Effect of Ion Pairing on Charge Transfer in the Bicyclooctatetraenyl Dianion

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Abstract: The rate constants for bond shift (k_{BS}) and intramolecular charge transfer (k_{CT}) in alkali metal salts of bicyclooctatetraenyl dianions ($\mathbf{1}^{2-}$) in THF-d_8 were determined by dynamic NMR spectroscopy. The values of k_{BS} and k_{CT} increase in the order K < Na ≤ Rb < Cs and K < Rb < Na < Cs ≪ Li, respectively. It is concluded that the K, Rb, and Cs salts react as contact ion pairs (CIPs) while the Li and Na salts react as solvent-separated ion pairs (SSIPs). Increases in k_{BS} and k_{CT} are observed in $\mathbf{1}^{2-}/2\mathrm{K}^+$ on going to more polar solvents (NH$_3$/CH$_3$NH$_2$ and THF-d_8/DMEU). Comparison with kinetic studies of four other dianions has led to the conclusion that $\mathbf{1}^{2-}/2\mathrm{Na}^+$ is the first example of a Na salt of a dianion to undergo charge transfer by SSIPs. This is attributed to the difficulty in forming a Na-bridged CIP transition structure in $\mathbf{1}^{2-}/2\mathrm{Na}^+$ that can compete with an SSIP transition structure.

Introduction

The role of counterions and solvents on ion pairing effects in intramolecular charge-transfer reactions of donor−acceptor model compounds has received increasing attention in recent years.[1] Nevertheless, this important field has only begun to be understood. Earlier work has shown that intramolecular two-electron exchange between a cyclooctatetraene dianion (COT^{2-}) and a neutral COT can occur in (a) sandwich structures where the rings are π-coordinated by a transition element[2] and (b) structures where the COT^{2-} and COT rings are connected by σ or $\sigma + \pi$ bonds.[3] In this contribution we present a study of the effect of counterion and solvent on the rate constants for bond shift and intramolecular charge transfer in the bicyclooctatetraenyl dianion ($\mathbf{1}^{2-}/2\mathrm{M}^+$, where M = Li, Na, K, Rb, Cs).[3a,b] We have shown that both cation size and the type of ion pairing play important roles in determining the rates of these reactions.

$\mathbf{1}^{2-}/2\mathrm{M}^+$

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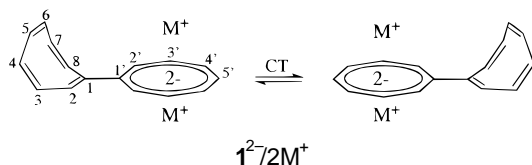
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(1) (a) Piotrowiak, P.; Miller, J. R. *J. Phys. Chem.* **1993,** *97,* 13052. (b) Piotrowiak, P. *Inorg. Chim. Acta* **1994,** *225,* 269.

(2) (a) Schwartz, J.; Sadler, J. E. *J. Chem. Soc., Chem. Commun.* **1973,** 172. (b) Schrock, R. R.; Guggenberger, L. J.; English, A. D. *J. Am. Chem. Soc.* **1976,** *98,* 903. (c) Rogers, D. M.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1991,** *10,* 2419. (d) Cloke, F. G. N.; Green, J. C.; Hitchcock, P. B.; Joseph, S. C. P.; Mountford, P.; Kaltsoyannis, N.; McCamley, A. *J. Chem. Soc., Dalton Trans.* **1994,** 2867.

(3) (a) Staley, S. W.; Dustman, C. K.; Facchine, K. L.; Linkowski, G. E. *J. Am. Chem. Soc.* **1985,** *107,* 4003. (b) Staley, S. W.; Eliasson, B.; Kearney, P. C.; Schreiman, I.; Lindsey, J. S. In *Molecular Electronic Devices*; Carter, J. L., Siatkowski, R. E., Wohltjen, H., Eds.; Elsevier: Amsterdam, 1988; pp 543−554. (c) Boman, P.; Eliasson, B. *Acta Chem. Scand.* **1996,** *50,* 816. (d) Staley, S. W.; Kehlbeck, J. D.; Grimm, R. A.; Sablosky, R. A.; Boman, P.; Eliasson, B. *J. Am. Chem. Soc.* **1998,** *120,* 9793. (e) Boman, P.; Eliasson, B.; Grimm, R. A.; Martin, G. S.; Strnad, J. T.; Staley, S. W. *J. Am. Chem. Soc.* **1999,** *121,* 1558.

