Dianions of 4-phenylbut-1-ene. Evidence for complex-induced proximity effects in the double metallation of hydrocarbons

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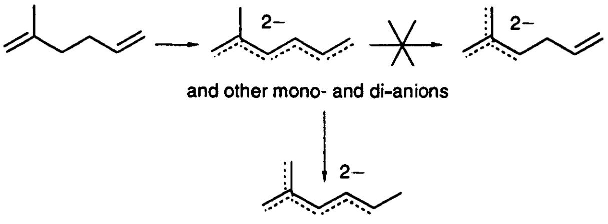
Metallation of 2-methyl-4-phenylbut-1-ene 1 resulted in the formation of a dianion linearly conjugated with the phenyl ring rather than the cross-conjugated dianion often seen in these systems. Examination of the reaction mixtures at varying periods of time revealed that the initial deprotonation was not at the benzylic carbon. Complexation of *n*-butyllithium–tetramethylethylenediamine (TMEDA) with the aromatic ring of 1 (a complex-induced proximity effect, CIPE) enhances the rate of metallation at the carbon β to the aromatic ring and α to the double bond of 1, as demonstrated in competitive metallations of 1 with ethylbenzene and of 1 with hexa-1,5-diene. This is the first report of a complex-induced proximity effect in the double metallation of a hydrocarbon in which complexation occurred with the neutral hydrocarbon.

Introduction

We have been interested for some time in the factors controlling metallation in unsaturated hydrocarbons.[1] We and others[2] found that cross-conjugated dianions[3] were formed at the expense of linearly conjugated dianions. Particular interest was paid to the 6π-electron dianion of isobutylene[4,1a] because of its potential for Y-aromaticity.[5] In many of the systems in which a competition between formation of cross-conjugated dianion and linearly conjugated dianion was observed, the linearly conjugated dianion was shown to be the kinetically formed dianion with subsequent isomerization of it to a cross-conjugated dianion. In previous work[1e] we attempted to promote formation of an initially formed linearly-conjugated dianion over the potentially Y-aromatic 6π-electron cross-conjugated dianion by incorporating both isobutylene and hexadiene moieties into the same carbon framework. The hexatriene dianion forms extraordinarily rapidly from hexa-1,5-diene[6] and we anticipated that we would see initial formation of linearly conjugated dianion with isomerization to the 6π-electron dianion, as shown in Scheme 1 for 2-methylhexa-1,5-diene. Instead, we saw isomerization to an 8π-electron cross-conjugated dianion.[1e]

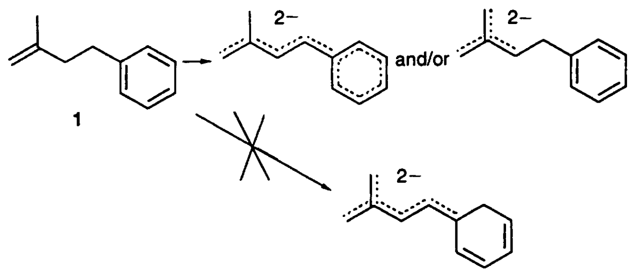


Scheme 1

It was our intent to thwart the isomerization to the 8π-electron cross-conjugated dianion by incorporating in the hexadiene system an aromatic ring, which would sacrifice its aromaticity upon isomerization to an 8π-electron cross-conjugated dianion, as shown in Scheme 2. It is results from that system which are described below.

Results and discussion

The hydrocarbon, 2-methyl-4-phenylbut-1-ene **1**, was metallated by butyllithium in *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA) and the reaction mixture quenched with chlorotrimethylsilane[7] after varying periods of time, 4–158 h, as shown in Table 1, giving products **2**–**9**. In addition to those products, which were identified through their ^{1}H NMR and mass spectra, two higher molecular mass compounds were observed, corresponding to hydrocarbons with three and four trimethylsilyl groups, respectively. Because they were present in low yield, they were not fully characterized.



