Hemilabile Ligands in Organolithium Chemistry: Substituent Effects on Lithium Ion Chelation.

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Supporting Information

I ^{6}Li NMR spectra of [^{6}Li,^{15}N]LDA recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA and 5.0 equiv of ligands **H-R**.

II Plot of k_{obsd} vs. [*n*-BuOMe] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M).

III Plot of k_{obsd} vs. [LDA] in *n*-BuOMe (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M).

IV Plot of k_{obsd} vs. [$MeOCH_2CH_2NMe_2$] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M).

V Plot of k_{obsd} vs. [LDA] in $MeOCH_2CH_2NMe_2$ (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M).

VI Plot of k_{obsd} vs. [LDA] in $MeOCH_2CH_2NMe_2$ (7.3 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M).

VII Plot of k_{obsd} vs. [$EtOCH_2CH_2NMe_2$] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M).

VIII Plot of k_{obsd} vs. [LDA] in $EtOCH_2CH_2NMe_2$ (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M).

IX Plot of k_{obsd} vs. [$MeOCH_2CH_2NEt_2$] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M).

X Plot of k_{obsd} vs. [LDA] in $MeOCH_2CH_2NEt_2$ (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M).

XI Plot of k_{obsd} vs. [Me_2NEt] in $MeOCH_2CH_2NMe_2$ (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M).

XII Plot of k_{obsd} vs. [DME] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (1, 0.004 M) by LDA (0.10 M).

XIII Plot of k_{obsd} vs. [LDA] in DME (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M).

XIV Plot of k_{obsd} vs. [*t*-$BuOCH_2CH_2OMe$] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M).

XV Plot of k_{obsd} vs. [LDA] in *t*-$BuOCH_2CH_2OMe$ (0.5 M) and hexane co-solvent for the β-elimination of 1- bromocyclooctene (**1**, 0.004 M).

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XXXIX Calculated enthalpies (kcal/mol) ΔH_4, ΔH_5, and ΔH_6 for Me_2NLi coordinated to ligands **A-G** and **K-V** (Scheme 3).

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XLI Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for H_2NLi coordinated to ligands substituted on the two-carbon backbone (**K-V**).

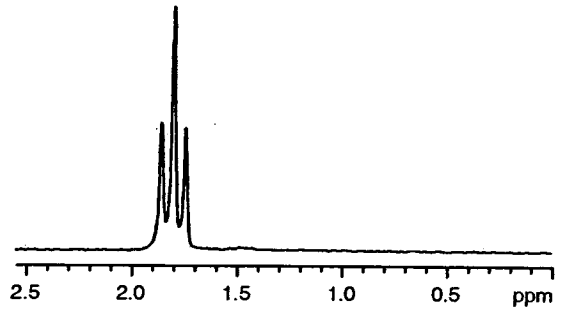
XLII Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for *i*-Pr_2NLi coordinated to ligands of general structure $MeOCH_2CH_2NR_2$ (**A-G**).

XLIII Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for *i*-Pr_2NLi coordinated to ligands substituted on the two-carbon backbone (**K-V**).

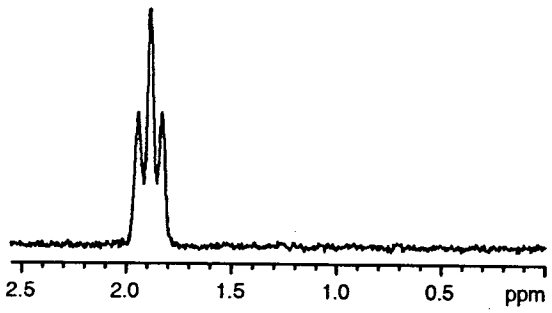
XLIV Calculated energies of reactants and transition structures for the β-elimination of (Z)-2-bromo-2-butene using Gaussian 98W at the B3LYP level of density functional theory with the 631A basis set.

XLV Optimized structures for the β-elimination of (Z)-2-bromo-2-butene using Gaussian 98W at the B3LYP level of density functional theory with the 631A basis set.