Experimental Section

General. Bicyclooctatetraenyl (**1**) was synthesized from bromocyclooctatetraene and lithiocyclooctatetraene according to a published procedure.[4] The crude product was filtered warm and recrystallized at least twice from diethyl ether. 2-Methyltetrahydrofuran (2-MTHF) was refluxed over K metal and distilled prior to use. Dimethylethyleneurea (DMEU, 1,3-dimethyl-2-imidazolidinone) was dried over 4 Å molecular sieves and distilled. The other solvents were used without further purification. Solutions of **1** in 5 mm NMR tubes were degassed and the dianions were prepared in sealed tubes by reduction with the appropriate alkali metal as described elsewhere.[3c−e]

The NMR experiments were performed on General Electric GN-300, Bruker AC-P 250, and Bruker AMX2 500 spectrometers, operating at 75, 62, and 125 MHz, respectively, for ^{13}C. The digital resolution in the spectra was generally close to 0.2 Hz after zero filling. A minimum of two samples were studied for each different alkali metal system and for the different solvents, except for the THF-d_8/DMEU system, where only one sample was used. Each experiment was performed at least twice. Experiments with $\mathbf{1}^{2-}/2\mathrm{K}^+$ and $\mathbf{1}^{2-}/2\mathrm{Cs}^+$ were performed on NMR instruments in both Umeå and Pittsburgh with identical results. The temperature was determined before or after each measurement using methanol.[5]

NMR chemical shifts are given in ppm relative to internal cyclohexane (δ ^{1}H 1.43, δ ^{13}C 27.70), except for the NH$_3$/CH$_3$NH$_2$ samples where trimethylamine (δ ^{13}C 47.93) was used as an internal reference. NMR data for **1** (THF-d_8, 0.5 M): ^{1}H NMR (−45 °C) 5.7−6.0 (m, 13 H, H$_2$−H$_8$, H$_{2'}$−H$_{7'}$), 6.20 (d, J = 11 Hz, 1 H, H$_{8'}$); ^{13}C NMR (−45 °C)[6] 141.9 (C$_1$), 141.9 (C$_{1'}$), 133.4, 133.0, 132.8, 132.7, 132.6, 132.6 (C$_{8'}$), 132.5, 132.5, 132.4, 132.0, 132.0, 131.7, 129.4, 129.0; ^{13}C NMR (+22 °C) 142.2, 132.9, 132.5, 131.7, 129.2.

$\mathbf{1}^{2-}/2\mathrm{Li}^+$ (THF-d_8, 0.3 M): ^{1}H NMR (+25 °C)[7] 5.96 (d, J = 9 Hz, 4 H, H$_2$, H$_{2'}$, H$_8$, H$_{8'}$), 5.75 (t, J = 9 Hz, 4 H, H$_3$, H$_{3'}$, H$_7$, H$_{7'}$), 5.64 (t, J = 9 Hz, 2 H, H$_5$, H$_{5'}$), 5.51 (t, J = 9 Hz, 4 H, H$_4$, H$_{4'}$, H$_6$, H$_{6'}$); ^{13}C NMR (−110 °C)[8] 155.4 (C$_1$), 132.4 (C$_5$), 104.6 (C$_{1'}$), 94.1 (C$_{5'}$), 93.2, 92.0, 86.4.

$\mathbf{1}^{2-}/2\mathrm{Na}^+$ (THF-d_8, 0.2 M): ^{1}H NMR (+25 °C) 5.5−6.1 (m); ^{13}C NMR (−68 °C) 155.5 (C$_1$), 140.9, 137.4, 132.8 (C$_5$), 132.8, 126.8, 126.8, 113.2 (C$_2$), 99.4 (C$_{1'}$), 92.8 (C$_{5'}$), 90.1, 88.5, 86.2.

$\mathbf{1}^{2-}/2\mathrm{K}^+$ (THF-d_8, 0.3 M): ^{1}H NMR (−75 °C) 6.50 (d, J = 11.5 Hz, 1 H, H$_8$), 5.4−6.0 (m, 13 H); ^{13}C NMR (−75 °C) 156.6 (C$_1$), 140.9,

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(4) Cope, A. C.; Marshall, D. J. *J. Am. Chem. Soc.* **1953,** *75,* 3208.

(5) Van Geet, A. L. *Anal. Chem.* **1970,** *42,* 679.

137.5, 133.0 (C_5), 133.0, 127.5, 126.4, 114.5 (C_2), 103.0 ($C_{1'}$), 95.0 ($C_{5'}$), 92.7, 91.7, 89.9.

$\mathbf{1}^{2-}/2K^+$ (4.7:1 THF-d_8/DMEU, 0.3 M): ^{1}H NMR (+4 °C) 5.5−6.0 (m); ^{13}C NMR (−75 °C) 156.9 (C_1), 141.2, 137.9, 133.2 (C_5), 133.2, 127.6, 126.3, 114.1 (C_2), 103.0 ($C_{1'}$), 95.2 ($C_{5'}$), 92.9, 91.8, 89.9.