Scheme 2

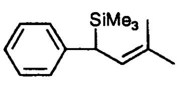
Table 1 Products from metallation of **1**[a]

t/h	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	Other[b]
4	41	—	4	3	14	30	7	2	—	1
14	14	1	4	3	10	45	18	2	1	3
26	11	3	4	2	9	46	20	2	1	2
38	10	7	3	2	9	45	19	2	1	3
62	6	9	3	2	7	45	21	2	1	3
158	1	16	6	1	3	43	22	2	1	3

[a] Reported as mol% of the reaction mixture; mass balance for each reaction averages 82% of starting material by GC analysis with tetradecane as internal standard. [b] Tri- and tetra-silylated products were also produced but were not characterized because of their low yield.

A more effective way of assessing the progress of the metallation comes from a consideration of the anions giving rise to the products isolated. Those anions are shown as **10**–**14** and in most cases their relationship to the silylated products is obvious.

However, compound **2** must result from conversion of dianion **13** to monoanion through its metallation of starting material or monoanion or through proton abstraction from TMEDA since there is no monoanion directly accessible from the starting material that could give **2** upon silylation. All other monosilylated products could be formed by monometallation/silylation of the starting materials and are attributed to the monoanion. The mol% of each anionic species and of the



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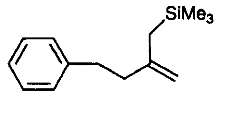

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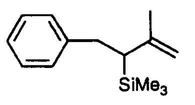

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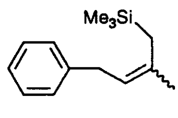

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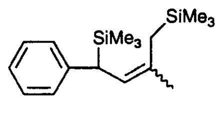

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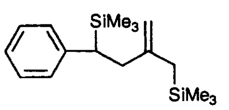

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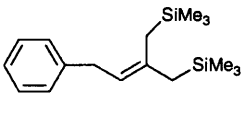

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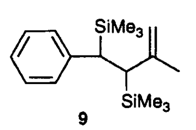

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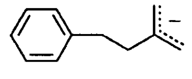

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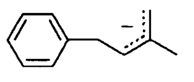

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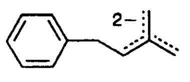

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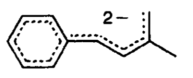

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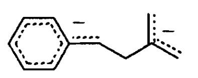

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Table 2 Anion formation from metallation of **1**

t/h	**1**	**10**	**11**	**12**	**13**	**14**	Other[a]
4	41	4	17	2	30	7	1
14	14	4	13	2	47	18	3
26	11	4	11	2	50	20	2
38	10	3	11	2	53	19	3
62	6	3	9	2	55	21	3
158	1	6	4	2	60	22	3

[a] Tri- and tetra-substituted anions the polysilylated products of which were not characterized because of their low yield.

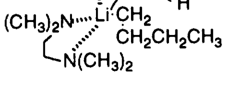
starting material as a function of time is listed in Table 2. It is apparent that the amount of starting material decreases with a concomitant increase in the amount of dianion **13**, which is consistent with the prediction that the linearly conjugated dianion should be the kinetic product. There is no indication that the linearly conjugated dianion isomerizes to the cross-conjugated 6π-electron dianion **12** because the mol% of that dianion remains constant at 2%. The only other dianionic species which is an important part of the reaction mixture is dianion **14**, which *might* arise by an initial deprotonation of starting material at the benzylic position. A second metallation would give either **14** or linearly conjugated **13**.

