Formation of Benzynes from 2,6-Dihaloaryllithiums:

Mechanistic Basis of the Regioselectivity

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Supporting Information

NMR Spectroscopy

I ^{13}C NMR spectrum of 2-chloro-6-fluorophenyllithium (**6**) in neat THF.

II ^{6}Li NMR spectrum of 2-chloro-6-fluorophenyllithium (**6**) in THF (10.3 M).

III ^{6}Li NMR spectra of 2-chloro-6-fluorophenyllithium (**6**) in THF (5.0 and 0.3 M).

Kinetics of Benzyne Formation

IV Plot of $k_{obsd(\mathbf{6})}$ versus [**6**] in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzyne.

V Plot of $k_{obsd(\mathbf{6})}$ versus [**6**] in THF (6.8 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzyne.

DFT Calculations

Experimental Section.

NMR Spectroscopy

I. ^{13}C NMR spectrum in neat THF at $-100\ ^\circ$C of 0.4 M [^{6}Li]2-chloro-6-fluorophenyllithium (**6**).

II. ^{6}Li NMR spectrum in THF (10.3 M) with toluene cosolvent at -100 $^\circ$C of 0.2 M [^{6}Li]2-chloro-6-fluorophenyllithium (**6**).
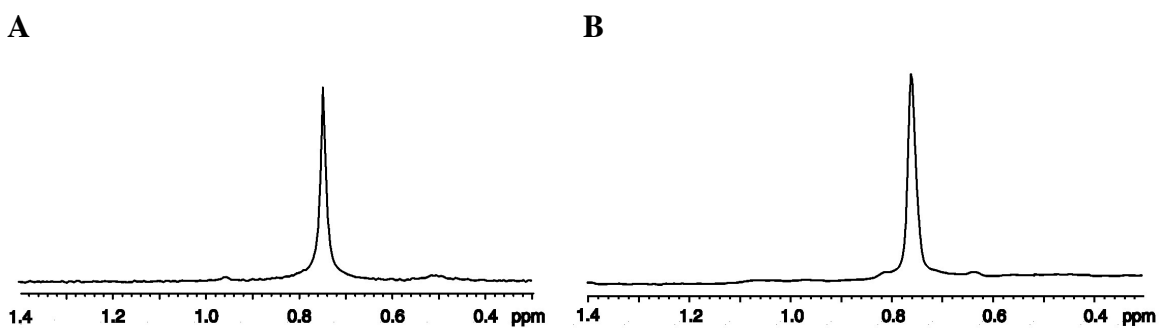
III. ^{6}Li NMR spectra in THF and toluene/pentane cosolvent at -85 $^\circ$C: (**A**) 0.10 M [^{6}Li]2-chloro-6-fluorophenyllithium (**6**) in [THF] = 5.0 M; (**B**) 0.10 M [^{6}Li]2-chloro-6-fluorophenyllithium (**6**) in [THF] = 0.30 M.