$\mathbf{1}^{2-}/2K^+$ (ND$_3$, 0.3 M): ^{1}H NMR (+20 °C)[7] 6.01 (d, 4 H, H_2, $H_{2'}$, H_8, $H_{8'}$), 5.86 (t, 4 H, H_3, $H_{3'}$, H_7, $H_{7'}$), 5.77 (t, 2 H, H_5, $H_{5'}$), 5.66 (t, 4 H, H_4, $H_{4'}$, H_6, $H_{6'}$).

$\mathbf{1}^{2-}/2K^+$ (1:1 NH$_3$/CH$_3$NH$_2$, 0.3 M): ^{13}C NMR (−81 °C) 156.0 (C_1), 140.3, 137.2, 132.8 (C_5), 132.8, 127.6, 127.2, 114.0 (C_2), 102.5 ($C_{1'}$), 95.1 ($C_{5'}$), 92.8, 91.4, 89.7.

$\mathbf{1}^{2-}/2Rb^+$ (THF-d_8, 0.3 M, −80 °C): ^{1}H NMR 5.4−6.1 (m); ^{13}C NMR 156.8 (C_1), 140.9, 137.6, 133.0, 132.9 (C_5), 127.4, 126.1, 113.8 (C_2), 104.2 ($C_{1'}$), 96.0 ($C_{5'}$), 93.9, 92.9, 91.0.

$\mathbf{1}^{2-}/2Cs^+$ (THF-d_8, 0.3 M, −79 °C): ^{1}H NMR 5.4−6.1 (m); ^{13}C NMR 157.1 (C_1), 141.0, 137.7, 133.2, 132.9 (C_5), 127.7, 126.3, 114.3 (C_2), 106.2 ($C_{1'}$), 97.7 ($C_{5'}$), 95.6, 94.9, 92.9.

Samples of $\mathbf{1}^{2-}/2K^+$ that were studied at more than one concentration include the following: $\mathbf{1}^{2-}/2K^+$/THF-d_8, 0.3 and 0.6 M; $\mathbf{1}^{2-}/2K^+$/THF-d_8/DMEU, 0.3 and 0.7 M; and $\mathbf{1}^{2-}/2K^+$/NH$_3$/CH$_3$NH$_2$, 0.3 and 0.5 M.

NMR Signal Assignment, Kinetics, and Error Analysis. The ^{13}C NMR signals were partially assigned using the methods described earlier,[3] i.e., on the basis of charge/chemical shift correlations, line widths, and magnetization transfer between exchanging nuclei.[3c−e] The 11.5 Hz doublet at δ 6.5 in $\mathbf{1}^{2-}/2K^+$/THF-d_8 was assigned to H_8 since it is the only >11 Hz doublet expected. Selective decoupling of H_8 gave the assignment of C_8. The most upfield of the signals for the carbons in the neutral ring of $\mathbf{1}^{2-}/2K^+$/THF-d_8 was assigned to C_2 on the basis of the electric field effect caused by the adjacent dianion ring.

The rate constants for bond shift were determined by line width studies in the slow exchange region, using the equation $k = \pi\Delta\nu_{1/2ex}$, where $\Delta\nu_{1/2ex}$ is the exchange broadening at half-peak height.[9] The exchange broadening due to bond shift was obtained by subtracting from the line width of the specific peak its line width at a lower temperature where exchange was absent, and by correcting for effects from changes of solvent viscosity and magnetic field homogeneity by using line widths for resonances not affected by exchange. If the line width could not be determined in the absence of exchange, the measured line width was corrected by subtracting the line width of a peak not affected by exchange, e.g., the line widths of cyclohexane or the protonated carbons in the dianion ring. The line widths were determined by least-squares fits to Lorentzian line shapes using standard NMR software routines. Values of k_{CT} were obtained from magnetization transfer studies as well as from line width studies. The rate constants determined by line width studies and from magnetization transfer were typically between 3 and 60 s^{-1} and 0.05 and 5 s^{-1}, respectively.

Two different types of magnetization transfer experiments were performed, inversion transfer[10] (IT) on the General Electric NMR instrument and spin saturation transfer[11] (SST) on the Bruker instruments. In inversion transfer, the population of one nucleus of an exchanging pair is selectively inverted, followed by a variable delay and observation of the system after a nonselective 90° pulse. The peak heights of the two exchanging nuclei vs delay time are described by two nonexponential curves. When the rate constant together with the instantaneous and equilibrium intensities and the relaxation rates of the two nuclei are simultaneously fitted to two nonlinear equations as formulated by Campbell,[10a] the rate constant for the exchange is obtained. The seven variables were optimized by using the program Minsq from MicroMath Scientific Software. In the IT studies, C_5 and

$C_{5'}$ were monitored rather than C_1 and $C_{1'}$ because of the better sensitivity that the protonated carbons offer.

In the SST experiment, the signal intensity for one nucleus is a function of the relaxation time of the nucleus and the time for population exchange with the other, initially saturated, nucleus.[3c,11] Both protonated and quaternary carbons were studied in the SST experiments. The activation parameters were calculated from the rate constants and the Eyring equation.

