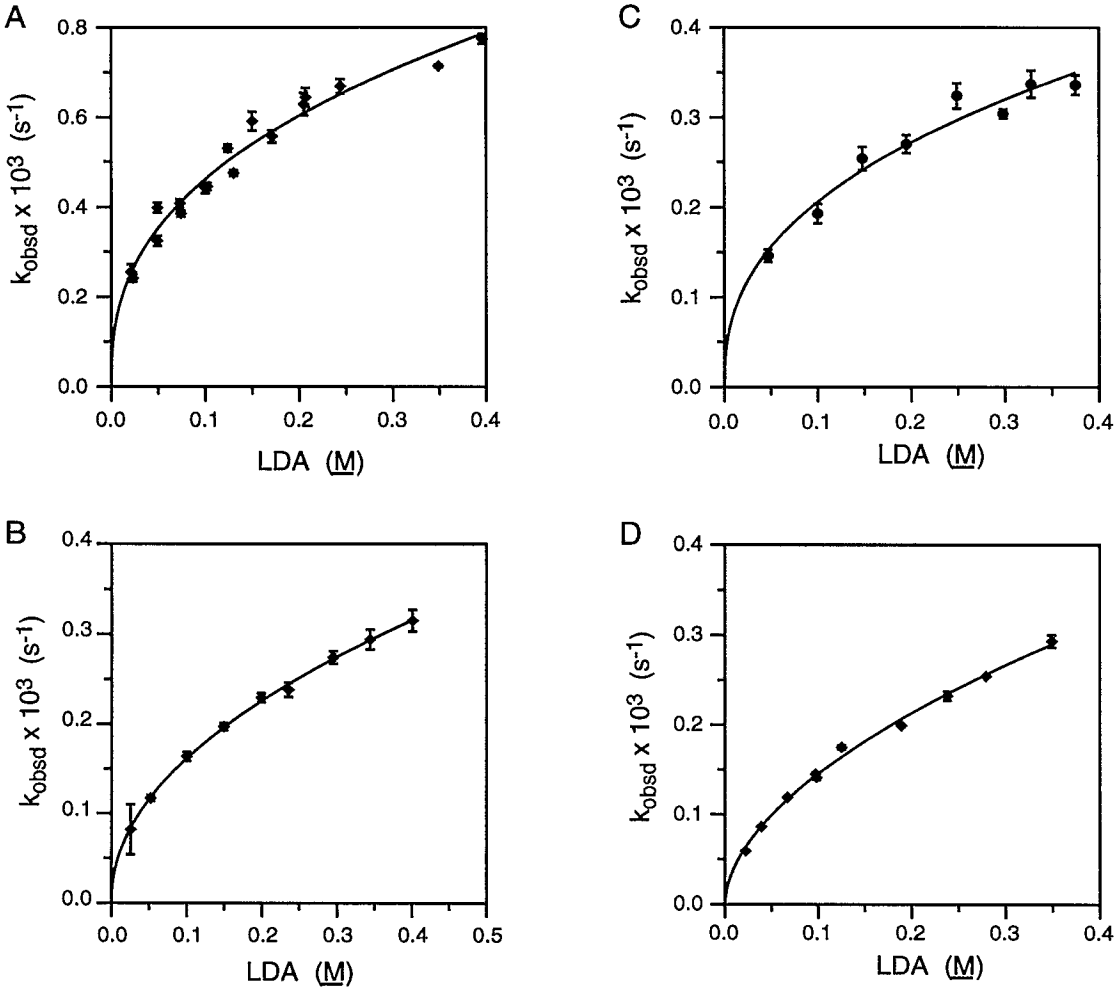

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