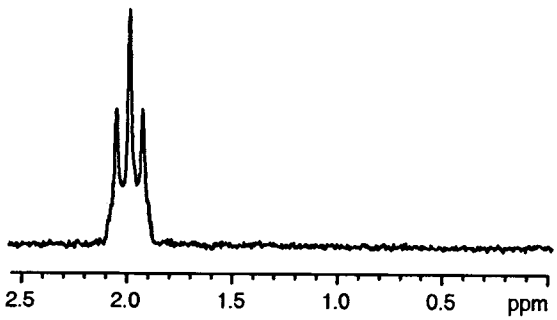
H $J_{Li\text{-}N} = 5.0$ Hz



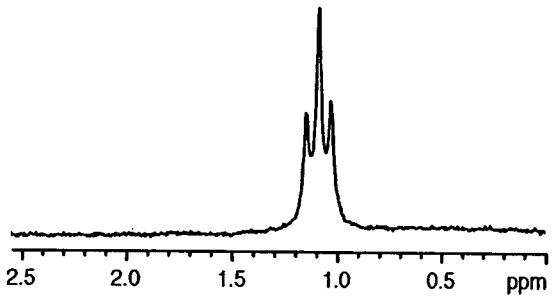
I $J_{Li\text{-}N} = 5.0$ Hz



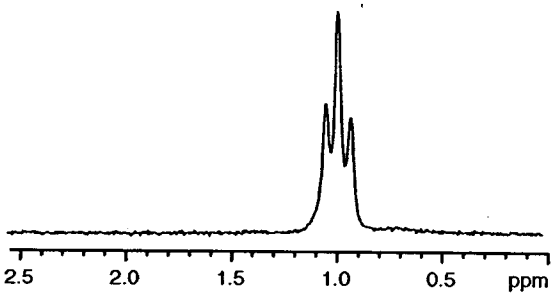
J $J_{Li\text{-}N} = 5.1$ Hz



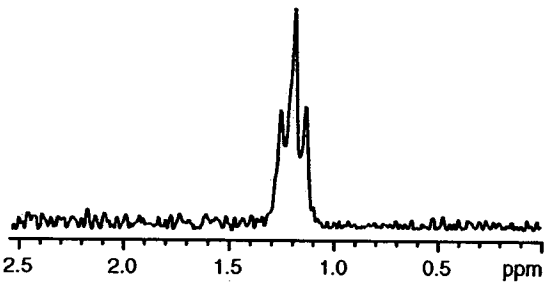
K $J_{Li\text{-}N} = 4.9$ Hz



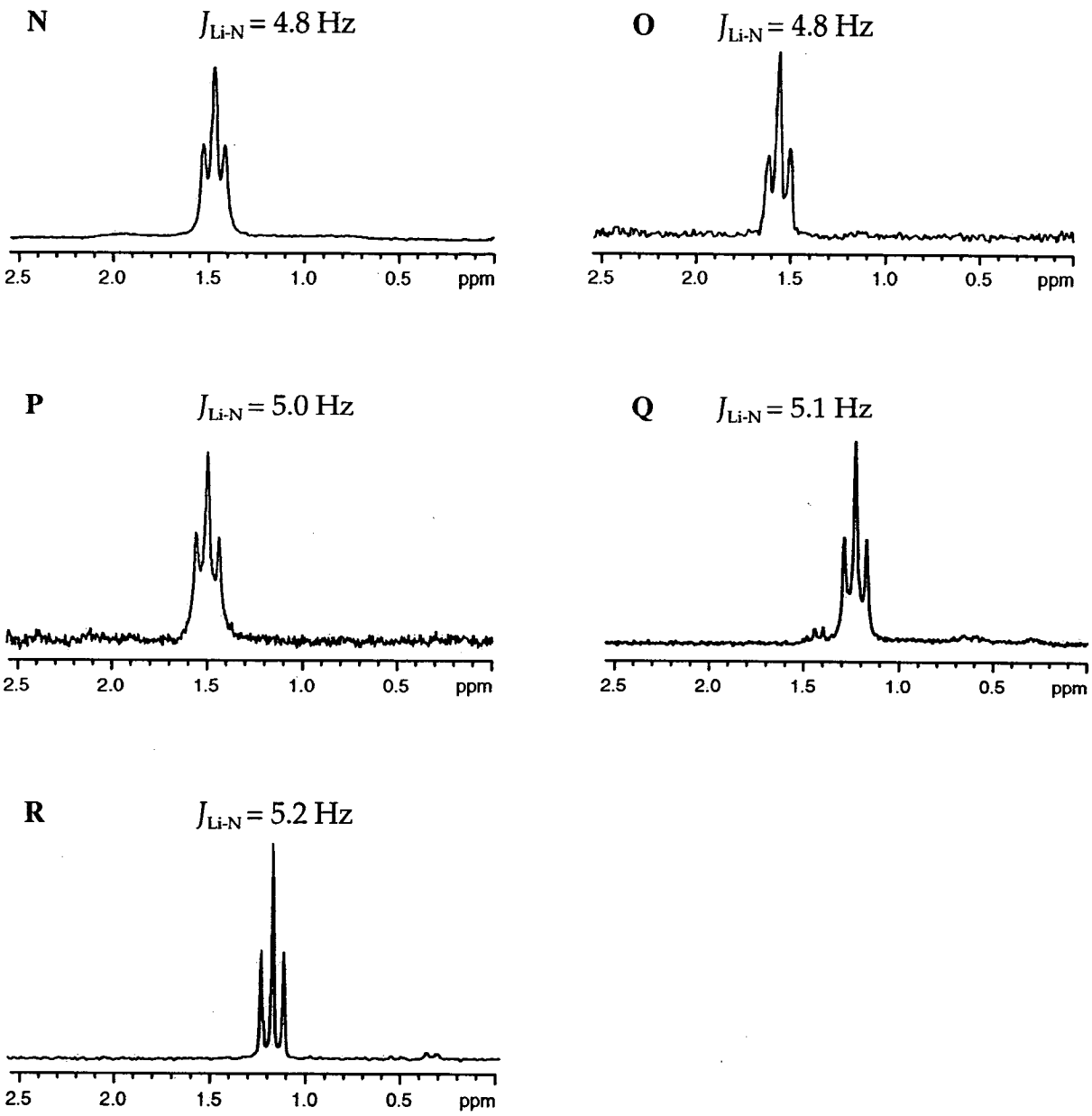
L $J_{Li\text{-}N} = 4.9$ Hz



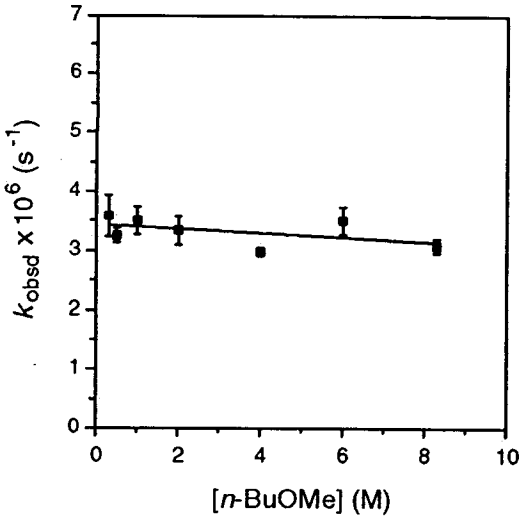
M $J_{Li\text{-}N} = 5.0$ Hz



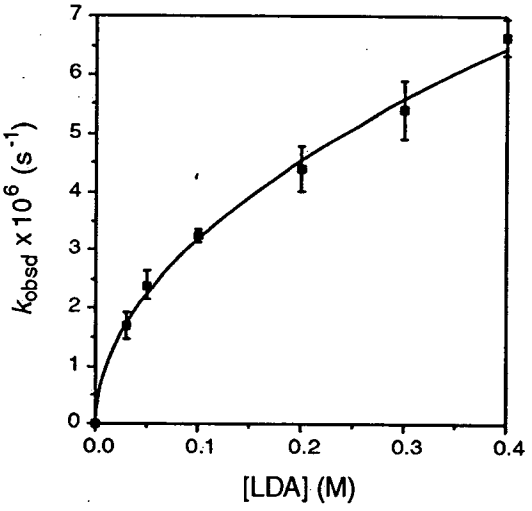
I. ^{6}Li NMR spectra of [^{6}Li,^{15}N]LDA recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at –90 °C. The samples also contain 5.0 equiv of ligands **H-M**.



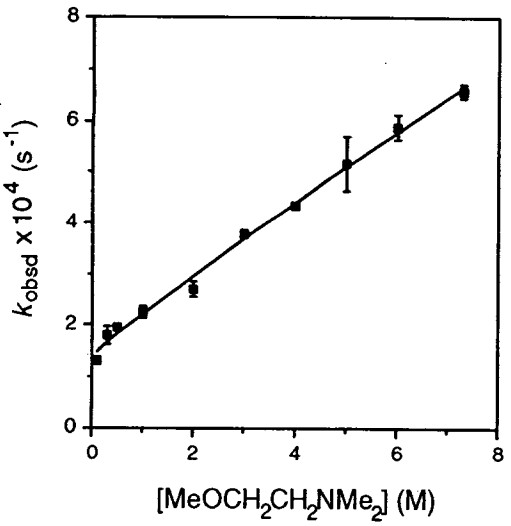
I. (Continuation) ^{6}Li NMR spectra of [^{6}Li,^{15}N]LDA recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at –90 °C. The samples also contain 5.0 equiv of ligands **N-R**.



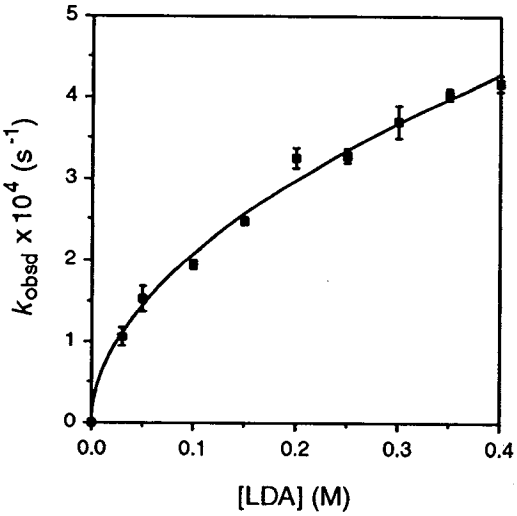
II. Plot of k_{obsd} vs. [*n*-BuOMe] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M) at 0 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k\,[n\text{-BuOMe}] + k'$ ($k = -3 \pm 3 \times 10^{-8}$, $k' = 3.4 \pm 0.1 \times 10^{-6}$).



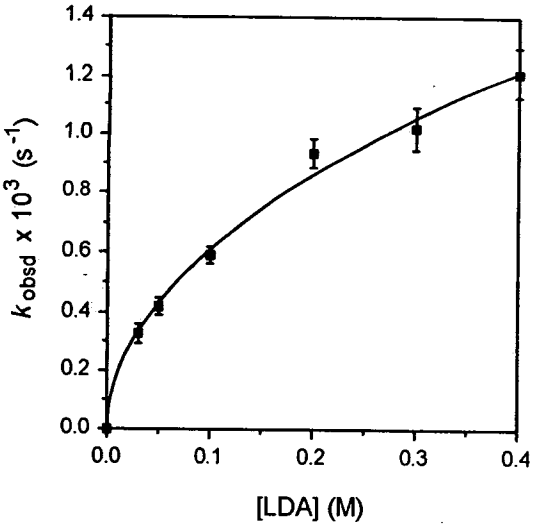
III. Plot of k_{obsd} vs. [LDA] in *n*-BuOMe (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) at 0 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k\,[\text{LDA}]^n$ ($k = 1.0 \pm 0.1 \times 10^{-5}$, $n = 0.51 \pm 0.02$).



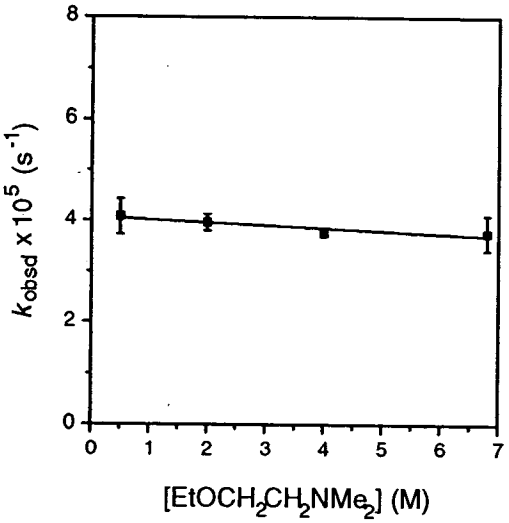
IV. Plot of k_{obsd} vs. [$MeOCH_2CH_2NMe_2$] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to k_{obsd} = k [$MeOCH_2CH_2NMe_2$]^n + k' ($k = 8 \pm 1 \times 10^{-5}$, $k' = 1.4 \pm 0.1 \times 10^{-4}$, n = 0.93 ± 0.07).



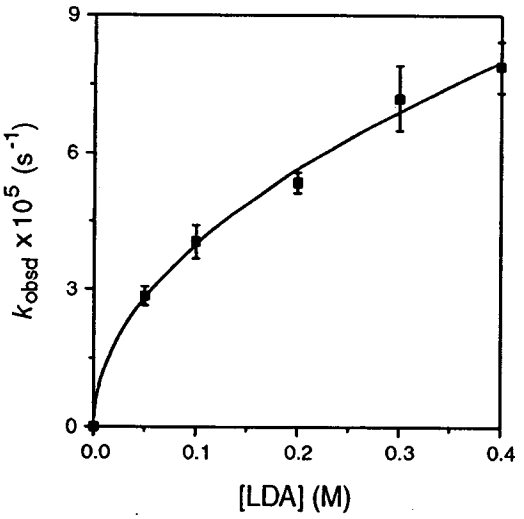
V. Plot of k_{obsd} vs. [LDA] in $MeOCH_2CH_2NMe_2$ (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k$ [LDA]^n ($k = 6.9 \pm 0.3 \times 10^{-4}$, n = 0.52 ± 0.03).