Temperature region, number of experiments (n), and regression coefficients (r) for plots of $\ln(k/T)$ vs $1/T$ for bond shift and charge-transfer analyses of $\mathbf{1}$ and $\mathbf{1}^{2-}/2M^+$ were as follows. $\mathbf{1}$: BS, −5 to +58 °C, $n = 10$. $\mathbf{1}^{2-}$/Li$^+$: CT, −110 °C. $\mathbf{1}^{2-}$/Na$^+$: BS, −68 to −52 °C, $n = 6$, $r = 0.987$; CT, −39 to −26 °C, $n = 9$, $r = 0.999$. $\mathbf{1}^{2-}$/K$^+$, THF-d_8: BS, −65 to −35 °C, $n = 13$, $r = 0.991$; CT, −29 to +27 °C, $n = 12$, $r = 0.996$. $\mathbf{1}^{2-}$/K$^+$, THF-d_8/DMEU: BS, −66 to −64 °C, $n = 2$; CT, −33 to −16 °C, $n = 8$, $r = 0.992$. $\mathbf{1}^{2-}$/K$^+$, NH$_3$/CH$_3$NH$_2$: BS, −85 to −70 °C, $n = 4$, $r = 0.998$; CT, −70 to −55 °C, $n = 4$, $r = 0.991$. $\mathbf{1}^{2-}$/Rb$^+$: BS, −83 to −63 °C, $n = 10$, $r = 0.996$; CT, −42 to −1 °C, $n = 20$, $r = 0.994$. $\mathbf{1}^{2-}$/Cs$^+$: BS, −92 to −78 °C, $n = 7$, $r = 0.990$; CT, −70 to −20 °C, $n = 25$, $r = 0.982$.

The uncertainties in the rate constants were estimated from replicate measurements, which were performed because differential error analysis yielded unreasonably small uncertainties in the rate constants. The replicate measurements gave an error in the line widths of ±10% at a 95% confidence interval. For SST and IT, replicate experiments gave a 20% error in the rate constants at a 95% confidence interval. We estimate that the maximum error in temperature was ±1 °C, which constitutes a significant contribution to the experimental error. Still, the major part of this error is likely to arise from variations in the electronics that control the NMR pulse lengths and strengths, and in unknown chemical differences between ostensibly identical samples.

Molecular Orbital Calculations. Ab initio molecular orbital (MO) calculations were performed with Spartan 4.1[12] using the 3-21G$^{(*)}$ basis set.[13,14] Semiempirical PM3 MO calculations were performed with MOPAC 93.[15]

Results and Discussion

The primary issue that we address in this study is the effect of different cations on the rates of bond shift (BS) and charge transfer (CT) in $\mathbf{1}^{2-}$. In the case of $\mathbf{1}^{2-}/2K^+$, samples in three different solvent systems were prepared with different concentrations of dianion (see Experimental Section) to investigate the ratio between inter- and intramolecular CT. The rate constants for these samples were the same within the experimental variation found for the other samples. We therefore conclude that CT in this study is an *intra*molecular process.

As seen in Table 1, the rate constants for BS in the neutral ring of $\mathbf{1}^{2-}$ increase at −65 °C in the order K < Na ≤ Rb < Cs while those for CT increase in a similar, but not identical, order (K < Rb < Na < Cs ≪ Li). This behavior is undoubtedly a function of the ion pair structure of the reacting species. In addition, a change of the solvent for $\mathbf{1}^{2-}/2K^+$ from THF-d_8 to 4.7:1 THF-d_8/DMEU and to 1:1 NH$_3$/CH$_3$NH$_2$ shows increased rate constants for both BS and CT (Table 2). This is expected for a change in ion pairing toward somewhat looser ion pairs in the two solvent mixtures, which solvate cations better than THF-d_8. While we cannot directly observe the ion pair structure

(6) A spectrum with 16 signals results from two diastereomers of $\mathbf{1}$ with slow ring inversion on the NMR time scale.

(7) Fast intramolecular electron and cation exchange on the NMR time scale.

(8) With the exception of C_1 and C_5, the signals for the neutral ring are broadened considerably due to bond shift dynamics.

(9) For an overview of dynamic NMR methods, see: Sandström, J. In *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(10) (a) Campbell, I. D.; Dobson, C. M.; Ratcliffe, R. G.; Williams, R. J. P. *J. Magn. Reson.* **1978**, *29*, 397. (b) Baine, P.; Gerig, J. T.; Stock, A. D. *Org. Magn. Reson.* **1981**, *17*, 41.

(11) (a) Hoffman, R. A.; Forsén, S. *Prog. Nucl. Magn. Reson. Spectrosc.* **1966**, *1*, 15. (b) Mann, B. E. *J. Magn. Reson.* **1977**, *25*, 17.