It was a great surprise that none of the monosilylated products corresponded to silylation of the benzylic anion obtained directly from the starting material. Benzyl hydrogens in toluene are 2.7 pK_a units more acidic than those in propene,[8] which indicates the greater thermodynamic stability of benzyl anion over allyl anion. In the hydrogen isotope exchange reactions with lithium cyclohexylamide,[8] benzyl hydrogens in toluene are six times more reactive than the allyl hydrogens; however, the reverse is apparently true in **1**. To probe for the formation of benzylic monoanion, **1** was reacted with only 1 equiv. of base and the reaction mixture quenched at shorter times. When the reaction mixture was prepared and allowed to warm to room temp. for 15 min, it contained 88 mol% starting material, 7 mol% monoanions **10** and **11**, and 5 mol% dianion **13**. After 30 min, the reaction mixture contained 77 mol% starting material, 12 mol% **10** and **11**, and 11 mol% **13**. Even when the reaction mixture with 1 equiv. of base was quenched at 0 °C 10 min after combination of reagents, no product corresponding to monosilylated benzylic anion was observed. If the benzylic monoanion is indeed formed, its metallation to **13** must be much faster than its formation.

An independent probe for the rate of formation of benzylic anions under these conditions was sought. Equimolar solutions of ethylbenzene and **1** were combined with 2 equiv. of metallating system for each starting material (4 equiv. of base total) and quenched after 2 h of reaction. Over three quarters of the ethylbenzene (78 mol%) remained unreacted, while 19 mol% was monosilylated, primarily at the benzylic position but with a small amount of ring silylated product. Ring metallation has been observed previously[9] along with metallation at the benzylic carbon. Metallation of **1** occurred to a much greater extent with only 46% of the starting material remaining. The products from silylation can be attributed to two monoanions, **10** (6 mol%) and **11** (16 mol%) and to two dianions, **13** (30 mol%) and **14** (6 mol%). If metallation of **1** occurs *via* formation of the benzylic anion followed by a second rapid metallation to give **13** and **14**, the yields of silylated products from **13** and **14** would be comparable to that of monosilylated ethylbenzene. In fact almost twice as much **13**/**14** is formed as monoanion of ethylbenzene.

We also examined the competition between **1** and hexa-1,5-diene for metallating systems. One equiv. of each starting hydrocarbon was combined with a total of 2 equiv. of metallating system so that the amount of disilylated product from each starting material would reflect a true competition for the metallating system. The quench with chlorotrimethylsilane after 4 h resulted in 3 mol% monosilylated hexadiene product and 30 mol% disilylated hexa-1,5-diene, with 68 mol% hexa-1,5-diene remaining unreacted. The metallation of **1** revealed 62 mol% of **1** unreacted, with the remainder of the reaction mixture divided between monoanion **10** (12 mol%) and dianions **13** (23 mol%) and **14** (3 mol%). In effect hexa-1,5-diene and **1** are almost equally competitive for metallating systems as approximately the same mol% remains after 4 h. If the benzylic proton on **1** was lost first, followed by a second rapid metallation to give **13** and **14**, the yields of silylated products from **13** and **14** would be substantially greater than disilylated products from hexa-1,5-diene, which is not what was observed.

A reasonable explanation for the speed of the metallation of both **1** and of hexa-1,5-diene involves a prior association between the butyllithium–TMEDA complex and the π-system of the aromatic ring in **1** and the π-system of one of the double bonds in hexa-1,5-diene. This association then allows the base to be delivered to a proton allylic to the remaining double bond, giving rise to anion **11** in the case of **1**. It should be noted that anion **11** is the anion formed in highest yield at all time periods except after 158 h of reaction, even though the hydrogen lost is secondary and less acidic than the primary hydrogen the loss of which would give **10**. Anion **11** is then deprotonated a second time to give either **12** or **13**, with the majority of deprotonation occurring to give **13**. The deprotonation to give anion **11** would involve a pseudo-six-membered ring, as shown below.