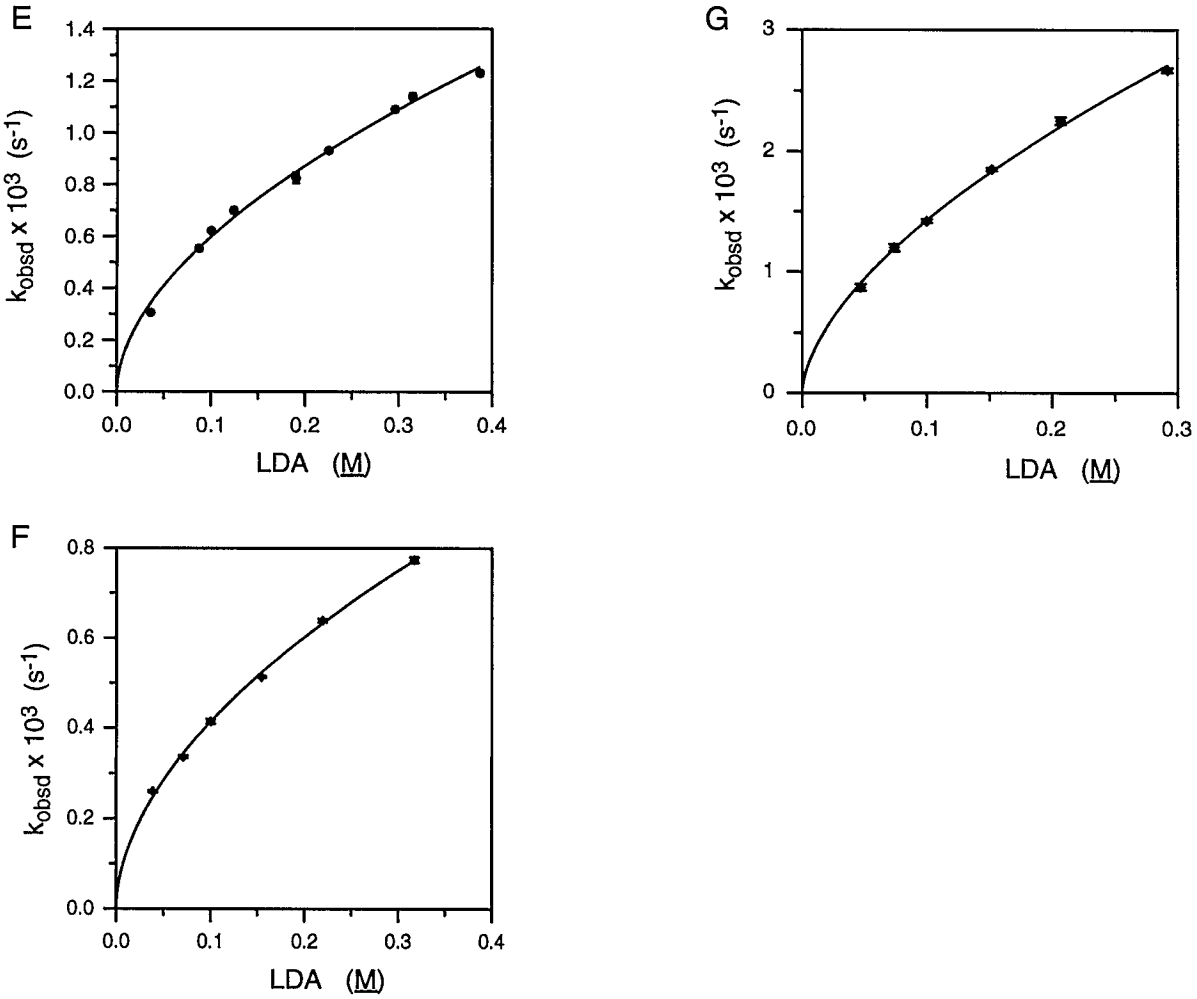
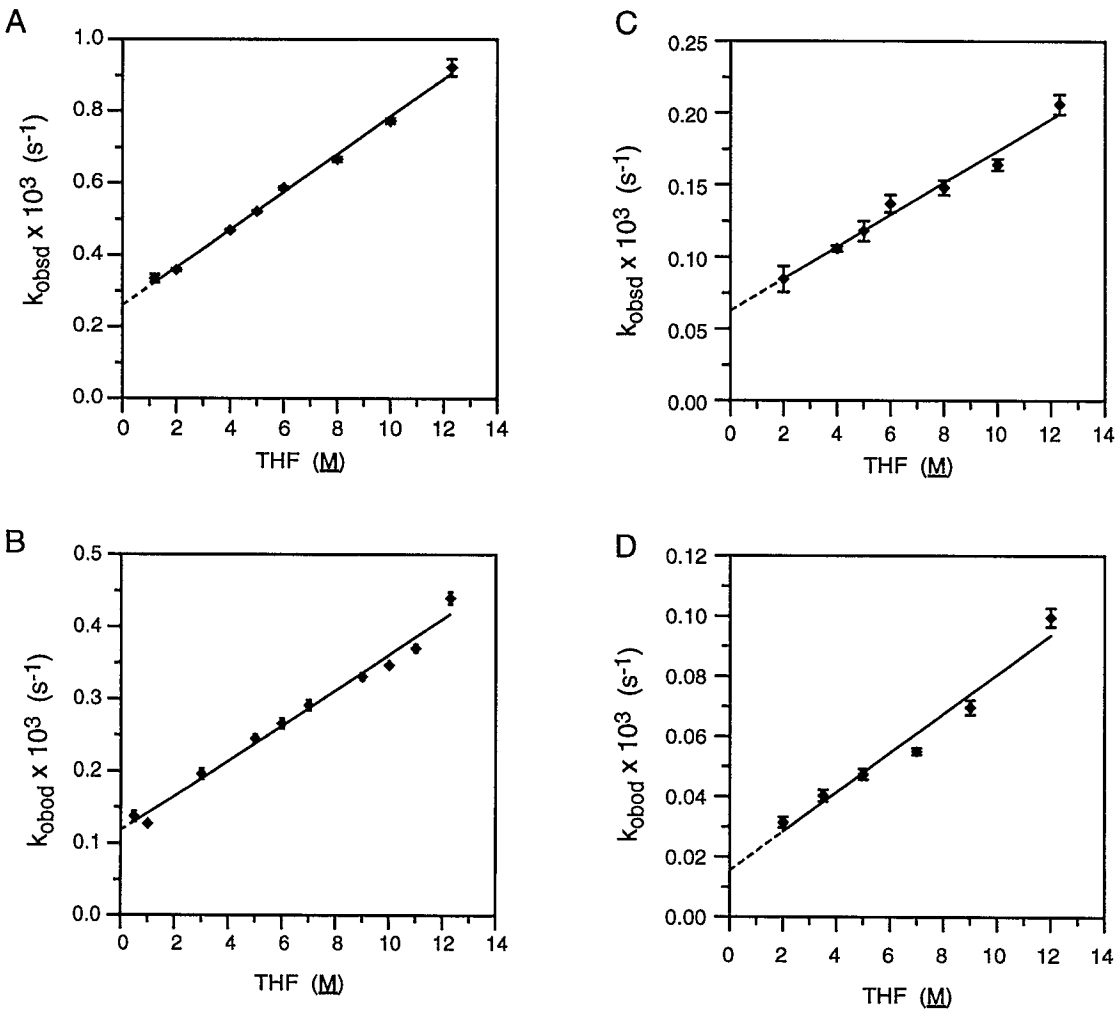
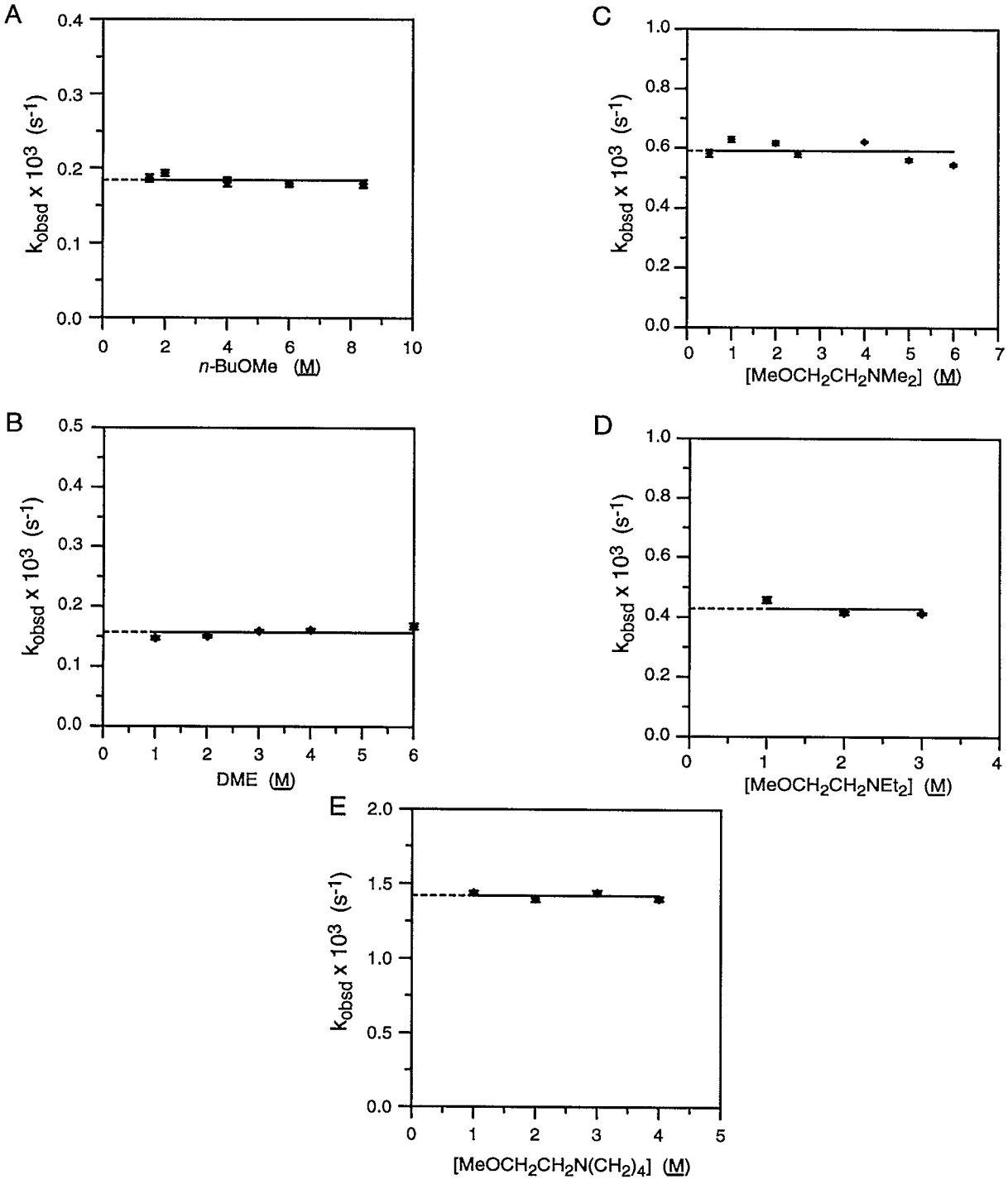


