than that of C2−C4 at 1.357(3) Å, which implies a greater π contribution to the C2−C4 bond versus theC2-C3 bond due to the proximity of Li to C3.

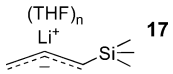
Lithium lies off the axis normal to the allyl plane at C3 with a torsional angle C1−C2−C3−Li of 55.64(16)°. Interestingly, the phenyl plane is twisted anticlockwise with respect to the allyl plane, see arrow on **7**, with the torsional angle C2−C3−C5−C6 being −17.8(3)°.

The solution NMR data for **7** are consistent with its X-ray structure. Thus, a ^{7}Li {^{1}H} HOESY[5] experiment shows a strong interaction between ^{7}Li and C3**H**, as well as with protons on the methoxy methyls. A NOESY experiment reveals proximity of the allyl methylene proton at 3.776 δ to the phenyl ortho and meta protons at, respectively, 6.170 δ and 6.092 δ. This result assigns the allyl methylene proton of **7** in solution at 3.776 δ as endo with phenyl also endo as in the X-ray structure. To compare the influence of internal coordination in **7** to that of external coordination on the structure of 1-phenyl-allyllithium, we have reinvestigated externally solvated **5** and **6**.

The ^{13}C shifts we obtained for **5** and **6** are closely similar to those reported by Ahlbrecht[6] and Schlosser.[7] Lithium-7 NMR at 140 K of 1-phenylallyllithium, prepared with four equiv of HMPT[8] in THF solution, consists of an equally spaced 1:4:6:4:1 quintet. With increasing temperature, this multiplet progressively averages to a single line by 170 K. These observations establish that lithium is complexed to four HMPTs[8] with ^{2}J (^{7}Li, ^{31}P) = 7.7 Hz and that the system undergoes a fast intermolecular Li^{+}, HMPT coordination exchange by 170 K.[9]

The two previous reports on NMR of **5** and **6** describe these preparations as incorporating *exo*-phenyl,[6,7] without supporting evidence. Our measurement of the *C*2**H**, C3**H** vicinal coupling constant of 12 Hz puts it half way between the cis and trans vicinal coupling constants connecting the allyl methylene hydrogens with the central *C*2**H** hydrogen of respectively 9 and 15 Hz. Neither of our preparations of **5** and **6** exhibited NOESY interactions between either of the allyl methylene protons and aromatic protons. By contrast, as noted above, the allylic methylene proton in **7** at 3.776 δ shows a strong NOESY interaction with aromatic protons. The latter allyl proton is significantly deshielded compared to the allyl methylene proton shifts in **5** and **6**, due to its proximity to the *endo*-phenyl in **7**. Taken together, these observations place phenyl exo in **5** and **6**.

Given the clear differences in solvation of Li^{+} in **5**, **6**, and **7**, it is interesting that all three species exhibit similar allyl ^{13}C shifts, see the structures with shifts in Table 1. From the magnitude of these shifts, it would appear that all three compounds incorporate delocalized anions despite the proximity of Li^{+} to C3 in **7** and the clear separation of lithium in Li(HMPT)$_4^{+}$ from the allylic anion in **5**. By contrast, while externally coordinated **17** is clearly fully delocalized[9] its internally coordinated analog **4** was shown to be partly localized due to the abberant site of Li^{+} in **4** compared to that in **17**.



17

Thus, while SSEPOC is significant in **4**, aryl−allyl conjugation renders the effect relatively unimportant in **7**.

The X-ray crystal structure of **8** reveals that lithium is fully coordinated to the tethered ligand, one terminal allyl carbon, and to oxygen of one THF, see the Ortep plot in Figure 3. Both methoxy oxygens and one terminal allyl carbon are near coplanar with centered lithium. Nitrogen lies nearly normal to the latter plane with oxygen of THF on the opposite side. Interestingly, structures **7** and **8** are very similar.