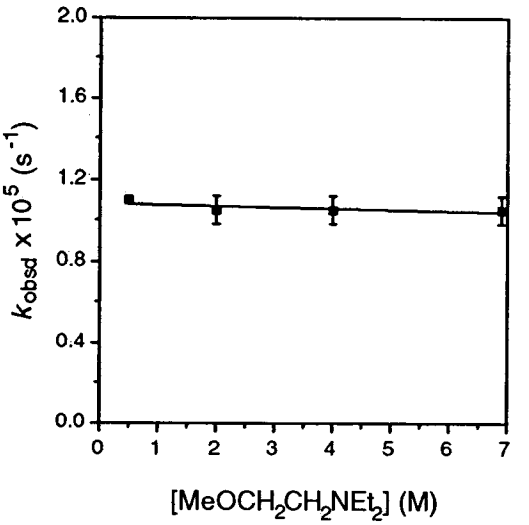
VI. Plot of k_{obsd} vs. [LDA] in $MeOCH_2CH_2NMe_2$ (7.3 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k\,[LDA]^n$ ($k = 2.3 \pm 0.1 \times 10^{-3}$, $n = 0.54 \pm 0.02$).



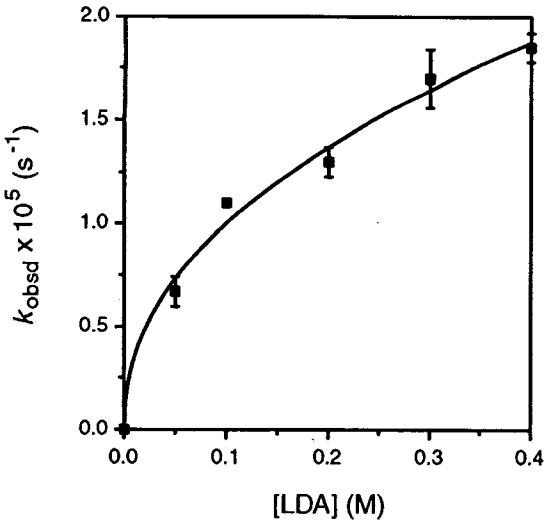
VII. Plot of k_{obsd} vs. [$EtOCH_2CH_2NMe_2$] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k\,[EtOCH_2CH_2NMe_2]^n + k'$ ($k = -5.5 \pm 1.8 \times 10^{-7}$, $k' = 4.1 \pm 0.1 \times 10^{-5}$).



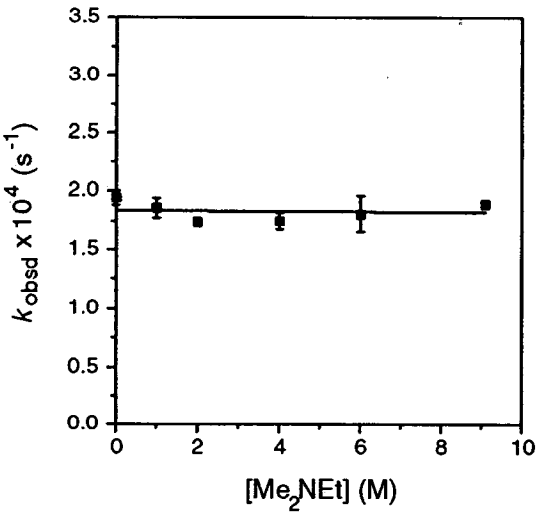
VIII. Plot of k_{obsd} vs. [LDA] in $EtOCH_2CH_2NMe_2$ (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) at –40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k\,[LDA]^n$ ($k = 1.2 \pm 0.1 \times 10^{-4}$, $n = 0.50 \pm 0.03$).



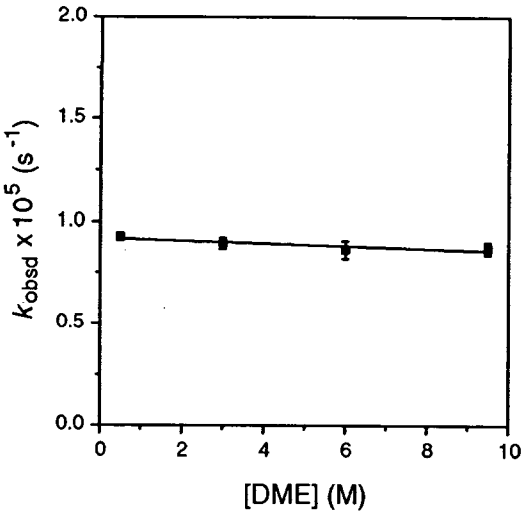
IX. Plot of k_{obsd} vs. [$MeOCH_2CH_2NEt_2$] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k\,[MeOCH_2CH_2NEt_2] + k'$ ($k = 2 \pm 9 \times 10^{-8}$, $k' = 1.09 \pm 0.04 \times 10^{-5}$).



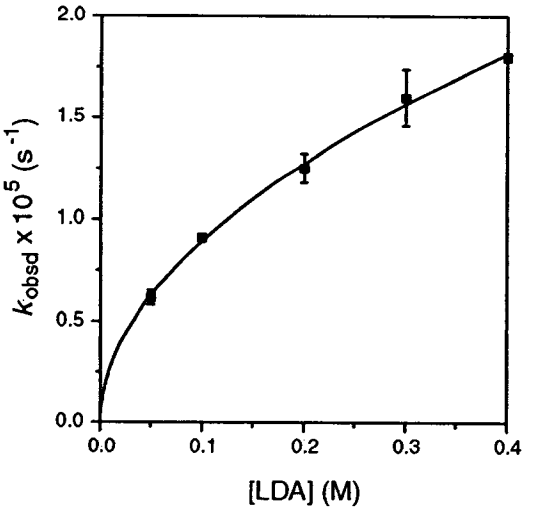
X. Plot of k_{obsd} vs. [LDA] in $MeOCH_2CH_2NEt_2$ (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) at –40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k\,[LDA]^n$ ($k = 2.8 \pm 0.2 \times 10^{-5}$, $n = 0.45 \pm 0.04$).



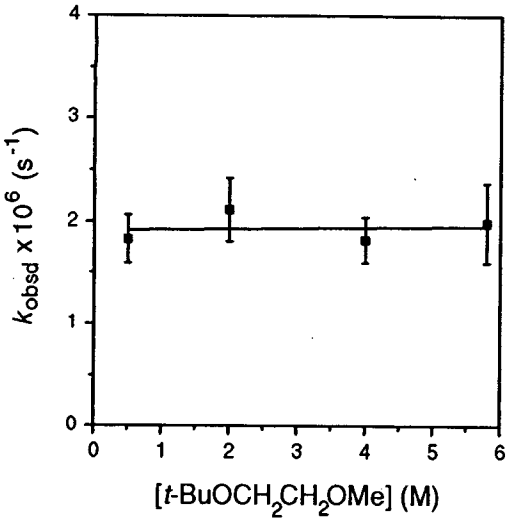
XI. Plot of k_{obsd} vs. Me_2NEt in $MeOCH_2CH_2Me_2$ (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k\,[Me_2NEt] + k'$ ($k = 1.4 \pm 0.2 \times 10^{-7}$, $k' = 1.8 \pm 0.1 \times 10^{-4}$).



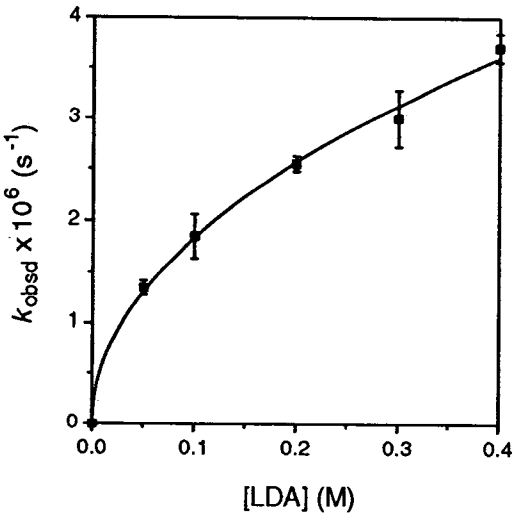
XII. Plot of k_{obsd} vs. [DME] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k$ [DME] + k' ($k = -6.7 \pm 2.6 \times 10^{-8}$, $k' = 9.2 \pm 0.2 \times 10^{-6}$).