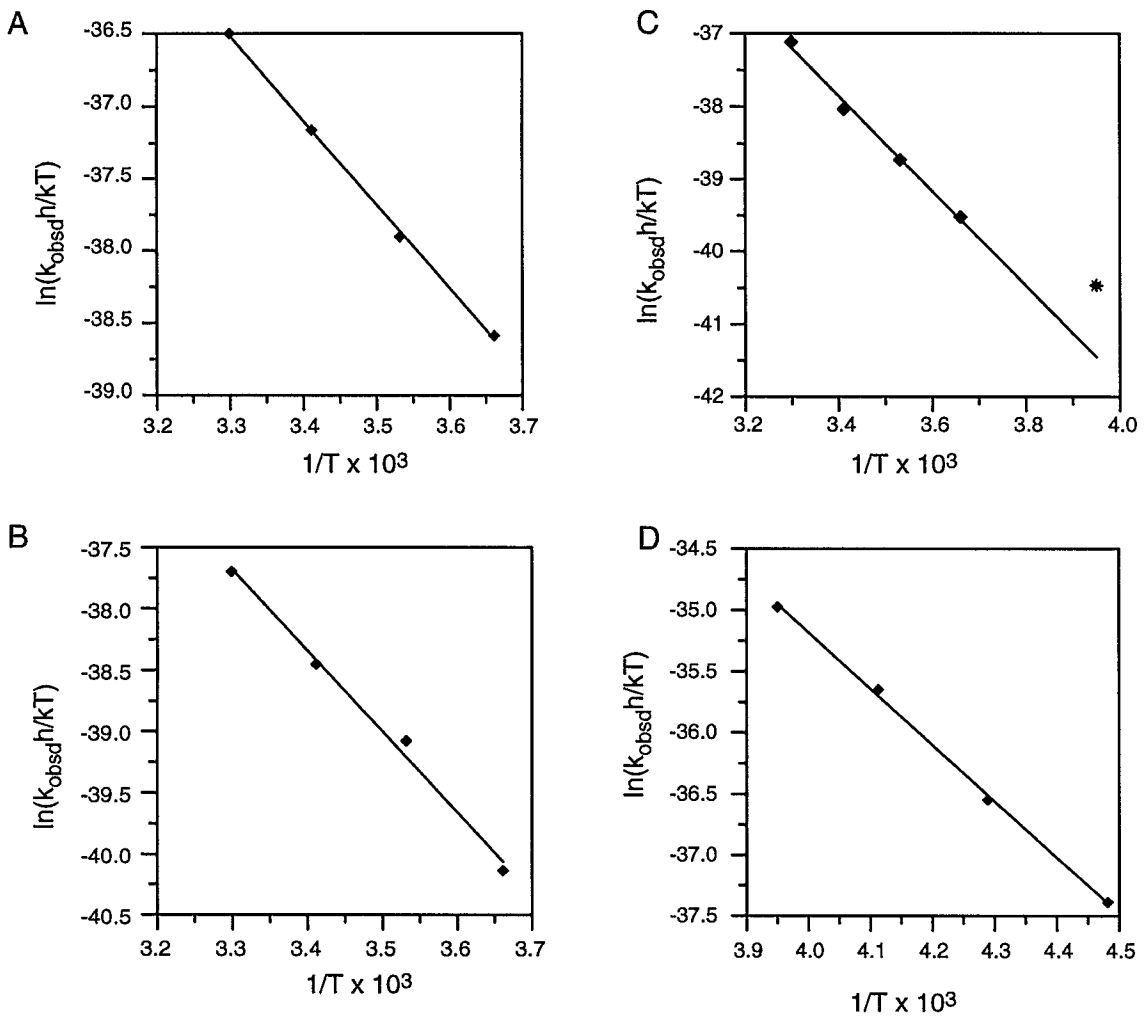
I. Plots of k_{obsd} versus [LDA] for the elimination of (±)-*exo*-2-bromonorbornane (0.004 M) by LDA in solution with: **A** THF (12.3 M, neat) at 20 °C; **B** THF (2.0 M) in toluene co-solvent at 20 °C; **C** *n*-BuOMe (2.0 M) in toluene co-solvent at 20 °C; **D** dimethoxyethane (2.0 M) in toluene co-solvent at -20 °C; **E** $MeOCH_2CH_2NMe_2$ (2.0 M) in toluene co-solvent at -40 °C; **F** $MeOCH_2CH_2NEt_2$ (2.0 M) in toluene co-solvent at -20 °C; **G** $MeOCH_2CH_2N(CH_2)_4$ (2.0 M) in toluene co-solvent at -20 °C. The curves depict the results of unweighted linear least-squares fits to $f(x) = ax^b$.