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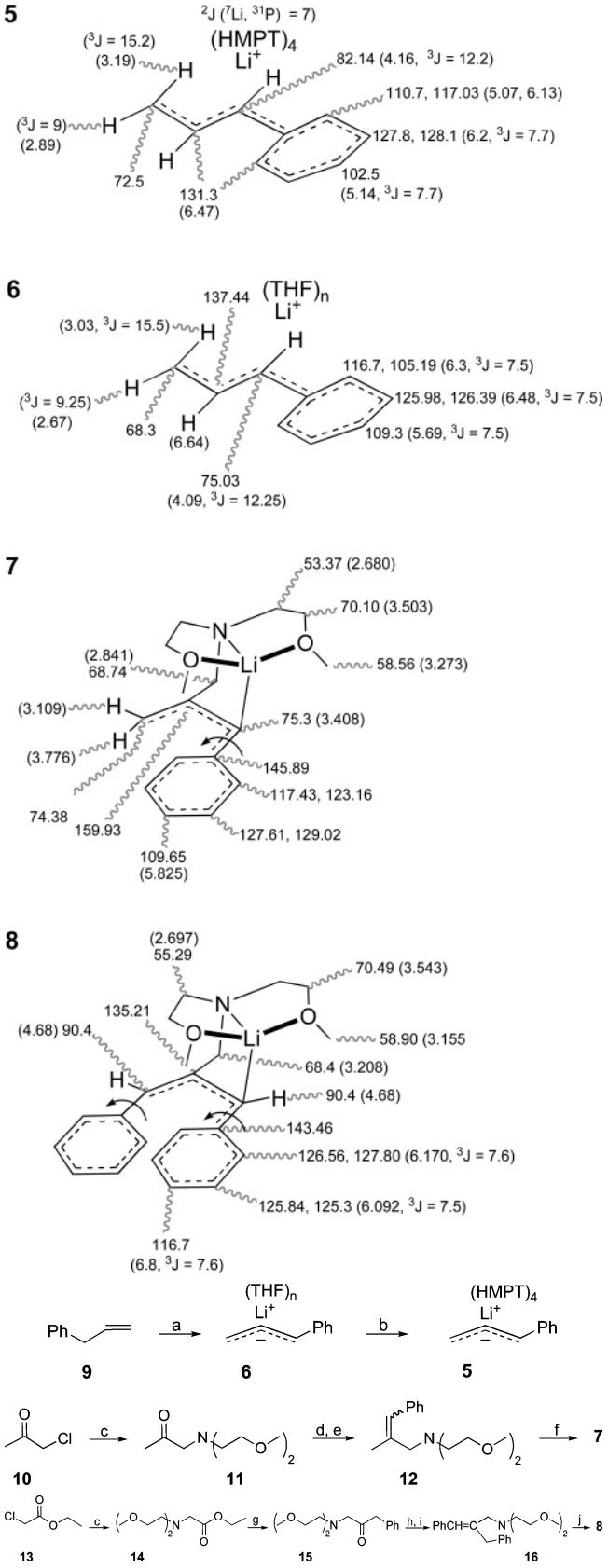
Table 1. Compounds **5**, **6**, **7** and **8**. Proposed Structures with ^{13}C and (^{1}H) Chemical Shifts, δ Scale, J in Hz



[a] n-BuLi, hexanes, THF, −10 °C. [b] HMPT. [c] $(CH_3OCH_2CH_2)_2NH$. [d] NaH, DMSO, 24h ↑↓. [e] $Ph_3P^+CH_2Ph\ Cl^-$ 0 °C. [f] n-BuLi, Et_2O, hexanes. [g] $PhCh_2MgCl$, THF, −10 °C. [h] NaH, DMSO, 80 °C. [i] $Ph_3P^+CH_2Ph\ Cl^-$, RT. [j] n-BuLi, Et_2O.