XIII. Plot of k_{obsd} vs. [LDA] in DME (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k$ [LDA]^n ($k = 2.9 \pm 0.1 \times 10^{-5}$, n = 0.51 ± 0.01).



XIV. Plot of k_{obsd} vs. [t-BuOCH$_2$CH$_2$OMe] in hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k$ [t-BuOCH$_2$CH$_2$OMe] + k' (k = -0.7 ± 4.2 x 10^{-8}, k' = 1.9 ± 0.2 x 10^{-6}).



XV. Plot of k_{obsd} vs. [LDA] in t-BuOCH$_2$CH$_2$OMe (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k$ [LDA]^n (k = 5.6 ± 0.2 x 10^{-6}, n = 0.49 ± 0.03).

XVI. Table of data for plot in Section II

[*n*-BuOMe] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.30	0.0000038 ± 4E-7	0.0000033 ± 3E-7	0.0000036 ± 4E-7
0.50	0.0000033 ± 3E-7	0.0000032 ± 3E-7	0.0000032 ± 3E-7
1.00	0.0000037 ± 3E-7	0.0000033 ± 3E-7	0.0000035 ± 1E-7
2.00	0.0000035 ± 4E-7	0.0000032 ± 3E-7	0.0000033 ± 3E-7
4.00	0.0000030 ± 3E-7	0.0000029 ± 3E-7	0.0000030 ± 3E-7
6.00	0.0000033 ± 3E-7	0.0000037 ± 2E-7	0.0000035 ± 3E-7
8.30	0.0000030 ± 2E-7	0.0000032 ± 3E-7	0.0000031 ± 3E-7

XVII. Table of data for plot in Section III

[LDA] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.03	0.0000018 ± 2E-7	0.0000015 ± 2E-7	0.0000017 ± 2E-7
0.05	0.0000026 ± 3E-7	0.0000022 ± 2E-7	0.0000024 ± 2E-7
0.10	0.0000033 ± 3E-7	0.0000032 ± 3E-7	0.0000032 ± 3E-7
0.20	0.0000041 ± 5E-7	0.0000047 ± 5E-7	0.0000044 ± 4E-7
0.30	0.0000057 ± 6E-7	0.0000050 ± 5E-7	0.0000054 ± 5E-7
0.40	0.0000064 ± 3E-7	0.0000069 ± 7E-7	0.0000066 ± 3E-7

XVIII. Table of data for plot in Section IV

[$MeO(CH_2)_2NMe_2$] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.10	0.00013 ± 2E-5	0.00013 ± 1E-5	0.00013 ± 1E-5
0.30	0.00019 ± 2E-5	0.00017 ± 2E-5	0.00018 ± 2E-5

0.50	0.00020 ± 2E-5	0.00019 ± 2E-5	0.00019 ± 2E-5
1.00	0.00022 ± 2E-5	0.00023 ± 1E-5	0.00022 ± 2E-5
2.00	0.00026 ± 1E-5	0.00028 ± 1E-5	0.00027 ± 1E-5
3.00	0.0004 ± 1E-4	0.00038 ± 2E-5	0.00038 ± 2E-5
4.00	0.00043 ± 2E-5	0.00044 ± 1E-5	0.00043 ± 1E-5
5.00	0.00048 ± 3E-5	0.00055 ± 3E-5	0.00052 ± 3E-5
6.00	0.00061 ± 2E-5	0.00057 ± 2E-5	0.00059 ± 2E-5
7.30	0.00067 ± 3E-5	0.00065 ± 3E-5	0.00066 ± 3E-5

XIX. Table of data for plot in Section V

[LDA] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.03	0.00010 ± 1E-5	0.00011 ± 2E-5	0.00011 ± 1E-5
0.05	0.00016 ± 2E-5	0.00014 ± 2E-5	0.00015 ± 2E-5
0.10	0.00020 ± 2E-5	0.00019 ± 2E-5	0.00019 ± 2E-5
0.15	0.00024 ± 2E-5	0.00025 ± 2E-5	0.00025 ± 2E-5
0.20	0.00033 ± 1E-5	0.00032 ± 1E-5	0.00032 ± 1E-5
0.25	0.00032 ± 2E-5	0.00033 ± 1E-5	0.00033 ± 1E-5
0.30	0.00035 ± 2E-5	0.00038 ± 1E-5	0.00037 ± 2E-5
0.35	0.00041 ± 1E-5	0.00040 ± 1E-5	0.00040 ± 1E-5
0.40	0.00042 ± 1E-5	0.00041 ± 1E-5	0.00042 ± 1E-5

XX. Table of data for plot in Section VI

[LDA] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.03	0.00036 ± 1E-5	0.00032 ± 3E-5	0.00034 ± 2E-5
0.05	0.00051 ± 5E-5	0.00045 ± 2E-5	0.00048 ± 4E-5
0.10	0.00067 ± 1E-5	0.00065 ± 3E-5	0.00066 ± 1E-5
0.20	0.0010 ± 1E-4	0.00095 ± 8E-5	0.00098 ± 7E-5

0.30	0.00124 ± 8E-5	0.0011 ± 1E-4	0.0012 ± 1E-4
0.40	0.00147 ± 8E-5	0.00142 ± 9E-5	0.00144 ± 3E-5

XXI. Table of data for plot in Section VII

[$EtO(CH_2)_2NMe_2$] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.50	0.000043 ± 5E-6	0.000038 ± 6E-6	0.000041 ± 5E-6
2.00	0.000041 ± 3E-6	0.000038 ± 5E-6	0.000040 ± 5E-6
4.00	0.000038 ± 3E-6	0.000037 ± 3E-6	0.000037 ± 3E-6
6.80	0.000035 ± 2E-6	0.000040 ± 1E-6	0.000037 ± 2E-6

XXII. Table of data for plot in Section VIII

[LDA] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.050	0.000027 ± 2E-6	0.000030 ± 3E-6	0.000028 ± 3E-6
0.100	0.000043 ± 5E-6	0.000038 ± 6E-6	0.000041 ± 5E-6
0.200	0.000055 ± 5E-6	0.000052 ± 2E-6	0.000053 ± 3E-6
0.300	0.000077 ± 5E-6	0.000067 ± 3E-6	0.000068 ± 3E-6
0.400	0.000075 ± 8E-6	0.000083 ± 5E-6	0.000080 ± 5E-6

XXIII. Table of data for plot in Section IX

[$MeO(CH_2)_2NEt_2$] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.50	0.000011 ± 1E-6	0.000011 ± 1E-6	0.000011 ± 1E-6
2.00	0.000010 ± 1E-6	0.000011 ± 1E-6	0.000010 ± 1E-6
4.00	0.000011 ± 1E-6	0.000010 ± 1E-6	0.000011 ± 1E-6
6.90	0.000011 ± 1E-6	0.000010 ± 1E-6	0.000010 ± 1E-6

XXIV. Table of data for plot in Section X

[LDA] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.050	0.0000062 ± 2E-7	0.0000072 ± 6E-7	0.0000067 ± 7E-7
0.100	0.000011 ± 1E-6	0.000011 ± 1E-6	0.000011 ± 1E-6
0.200	0.000013 ± 1E-6	0.000013 ± 1E-6	0.000013 ± 1E-6
0.300	0.000016 ± 1E-6	0.000018 ± 2E-6	0.000017 ± 1E-6
0.400	0.000019 ± 2E-6	0.000018 ± 2E-6	0.000019 ± 1E-6

XXV. Table of data for plot in Section XI

[Me_2NEt] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.00	0.00020 ± 2E-5	0.00019 ± 2E-5	0.00019 ± 2E-5
1.00	0.00018 ± 2E-5	0.00019 ± 1E-5	0.00019 ± 2E-5
2.00	0.00018 ± 1E-5	0.00017 ± 1E-5	0.00017 ± 1E-5
4.00	0.00017 ± 1E-5	0.00018 ± 2E-5	0.00017 ± 1E-5
6.00	0.00017 ± 2E-5	0.00019 ± 2E-5	0.00018 ± 2E-5
9.10	0.00019 ± 2E-5	0.00019 ± 2E-5	0.00019 ± 2E-5

XXVI. Table of data for plot in Section XII

[DME] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.50	0.000009 ± 1E-6	0.0000092 ± 7E-7	0.0000091 ± 9E-7
3.00	0.0000092 ± 9E-7	0.000009 ± 1E-6	0.0000090 ± 4E-7
6.00	0.0000089 ± 9E-7	0.0000083 ± 7E-7	0.0000086 ± 6E-7
9.50	0.0000089 ± 3E-7	0.0000085 ± 6E-7	0.0000087 ± 3E-7

XXVII. Table of data for plot in Section XIII

[LDA] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.050	0.0000059 ± 7E-7	0.0000064 ± 8E-7	0.0000061 ± 7E-7
0.100	0.000009 ± 1E-6	0.0000092 ± 7E-7	0.0000091 ± 9E-7
0.200	0.000013 ± 1E-6	0.000012 ± 1E-6	0.000012 ± 1E-6
0.300	0.000015 ± 1E-6	0.000017 ± 2E-6	0.000016 ± 1E-6
0.400	0.000018 ± 2E-6	0.000018 ± 2E-6	0.000018 ± 2E-6