II. Plots of k_{obsd} versus [THF] in toluene co-solvent for the elimination of (±)-*exo*-2-bromonorbornane (0.004 M) by LDA (0.10 M). The plots show data obtained at: **A** 30 °C; **B** 20 °C; **C** 10 °C; **D** 0 °C. The curves depict the results of unweighted linear least-squares fits to f(x) = ax+b.



III. Plots of k_{obsd} versus [ligand] in toluene co-solvent for the elimination of (±)-*exo*-2-bromonorbornane (0.004 M) by LDA (0.10 M). The plots show data obtained for: **A** *n*-BuOMe at 20 °C; **B** dimethoxyethane at -20 °C; **C** $MeOCH_2CH_2NMe_2$ at -40 °C; **D** $MeOCH_2CH_2NEt_2$ at -20 °C; **E** $MeOCH_2CH_2N(CH_2)_4$ at -20 °C. The curves depict the results of unweighted linear least-squares fits to f(x) = a.



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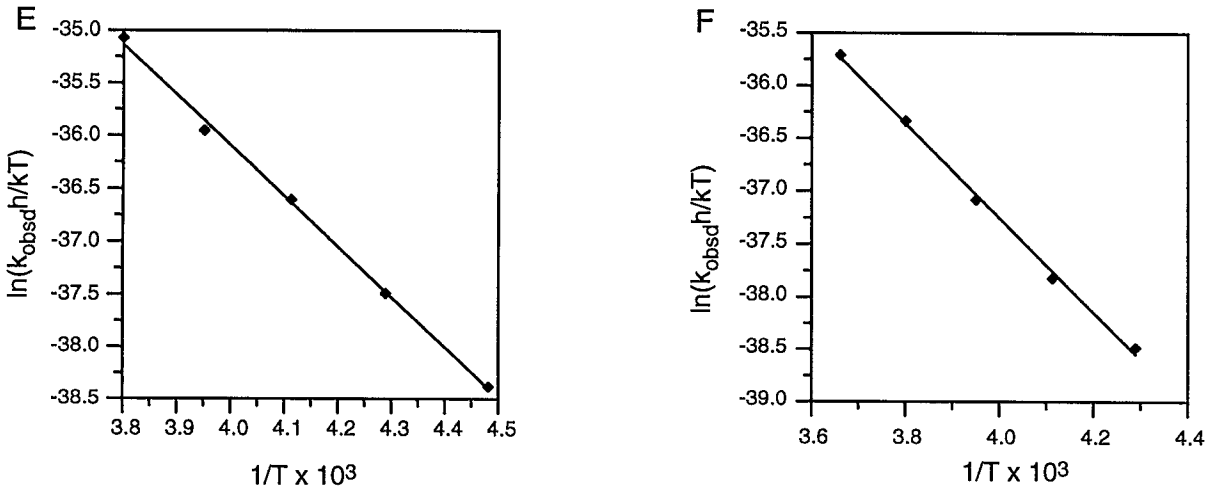
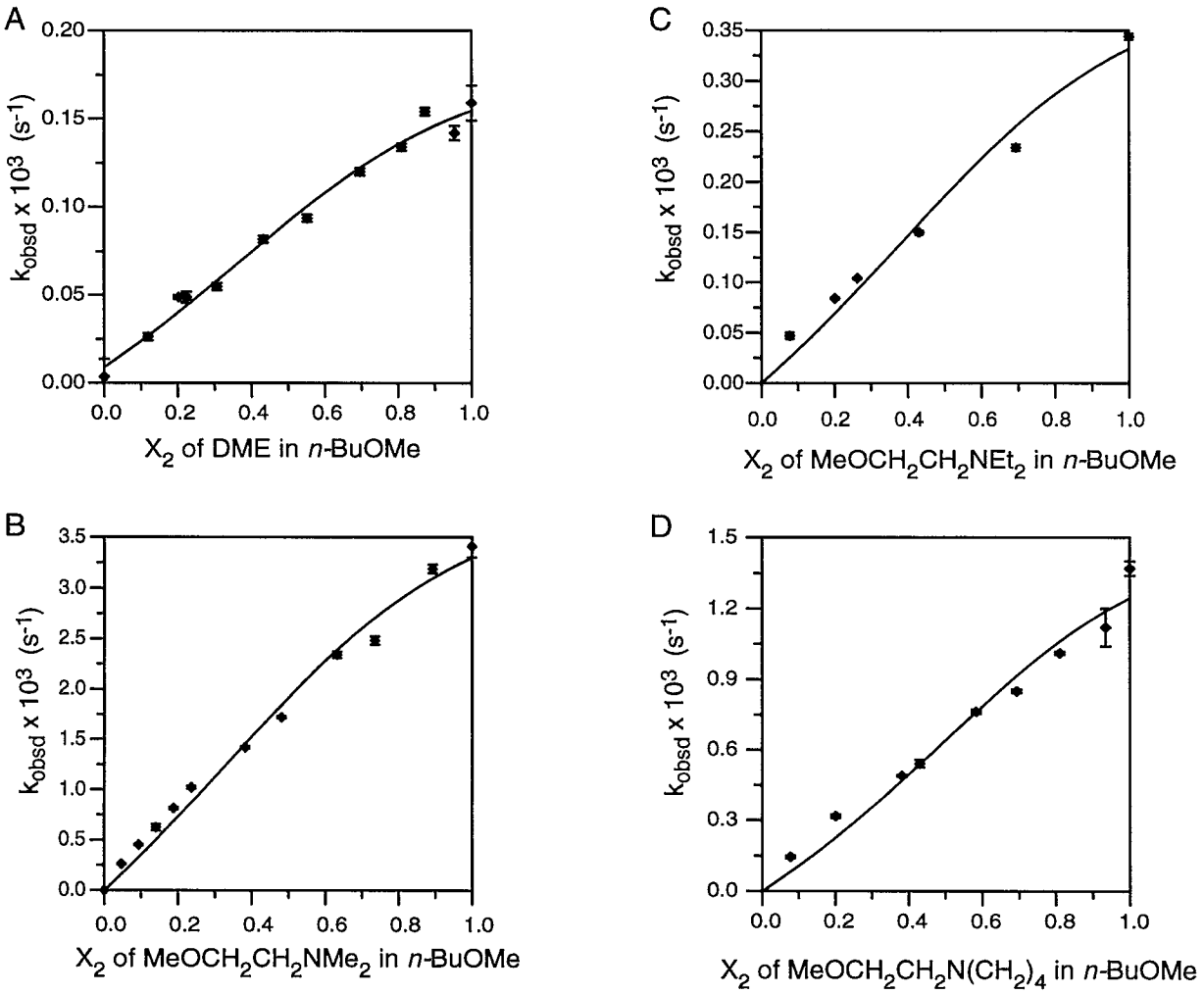


IV. Observed pseudo-first-order rate constants (k_{obsd}) measured as a function of temperature for the elimination of (±)-*exo*-2-bromonorbornane (0.004 M) by LDA (0.10 M): **A** neat THF (12.3 M) measured from 0 to 30 °C; **B** no free THF in toluene co-solvent measured from 0 to 30 °C; **C** *n*-BuOMe (2.0 M) in toluene co-solvent measured from 0 to 30 °C; **D** $MeOCH_2CH_2NMe_2$ (2.0 M) in toluene co-solvent measured from -50 to -20 °C; **E** $MeOCH_2CH_2NEt_2$ (2.0 M) in toluene co-solvent measured from -40 to 0 °C; **F** $MeOCH_2CH_2N(CH_2)_4$ (2.0 M) in toluene co-solvent