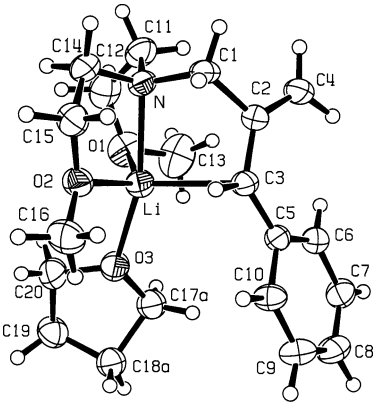


Figure 1. ORTEP diagram of compound **7**. Selected bond distances, Å and angles °: C2−C3 1.432(2), C2−C4 1.357(3), C3−Li 2.359(4), C4−C2−C3 130.69(17), C1−C2−C3−Li 55.64(16), C2−C3−C5−C6−17.8-(3).

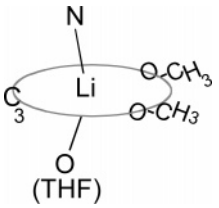


Figure 2. Coordination arrangement around lithium in **7**.

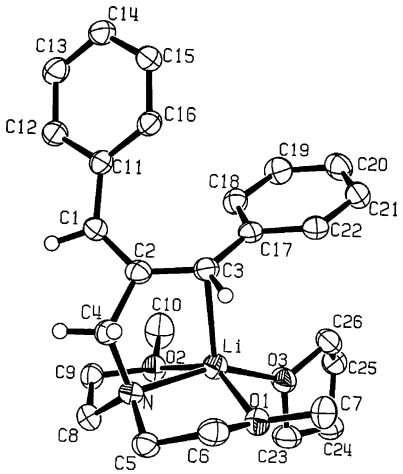
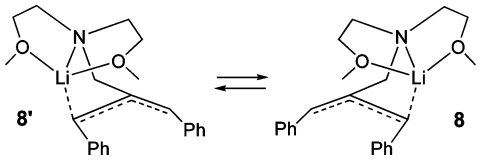


Figure 3. ORTEP diagram of compound **8**. Most hydrogen atoms have been removed for clarity; selected bond distances, Å and angles °: C1−C2 1.382(2), C2−C3 1.416(2), Li−C3 2.370(3), C1−C2−C3 130.92(12), C4−C2−C3−Li 54.92(12), C2−C3−C17−C18−15.3(2), C2−C1−C11−C16−14.8(2).

Both phenyls in **8** are endo with each phenyl rotated with respect to the allyl plane by −15.3(2)° (C2−C3−C17−C18) and −14.8(2)° (C2−C1−C11−C16) at C3 and C1, respectively. See arrows on the structure in Table 1. Lithium is closest to one allyl terminus, C3 with the C4−C2−C3−Li torsional angle of 54.92(12)° (Ortep numbering). Due to the proximity of Li^+ to one terminal allyl carbon C3, the C2−C3 bond of 1.416-(2)Å is slightly longer than the C1−C2 bond of 1.382(2)Å.

The solution NMR data for **8** are consistent with the X-ray crystallographic structure and also reveal some interesting dynamic effects. Thus, the single narrow resonance at 90.4 δ, observed at 290 K and assigned to both terminal allyl carbons,

broadens with decreasing temperature and disappears into the baseline by 180 K. This is most likely the result of a fast lithium 1,3 sigmatropic shift which effectively inverts the configuration, see eq 1.



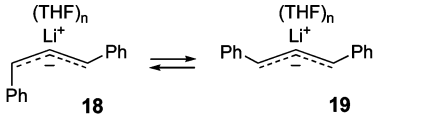
(1)

Similar effects have been observed among other internally coordinated allylic lithium compounds that are symmetrically substituted as well as unsubstituted.[4]

A ^{7}Li {^{1}H} HOESY experiment at 300 K of **8** shows strong interactions of ^{7}Li with both terminal allyl C**H**'s and to the hydrogens of both methoxyl methyls. This confirms that the X-ray structure also prevails in solution.