Kinetics of Benzyne Formation
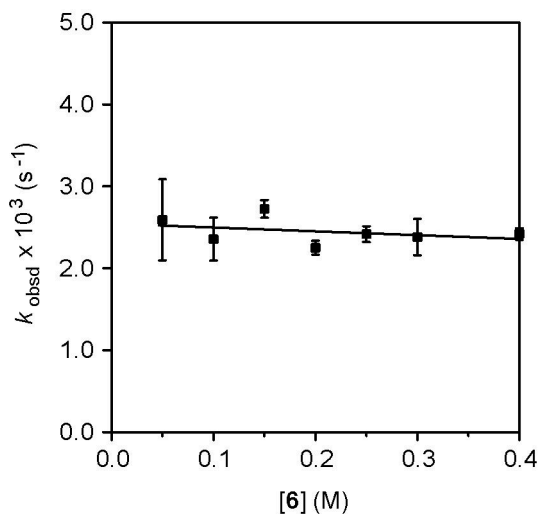
IV. Plot of $k_{obsd(6)}$ versus [**6**] in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzyne at -25 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd(6)} = k[\mathbf{6}] + k'$ ($k = 5 \pm 5$ x 10^{-4}, $k' = 2.5 \pm 0.1$ x 10^{-3}).
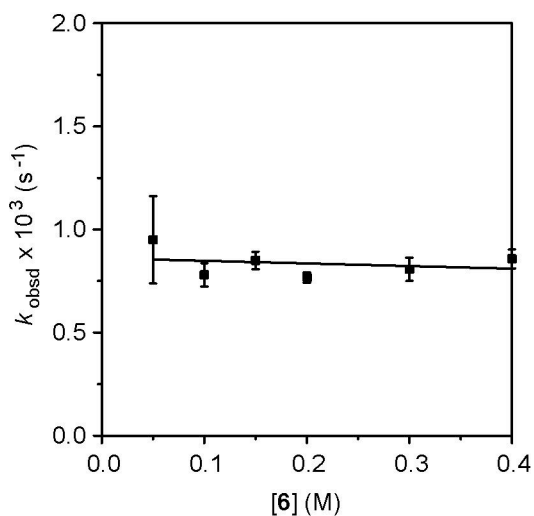
V. Plot of $k_{obsd(6)}$ versus [**6**] in THF (6.8 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzyne at -25 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd(6)} = k[\mathbf{6}] + k'$ ($k = 1 \pm 2$ x 10^{-4}, $k' = 8.6 \pm 0.6$ x 10^{-4}).
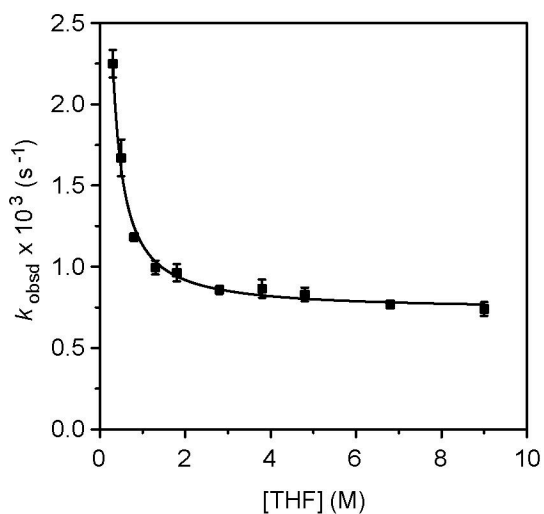
VI. Plot of $k_{obsd(6)}$ versus [THF] in toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzyne from **6** (0.2 M) at -25 $^{\circ}$C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd(6)} = k[\text{THF}]^n + k'$ ($k = 4.0 \pm 0.4$ x 10^{-5}, n = -1.12 $\pm$ 0.09, $k' = 7.3 \pm 0.3$ x 10^{-4}).

VII. Plot of $k_{obsd(2)}$ versus [THF] in toluene cosolvent for the formation of 3-chlorobenzyne from **6** (0.2 M) at -25 $^{\circ}$C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd(2)} = k[\text{THF}]^n + k'$ ($k = 4.2 \pm 0.6$ x 10^{-4}, n = -1.1 $\pm$ 0.1, $k' = 1 \pm 4$ x 10^{-5}).
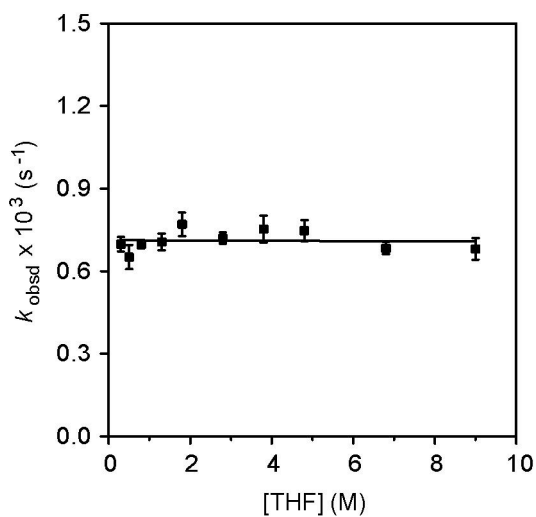
VIII. Plot of $k_{obsd(3)}$ versus [THF] in toluene cosolvent for the formation of 3-fluorobenzyne from **6** (0.2 M) at -25 $^{\circ}$C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd(3)} = k$[THF] $+ k'$ ($k = $ -1 $\pm$ 4 x 10^{-6}, $k' = 7.1 \pm 0.2$ x 10^{-4}).
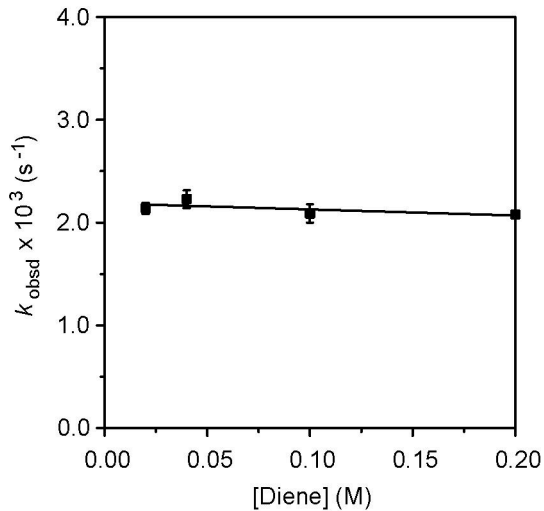
IX. Plot of $k_{obsd(6)}$ versus [spiro[2.4]hepta-4,6-diene] in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro and 3-fluorobenzyne from **6** (0.2 M) at -25 $^{\circ}$C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd(6)} = k$[diene] $+ k'$ ($k = $ -1 $\pm$ 4 x 10^{-4}, $k' = 2.2 \pm 0.1$ x 10^{-3}).