measured from -50 to -10 °C. The curves correspond to linear least-squares fits to the equation: $\ln\{k_{obsd}h/kT\} = -\Delta H^{o}_{act}/RT + \Delta S^{o}_{act}/R$. The activation parameters (Table 1) were derived from a non-linear least-squares fit to the expression: $k_{obsd} = kT/h[\exp(-\Delta H^{o}_{act}/RT)\exp(\Delta S^{o}_{act}/R)]$.



V. Observed rate constants for dehydrobromination of (±)-exo-2-bromonorbornane (0.004 M) by LDA (0.1 M) vs. mole fraction, X_2, of chelating ligand in *n*-BuOMe at -20 °C. The curves correspond to a non-linear squares fit to the equation shown below. (See part XI for derivation and eq 10 in the manuscript.) The chelating ligands shown are: **A**. Dimethoxyethane; **B**. $MeOCH_2CH_2NMe_2$; **C**. $MeOCH_2CH_2NEt_2$; **D**. $MeOCH_2CH_2N(CH_2)_4$.

$$k_{obsd} = \left\{ k_1 K_B^{1/2} + k_2 K_D^{1/2} \left(2K_A \frac{[X_2]}{[1-X_2]} \right) \right\} \left\{ \frac{A_T}{1 + K_A \frac{[X_2]}{[1-X_2]} + \left(2K_A \frac{[X_2]}{[1-X_2]} \right)^2} \right\}^{1/2}$$

VI. Tables of data for plots in Section I.

Data for Figure IA

[LDA] (M)	k_{obsd} (s^{-1})	error (s^{-1})
0.021	0.00025	1.7E-5
0.023	0.00024	8.0E-6
0.049	0.00032	1.1E-5
0.049	0.00039	1.1E-5
0.073	0.00040	9.0E-6
0.074	0.00038	7.0E-6
0.10	0.00044	1.2E-5
0.10	0.00044	8.0E-6
0.12	0.00053	8.0E-6
0.13	0.00047	6.0E-6
0.15	0.00059	2.1E-5
0.17	0.00055	1.4E-5
0.20	0.00062	2.5E-5
0.20	0.00064	2.1E-5
0.24	0.00066	1.6E-5
0.34	0.00071	3.0E-6
0.39	0.00077	1.1E-5