(12) Wavefunction, Inc.: 18401 Von Karman Ave., Suite 370, Irvine, CA 92715 USA.

(13) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(14) (a) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (b) Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1986**, *7*, 359.

(15) CS MOPAC v. 3.50; Cambridge Soft Corp.: 875 Massachusetts Ave., Cambridge, MA 02139 USA.

Table 1. Kinetic Parameters for Bond Shift and Intramolecular Charge Transfer in Bicyclooctatetraenyl Systems in THF-d_8 at −65 °C[a]

compd	k_{BS}	$\Delta G^{\ddagger}_{BS}$	$\Delta H^{\ddagger}_{BS}$	k_{CT}	$\Delta G^{\ddagger}_{CT}$	$\Delta H^{\ddagger}_{CT}$	$\Delta S^{\ddagger}_{CT}$
1	9.8 (+39 °C)	16.9 ± 0.1 (+39 °C)					
1^{2-}/Li$^+$	b	b		≥14 (−110 °C)	≤8.5 ± 0.5 (−110 °C)		
1^{2-}/Na$^+$	20.2	10.8 ± 0.1	8.0	0.34	12.5 ± 0.1[c]	10.8	−8
1^{2-}/K$^+$	2.75	11.6 ± 0.1	10.7 ± 1.5	0.0095	14.0 ± 0.1[c]	12.7 ± 1.3	−6 ± 5
1^{2-}/Rb$^+$	29.3	10.6 ± 0.1	9.1 ± 2.5	0.038	13.4 ± 0.1[c]	12.1 ± 1.6	−6 ± 6
1^{2-}/Cs$^+$	105	10.1 ± 0.1[d]	9.2 ± 3.2	1.17	12.0 ± 0.1	9.8 ± 1.3	−10 ± 5

[a] Other temperatures within parentheses; k in s^{-1} (see text for uncertainties), $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ in kcal/mol, $\Delta S^{\ddagger}$ in cal/(mol·K). [b] Resolved signals for the carbons that are exchanged by bond shift were not observed, even at the lowest temperature (−110 °C). [c] Value extrapolated from higher temperatures. [d] Value extrapolated from lower temperatures.

Table 2. Effect of Solvent on Kinetic Data for Bond Shift and Intramolecular Charge Transfer in 1^{2-}/2K$^+$ at −65 °C[a]

solvent	k_{BS}	$\Delta G^{\ddagger}_{BS}$	k_{CT}	$\Delta G^{\ddagger}_{CT}$
THF-d_8	2.75	11.6 ± 0.1	0.0095[b]	14.0 ± 0.1[b]
THF-d_8/DMEU[c]	14.2	10.9 ± 0.3	0.079[b]	13.1 ± 0.3[b]
NH$_3$/CH$_3$NH$_2$	140[d]	10.0 ± 0.3[d]	9.0	11.1 ± 0.3

[a] k in s^{-1}; $\Delta G^{\ddagger}$ in kcal/mol. [b] Value extrapolated from higher temperatures. [c] Dimethylethyleneurea (1,3-dimethyl-2-imidazolidinone). [d] Value extrapolated from lower temperatures.

Table 3. ^{13}C NMR Data for Bicyclooctatetraenyl Systems in THF-d_8

compd	T (°C)	$\delta C_1 - \delta C_2$	δ_{av} ^{13}C neutral ring	δ_{av} ^{13}C dianion ring
1	−45	≤12.9[a]	133.29	
1^{2-}/2Li$^+$	−110	b	b	92.73
1^{2-}/2Na$^+$	−68	42.28	133.30	90.22
1^{2-}/2K$^+$	−81	42.10	133.67	93.31
1^{2-}/2Rb$^+$	−80	42.97	133.57	94.45
1^{2-}/2Cs$^+$	−79	42.80	133.65	96.18

[a] The signals of C_2–C_8 have not been assigned. The total δ interval for the neutral ring carbons is 12.9 ppm. [b] Signals for carbons that undergo bond shift are broadened into the baseline.

of the transition state, a study of the corresponding ground states has proven informative.

Ion Pairing in the Ground State. Following Cox et al.,[16] we consider a model for 1^{2-}/2M$^+$ that involves at least three different structures: (a) both cations exist in a tight or contact ion triplet with a cyclooctatetraenyl dianion ring, (b) one cation exists in a loose or solvent-separated ion pair (SSIP) while the second is contact ion paired (CIP), and (c) both cations are separated from the dianion ring by a layer of solvent molecules. Cox and co-workers concluded that the Na, K, and Rb salts of the cyclooctatetraene dianion are dicontact ion paired in THF and DME and that a small fraction of SSIPs is formed with the dilithium salt.[16]