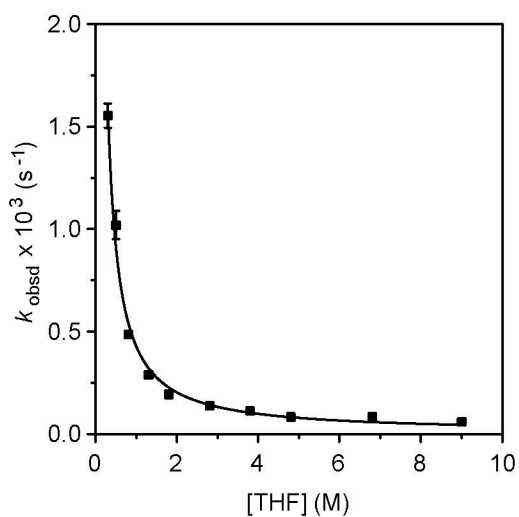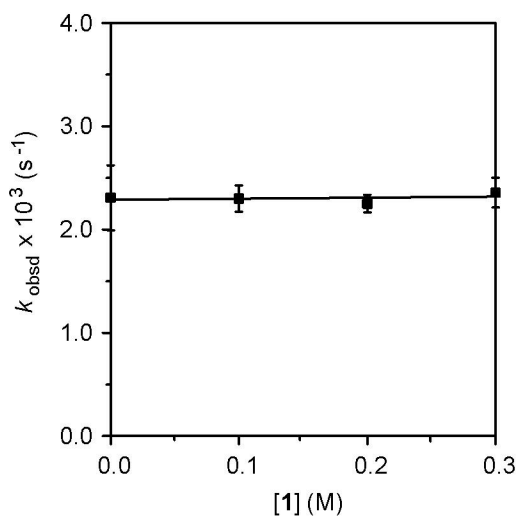**X.** Plot of $k_{obsd(6)}$ versus [**1**] in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro and 3-fluorobenzyne from **6** (0.2 M) at -25 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd(6)} = k[\mathbf{1}] + k'$ ($k = 1 \pm 2$ x 10^{-4}, $k' = 2.3 \pm 0.1$ x 10^{-3}).

XI. Table of data for plot in Section IV

[**6**] (M)	$k_{obsd(6)}$ 1 (s^{-1})	$k_{obsd(6)}$ 2 (s^{-1})	$k_{obsd(6)}$ (avg) (s^{-1})
0.050	0.0029 ± 3E-4	0.0022 ± 2E-4	0.0026 ± 5E-4
0.100	0.0022 ± 1E-4	0.0025 ± 2E-4	0.0023 ± 3E-4
0.150	0.0026 ± 1E-4	0.0028 ± 3E-4	0.0027 ± 1E-4
0.200	0.0022 ± 2E-4	0.0023 ± 2E-4	0.0022 ± 1E-4
0.250	0.0025 ± 3E-4	0.0023 ± 2E-4	0.0024 ± 1E-4
0.300	0.0025 ± 2E-4	0.0022 ± 2E-4	0.0024 ± 2E-4
0.400	0.0024 ± 2E-4	0.0025 ± 3E-4	0.0024 ± 1E-4

XII. Table of data for plot in Section V

[6] (M)	$k_{obsd(6)}$ 1 (s^{-1})	$k_{obsd(6)}$ 2 (s^{-1})	$k_{obsd(6)}$ (avg) (s^{-1})
0.050	0.0008 ± 1E-4	0.0011 ± 1E-4	0.0009 ± 2E-4
0.100	0.00082 ± 5E-5	0.00074 ± 3E-5	0.00078 ± 6E-5
0.150	0.00088 ± 4E-5	0.00082 ± 5E-5	0.00085 ± 4E-5
0.200	0.00075 ± 8E-5	0.00078 ± 5E-5	0.00077 ± 2E-5
0.300	0.0008 ± 1E-4	0.00077 ± 4E-5	0.00081 ± 5E-5
0.400	0.0008 ± 1E-4	0.00089 ± 1E-5	0.00086 ± 5E-5