Data for Figure IB

[LDA] (M)	k_{obsd} (s^{-1})	error (s^{-1})
0.025	8.2E-5	2.8E-5
0.052	0.00011	3.0E-6
0.10	0.00016	2.0E-6
0.14	0.00019	7.0E-6
0.19	0.00022	5.0E-6
0.23	0.00023	8.0E-6
0.29	0.00027	7.0E-6
0.34	0.00029	1.1E-5
0.40	0.00031	1.2E-5

VI. Tables of data for plots in Section I. (continued)

Data for Figure IC

[LDA] (M)	k_{obsd} (s^{-1})	error (s^{-1})
0.047	0.00014	7.0E-6
0.10	0.00019	1.1E-5
0.14	0.00025	1.3E-5
0.19	0.00027	1.0E-5
0.24	0.00032	1.4E-5
0.29	0.00030	5.0E-6
0.32	0.00033	1.5E-5
0.37	0.00033	1.1E-5

Data for Figure ID

[LDA] (M)	k_{obsd} (s^{-1})	error (s^{-1})
0.067	0.00012	1.0E-6
0.097	0.00014	1.0E-6
0.12	0.00017	2.0E-6
0.18	0.00019	1.0E-6
0.23	0.00023	5.0E-6
0.27	0.00025	1.0E-6
0.34	0.00029	7.0E-6

Data for Figure IE

[LDA] (M)	k_{obsd} (s^{-1})	error (s^{-1})
0.036	0.00030	8.0E-6
0.087	0.00055	1.0E-5
0.10	0.00062	5.0E-6
0.12	0.00069	1.0E-5
0.19	0.00082	2.0E-5
0.22	0.00093	8.0E-6
0.29	0.00109	1.0E-5
0.31	0.00114	1.1E-5
0.38	0.00123	9.0E-6

VI. Tables of data for plots in Section I. (continued)

Data for Figure IF

[LDA] (M)	k_{obsd} (s^{-1})	error (s^{-1})
0.039	0.00026	2.0E-6
0.071	0.00033	3.0E-6
0.10	0.00041	5.0E-6
0.15	0.00051	2.0E-6
0.21	0.00063	4.0E-6
0.31	0.00077	6.0E-6

Data for Figure IG

[LDA] (M)	k_{obsd} (s^{-1})	error (s^{-1})
0.047	0.00086	2.7E-5
0.074	0.0012	3.0E-5
0.10	0.0014	1.5E-5
0.15	0.0018	1.3E-5
0.20	0.0022	3.0E-5
0.29	0.0026	1.8E-5

VII. Tables of data for plots in Section II.

Data for Figure IIA

[THF] (M)	k_{obsd} (s^{-1})	error on k_{obsd}
1.2	0.00033	1.1E-5
2.0	0.00035	4.0E-6
4.0	0.00046	2.0E-6
5.0	0.00052	3.0E-6
6.0	0.00058	3.0E-6
8.0	0.00066	7.0E-6
10.	0.00077	7.0E-6
12.3	0.00092	2.4E-5

Data for Figure IIB

[THF] (M)	k_{obsd} (s^{-1})	error on k_{obsd}
1.0	0.00012	3.0E-6
3.0	0.00019	7.0E-6
5.0	0.00024	5.0E-6
6.0	0.00026	7.0E-6
7.0	0.00029	7.0E-6
9.0	0.00033	5.0E-6
10.	0.00034	3.0E-6
11.	0.00037	5.0E-6
12.3	0.00044	8.0E-6

Data for Figure IIC

[THF] (M)	k_{obsd} (s^{-1})	error on k_{obsd}
2.0	8.46E-5	9.0E-6
4.0	0.00010	2.0E-6
5.0	0.00011	7.0E-6
6.0	0.00013	6.0E-6
8.0	0.00014	5.0E-6
10.	0.00016	4.0E-6
12.3	0.00020	7.0E-6

Data for Figure IID

[THF] (M)	k_{obsd} (s^{-1})	error on k_{obsd}
2.0	0.00031	1.8E-6
3.5	0.00040	2.0E-6
5.0	0.00047	1.7E-6
7.0	0.00054	1.1E-6
9.0	0.00069	2.4E-6
12.	0.00099	3.1E-6

VIII. Tables of data for plots in Section III.

Data for Figure IIIA

[*n*-BuOMe] (M)	k_{obsd} (s^{-1})	error on k_{obsd}
1.5	0.00018	5.0E-6
2.0	0.00019	4.0E-6
4.0	0.00018	6.0E-6
6.0	0.00017	4.0E-6
8.4	0.00017	5.0E-6

Data for Figure IIIB

[$MeOCH_2CH_2OMe$]	k_{obsd} (s^{-1})	error on k_{obsd}
0.5	0.00058	1.2E-5
1.0	0.00062	9.0E-6
2.0	0.00061	7.0E-6
2.5	0.00058	1.0E-5
4.0	0.00062	2.0E-6
5.0	0.00056	5.0E-6
6.0	0.00054	4.0E-6

Data for Figure IIIC

[$MeOCH_2CH_2NMe_2$]	k_{obsd} (s^{-1})	error on k_{obsd}
1.0	0.00014	3.0E-6
2.0	0.00015	2.0E-6
3.0	0.00015	2.0E-6
4.0	0.00016	2.0E-6
6.0	0.00016	5.0E-6

Data for Figure IIID

[$MeOCH_2CH_2NEt_2$]	k_{obsd} (s^{-1})	error on k_{obsd}
1.0	0.00045	1.0E-5
2.0	0.00041	5.0E-6
3.0	0.00041	3.0E-6