XXVIII. Table of data for plot in Section XIV

[*t*-BuO$(CH_2)_2$OMe] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.50	0.0000017 ± 2E-7	0.0000020 ± 2E-7	0.0000018 ± 2E-7
2.00	0.0000019 ± 1E-7	0.0000023 ± 4E-7	0.0000021 ± 2E-7
4.00	0.0000017 ± 1E-7	0.0000020 ± 2E-7	0.0000018 ± 1E-7
5.80	0.0000023 ± 3E-7	0.0000017 ± 2E-7	0.0000020 ± 2E-7

XXIX. Table of data for plot in Section XV

[LDA] (M)	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
0.050	0.0000014 ± 2E-7	0.0000013 ± 1E-7	0.0000013 ± 1E-7
0.100	0.0000017 ± 2E-7	0.0000020 ± 2E-7	0.0000018 ± 2E-7
0.200	0.0000025 ± 3E-7	0.0000026 ± 2E-7	0.0000026 ± 2E-7
0.300	0.0000028 ± 2E-6	0.0000032 ± 3E-7	0.0000030 ± 2E-7
0.400	0.0000036 ± 4E-7	0.0000038 ± 4E-7	0.0000037 ± 4E-7

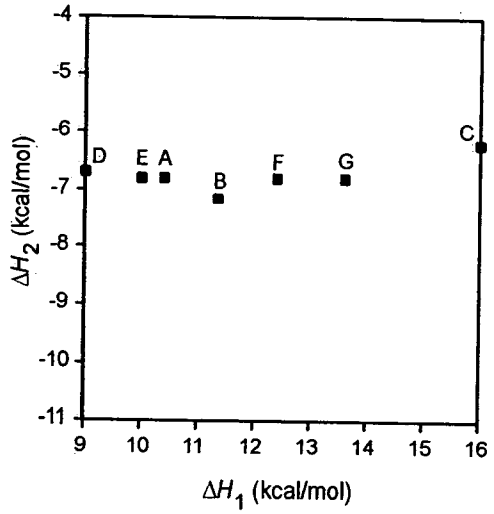
XXX. Table of data for k_{obsd} in various ligands (0.5 M) and hexane co-solvent for the β-elimination of 1-bromocyclooctene (**1**, 0.004 M) by LDA (0.10 M) at -40 °C.

Ligand	$k_{obsd}1$ (s^{-1})	$k_{obsd}2$ (s^{-1})	k_{obsd} (avg) (s^{-1})
n-BuOMe	0.00000010 ± 1E-8	0.00000014 ± 2E-8	0.00000012 ± 2E-8
A $MeOCH_2CH_2NMe_2$	0.00020 ± 2E-5	0.00019 ± 2E-5	0.00019 ± 2E-5
B $MeOCH_2CH_2NEt_2$	0.000011 ± 1E-6	0.000011 ± 1E-6	0.000011 ± 1E-6
C $MeOCH_2CH_2N$*i*-Pr_2	0.000008 ± 1E-6	0.0000085 ± 5E-7	0.0000082 ± 8E-7
D $MeOCH_2CH_2N(CH_2)_2$	0.000048 ± 4E-6	0.000061 ± 6E-6	0.000055 ± 5E-6
E $MeOCH_2CH_2N(CH_2)_3$	0.00015 ± 2E-5	0.00012 ± 1E-5	0.00013 ± 1E-5
F $MeOCH_2CH_2N(CH_2)_4$	0.000018 ± 2E-6	0.000021 ± 1E-6	0.000019 ± 1E-6
G $MeOCH_2CH_2N(CH_2)_5$	0.000010 ± 1E-6	0.000010 ± 1E-6	0.000010 ± 1E-6
H $EtOCH_2CH_2NMe_2$	0.000043 ± 5E-6	0.000038 ± 6E-6	0.000041 ± 5E-6
I *i*-$PrOCH_2CH_2NMe_2$	0.000010 ± 1E-6	0.000013 ± 1E-6	0.000012 ± 1E-6
J *t*-$BuOCH_2CH_2NMe_2$	0.0000028 ± 1E-7	0.0000023 ± 2E-7	0.0000025 ± 1E-7
K $MeOCH_2CMe_2NMe_2$	0.000028 ± 3E-6	0.000025 ± 3E-6	0.000027 ± 3E-6
L $MeOC(Me)_2CH_2NMe_2$	0.00010 ± 1E-5	0.00012 ± 1E-5	0.00011 ± 1E-5
M $MeOCH_2CHMeNMe_2$	0.00038 ± 2E-5	0.00040 ± 1E-5	0.00039 ± 1E-5
N $MeOCH_2CH(Et)NMe_2$	0.00033 ± 5E-5	0.00028 ± 2E-5	0.00032 ± 3E-5
O $MeOCH_2CH$(*i*-Pr)NMe_2	0.00010 ± 1E-5	0.00009 ± 9E-5	0.00010 ± 1E-5
P $MeOCH(Me)CH_2NMe_2$	0.00058 ± 3E-5	0.00060 ± 4E-5	0.00059 ± 4E-5
Q $MeOCH(Et)CH_2NMe_2$	0.00028 ± 3E-5	0.00031 ± 3E-5	0.00029 ± 3E-5
R $MeOCH$(*i*-Pr)CH_2NMe_2	0.00008 ± 1E-5	0.00010 ± 1E-5	0.00009 ± 1E-5
S	0.000014 ± 2E-5	0.000018 ± 2E-6	0.000016 ± 1E-6
T	0.000020 ± 1E-6	0.000020 ± 2E-6	0.000020 ± 1E-6
U	0.000017 ± 2E-5	0.000019 ± 2E-5	0.000018 ± 2E-5
V	0.000012 ± 1E-5	0.000011 ± 1E-5	0.000012 ± 1E-5
W $MeOCH_2CH_2CH_2NMe_2$	0.0000020 ± 2E-7	0.0000018 ± 2E-7	0.0000019 ± 2E-7
X $MeOCH_2C(Me)_2CH_2NMe_2$	0.0000070 ± 5E-7	0.0000075± 8E-7	0.0000072 ± 7E-7
Y	0.0000011 ± 1E-7	0.0000015 ± 2E-7	0.0000013 ± 1E-7
Z	0.000015 ± 2E-7	0.000012 ± 1E-7	0.000014 ± 1E-7
AA	0.000015 ± 2E-6	0.000015 ± 2E-6	0.000016 ± 2E-6

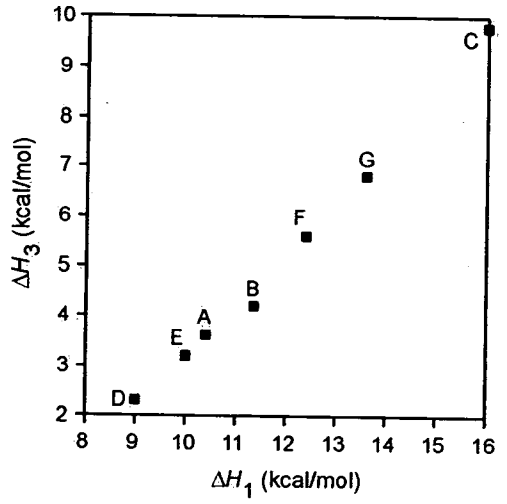
BB	0.00013 ± 1E-4	0.00011 ± 1E-4	0.00012 ± 1E-4
CC $MeOCH_2CH_2OMe$	0.000009 ± 1E-6	0.0000092 ± 7E-7	0.0000093 ± 9E-7
DD *t*-$BuOCH_2CH_2OMe$	0.0000017 ± 2E-7	0.0000020 ± 2E-7	0.0000018 ± 2E-7
EE $MeOCH(Me)CH_2OMe$	0.000034 ± 4E-6	0.000030 ± 3E-6	0.000032 ± 3E-6
FF	0.000012 ± 1E-7	0.000014 ± 1E-7	0.000013 ± 1E-7
GG $(MeO)_2CHCH_2OMe$	0.000008 ± 1E-6	0.000009 ± 1E-6	0.000009 ± 1E-6
HH $(MeO)_2CHCH_2NMe_2$	0.000033 ± 3E-6	0.000032 ± 3E-6	0.000032 ± 3E-6
II	0.000016 ± 1E-7	0.000014 ± 2E-7	0.000015 ± 2E-7
JJ $(MeOCH_2CH_2)_2O$	0.000008 ± 1E-6	0.000007 ± 1E-6	0.000008 ± 1E-6
KK $[Me(OCH_2CH_2)_2]_3N$	0.000033 ± 2E-6	0.000030 ± 4E-6	0.000032 ± 2E-6
LL	0.000009 ± 9E-6	0.00001 ± 1E-5	0.00001 ± 1E-5
MM TDB	0.000017 ± 1E-6	0.000018 ± 3E-6	0.000018 ± 2E-6
NN TDA	0.000029 ±3E-6	0.000033 ± 2E-6	0.000031 ± 2E-6
OO 12-Crown-4	0.0000023 ± 2E-7	0.0000027 ± 3E-7	0.0000025 ± 2E-7
PP 15-Crown-5	0.0000060 ± 7E-7	0.0000056 ± 6E-7	0.0000058 ± 6E-7
QQ 18-Crown-6	0.000013 ± 2E-7	0.000010 ± 1E-7	0.000011 ± 1E-7

XXXI. Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for Me_2NLi coordinated to ligands of general structure $MeOCH_2CH_2NR_2$ (Scheme 2).[ref1] The average deviation of the enthalpies is represented by avg dev. The heats of formation (kcal/mol) of ligands **A-G** in their most stable conformations are represented by $H_{f(Ligand)}$. $(Me_2NLi)_2$ = -60.5 kcal/mol.