An alternative explanation suggested by a referee is that **1** metallates very slowly to a benzyl monoanion, perhaps because **1** forms a sandwich around the metallating agent which slows the metallation to benzyl monoanion compared to the metallation of ethylbenzene. To examine both kinetic schemes, constants for each metallation were determined using the CKS

Table 3 Simulated[a] rate data for metallation of **1**

	10^5k	Relative rate
k_{10}	0.64	3.2
k_{11}	2.56	12.8
k_{12}	0.2	1
$k_{12'}$	0.2	1
k_{13}	4.5	22.5
k_{14}	9.0	45.0

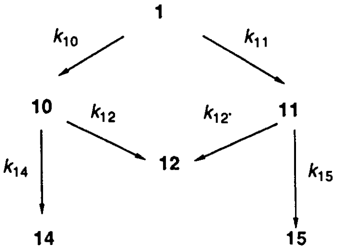
[a] Initial concentration of **1** was set to 1.0 mol l^{-1}; initial concentration of butyllithium–TMEDA was set to 2.0 mol l^{-1}.

Table 4 Relative amounts of species from competitive metallation of **1** and **15** at 2.0 h

Species	Amount (exp.)	Amount (simulation)[a]
1	46%	45.0%
10	6	3.9
11	11	24.1
13	30	18.6
14	6	7.2
15	78	78.0
16	19	21.5

[a] Initial concentration of **1** and of **15** were set to 1.0 mol l^{-1}; initial concentration of butyllithium–TMEDA was set to 4.0 mol l^{-1}.

program of Hinsberg and Houle.[10] The overall scheme for metallation of **1** is shown in Scheme 3. Rate constants were systematically varied to best fit the mechanism of Scheme 3 with the experimental data. The best-fit data are given in Table 3. Simulations were carried out for the competitive reaction with ethylbenzene **15** by butyllithium–TMEDA to give monoanion **16**. The best-fit rate constant (k_{16}) for metallation of **15** is 1.0×10^{-5} l mol^{-1} s^{-1}. The relative amounts of chemical species at 2.0 h elapsed time are given in Table 4. Simulations were also carried out for metallation of hexa-1,5-diene **17** in competition with **1**. The rate constant for metallation of **17** to monoanion **18** (k_{18}) was 2.5×10^{-5} l mol^{-1} s^{-1} with subsequent metallation to dianion **19** occurring with a rate constant (k_{19}) of 70×10^{-5} l mol^{-1} s^{-1}. The relative amounts of chemical species at 4.0 h are given in Table 5. The kinetic analysis is consistent with the overall rate of allylic metallation of **1** being about a factor of three faster than benzylic metallation of ethylbenzene [the value of $(k_{10} + k_{11})/k_{16}$ is approximately 3]. Kinetic analysis of the competitive reaction between **1** and **17** is consistent with the rates of allylic metallation of these two compounds being almost equal [the value of $(k_{10} + k_{11})/k_{18}$ is approximately unity)].



Scheme 3

Table 5 Relative amounts of species from competitive metallation of **1** and **17** at 4.0 h

Species	Amount (exp.)	Amount (simulation)[a]
1	62.0%	56.9%
10	12.0	3.9
11	0.0	22.1
13	23.0	11.8
14	3.0	4.7
17	68.0	64.0
18	3.0	2.5
19	30.0	33.0

[a] Initial concentration of **1** and of **17** were set to 1.0 mol l^{-1}; initial concentration of butyllithium–TMEDA was set to 2.0 mol l^{-1}.

The smaller rate constant for metallation of **15** compared to **1** and the relatively similar rate constants for metallation of **17** compared to **1** support the suggestion of prior association between the butyllithium–TMEDA complex and the π-system of the aromatic ring in **1** and π-system of one of the double bonds in hexa-1,5-diene. The slightly greater rate of metallation of **1** ($k_{10} + k_{11}$) over metallation of **17** suggests that complexation with the aromatic ring is more advantageous than complexation with a double bond. Such a directed metallation would be considered a 'complex induced proximity effect' (CIPE).[11] As such, it represents, to the best of our knowledge, the first time that CIPE has been observed in a complex between a π-system and an organolithium reagent. Although CIPE has been suggested as an explanation for the dilithiation of certain olefins and aromatic hydrocarbons in which 'the first metallation provides a lithium species which acts to direct the second deprotonation in an aggregated species',[11] here, we are suggesting that the association occurs with the neutral π-system itself, not with a metallated system. The observation of CIPE in neutral hydrocarbon systems extends the scope of this useful concept in carbanionic chemistry.