The structure and behavior of internally coordinated 1,3-diphenylallyllithium **8**, is entirely different from its externally solvated analogs. Thus, in Hoppe's X-ray structure of 1,3-diphenylallyllithium·sparteine, both phenyls are exo and are coplanar with the allyl framework, and the C−C allyl bond lengths, at 1.380 Å and 1.392 Å, are almost the same.[10] This implies that the latter structure is slightly more delocalized than **8**.

In addition, Boche's solution NMR studies of 1,3-diphenylallyllithium show it to consist of an equilibrium mixture of interconverting isomers 1,3-endo, exo-**18**, and 1,3-exo, exo-**19**, see eq 2, with the latter predominating at lower temperatures.[11]



(2)

ΔH^{o} = -1.57
ΔS^{o} = +12

$\Delta H^{\ddagger}$ = 17.3 ± 1 kcal•mol^{-1}
$\Delta S^{\ddagger}$ = +2 ± 3 eu

Analysis of changes among the proton NMR line shapes provided the thermodynamic and activation parameters for the **18** ⇄ **19** interconversion. These are listed below (eq 2).

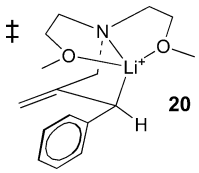
The aromatic ^{13}C NMR line shapes of compounds **5**, **6**, **7**, and **8** undergo changes with temperature reflective of the dynamics of rotation of phenyls with respect to the allyl planes. Thus, at low temperature, the ^{13}C NMR of the ortho and meta carbons of **5**, **6**, and **7** each give rise to a 1:1 doublet, whereas resonances for the ipso and para carbons consist of a single sharp line each. With increasing temperature above 200 K, the latter doublets progressively average to single lines at their respective centers, the ipso and para resonances remaining unchanged. Line shape analysis provides the activation parameters for phenyl rotation listed in Table 2.

In the case of **8** at 200 K, both phenyls together give rise to two 1:1 ^{13}C NMR doublets, one for the ortho carbons and a second one for the meta carbons, the result of slow rotation of phenyls under conditions of the fast 1,3-sigmatropic shift which averages the individual ortho and meta carbon shifts of the two phenyls. With increasing temperature, the two latter doublets average to single lines at their respective centers. Activation parameters for overall rotation of both phenyls are listed in Table 2.

Table 2. Activation Parameters for Phenyl Rotation

cpd	$\Delta H^{\ddagger}$ kcal•mol^{-1}	$\Delta S^{\ddagger}$ eu
5	19.8 ± 1.5	+22.7 ± 4
6	14.6 ± 1.0	+11.7 ± 2
7	10.2 ± 0.8	−2.5 ± 0.5
8	8.9 ± 0.7	−8.4 ± 1.5

Inspection of Table 2 reveals that decrease of the $\Delta H^{\ddagger}$ values for phenyl rotation follows increasing proximity of Li^{+} to the carbanion in the order **5**, **6**, **7**, and **8**, where in the last two structures, the **L**i−**C**$_3$(−Ph) separations are similar. This implies that lithium participates in the mechanism of phenyl rotation at least for **6**, **7**, and **8**. Such an effect would be minimal in the case of **5** due to the large separation of lithium in Li(HMPT)$_4^{+}$ from the carbanion. Thus, the barrier to phenyl rotation in **5** should be regarded as that of a carbanion that is well-separated from and unperturbed by lithium. By contrast, in the case of **6**, **7**, and **8**, the proximity of Li^{+} to phenyl bound allyl carbon may well facilitate phenyl rotation. Thus, we propose that developing increase in the Li....C$_\alpha$ covalency would promote tetrahedral stereochemistry at C$_\alpha$, thus decoupling the conjugation between phenyl and allyl. This would provide a lower energy path to phenyl rotation in **6**, **7** and **8** compared to the "free" anion in **5**. In this model phenyl rotation in **6**, **7**, and **8** is chemically driven. An illustration depicting the proposed transition state for phenyl rotation in **7** is shown as **20**.