Data for Figure IIIE

[$MeOCH_2CH_2N(CH_2)_4$]	k_{obsd} (s^{-1})	error on k_{obsd}
1.0	0.0014	1.2E-5
2.0	0.0014	2.0E-5
3.0	0.0014	1.6E-5
4.0	0.0014	1.4E-5

IX. Tables of data for plots in Section IV

Data for Figure IVA

T (K)	k_{obsd} (s^{-1})	$\ln(k_{obsd}h/kT)$	1/T (K^{-1})
273	9.9E-5	-39	0.0036
283	0.00020	-38	0.0035
293	0.00044	-37	0.0034
303	0.00088	-37	0.0032

Data for Figure IVB

T (K)	k_{obsd} (s^{-1})	$\ln(k_{obsd}h/kT)$	1/T (K^{-1})
273	2.1E-5	-40	0.0036
283	6.3E-5	-39	0.0035
293	0.00012	-38	0.0034
303	0.00026	-37	0.0033

Data forFigure IVC

T (K)	k_{obsd} (s^{-1})	$\ln(k_{obsd}h/kT)$	1/T (K^{-1})
273	3.9E-5	-39	0.0036
283	8.9E-5	-38	0.0035
293	0.00018	-38	0.0034
303	0.00048	-37	0.0032

Data for Figure IVD

T (K)	k_{obsd} (s^{-1})	$\ln(k_{obsd}h/kT)$	1/T (K^{-1})
223	0.00026	-37	0.0044
233	0.00065	-36	0.0042
243	0.0016	-35	0.0041
253	0.0034	-34	0.0039

Data for Figure IVE

T (K)	k_{obsd} (s^{-1})	$\ln(k_{obsd}h/kT)$	1/T (K^{-1})
223	0.00010	-38	0.0044
233	0.00025	-37	0.0042
243	0.00064	-36	0.0041
253	0.0012	-35	0.0039
263	0.0032	-35	0.0038

IX. Tables of data for plots in section IV (continued)

Data for Figure IVF

T (K)	k_{obsd} (s^{-1})	$\ln(k_{obsd}h/kT)$	1/T (K^{-1})
233	9.4E-5	-38	0.0042
243	0.00019	-37	0.0041
253	0.00041	-37	0.0039
263	0.00090	-36	0.0038
273	0.0017	-35	0.0036

X. Tables of data for plots in Section V.

Data for Figure VA

X_2, $MeOCH_2CH_2OME$	k_{obsd} (s^{-1})	error on k_{obsd} (s^{-1})
0.00	3.5E-6	1.0E-5
0.11	2.6E-5	2.0E-6
0.20	4.8E-5	1.0E-6
0.22	4.8E-5	3.0E-6
0.30	5.4E-5	2.0E-6
0.43	8.1E-5	2.0E-6
0.55	9.3E-5	2.0E-6
0.69	0.00012	2.0E-6
0.80	0.00013	2.0E-6
0.87	0.00015	2.0E-6
0.95	0.00014	4.0E-6
1.00	0.00015	1.0E-5

Data for Figure VB

X_2, $MeOCH_2CH_2NMe_2$	k_{obsd} (s^{-1})	error on k_{obsd} (s^{-1})
0.046	0.00026	5.0E-6
0.093	0.00045	5.0E-6
0.14	0.00062	3.0E-5
0.18	0.00081	1.3E-5
0.23	0.0010	1.3E-5
0.38	0.0014	1.0E-5
0.48	0.0017	1.0E-5
0.63	0.0023	3.1E-5
0.73	0.0024	4.0E-5
0.89	0.0031	4.0E-5
1.0	0.0034	0.00011

Data for Figure VC

X_2, $MeOCH_2CH_2NEt_2$	k_{obsd} (s^{-1})	error on k_{obsd} (s^{-1})
0.077	4.7E-5	3.0E-6
0.20	8.4E-5	1.0E-6
0.26	0.00010	1.0E-6
0.42	0.00015	2.0E-6
0.69	0.00023	3.0E-6
1.0	0.00034	3.0E-6

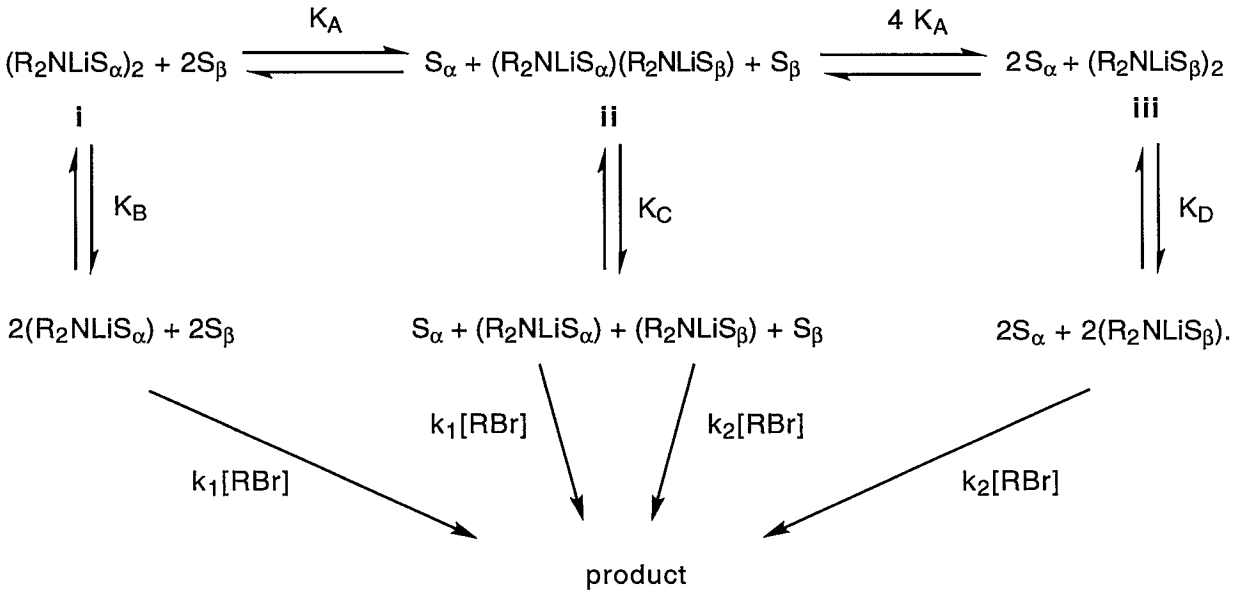
Figure X. Tables of data for plots in Section V. (continued)