Experimental

General

The source and purification of solvents and the analytical equipment used were described previously.[1e] The high resolution MS data obtained were for pure compounds after GC separation except for **6** which was obtained as a mixture of geometrical isomers. *J* values are reported in Hz.

Metallation/quench of 1

In a typical reaction, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA, 7.2 ml, 48.0 mmol) and butyllithium (30.4 ml, 48.0 mmol) were combined in a septum-capped 50 ml graduated cylinder under argon. After mixing, the yellow metallating system was divided among eight septum-capped argon filled test tubes. To each tube of metallating systems at 0 °C was added **1** (0.46 ml, 3.0 mmol) and tetradecane (0.078 ml) which would serve as an internal standard for GC analysis. The dark-red solutions were allowed to warm to room temp. and were quenched at varying times by the addition of chlorotrimethylsilane (0.91 ml, 7.2 mmol). After disappearance of the deep colour of the solution, methanol (0.41 ml, 10 mmol) was added to react with excess chlorotrimethylsilane. After stirring overnight, water was added to dissolve the white precipitate.

For GC analysis, the procedure followed was that previously cited.[1e] The internal standard showed an average mass balance of 82%. For ^{1}H NMR analysis, the reaction mixture after extraction was concentrated by fractional distillation and the products were separated and collected by preparative GC.

(*E*)-2-Methyl-4-phenyl-3-trimethylsilylbutene, 2

δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.06 (9 H, s, SiC*H*$_3$), 1.63 (3 H, d, *J* 1.33, C*H*$_3$-C=CH), 1.763 (3 H, d, *J* 1.22, C*H*$_3$-C=CH), 3.13 (1 H, d, *J* 11.3, C*H*SiCH$_3$), 5.58 (1 H, d of apparent septets, *J* 11.3, *J* 1.4, C*H*=C), 7.08 (2 d, *J* 7.6, Ar-*H*), 7.23 (3 H, m, Ar-*H*); *m*/*z* 218 (M^+, 8%), 145 (8), 144 (12), 74 (14), 73 (100); HRMS *m*/*z* calc. for $C_{14}H_{22}Si$ 218.0784, found 218.0792.

4-Phenyl-2-(trimethylsilylmethyl)but-1-ene, 3

δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.06 (9 H, s, C*H*$_3$Si), 1.78 (2 H, s, C*H*$_2$Si), 2.32 (2 H, t, *J* 8.4, CH$_2$C=C), 2.76 (2 H, t, *J* 8.3,

CH_2CH_2), 4.74 (2 H, br d, J 5.1, CH_2=C), 7.2–7.4 (5 H, m, Ar), lit.,[12] δ 0.07 (9 H, s), 1.56 (2 H, s), 2.12–2.35 (2 H, m), 2.62–2.84 (2 H, m), 4.52–4.63 (2 H, m), 7.0–7.13 (5 H, m); m/z 218 (M^+, 1%), 203 (6, $M^+ - CH_3$), 145 (13), 73 (100, $SiMe_3$), lit.,[10] 218 (M^+, 12%), 203 (6), 73 (100).

2-Methyl-4-phenyl-3-trimethylsilylbut-1-ene, 4

δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.06 (9 H, s, CH_3Si), 1.55 (3 H, s, CH_3C=C), 2.32 (1 H, t, J 8.4, CHSi), 2.75 (2 H, bt, J 8.4, CH_2CH), 4.73 (2 H, bd, J 4.3, CH_2=C), 7.10–7.45 (5 H, m, Ar), m/z 218 (M^+, 1%), 203 (100, $M^+ - CH_3$), 163 (35), 148 (32), 144 (47), 73 (47, $SiMe_3$); HRMS m/z calc. for $C_{13}H_{19}Si$ (M − 15) 203.1256, found 203.1261.