Transition states for phenyl rotation such as **20** should also apply to **8** and, to a lesser extent, to externally coordinated **6**. The latter also showed proximity of Li^{+} to carbon bound phenyl.

Similar transition states to **20** have been proposed in studies of rotation of allyllithium[12] and of benzylic lithium compounds.[13]

Concluding Remarks

NMR and crystallographic studies of a variety of arylallyllithiums, both internally coordinated **7** and **8**, and externally coordinated **5** and **6**, and of the published equilibrium system **18** and **19** show all to be substantially delocalized despite wide variations in the separations of lithium from the anions. All phenyls within internally coordinated **7** and **8** are endo, whereas external coordination of **5** and **6** largely favors the exo phenyl structure. Endo stereochemistry minimizes repulsion between the pendant ligand and the substituent phenyl, whereas allyl delocalization is common among **5**, **6**, **7**, and **8**, their dynamic

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behavior varies substantially. Thus, their barriers to phenyl rotation in **5**, **6**, **7**, and **8** around their $C_{ipso}-C_{allyl}$ bonds decrease substantially with decreasing separation of lithium from the C-phenyl carbon, see Table 2. It is concluded that at least for **6**, **7**, and **8**, which may be regarded as contact ion pairs, lithium is involved in the mechanism for phenyl rotation. The barrier in **5** is ascribed as that of the anion since the $Li(HMPT)_4^+$ complex keeps the Li^+ and the anion well-separated.

Compound **8** is also subject to an unusually rapid 1,3-lithium sigmatropic shift, which averages the ^{13}C shifts of the terminal allyl carbons, even at low temperature.

Experimental Section

1-Phenylallyllithium·(HMPT)$_4$, 5. An NMR tube was flame-dried under vacuum and then charged with 1-phenylallyllithium THF complex (40 mg) under argon. After that, the NMR tube was cooled to −100 °C. Then, HMPT (107.52 mg) was added before it was transferred to a high vacuum line (10^{-6} Torr) trapped with liquid nitrogen. Volatile impurities were pumped out into a liquid nitrogen trap. After 3 h, THF-d_8 (0.5 mL) was vacuum transferred into the NMR tube cooled by a liquid nitrogen bath. Under high vacuum, the NMR tube was sealed with a small hot flame. The ratio of allyl·Li/HMPT was 1/5.5. NMR data are summarized in Table 1.

1-Phenylallyllithium·(THF)$_8$, 6. To a solution of 1-phenylpropene (709 mg, 6.0 mmol) in 6 mL of THF was added a solution of *n*-butyllithium in hexanes (4.06 mL, 1.6 M, 6.5 mmol) at −10 °C. The mixture was stirred at room temperature for 24 h and was then cooled to −78 °C. Then solvent was removed in vacuum to give a gel-like material. Pentane (7 mL) was added, and the mixture was stirred for 2 h. The mixture was then cooled to −78 °C, and the solvent was removed with a syringe. After that, a 7-mL portion of pentane was added with stirring until a yellow solid formed. The solvent was removed, and the yellow solid was washed three times with 6 mL pentane. An NMR tube was flame-dried under vacuum and then charged with 40 mg product before it was transferred to a high vacuum line (10^{-6} Torr) trapped with liquid nitrogen. Volatile impurities were pumped out into a liquid nitrogen trap. After 3 h, THF-d_8 (0.5 mL) was vacuum transferred into the NMR tube cooled by a liquid nitrogen bath. Under high vacuum, the NMR tube was sealed with a small hot flame. NMR data are summarized in Table 1.

2-(Bis(2-methoxyethyl))aminomethyl)-1-phenylallyllithium, 7. A 25-mL Schlenk tube was charged with 3 mL dry diethyl ether and compound **12** (394.5 mg, 1.5 mmol). After cooling to −78 °C *n*-butyllithium (0.94 mL, 1.6 M in hexanes, 1.5 mmol) was added by syringe. A red solid formed immediately. After warming the mixture to rt, 3 mL THF was added. The solution was stirred at rt for 2 h. Solvent was removed under vacuum, and the residue was recrystallized from ether/THF to give a red solid. An NMR tube was flamed out under argon and loaded with 54 mg of the title compound. Volatile components were removed under high vacuum. After pumping for 3 h, 0.5 mL THF-d_8 was vacuum transferred into the NMR tube, and the latter was sealed off with a small hot flame while frozen and under vacuum. NMR data are summarized in Table 1.