Data for Figure VD

X_2, $MeOCH_2CH_2N(CH_2)_4$	k_{obsd} (s^{-1})	error on k_{obsd} (s^{-1})
0.077	0.00014	6.0E-6
0.20	0.00031	8.0E-6
0.38	0.00048	5.0E-6
0.42	0.00054	1.6E-5
0.58	0.00076	9.0E-6
0.69	0.00084	7.0E-6
0.81	0.0010	6.0E-6
0.93	0.0011	8.0E-5
1.0	0.0013	3.0E-5

XI. Derivation of expression for solvent binding constant determination (eq 10 in manuscript):

Scheme 1



For convenience, we let A = R_2NLi, S_α = S, and S_β = S' and describe Scheme I by eq 1-7.

$$A_2S_2 + S' \overset{K_A}{\rightleftharpoons} A_2SS' + S \qquad (1)$$

$$A_2SS' + S' \overset{4K_A}{\rightleftharpoons} A_2S'_2 + S \qquad (2)$$

$$A_2S_2 \overset{K_B}{\rightleftharpoons} 2\ AS \qquad (3)$$

$$A_2SS' \overset{K_C}{\rightleftharpoons} AS + AS' \qquad (4)$$

$$A_2S'_2 \overset{K_D}{\rightleftharpoons} 2\ AS' \qquad (5)$$

$$AS + RX \xrightarrow{k_1} \text{product} \qquad (6)$$

$$AS' + RX \xrightarrow{k_2} \text{product} \qquad (7)$$

$$\frac{d[\text{product}]}{dt} = \left(k_1[AS] + k_2[AS'] \right)[RX] \qquad (8)$$

$$k_{obsd} = k_1[AS] + k_2[AS'] \qquad (9)$$

From eq 3 and 5,

$$[AS] = K_B^{1/2}[A_2S_2]^{1/2} \qquad (10)$$

$$[AS'] = K_D^{1/2}[A_2S'_2]^{1/2} \qquad (11)$$

Substitution of [AS] and [AS'] from eq 10 and 11 into eq 9 affords

$$k_{obsd} = k_1 K_B^{1/2}[A_2S_2]^{1/2} + k_2 K_D^{1/2}[A_2S'_2]^{1/2} \qquad (12)$$

$$K_A = \frac{[A_2SS'][S]}{[A_2S_2][S']} \qquad (13)$$

$$4K_A = \frac{[A_2S'_2][S]}{[A_2SS'][S']} \qquad (14)$$

$$A_T = [A_2S_2] + [A_2SS'] + [A_2S'_2] \qquad (15)$$

Rearranging eq 13

$$[A_2SS'] = K_A[A_2S_2]\frac{[S']}{[S]} \qquad (16)$$

Rearranging eq 14 and substituting in [A_2SS'] from eq 16 gives

$$[A_2S'_2] = [A_2S_2]\left(2K_A\frac{[S']}{[S]}\right)^2 \qquad (17)$$

By substituting 16 and 17 into eq 15 and rearranging we get

$$[A_2S_2] = \left\{\frac{A_T}{1 + K_A\frac{[S']}{[S]} + \left(2K_A\frac{[S']}{[S]}\right)^2}\right\} \qquad (18)$$

Substituting $[A_2S_2]$ from eq 18 into eq 16 and 17 gives eq 19 and 20, respectively.

$$[A_2SS'] = K_A \frac{[S']}{[S]} \left\{ \frac{A_T}{1 + K_A \frac{[S']}{[S]} + \left(2K_A \frac{[S']}{[S]}\right)^2} \right\} \tag{19}$$

$$[A_2S'_2] = \left(2K_A \frac{[S']}{[S]}\right)^2 \left\{ \frac{A_T}{1 + K_A \frac{[S']}{[S]} + \left(2K_A \frac{[S']}{[S]}\right)^2} \right\} \tag{20}$$

Substituting $[A_2S_2]$ and $[A_2S'_2]$ from eq 18 and 20 into eq 12 gives

$$k_{obsd} = \left\{ k_1 K_B^{1/2} + k_2 K_D^{1/2} \left(2K_A \frac{[S']}{[S]}\right) \right\} \left\{ \frac{A_T}{1 + K_A \frac{[S']}{[S]} + \left(2K_A \frac{[S']}{[S]}\right)^2} \right\}^{1/2} \tag{21}$$

Defining [S'] and [S] in terms mole fractions X_1 and X_2 for S and S' (eq 22 and 23) and substituting into eq 21 affords eq 25.

$$X_2 = \frac{[S']}{[S'] + [S]} \tag{22}$$

$$X_1 = 1 - X_2 \tag{23}$$

$$k_{obsd} = \left\{ k_1 K_B^{1/2} + k_2 K_D^{1/2} \left(2K_A \frac{[X_2]}{[1 - X_2]}\right) \right\} \left\{ \frac{A_T}{1 + K_A \frac{[X_2]}{[1 - X_2]} + \left(2K_A \frac{[X_2]}{[1 - X_2]}\right)^2} \right\}^{1/2} \tag{24}$$

Eq 24 (eq 9 in manuscript) describes the pseudo-first-order rate constant, k_{obsd}, in terms of the mole fraction of S' (X_2), mechanistic constants k_1K_B and k_2K_D, and relative solvent binding constant K_A.