(*E*)-2-Methyl-4-phenyl-1-trimethylsilylbut-2-ene, *cis*-5

δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.06 (9 H, s, CH_3Si), 1.54 (2 H, s, CH_2Si), 1.73 (3 H, s, CH_3C=C), 3.35 (2 H, d, J 7.3, CHAr), 5.15 (1 H, apparent t, J 7.2, CH=C), 7.01–7.3 (5 H, m), lit.,[13] 0.05 (9 H, s), 1.57 (2 H, s), 1.73 (3 H, s), 3.37 (2 H, d), 5.15 (1 H, t), 7.15 (5 H, s); m/z 218 (M^+, 3%), 144 (8), 73 (100, $SiMe_3$), 59 (11).

(*Z*)-2-Methyl-4-phenyl-1-trimethylsilylbut-2-ene, *trans*-5

δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.02 (9 H, s, CH_3Si), 1.63 (2 H, s, CH_2Si), 1.71 (3 H, s, CH_3C=C), 3.28 (2 H, d, J 7.3, CHAr), 5.22 (1 H, apparent t, J 7.2, CH=C), 7.01–7.3 (5 H, m), lit.,[13] 0.05 (9 H, s), 1.65 (2 H, s), 1.73 (3 H, s), 3.30 (2 H, d), 5.20 (1 H, t), 7.17 (5 H, s); m/z 218 (M^+, 3%), 91 (9), 73 (100, $SiMe_3$), 59 (11).

(*E*)- and (*Z*)-2-Methyl-4-phenyl-1,4-bis(trimethylsilyl)but-2-ene, 6[14]

Product in larger amount, δ_H(300 MHz; $CDCl_3$; $SiMe_4$) −0.05 (9 H, s, CH_3Si), 0.02 (9 H, s, CH_3Si), 1.61 (2 H, s, CH_2Si), 1.74 (3 H, s, CH_3C=C), 3.1 (1 H, d, J 11.0, CHSi), 5.48 (1 H, d, J 11.2, CH=C), 6.99–7.20 (3 H, m, Ar), 7.35–7.51 (2 H, m, Ar); product in smaller amount, δ_H(300 MHz; $CDCl_3$; $SiMe_4$) −0.06 (9 H, s, CH_3Si), 0.02 (9 H, s, CH_3Si), 1.62 (2 H, s, CH_2Si), 1.74 (3 H, s, CH_3C=C), 2.96 (1 H, d, J 11.1, CHSi), 5.42 (1 H, d, J 11.2, CH=C), 6.99–7.20 (3 H, m, Ar), 7.35–7.51 (2 H, m, Ar); m/z for mixture, 290 (M^+, 5%), 217 (13, $M^+ - SiMe_3$), 187 (8), 129 (6), 73 (100, $SiMe_3$), 59 (11%); HRMS of the mixture, m/z calc. for $C_{17}H_{30}Si_2$ 290.1886, found 290.1880.

4-Phenyl-4-trimethylsilyl-2-trimethylsilylmethylbut-1-ene, 7

δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.00 (9 H, s, CH_3Si), 0.02 (9 H, s, CH_3Si), 1.03 (2 H, s, CH_2Si), 2.32 (1 H, dd, J 11.8, 3.8, CHSi), 2.46 (2 H, m, CH_2C=C), 4.23 (1 H, s, CH=C), 4.50 (1 H, s, CH=C), 6.99–7.20 (3 H, m, Ar), 7.38–7.55 (2 H, m, Ar); m/z 290 (M^+, 10%), 203 (5), 187 (8), 161 (6), 135 (8), 73 (100, $SiMe_3$), 59 (13); HRMS m/z calc. for $C_{17}H_{30}Si_2$ 290.1886, found 290.1892.