XIII. Table of data for plot in Section VI

[THF] (M)	$k_{obsd(6)}$ (s^{-1})	$k_{obsd(6)}$ 2 (s^{-1})	$k_{obsd(6)}$ (avg) (s^{-1})
0.30	0.0022 ± 2E-4	0.0023 ± 2E-4	0.0022 ± 1E-4
0.50	0.0017 ± 1E-4	0.0016 ± 2E-4	0.0017 ± 1E-4
0.80	0.0012 ± 1E-5	0.0012 ± 1E-4	0.0012 ± 1E-4
1.30	0.0010 ± 1E-5	0.00096 ± 8E-5	0.00099 ± 4E-5
1.80	0.00092 ± 5E-5	0.0010 ± 1E-4	0.00096 ± 5E-5
2.80	0.00087 ± 4E-5	0.00084 ± 5E-5	0.00086 ± 2E-5

3.80	$0.00082 \pm$ 4E-6	$0.00090 \pm$ 3E-5	$0.00086 \pm$ 6E-5
4.80	$0.0009 \pm$ 1E-4	$0.00080 \pm$ 5E-5	$0.00083 \pm$ 4E-5
6.80	$0.00075 \pm$ 8E-5	$0.00078 \pm$ 5E-5	$0.00077 \pm$ 2E-5
9.00	$0.00071 \pm$ 6E-5	$0.00077 \pm$ 8E-5	$0.00074 \pm$ 4E-5

XIV. Table of data for plot in Section VII

[THF] (M)	$k_{obsd(2)}$ 1 (s^{-1})	$k_{obsd(2)}$ 2 (s^{-1})	$k_{obsd(2)}$ (avg) (s^{-1})
0.30	$0.0015 \pm$ 1E-4	$0.0016 \pm$ 1E-4	$0.0015 \pm$ 1E-4
0.50	$0.0011 \pm$ 1E-4	$0.00097 \pm$ 6E-5	$0.0010 \pm$ 1E-4
0.80	$0.00048 \pm$ 5E-5	$0.00049 \pm$ 5E-5	$0.00048 \pm$ 1E-5
1.30	$0.00030 \pm$ 4E-5	$0.00028 \pm$ 3E-5	$0.00029 \pm$ 1E-5
1.80	$0.00018 \pm$ 2E-5	$0.00020 \pm$ 2E-5	$0.00019 \pm$ 1E-5
2.80	$0.00014 \pm$ 2E-5	$0.00013 \pm$ 1E-5	$0.00014 \pm$ 1E-5
3.80	$0.00011 \pm$ 1E-5	$0.00012 \pm$ 1E-5	$0.00011 \pm$ 1E-5
4.80	$0.000086 \pm$ 8E-6	$0.00008 \pm$ 1E-5	$0.000083 \pm$ 4E-6
6.80	$0.000082 \pm$ 9E-6	$0.000086 \pm$ 8E-6	$0.000084 \pm$ 3E-6
9.00	$0.000057 \pm$ 8E-6	$0.000062 \pm$ 7E-6	$0.000059 \pm$ 3E-6

XV. Table of data for plot in Section VIII

[THF] (M)	$k_{obsd(3)}$ 1 (s^{-1})	$k_{obsd(3)}$ 2 (s^{-1})	$k_{obsd(3)}$ (avg) (s^{-1})
0.30	$0.00068 \pm$ 6E-5	$0.00072 \pm$ 5E-5	$0.00070 \pm$ 3E-5
0.50	$0.00068 \pm$ 6E-5	$0.00062 \pm$ 5E-5	$0.00065 \pm$ 4E-5

0.80	$0.00069 \pm 7E\text{-}5$	$0.00071 \pm 7E\text{-}5$	$0.00070 \pm 1E\text{-}5$
1.30	$0.00073 \pm 8E\text{-}5$	$0.00068 \pm 7E\text{-}5$	$0.00070 \pm 3E\text{-}5$
1.80	$0.00074 \pm 8E\text{-}5$	$0.00080 \pm 8E\text{-}5$	$0.00077 \pm 4E\text{-}5$
2.80	$0.00073 \pm 8E\text{-}5$	$0.00071 \pm 6E\text{-}5$	$0.00072 \pm 2E\text{-}5$
3.80	$0.00072 \pm 7E\text{-}5$	$0.00079 \pm 7E\text{-}5$	$0.00075 \pm 5E\text{-}5$
4.80	$0.00077 \pm 8E\text{-}5$	$0.00072 \pm 7E\text{-}4$	$0.00075 \pm 4E\text{-}5$
6.80	$0.00067 \pm 7E\text{-}5$	$0.00070 \pm 5E\text{-}5$	$0.00068 \pm 2E\text{-}5$
9.00	$0.00065 \pm 8E\text{-}5$	$0.00071 \pm 8E\text{-}5$	$0.00068 \pm 4E\text{-}5$