2-(Bis(2-methoxyethyl)aminomethyl)-1,3-diphenylallyllithium, 8. Butyllithium (1.01 mL, 1.6 M, 1.62 mmol) in hexane was syringed into a 20-mL Schlenk tube previously charged with 3 mL diethyl ether and **16** (0.55 g, 1.62 mmol) cooled to −78 °C, all under an atmosphere of argon. The solution was stirred at rt for 2 h. Solvent was removed in vacuo to yield a red solid, the title compound, which was then recrystallized from diethyl ether/THF. An NMR tube loaded with 69 mg of **8** was transferred to a high vacuum line and volatile impurities were pumped at 10^{-6} Torr, over 3 h, into a trap cooled with liquid nitrogen. Then, THF-d_8 was vacuum transferred into the NMR tube, which was then sealed off under high vacuum. NMR data are summarized in Table 1.

Bis(2-methoxyethyl)aminoacetone, 11. A mixture of chloroacetone (18.5 g, 0.2 mol) bis(2-methoxyethyl)amine (26.7 g, −0.2 mol) triethylamine (40.4 g, 0.4 mol) and 100 mL acetone was refluxed for 4 h. The solvent was removed in vacuum, and the residue was treated with 200 mL water which was extracted with chloroform three times (150 mL × 3). The combined organic phase was dried with $MgSO_4$. The solvent was removed in vacuum and the residue was distilled bp 65 °C− 68 °C/10 Torr, to give 32 g of the title compound in 85.7% yield. ^1H NMR, $CDCl_3$: 3.332 (t, 4H, $(OCH_2)_2$), 3.184 (s, 6H, $(OCH_3)_2$), 2.720 (t, 4H, $(NCH_2CH_2O)_2$), 1.98 (s, $CH_3C{=}O$). ^{13}C NMR: 208.91, 71.92, 66.11, 58.92, 54.03, 27.43.

3-(Bis(2-methoxyethyl)amino)-2-methyl-1-phenylpropene, 12. Sodium hydride (1.8 g (60% in mineral oil), 0.05 mol) was introduced into 50 mL DMSO and the mixture was heated to 80 °C for 1 h. After cooling, the resulting solution with an ice bath, a suspension of triphenylbenzylphosphonium chloride (17.5 g, 0.045 mol) in 120 mL THF was added, and the mixture was stirred for 1.5 h at rt. Then, under an argon atmosphere, to this mixture was added bis(2-methoxyethyl)-amionacetone and the mixture was refluxed for 24 h. The THF was removed under vacuum, and 40 mL of water was added. This mixture was extracted three times with 50 mL ether. The combined organic phases were washed once with brine and dried with $MgSO_4$. After removal of solvent, the residue was distilled bp (117−121 °C/0.6 Torr), giving 6.3 g of the title compound with $Z/E = 1/4$ as determined with proton NMR. Proton NMR $CDCl_3$: 7.22−7.05 (m, 5H, Ph), 6.358 (s, 1H, C=C−H), 3.411 (t, 4H, $(OCH_2)_2$, E), 3.307 (t, 4H, $(OCH_2)_2$ Z), 3.260 (s, OCH_3), 2.670 (t, 4H, NCH_2CH_2, E), 2.525 (t, 4H, NCH_2CH_2, Z), 1.859 (s, CH_3, Z), 1.818 (s, CH_3, E).