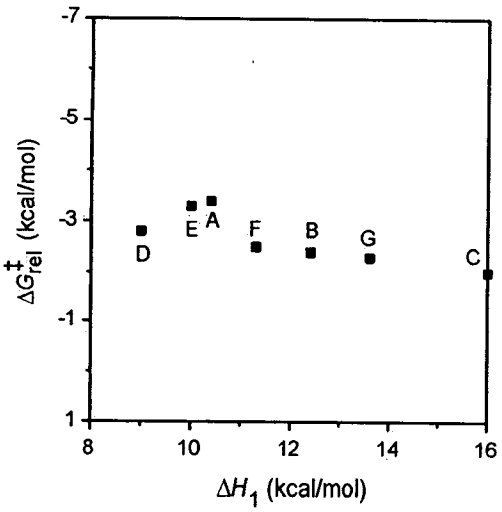
Ligand	$H_{f(Ligand)}$	ΔH_1	ΔH_2	ΔH_3
A	-44.1	10.4	-6.8	3.6
B	-51.0	11.3	-7.1	4.2
C	-50.3	16.0	-6.2	9.8
D	-17.9	9.0	-6.7	2.3
E	-37.9	10.0	-6.8	3.2
F	-54.6	12.4	-6.8	5.6
G	-55.9	13.6	-6.8	6.8
avg dev	---	2.4	0.3	2.6



XXXII. Plot of calculated ΔH_1 versus ΔH_2 (kcal/mol) for Me_2NLi coordinated to ligands of general structure $MeOCH_2CH_2NR_2$ (**A-G**).



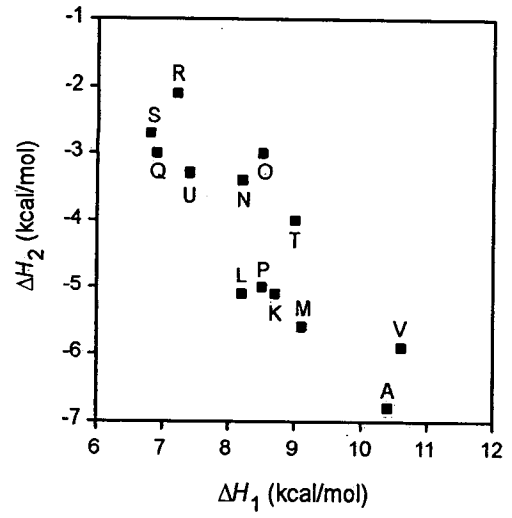
XXXIII. Plot of calculated ΔH_1 versus ΔH_3 (kcal/mol) for Me_2NLi coordinated to ligands of general structure $MeOCH_2CH_2NR_2$ (**A-G**).



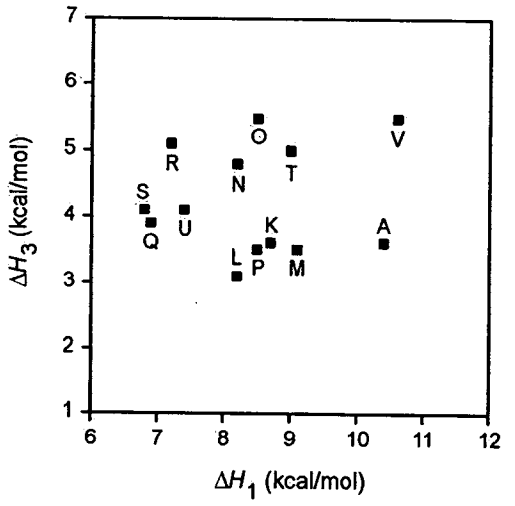
XXXIV. Plot of calculated ΔH_1 for Me_2NLi coordinated to ligands of general structure $MeOCH_2CH_2NR_2$ (**A-G**) versus free energies of activation $\Delta G^{\ddagger}_{rel}$ (kcal/mol) relative to *n*-BuOMe for the β-elimination of 1-bromocyclooctene (**1**).

XXXV. Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for Me_2NLi coordinated to ligands substituted on the two-carbon backbone. The average deviation of the enthalpies is represented by avg dev. The heats of formation (kcal/mol) of ligands **K-V** in their most stable conformations are represented by $H_{f(Ligand)}$. $(Me_2NLi)_2$ = -60.5 kcal/mol.

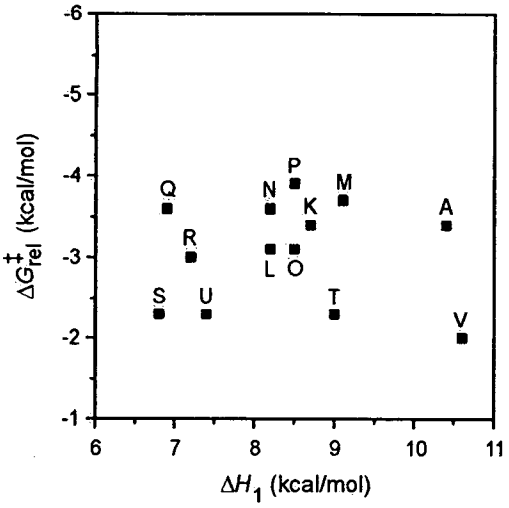
Ligand	$H_{f(Ligand)}$	ΔH_1	ΔH_2	ΔH_3
K	-35.0	8.7	-5.1	3.6
L	-38.9	8.2	-5.1	3.1
M	-43.3	9.1	-5.6	3.5
N	-46.9	8.2	-3.4	4.8
O	-44.2	8.5	-3.0	5.5
P	-44.4	8.5	-5.0	3.5
Q	-47.5	6.9	-3.0	3.9
R	-47.1	7.2	-2.1	5.1
S	-41.9	6.8	-2.7	4.1
T	-42.3	9.0	-4.0	5.0
U	-8.0	7.4	-3.3	4.1
V	-8.3	10.6	-5.9	5.5
avg dev	---	1.1	1.3	0.8



XXXVI. Plot of calculated ΔH_1 versus ΔH_2 (kcal/mol) for Me_2NLi coordinated to ligands substituted on the two-carbon backbone (**K-V**).



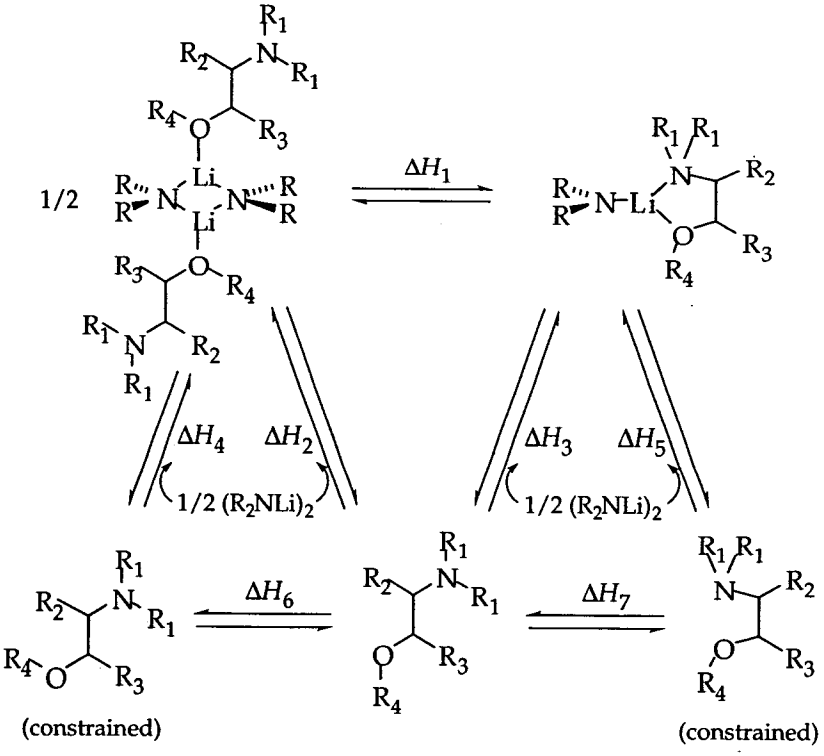
XXXVII. Plot of calculated ΔH_1 versus ΔH_3 (kcal/mol) for Me_2NLi coordinated to ligands substituted on the two-carbon backbone (**K-V**).