XVI. Table of data for plot in Section IX

[Diene] (M)	$k_{obsd(6)}\ 1\ (s^{-1})$	$k_{obsd(6)}\ 2\ (s^{-1})$	$k_{obsd(6)}\ (avg)\ (s^{-1})$
0.02	$0.0022 \pm 2E\text{-}4$	$0.00212 \pm 4E\text{-}5$	$0.00216 \pm 5E\text{-}5$
0.04	$0.0022 \pm 2E\text{-}4$	$0.0023 \pm 2E\text{-}4$	$0.00225 \pm 8E\text{-}5$
0.10	$0.0020 \pm 1E\text{-}4$	$0.00217 \pm 4E\text{-}5$	$0.00211 \pm 9E\text{-}5$
0.20	$0.00207 \pm 3E\text{-}5$	$0.0021 \pm 2E\text{-}4$	$0.00210 \pm 4E\text{-}5$

XVII. Table of data for plot in Section X

[1] (M)	$k_{obsd(6)}$ 1 (s^{-1})	$k_{obsd(6)}$ 2 (s^{-1})	$k_{obsd(6)}$ (avg) (s^{-1})
0.00	0.0025 $\pm$ 3E-4	0.0021 $\pm$ 2E-4	0.0023 $\pm$ 3E-4
0.10	0.0022 $\pm$ 2E-4	0.0024 $\pm$ 3E-4	0.0023 $\pm$ 1E-4
0.20	0.0022 $\pm$ 2E-4	0.0023 $\pm$ 2E-4	0.00225 $\pm$ 8E-5
0.30	0.00225 $\pm$ 3E-5	0.0025 $\pm$ 2E-4	0.0024 $\pm$ 1E-4

XVIII. Table of data for observed ratio of [4]:[5] versus [THF] in toluene cosolvent for the formation of 3-chloro and 3-fluorobenzyne from **6** (0.2 M).

[THF] (M)	ratio [4]:[5] (avg)
0.30	0.69 $\pm$ 0.08
0.50	0.61 $\pm$ 0.07
0.80	0.41 $\pm$ 0.05
1.30	0.29 $\pm$ 0.02
1.80	0.20 $\pm$ 0.02
2.80	0.16 $\pm$ 0.02
3.80	0.13 $\pm$ 0.01
4.80	0.10 $\pm$ 0.01
6.80	0.11 $\pm$ 0.01
9.00	0.08 $\pm$ 0.01

DFT Calculations

XIX   Optimized structures for the serial solvation of 2-chloro-6-fluorophenyllithium using Gaussian 98W at the B3LYP level of DFT theory with the 6-31G* basis set. Only the most stable isomers are shown. THF is modeled by Me_2O. Vibrational frequencies calculated at the same level characterize these stationary points as minima (NIMAG = 0). Enthalpies (ΔH, kcal/mol) include thermal corrections at 248 °C.
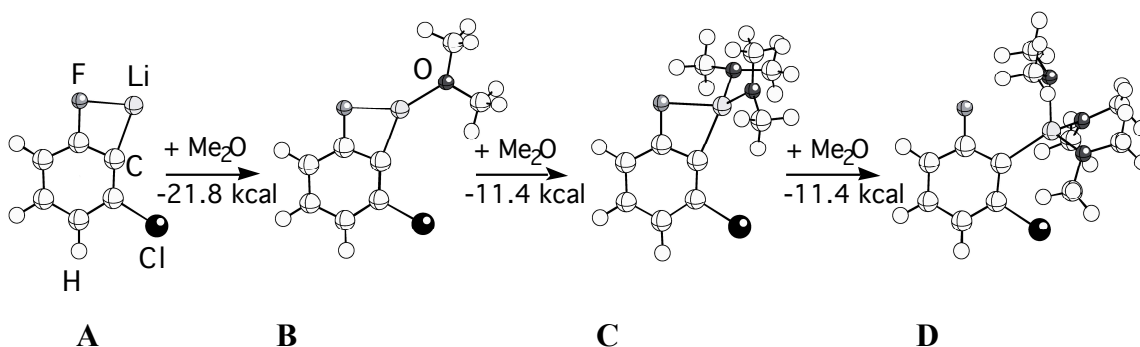
	_H_ (Hartrees)
Me_2O	-154.94063
A	-797.92399
B	-952.89941
C	-1107.85826
D	-1262.81714