The average ^{13}C chemical shifts (δ_{av} ^{13}C) for the dianion ring given in Table 3 fully support this conclusion. There is a monotonic decrease in δ_{av} ^{13}C, i.e., an upfield shift, on going from the CIP Cs salt to an even tighter CIP Na salt. This can be understood on the basis of a small cation stabilizing the anion by interacting with the π orbitals, especially the HOMO, as compared with a large cation that interacts less with the π orbitals.[17] This reduces the paramagnetic contribution to the ^{13}C chemical shifts by stabilizing the π orbitals and increasing the energies of the magnetically allowed $\pi \rightarrow \sigma^*$ excitations.[18] In a

distinct reversal of this trend, δ_{av} ^{13}C for the Li salt shows a *downfield* shift of over 2 ppm relative to the Na salt. This indicates a shift toward SSIPs, which are expected to behave like CIPs of the larger, more diffuse, alkali metal cations.

Note that the average chemical shift for the carbons in the neutral ring is almost the same for the different salts, in contrast to that of the charged ring (Table 3). The average chemical shift for C_1 and C_2 is also very similar for the K–Cs salts but undergoes a slight upfield shift of ca. 1 ppm in the Na salt (Experimental Section). These observations indicate that there is essentially no transfer of charge into the neutral ring in the ground states of 1^{2-}/K$^+$−Cs$^+$, but possibly a small charge transfer in the Na salt.

The above NMR analysis is supported by single-crystal X-ray studies of various alkali metal salts possessing COT dianion rings. Thus, while the lithiums in [dibenzo[*a,e*]COT][Li·TMEDA]$_2$,[19] [Li(THF)$_2$][COT·Sm(CH(TMS)$_2$)$_2$],[20] and [Li·DME]$_2$[1,4-(TMS)$_2$COT][21] are contact ion paired, those in [Li(THF)$_4$][Ce(COT)$_2$][22] and [Li(THF)$_4$][Sm(1,4-(TMS)$_2$-COT)$_2$][23] are solvent-separated ion paired. The latter are to our knowledge the only known examples of SSIP alkali metal salts of COT in the solid state since [Na(THF)$_3$][Ce(COT)$_2$],[22] [Rb$_2$·diglyme][COT],[24] and seven different potassium salts of COT^{2-} or 1,3,5,7-tetramethylCOT^{2-}[25] all crystallize as CIPs.

One can, in principle, refine this simple CIP/SSIP model by considering CIPs with different degrees of solvation of the cations coordinated with the COT dianion ring. For example, while the X-ray structure of dipotassium diglyme 1,3,5,7-tetramethylcyclooctatetraene[25c] shows a dianion ring symmetrically bound by two potassium ions, each coordinated by a diglyme molecule, two related structures show different solvation of the cations. In C$_8$H$_8$K$_2$·diglyme,[25b] only one potassium ion of each C$_8$H$_8$K$_2$ unit is coordinated by diglyme molecules, while in C$_8$H$_8$K$_2$·(THF)$_3$[25e] both potassiums are coordinated by two bridging THF molecules but one of them is also coordinated to a third, nonbridging, THF. In the latter structure, the more coordinated potassium is slightly farther from

(16) Cox, R. H.; Harrison, L. W.; Austin, W. K., Jr. *J. Phys. Chem.* **1973**, *77*, 200.

(17) Carter, H. V.; McClelland, B. J.; Warhurst, E. *Trans. Faraday Soc.* **1960**, *56*, 455.

(18) (a) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803. (b) Eliasson, B.; Johnels, D.; Sethson, I.; Edlund, U.; Müllen, K. *J. Chem. Soc., Perkin Trans. 2* **1990**, 897. (c) Eliasson, B.; Edlund, U. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1837.

(19) Sygula, A.; Fronczek, F. R.; Rabideau, P. W. *J. Organomet. Chem.* **1996**, *526*, 389.

(20) Schumann, H.; Winterfeld, J.; Görlitz, F. H.; Pickardt, J. *J. Chem. Soc., Chem. Commun.* **1993**, 623.

(21) Poremba, P.; Schmidt, H.-G.; Noltemeyer, M.; Edelmann, F. T. *Organometallics* **1998**, *17*, 986.

(22) Kilimann, U.; Schäfer, M.; Herbst-Irmer, R.; Edelmann, F. T. *J. Organomet. Chem.* **1994**, *469*, C15.

(23) Poremba, P.; Reissmann, U.; Noltemeyer, M.; Schmidt, H. G.; Brüser, W.; Edelmann, F. T. *J. Organomet. Chem.* **1997**, *544*, 1.

(24) Noordik, J. H.; Degens, H. M. L.; Mooij, J. J. *Acta Crystallogr.* **1975**, *B31*, 2144.