Ethyl-bis(2-methoxyethyl)aminoacetate, 14. A mixture of bis(2-methoxyethyl)amine (24.5 g, 0.2 mol), ethyl chloracetate (40.4 g, 0.4 mol), triethylamine (40.4 g, 0.4 mol) and 100 mL of ethanol was refluxed for 12 h. Solvent was removed in vacuum and 150 mL water was added. The aqueous phase was extracted with chloroform, 3 × 150 mL, and the combined organic phase was dried with $MgSO_4$. Distillation at bp 70 °/0.05 Torr gave 36.7 g of the title compound in 83.8% yield: ^1H NMR, $CDCl_3$: 3.981 (g, 2H, CH_2CH_3), 3.324 (s, 2H, $NCH_2C{=}O$), 3.352 (t, 4H, $(OCH_2CH_2)_2$), 3.161 (s, 6H, $(OCH_3)_2$), 2.823 (t, 4H, $(CH_2CH_2N)_2$, 1.121 (t, 3H, CCH_3). ^{13}C NMR: 172.04, 71.86, 60.50, 59.09, 56.36, 54.43, 14.66.

1-Bis(2-methoxyethyl)amino-3-phenylpropanone, 15. Benzylmagnesium chloride prepared from benzyl chloride (10.1 g, 0.08 mol) and magnesium (2.1 g, 0.037 g/atom) in 80 mL THF was added dropwise at −10 °C to **14** (8.1 g, 0.037 mol) in 80 mL diethyl ether. After the reaction mixture was stirred for 2 h at rt, it was cooled with an ice bath and carefully treated with 100 mL of water. After acidification to pH 6 using 15% HCl the aqueous phase was extracted three times with 50 mL ether. The combined organic phase was washed with 100 mL water and then dried with $MgSO_4$. Removal of solvent followed by vacuum distillation bp 125−127 °C/0.1 Torr gave 8.3 g of the title compound in 83.8% yield. ^1H NMR, $CDCl_3$: 7.0−7.2 (m, 5H, Ph), 3.63 (s, 2H, CH_2Ph), 3.423 (s, 2H, $CH_2C{=}O$), 3.294 (t, 4H, $(OCH_2)_2$), 3.167 (s, 6H, $(OCH_3)_2$), 2.686 (t, 4H, $N(CH_2CH_2)_2$. ^{13}C NMR: 208.34, 137.13, 135.80, 129.93, 129.04, 127.32, 71.94, 64.43, 58.81, 55.11, 47.60.

***Z*- and *E*-1,3-Diphenyl-2-bis(2-methoxyethyl)aminomethylpropene, 16.** Sodium hydride (1.2 g, (60% in mineral oil), 0.033 mol) was introduced into 20 mL of redistilled DMSO, and the mixture was heated at 80 °C for 1 h and then cooled to room temperature. A suspension of triphenylbenzylphosphonium chloride (11.66 g, 0.033 mol) in 120 mL of THF was then added to the DMSO solution, and the mixture was stirred for 1.5 h at rt. Then, ketone **15** (7 g, 0.26 mol) was added under argon, and the mixture was refluxed for 24 h. The THF was removed under vacuum, 30 mL of water was added and the mixture was extracted three times with ether, 50 mL each. The combined organic phase was washed with brine once and then dried with $MgSO_4$. After purification by column chromatography 6.8 g of

the title product mixture mixture (**Z**∼30**E**) was obtained in 76.9% yield. ^{1}H NMR, $CDCl_3$: 7.09−7.3 (m, 10H, Ph), 6.484 (s, 1H, −C−H), 3.665 (s, 2H, C**H**$_2$Ph), 3.151 (s, 6H, $(OCH_3)_2$), 3.117 (s, 2H, −C−CH_2N), 2.534 (t, 4H, NC**H**$_2$$CH_2O)_2$, **Z**∼30**E** by NMR. ^{13}C NMR: 141.91, 140.42, 137.70, 129.93, 129.39, 129.17, 128.24, 126.41, 126.01, 71.19, 58.71, 53.77, 53.32, 41.86.

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Supporting Information Available: NMR and crystallographic data (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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