Geometries of stationary points are given below:

Me$_2$O

```
SCF Done:  E(RB+HF-LYP) =  -155.025044227      A.U. after     1 cycles
Zero-point correction=                         0.08030   (Hartree/Particle)
Thermal correction to Energy=                  0.083627
Thermal correction to Enthalpy=                0.084413
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	0.000000	-0.589888	-0.000009
2	6	0	-1.171072	0.195261	0.000015
3	6	0	1.171072	0.195261	-0.000009
4	1	0	1.232500	0.839668	0.892951
5	1	0	2.021947	-0.491384	-0.000033
6	1	0	1.232477	0.839704	-0.892944
7	1	0	-1.232496	0.839702	-0.892920
8	1	0	-2.021947	-0.491385	0.000010
9	1	0	-1.232480	0.839670	0.892975

	1	2	3
	A	A	A
Frequencies --	224.0277	250.1852	415.2505

A

```
SCF Done:  E(RB+HF-LYP) =  -798.002004980      A.U. after    14 cycles
Zero-point correction=                         0.071769 (Hartree/Particle)
Thermal correction to Energy=                  0.077227
Thermal correction to Enthalpy=                0.078012
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.193425	-0.864690	-0.000013
2	6	0	-1.416565	-0.239413	0.000003
3	9	0	-2.538598	-1.169689	-0.000019
4	6	0	-1.728034	1.108292	0.000023
5	6	0	-0.621208	1.963405	0.000034
6	6	0	0.676630	1.441627	0.000023
7	6	0	0.852017	0.053561	-0.000004
8	17	0	2.536845	-0.542211	-0.000014
9	3	0	-1.237038	-2.549999	-0.000035
10	1	0	-2.749682	1.473450	0.000029
11	1	0	-0.770017	3.039494	0.000052
12	1	0	1.535346	2.105143	0.000033

	1	2	3
	A	A	A
Frequencies --	134.6060	180.2365	218.7280

B

SCF Done: E(RB+HF-LYP) = -953.064378177   A.U. after   14 cycles
Zero-point correction=   0.154053 (Hartree/Particle)
Thermal correction to Energy=   0.164183
Thermal correction to Enthalpy=   0.164969

 Center   Atomic   Atomic   Coordinates (Angstroms)
 Number   Number   Type   X   Y   Z
----
    1   6   0   0.517707   -0.097437   -0.000476
    2   6   0   1.657750   0.695168   -0.000110
    3   6   0   2.967961   0.205485   0.000482
    4   6   0   3.168674   -1.178510   0.000714
    5   6   0   2.074672   -2.050366   0.000360
    6   6   0   0.834489   -1.435254   -0.000214
    7   9   0   -0.320455   -2.305072   -0.000618
    8   17   0   1.476361   2.484006   -0.000386
    9   3   0   -1.409738   -0.682707   -0.001178
   10   8   0   -3.164529   -0.001791   0.000023
   11   6   0   -3.253293   1.429716   0.000814
   12   6   0   -4.433844   -0.649305   0.000061
   13   1   0   2.190355   -3.129549   0.000518
   14   1   0   4.179222   -1.577679   0.001170
   15   1   0   3.814451   0.884673   0.000751
   16   1   0   -5.006245   -0.375859   0.895737
   17   1   0   -4.250755   -1.726097   -0.000339
   18   1   0   -2.230337   1.811378   0.000551
   19   1   0   -3.781265   1.775216   0.898331
   20   1   0   -3.782093   1.776163   -0.895851
   21   1   0   -5.006626   -0.375238   -0.895182
----
                       1   2   3
                       A   A   A
 Frequencies --   16.4185   24.5809   36.7070

C

```
SCF Done:  E(RB+HF-LYP) = -1108.11491248     A.U. after    2 cycles
Zero-point correction=                        0.236176 (Hartree/Particle)
Thermal correction to Energy=                 0.255708
Thermal correction to Enthalpy=               0.256652
```