XXXVIII. Plot of calculated ΔH_1 for Me_2NLi coordinated to ligands substituted on the two-carbon backbone (**K-V**) versus free energies of activation $\Delta G^{\ddagger}_{rel}$ (kcal/mol) relative to *n*-BuOMe for the β-elimination of 1-bromocyclooctene (**1**).

XXXIX. Calculated enthalpies (kcal/mol) ΔH_4, ΔH_5, and ΔH_6 for Me_2NLi coordinated to ligands **A-G** and **K-V** (Scheme 3, R = Me). The average deviation of the enthalpies is represented by avg dev. The heats of formation (kcal/mol) of ligands in their most stable conformations are represented by $H_{f(Ligand)}$. $(Me_2NLi)_2$ = -60.5 kcal/mol.

Ligand	$H_{f(Ligand)}$	ΔH_4	ΔH_5	ΔH_6	ΔH_7
A	-44.1	-8.1	0.9	1.3	-2.7
B	-51.0	-7.9	-0.3	0.8	-2.5
C	-50.3	-6.0	3.5	1.4	-6.3
D	-17.9	-8.1	-0.1	1.4	-2.4
E	-37.9	-8.2	0.8	1.4	-2.4
F	-54.6	-8.1	2.9	1.3	-2.7
G	-55.9	-8.1	2.6	1.3	-4.4
avg dev	---	0.8	1.5	0.2	1.5
K	-35.0	-6.9	1.3	1.8	-2.3
L	-38.9	-6.4	0.2	1.3	-2.9
M	-43.3	-6.3	1.2	0.7	-2.3
N	-46.9	-5.3	1.6	1.9	-3.2
O	-44.2	-6.2	1.8	3.3	-3.7
P	-44.4	-6.8	1.0	1.8	-2.5
Q	-47.5	-3.1	1.8	0.1	-2.9
R	-47.1	-5.1	2.8	3.0	-2.3
avg dev	---	1.2	0.7	1.1	0.5



Scheme 3

XL. Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for H_2NLi coordinated to ligands of general structure $MeOCH_2CH_2NR_2$ (Scheme 3, R = H). The average deviation of the enthalpies is represented by avg dev. The heats of formation (kcal/mol) of ligands **A-G** in their most stable conformations are represented by $H_{f(Ligand)}$. $(H_2NLi)_2$ = -47.6 kcal/mol.

Ligand	$H_{f(Ligand)}$	ΔH_1	ΔH_2	ΔH_3
A	-44.1	16.2	-5.7	10.5
B	-51.0	19.5	-6.2	13.3
C	-50.3	16.7	-7.6	9.1
D	-17.9	15.5	-6.0	9.4
E	-37.9	16.2	-5.9	10.3
F	-54.6	18.3	-5.8	12.5
G	-55.9	21.6	-5.7	15.9
avg dev	---	2.2	0.7	2.4

XLI. Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for H_2NLi coordinated to ligands substituted on the two-carbon backbone (Scheme 3, R = H). The average deviation of the enthalpies is represented by avg dev. The heats of formation (kcal/mol) of ligands **K-V** in their most stable conformations are represented by $H_{f(Ligand)}$. $(H_2NLi)_2$ = -47.6 kcal/mol.

Ligand	$H_{f(Ligand)}$	ΔH_1	ΔH_2	ΔH_3
K	-35.0	15.0	-4.2	10.8
L	-38.9	15.1	-4.9	10.2
M	-43.3	15.7	-5.3	10.4
N	-46.9	15.3	-4.2	11.1
O	-44.2	14.5	-2.5	12.0
P	-44.4	14.3	-3.6	10.7
Q	-47.5	13.6	-2.8	10.8
R	-47.1	11.7	-0.1	11.6
S	-41.9	11.8	-0.8	11.0
T	-42.3	14.8	-2.6	12.2
U	-8.0	14.8	-3.7	11.0
V	-8.3	18.2	-5.4	12.8
avg dev	---	1.7	1.3	1.7

XLII. Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for *i*-Pr_2NLi coordinated to ligands of general structure $MeOCH_2CH_2NR_2$ (Scheme 3, R = *i*-Pr). The average deviation of the enthalpies is represented by avg dev. The heats of formation (kcal/mol) of ligands **A-G** in their most stable conformations are represented by $H_{f(Ligand)}$. $(i\text{-}Pr_2NLi)_2$ = -94.4 kcal/mol.

Ligand	$H_{f(Ligand)}$	ΔH_1	ΔH_2	ΔH_3
A	-44.1	1.6	3.2	-4.4
B	-51.0	4.4	3.1	-1.6
C	-50.3	7.0	3.9	2.5
D	-17.9	-1.6	3.3	-7.3
E	-37.9	0.1	3.3	-5.7
F	-54.6	2.8	3.3	-2.9
G	-55.9	4.5	4.0	0.1
avg dev	---	2.9	0.3	3.4

XLIII. Calculated enthalpies (kcal/mol) of monomer aggregation (ΔH_1), dimer solvation (ΔH_2), and monomer solvation (ΔH_3) for *i*-Pr_2NLi coordinated to ligands substituted on the two-carbon backbone (Scheme 3, R = *i*-Pr). The average deviation of the enthalpies is represented by avg dev. The heats of formation (kcal/mol) of ligands **K-V** in their most stable conformations are represented by $H_{f(Ligand)}$. (*i*-Pr_2NLi)$_2$ = -94.4 kcal/mol. [d]Minima corresponding to disolvated dimer structures couldn't be located with retention of ligand.

Ligand	$H_{f(Ligand)}$	ΔH_1	ΔH_2	ΔH_3
K	-35.0	-2.7	5.7	-3.7
L	-38.9	---[d]	---	-3.7
M	-43.3	-0.8	4.3	-0.7
N	-46.9	0.2	4.1	-3.0
O	-44.2	-1.1	5.7	-2.1
P	-44.4	-0.5	4.5	-3.9
Q	-47.5	-2.8	5.6	-3.9
R	-47.1	---[d]	---[d]	-3.0
S	-41.9	-4.1	6.3	-3.8
T	-42.3	-1.3	5.7	-2.2

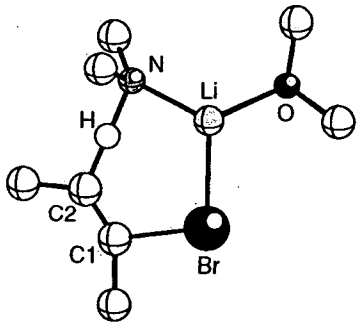
XLIII. (Continued)

U	-8.0	---[d]	---	-3.8
V	-8.3	---[d]	---	1.1
avg dev	---	1.4	0.8	1.5

XLIV. Calculated energies of reactants and transition structures for the β-elimination of 1-bromocyclooctene using Gaussian 98W at the B3LYP level of density functional theory with the 631A basis set.

	E (Hartrees)
Cis-2-bromo-2-butene (RBr)	-2728.22703
Me_2O	-154.94045
$Me_2OCH_2CH_2NMe_2$	-328.10947
DME	-308.70516
$(Me_2NLi)_2(Me_2O)_2$	-594.01449
$(Me_2NLi)_2(Me_2OCH_2CH_2NMe_2)_2$	-940.34891
$(Me_2NLi)_2(DME)_2$	-901.54220
15; $[(Me_2NLi)(Me_2O)(RBr)]^{\ddagger}$	-3025.21082
16; $[(Me_2NLi)(Me_2OCH_2CH_2NMe_2)(RBr)]^{\ddagger}$	-3198.39618
17; $[(Me_2NLi)(DME)(RBr)]^{\ddagger}$	-3178.98827
18; $[(Me_2NLi)(Me_2OCH_2CH_2NMe_2)(Me_2O)(RBr)]^{\ddagger}$	-3353.33286
19; $[(Me_2NLi)(DME)(Me_2O)(RBr)]^{\ddagger}$	-3333.93006
$[(Me_2N)(RBr)]^{-\ddagger}$	-2862.66993

XLV. Optimized structures for the β-elimination of (Z)-2-bromo-2-butene using Gaussian 98W at the B3LYP level of density functional theory with the 631A basis set. Energies relative to the starting materials are shown in kcal/mol. Hydrogens other than the one attached to C2 are omitted for clarity.