4-Phenyl-1-trimethylsilyl-2-trimethylsilylmethylbut-2-ene, 8

δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.01 (9 H, s, CH_3Si), 0.02 (9 H, s, CH_3Si), 1.71 (2 H, s, CH_2Si), 1.73 (2 H, bs, CH_2Si), 3.32 (2 H, d, J 7.0, CHAr), 5.24 (1 H, m, CH=C), 7.10–7.45 (5 H, m, Ar); m/z 290 (M^+, 1%), 202 (9), 187 (10), 142 (7), 73 (100, $SiMe_3$), 59 (15); HRMS m/z calc. for $C_{17}H_{30}Si_2$ 290.1886, found 290.1885.

2-Methyl-4-phenyl-3,4-bis(trimethylsilyl)but-1-ene, 9

δ_H(300 MHz; $CDCl_3$; $SiMe_4$) 0.02 (9 H, s, CH_3Si), 0.06 (9 H, s, CH_3Si), 1.54 (3 H, s, CH_3C=C), 2.74 (2 H, m, CHSi), 4.57 (1 H, s, CH=C), 4.66 (1 H, s, CH=C), 7.10–7.45 (5 H, m, Ar); m/z 290 (M^+, 2%), 202 (16), 187 (13), 142 (9), 73 (100, $SiMe_3$), 59 (15); HRMS m/z calc. for $C_{17}H_{30}Si_2$ 290.1886, found 290.1890.

Competitive reaction of 1 with hexa-1,5-diene

TMEDA (0.60 ml, 4.0 mmol) and butyllithium (2.5 ml, 4.0 mmol) were combined in a septum-capped test tube under argon. To this metallating system was added a mixture of **1** (0.31 ml, 2.0 mmol) and hexa-1,5-diene (0.24 ml, 2.0 mmol). The resulting solution was quenched at varying times by the addition of chlorotrimethylsilane (0.61 ml, 4.8 mmol). Work-up followed the procedure described for the metallation of **1**. The reaction mixture was characterized by GC and GC–MS. No attempt was made to isolate and characterize the products from metallation of hexa-1,5-diene except through their MS because the product distribution determined from MS was consistent with that reported previously.[15]

Competitive reaction of 1 with ethylbenzene

TMEDA (0.60 ml, 4.0 mmol) and butyllithium (2.5 ml, 4.0 mmol) were combined in a septum-capped test tube under argon. To this metallating system was added a mixture of **1** (0.152 ml, 1.0 mmol) and ethylbenzene (0.119 ml, 1.0 mmol). The resulting solution was quenched at varying periods of time by the addition of chlorotrimethylsilane (0.61 ml, 4.8 mmol). Work-up followed the procedure described for the metallation of **1**. The reaction mixture was characterized by GC and GC–MS. No attempt was made to isolate and characterize the products from metallation of ethylbenzene except through their MS because the product distribution determined from MS was consistent with that reported previously.[9]

Kinetics simulation of metallation of 1

For purposes of simulation, the initial concentration of **1** was set to 1.0 mol l^{-1}, and the concentration of butyllithium–TMEDA was set to 2.0 mol l^{-1}. Simulations were carried out using the kinetics simulation program CKS,[10] which uses a rigorously accurate stochastic algorithm to propagate the reacting system. Rate constants were systematically varied to best fit the mechanism of Scheme 3 with the experimental data.

Kinetics simulation of competitive metallation of 1 and 15

Simulations were carried out with the rate constants of Scheme 3 preserved unmodified, and the reaction scheme augmented with a step describing the metallation of **15** by butyllithium–TMEDA. The initial concentration of **1** and of **15** were set to 1.0 mol l^{-1}; the initial concentration of butyllithium–TMEDA was set to 4.0 mol l^{-1}.

Kinetics simulation of competitive metallation of 1 and 17

Simulations were carried out with the rate constants of Scheme 3 preserved unmodified and the reaction scheme augmented with two steps describing the metallation of **17** to form **18** and further metallation to form **19**. The initial concentrations of **1** and of **17** were set to 1.0 mol l^{-1}; the initial concentration of butyllithium–TMEDA was set to 2.0 mol l^{-1}.

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