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.941928	-0.004917	0.006531
2	6	0	-2.203597	0.394607	0.424847
3	6	0	-3.412979	-0.126936	-0.047072
4	6	0	-3.372515	-1.131278	-1.018607
5	6	0	-2.143289	-1.593294	-1.500385
6	6	0	-1.021205	-0.992964	-0.950024
7	9	0	0.247461	-1.448197	-1.435408
8	17	0	-2.339067	1.694548	1.669751
9	3	0	1.111564	-0.061364	-0.092483
10	8	0	2.349638	-1.171238	0.950354
11	8	0	2.139234	1.421288	-0.804696
12	6	0	1.424015	2.620173	-1.115815
13	6	0	3.352912	1.283858	-1.533547
14	6	0	1.982743	-2.545182	1.097865
15	6	0	2.914665	-0.620222	2.137273
16	1	0	-2.072095	-2.369119	-2.256733
17	1	0	-4.298707	-1.552209	-1.400715
18	1	0	-4.362701	0.239047	0.330154
19	1	0	3.159723	1.261759	-2.614802
20	1	0	3.807402	0.340082	-1.224188
21	1	0	0.493060	2.585753	-0.548322
22	1	0	1.199163	2.665216	-2.189590
23	1	0	1.500054	-2.842287	0.166558
24	1	0	1.278555	-2.669456	1.930662
25	1	0	2.200985	-0.673205	2.970091
26	1	0	3.150597	0.424845	1.925489
27	1	0	2.874965	-3.160040	1.275794
28	1	0	3.833969	-1.155470	2.410559
29	1	0	2.015391	3.499768	-0.828612
30	1	0	4.038038	2.112392	-1.307662

```
                        1                    2                    3
                        A                    A                    A
 Frequencies --    15.6234              27.2839              31.2522
```

D

```
SCF Done:  E(RB+HF-LYP) =  -1263.15555432     A.U. after    1 cycles
Zero-point correction=                        0.318964 (Hartree/Particle)
Thermal correction to Energy=                 0.337628
Thermal correction to Enthalpy=               0.338413
------------------------------------------------------------------
 Center     Atomic      Atomic            Coordinates (Angstroms)
 Number     Number       Type         X           Y           Z
------------------------------------------------------------------
    1          6           0        1.237202   -0.183550   -0.101580
    2          6           0        2.379766    0.606120   -0.113680
    3          6           0        3.700645    0.158558   -0.216079
    4          6           0        3.919881   -1.216726   -0.313210
    5          6           0        2.832849   -2.094241   -0.300318
    6          6           0        1.568395   -1.526871   -0.192752
    7          9           0        0.503343   -2.438785   -0.163327
    8         17           0        2.206331    2.413110    0.029336
    9          3           0       -0.865117    0.029217    0.034984
   10          8           0       -1.667152    1.900208    0.046561
   11          8           0       -1.571027   -0.702604    1.813882
   12          8           0       -2.113353   -0.718243   -1.416262
   13          6           0       -1.681818   -1.717046   -2.339968
   14          6           0       -3.399541   -0.205562   -1.730425
   15          6           0       -0.587545   -1.280256    2.675543
   16          6           0       -2.812640   -1.388955    1.880201
   17          6           0       -1.367372    2.703681   -1.095365
   18          6           0       -1.520667    2.625809    1.267254
   19          1           0        2.962245   -3.170738   -0.367208
   20          1           0        4.933122   -1.601323   -0.395573
   21          1           0        4.531412    0.856854   -0.217218
   22          1           0       -0.726277   -2.090196   -1.976835
   23          1           0       -1.569304   -1.289142   -3.345869
   24          1           0       -3.415516    0.225650   -2.742051
   25          1           0       -3.620298    0.575531   -1.001204
   26          1           0       -2.707589   -2.429305    1.542061
   27          1           0       -3.511773   -0.864021    1.226563
   28          1           0        0.329057   -0.707728    2.534081
   29          1           0       -0.402336   -2.326084    2.402321
   30          1           0       -1.486140    2.066267   -1.973809
   31          1           0       -0.336034    3.069820   -1.051284
   32          1           0       -0.495897    3.001635    1.372752
   33          1           0       -1.741727    1.926638    2.075260
   34          1           0       -2.065314    3.550702   -1.159531
   35          1           0       -2.228120    3.466711    1.299378
   36          1           0       -0.919848   -1.221232    3.721395
   37          1           0       -3.204603   -1.384351    2.907314
   38          1           0       -4.160687   -0.997522   -1.675024
   39          1           0       -2.409418   -2.540273   -2.380415
------------------------------------------------------------------
                     1                   2                   3
                     A                   A                   A
 Frequencies --   27.4884             29.5158             40.0022
```

Experimental Section

Reagents and Solvents. 1-Chloro-3-fluorobenzene (**1**) is commercially available. *n*-BuLi used in the kinetics was recrystallized [see ref 10 in text]. Spiro[2.4]hepta-4,6-diene was prepared and purified according to literature procedures [see ref 8 in text]. [⁶Li]*n*-BuLi was prepared and recrystallized as described previously [Chadwick, S. T.; Rennels, R. A.; Rutherford, J. L.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 8640]. THF, *n*-pentane and toluene were distilled from sodium/benzophenone. The pentane still contained 1% tetraglyme to dissolve the ketyl. The diphenylacetic acid used to check solution titers [Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879] was recrystallized from methanol and sublimed at 120 ºC under full vacuum. Air- and moisture sensitive materials were manipulated under argon or nitrogen using standard glove box, vacuum line, and syringe techniques.