(25) (a) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 3030. (b) Noordik, J. H.; van den Hark, T. E. M.; Mooij, J. J.; Klaassen, A. A. K. *Acta Crystallogr.* **1974**, *B30*, 833. (c) Goldberg, S. Z.; Raymond, K. N.; Harmon, C. A.; Templeton, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 1348. (d) Kinsley, S. A.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1985**, *4*, 52. (e) Hu, N.; Gong, L.; Jin, Z.; Chen, W. *J. Organomet. Chem.* **1988**, *352*, 61. (f) Boussie, T. R.; Eisenberg, D. C.; Rigsbee, J.; Streitwieser, A.; Zalkin, A. *Organometallics* **1991**, *10*, 1922.

Table 4. Geometrical Data and Natural Atomic Charges for HF/3-21G(*)-Optimized Structures

				total charge		
compd	ω (deg)[a]	α (deg)[b]	β (deg)[b]	C_1	C_2	$\Sigma(C_1-C_8) +$ (H_2-H_8)
1[c]	158	136.1	137.0	−0.053	−0.215	0.000
1[2−]/2Na[+] [d]	46.6	136.9	137.3	+0.006	−0.272	−0.045
1[2−]/2Na[+] [e]	37.8	136.7	137.2	+0.014	−0.309	−0.082
1[2−]/2K[+] [f]	43.0	136.9	137.2	+0.012	−0.288	−0.070
1[2−] [g]	h	h	h	+0.042	−0.385	−0.272

[a] Dihedral angle $C_2C_1C_{1'}C_{2'}$. 180° corresponds to the anti orientation of the C_1-C_2 and $C_{1'}-C_{2'}$ bonds. [b] α and β are interplanar angles between the least-squares plane $C_3C_4C_7C_8$ and the planes $C_1C_2C_3C_8$ and $C_4C_5C_6C_7$, respectively. [c] Data for the most stable conformer, which is 0.9 kcal/mol lower in energy than the next most stable conformer. [d] Na−Na distance optimized (3.61 Å). Charges at hydrogens in the neutral COT ring are in the range of 0.226−0.230. [e] Geometry optimization with the Na−Na distance constrained to 4.50 Å. Charges at hydrogens in the neutral COT ring are in the range of 0.221−0.236. [f] K−K distance optimized (4.573 Å). Charges at hydrogens in the neutral COT ring are in the range of 0.223−0.228. [g] Single-point energy calculation on optimized **1**[2−]/2K[+] with K ions excluded. Charges at hydrogens in the neutral COT ring are in the range of 0.190−0.234. [h] See the previous geometry optimization for the parameter value.

the COT dianion ring. These studies indicate that a number of possible symmetrical and unsymmetrical ion pairs within the three classes mentioned above can exist in solution. However, very little work has been done on this problem and therefore we will only employ a simple CIP/SSIP model.

To investigate the effect of cation complexion and size on geometry and charge, we have obtained geometry-optimized structures of **1**, unsolvated **1**[2−]/2Na[+] and **1**[2−]/2K[+] (as models for CIPs), and **1**[2−]/2Na[+] with the Na^{+}−Na^{+} distance fixed at 4.500 Å (as a model for an externally solvated CIP) by ab initio molecular orbital theory at the HF/3-21G(*) level of basis set (Table 4). Calculations of electron density at this level were also performed for these compounds and for **1**[2−] (as a model for an SSIP) using the geometry from the **1**[2−]/2K[+] optimization. (Geometry optimization of **1**[2−] results in a structure with both rings equally charged and somewhat folded.) Two geometric parameters of relevance are the degree of twist between the dianion ring and the C_1C_2 double bond of the neutral ring, as given by the dihedral angle $\omega(C_2C_1C_{1'}C_{2'})$, and the degree of flattening of the neutral ring, as indicated by the interplanar angles α and β between the $C_3C_4C_7C_8$ least-squares plane and the $C_1C_2C_3C_8$ and $C_4C_5C_6C_7$ planes, respectively.

The geometry of the neutral ring is essentially unchanged on going from **1** to **1**[2−]/2M[+], suggesting that dianion ring−neutral ring interactions are weak in the ground state. Nevertheless, several trends indicate that some interaction is present. Thus $\omega(C_2C_1C_{1'}C_{2'})$ decreases in the order **1**[2−]/2Na[+] > **1**[2−]/2K[+] > **1**[2−]/2Na[+](solvated), whereas the polarization of the C_1C_2 double bond ($\rho_{C1}-\rho_{C2}$) and the total charge transferred from the dianion ring to the neutral ring ($\Delta\rho_{tot}$) both increase in the order **1**[2−]/2Na[+] < **1**[2−]/2K[+] < **1**[2−]/2Na[+](solvated) < **1**[2−] (Table 4). The polarization of the C_1C_2 bond in **1**[2−] is also obvious from the difference $\delta C_1 - \delta C_2$ for the dianions as compared with neutral **1** (Table 3). A larger value of $\delta C_1 - \delta C_2$ signifies a stronger polarization of electron density toward C_2. The variation between the samples of **1**[2−] with different cations is small, but indicates that the Na and K salts have weaker polarization than the Rb and Cs salts, in accord with weaker anion−cation interactions in the latter salts.