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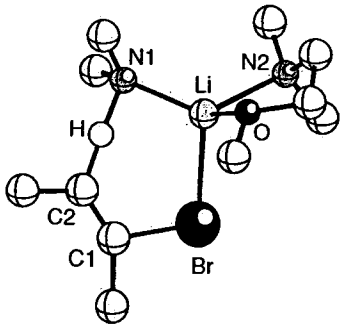

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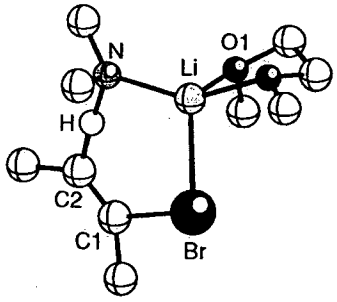

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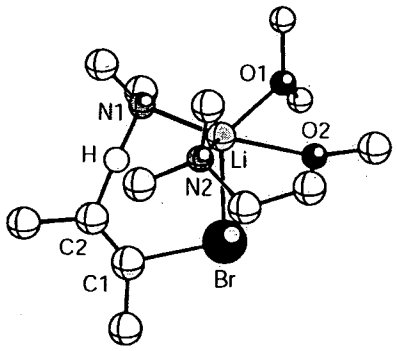

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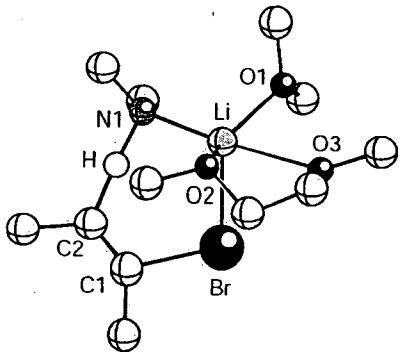

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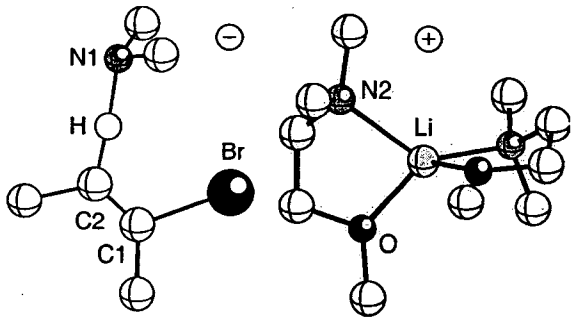


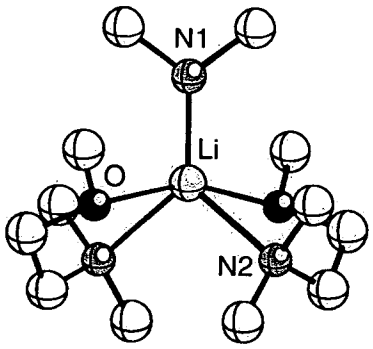
20; +100.2

Selected bond lengths (Å) for calculated transition structures **15, 16, 17, 18, 19,** and **20.**

Bond	**15**	**16**	**17**	**18**	**19**	**20**
Li-Br	2.38	2.48	2.49	2.56	2.55	---
Li-N(1)	1.92	1.94	1.93	2.03	2.03	---
Li-N(2)	---	2.15	---	2.40	---	2.12
Li-O(1)	1.92	2.02	2.05	2.22	2.13	1.98
Li-O(2)	---	---	2.04	2.38	2.24	---
Li-O(3)	---	---	---	---	2.52	---
Br-C(1)	2.31	2.21	2.22	2.18	2.17	2.05
C(1)-C(2)	1.28	1.29	1.29	1.30	1.30	1.31
C(2)-H	1.33	1.36	1.35	1.38	1.39	1.28
N(1)-H	1.39	1.36	1.38	1.34	1.33	1.47

XLVI. Calculated energies and optimized structures for bis-chelated complexes using Gaussian 98W at the B3LYP level of density functional theory with the 631A basis set. Hydrogens are omitted for clarity.

	E (Hartrees)
21; $[LiMe_2N{\cdot}(Me_2OCH_2CH_2NMe_2)_2]$	-798.27861
22; $[LiMe_2N{\cdot}(DME)_2]$	-759.46828
$[Li{\cdot}(Me_2OCH_2CH_2NMe_2)_2]^+$	-663.68129
$[Li{\cdot}(DME)_2]^+$	-624.87219
Li^+	-7.28313



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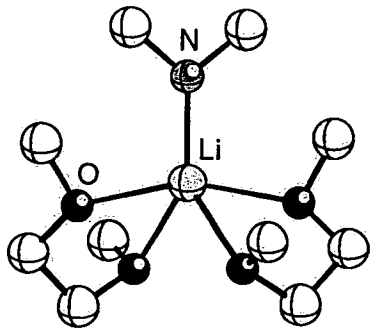

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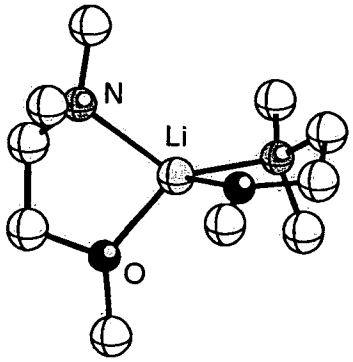
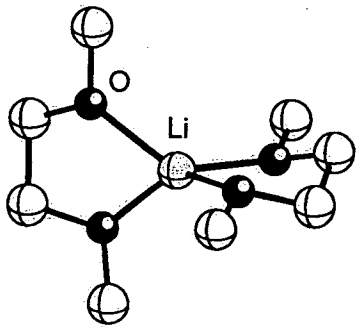


$[Li{\cdot}(Me_2OCH_2CH_2NMe_2)_2]^+$



$[Li{\cdot}(DME)_2]^+$

XLVII. Crystal data for bis-chelated $[(LiBF_4)(Me_2OCH_2CH_2NMe_2)_2]$ complex **23**.

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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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H5A H 0.118(3) 0.703(2) 0.8632(19) 0.066(7) Uiso 1 1 d . . .
C6 C 0.0075(2) 0.60550(13) 0.71032(14) 0.0366(4) Uani 1 1 d . . .
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C7 0.0274(7) 0.0466(10) 0.0343(9) 0.0080(8) -0.0053(6) 0.0040(7)
C8 0.0464(10) 0.0528(12) 0.0289(9) -0.0059(8) -0.0095(8) -0.0084(9)
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  into account individually in the estimation of esds in distances, angles
  and torsion angles; correlations between esds in cell parameters are only
  used when they are defined by crystal symmetry. An approximate (isotropic)
  treatment of cell esds is used for estimating esds involving l.s. planes.
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C6 C7 1.493(3) . ?

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  _geom_angle_atom_site_label_2
  _geom_angle_atom_site_label_3
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  _geom_angle_site_symmetry_3
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B1 F1 Li1 150.64(14) . . ?
C2 O1 C1 111.66(13) . . ?
C2 O1 Li1 111.70(12) . . ?
C1 O1 Li1 123.48(13) . . ?
C3 O2 C4 112.37(15) . . ?
C3 O2 Li1 105.19(12) . . ?
C4 O2 Li1 121.90(13) . . ?
C5 O3 C6 111.21(14) . . ?
C5 O3 Li1 125.47(13) . . ?
C6 O3 Li1 112.15(12) . . ?
C7 O4 C8 112.71(13) . . ?
C7 O4 Li1 103.14(12) . . ?
C8 O4 Li1 120.55(13) . . ?
O1 C2 C3 107.75(13) . . ?
O2 C3 C2 107.57(14) . . ?
O3 C6 C7 107.25(14) . . ?
O4 C7 C6 107.53(13) . . ?
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F4 B1 F2 109.62(14) . . ?
F4 B1 F3 110.96(16) . . ?
F2 B1 F3 110.74(15) . . ?
F4 B1 F1 109.05(14) . . ?
F2 B1 F1 107.70(15) . . ?
F3 B1 F1 108.69(14) . . ?
F1 Li1 O3 116.83(13) . . ?
F1 Li1 O1 124.24(15) . . ?
O3 Li1 O1 118.93(13) . . ?
F1 Li1 O2 96.66(12) . . ?
O3 Li1 O2 93.02(11) . . ?
O1 Li1 O2 81.13(10) . . ?
F1 Li1 O4 92.72(11) . . ?
O3 Li1 O4 81.14(10) . . ?
O1 Li1 O4 95.03(11) . . ?
O2 Li1 O4 170.46(14) . . ?

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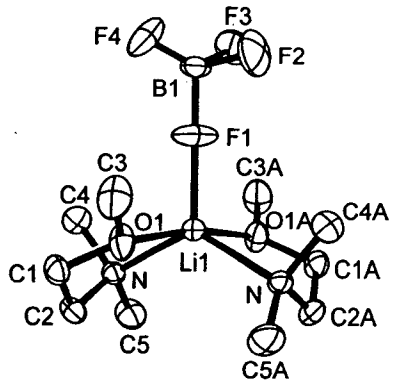

$LiBF_4(A)_2$; 23