NMR Spectroscopic Analyses. Samples for spectroscopic analyses were prepared by using a protocol described elsewhere [Romesberg, F. E.; Bernstein, M. P.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 3475]. ⁶Li and ¹³C NMR spectra were recorded on a Varian XL-400 spectrometer operating at 58.84 and 100.58 MHz, respectively. The ⁶Li and ¹³C resonances are referenced to 0.30 M [⁶Li]LiCl/MeOH (0.0 ppm, -100 ºC), and the THF β-methylene resonance (25.37 ppm, -100 ºC), respectively.

Kinetics. For a kinetic run corresponding to a single rate constant, a relatively concentrated (2.2 M) solution of *n*-BuLi in toluene at -78 ºC was prepared and titrated to determine the precise concentration. The solution was diluted to a concentration appropriate for the particular series and titrated a second time. A series of oven-dried, argon-flushed 5 mL serum vials (10 per rate constant) fitted with stir bars were charged with a stock solution containing 1-chloro-3-fluorobenzene (**1**), spiro[2.4]hepta-4,6-diene, THF, and *n*-octane as a GC standard. The reaction vials were held under argon at –25.0 ± 0.2 ºC. The reactions were initiated by adding aliquots of a stock solution of *n*-BuLi in

toluene, also refrigerated at –25 ºC, to achieve a concentration 0.2 M below the actual 1-chloro-3-fluorobenzene (**1**) concentration. The metalations were monitored by following the decrease of **1** relative to the internal standard at early percent conversion. The vessels were periodically quenched with 1:1 H_2O-THF at intervals chosen to ensure an adequate sampling of early conversion at 10% consumption of the starting material. The quenched aliquots were extracted into Et_2O and the extracts analyzed using an auto injecting GC fitted with a 60 meter DB-5 column. The initial rates were determined by linear least-squares analyses, and were shown to be reproducible within $\pm$ 10%. Following the formation of cycloadducts **4** and **5** afforded equivalent rate constants within $\pm$ 10%. Beyond 20% consumption of the starting material, GC analyses showed detectable amounts (< 5%) of butyl adducts resulting from nucleophilic addition of *n*-BuLi to the intermediate 3-halobenzyne [Coe, J. W.; Wirtz, M. C.; Bashore, C. G.; Candler, J. *Org. Lett.* **2004**, *6*, 1589]. The observed rate constants (k_{obsd}) were calculated by dividing the initial rates (linear slopes) by the corresponding concentrations of 2-chloro-6-fluorophenyllithium (**6**). The reported errors correspond to one standard deviation.

XX. Physical and Spectral Data.

5-Chloro-9,9-spirocyclopropyl-1,4-dihydro-1,4-methano-naphthalene (4).
Clear colorless oil. TLC: R_f = 0.60 (100% hexanes); MS *m/z* 202 (M)$^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 6.6 Hz, 1H), 6.89 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.87 - 6.82 (m, 3H), 3.56 (d, *J* = 2.1 Hz, 1H), 3.32 (br s, 1H), 0.67 - 0.52 (m, 2H), 0.50 - 0.43 (m, 2H). Anal. Calcd for $C_{13}H_{11}Cl$: C, 77.04; H, 5.47. Found: C, 75.78; H, 5.57. Anal. Calcd for $C_{13}H_{11}Cl \cdot 1/4H_2O$: C, 75.36; H, 5.59.

5-Fluoro-9,9-spirocyclopropyl-1,4-dihydro-1,4-methano-naphthalene (5).
Clear colorless oil. TLC: R_f = 0.60 (100% hexanes); MS *m/z* 186, 184 (M)$^+$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.0 Hz, 1H), 6.87 (m, 1H), 6.83 (br s, 2H), 6.63 (ddd, *J* = 8.7, 8.3, 0.9 Hz, 1H), 3.58 (d, *J* = 1.6 Hz, 1H), 3.32 (m, 1H), 0.66 - 0.61 (m, 2H), 0.60 - 0.45 (m, 2H). Anal. Calcd for $C_{13}H_{11}F$: C, 83.84; H, 5.95. Found: C, 83.40; H, 6.12.