The double bonds in each of these compounds are calculated to be polarized $C_1{\rightarrow}C_2$, $C_3{\rightarrow}C_4$, and $C_7{\leftarrow}C_8$, while C_5C_6, which is approximately perpendicular to the $C_1C_{1'}$ bond, is close to

being nonpolar. PM3 calculations, with different orientations of the molecule to obtain the local π electron density in each of these double bonds, indicate that all or most of the polarization arises from the "π" components of the double bonds.

Kinetics of Bond Shift and Charge Transfer. As noted above, the rate constants for bond shift and charge transfer in **1**[2−] are at a minimum for the dipotassium salt and increase on going to *both* smaller (K < Na < Li) and larger (K < Rb < Cs) cations (Table 1). This reversal in order of rate constants with increasing size of cation suggests that a change is occurring in the ion pairing for these processes. The counterion effect is similar in the two processes, although the magnitude of the effect is a bit larger for CT than for BS. As discussed below, it seems clear that looser ion pairs increase the rates of both BS and CT.

In view of the requirement for transferring two cations as well as two electrons during the CT process, it is likely that the latter occurs in a stepwise manner.[26] This is represented in its simplest form in eq 1. Note that the intermediate in eq 1 would

$$2M^+/COT^{2-}-COT \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^+/COT^--COT^-/M^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$
$$COT-COT^{2-}/2M^+ \quad (1)$$

be a diradical anion only if the two rings were perpendicular to each other. Instead, a partially twisted closed-shell species, represented by di-monoanion **2**, is a more reasonable structure.

2
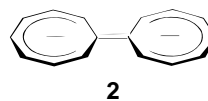
The order of reactivity as a function of counterion can be understood if Li and (perhaps to a lesser extent) Na react via SSIP transition states whereas K, Rb, and Cs are transferred via CIP transition states. SSIPs form more readily with the smaller cations, as compared with larger cations, owing to the greater concentration of positive charge and stronger solvation in the former.[27] SSIPs also undergo intramolecular charge transfer at a greater rate than CIPs because of reduced Coulombic attraction between the anion and the solvated cation.[28] Contrariwise, the greater dispersal of positive charge in the larger cations causes them to be less solvated and to exist as CIPs. Since Coulombic attraction between the dianion ring and the counterion in CIPs decreases for the larger cations, these salts undergo more rapid charge transfer via *CIP transition states*.

It should be noted that δ_{av} for the dianion ring and $\delta C_1 - \delta C_2$ (Table 3) both indicate that **1**[2−]/2Na[+] is a CIP. This is expected if only a small fraction of loose ion pairs is present with a negligible contribution to the (ground state) NMR data. Still, the effect on the rate of CT (and BS) can be large since CIP/SSIP interconversion is rapid and SSIPs undergo electron/ cation transfer faster than CIPs.

In summary, although **1**[2−]/2M[+] in THF-d_8 probably exists as CIPs for Na^{+}, K^{+}, Rb^{+}, and Cs^{+} and in a CIP/SSIP

(26) Pfennig, B. W.; Bocarsley, A. B. *Comments Inorg. Chem.* **1992**, *13*, 261.

(27) (a) Smid, J. In *Ions and Ion Pairs In Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. 1, pp 85−151. (b) Hogen-Esch, T. E. *Adv. Phys. Org. Chem.* **1977**, *15*, 153.

(28) A referee has suggested that the participation of free ions cannot be precluded, especially in the case of the solvent mixtures in Table 2. While we accept this point, we nevertheless believe that free ions are unlikely for *dianions* in these solvents.

equilibrium for Li^+, the CT *transition states* can be explained in terms of a different ion pairing, where Li^+ and Na^+ transfer as SSIPs and K^+, Rb^+, and Cs^+ transfer as CIPs.

Charge Transfer in Other Dianions. We are aware of the determination of alkali metal counterion effects in four other charge-transfer studies of dianions (eq 2−5). In the comproportionation of the tetraphenylethene (T) radical anion (eq 2)

$$T^{2-}/2M^+ + T \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2T^{-\bullet}/M^+ \qquad k_1: \ Li > Na \qquad (2)$$

(where $T^{-\bullet}$ is generated by flash photolysis of $T^{2-}/2M^+$ in THF), Szwarc and co-workers concluded that $T^{-\bullet}/Li^+$ and $T^{-\bullet}/Na^+$ both exist as SSIPs whereas both cations are CIPs in $T^{2-}/2Na^+$ and suggested that one of the lithium cations in $T^{2-}/2Li^+$ exists in an SSIP and the other as a CIP.[29] Finally, they concluded that the transition state (TS) corresponding to k_1 is SSIP for the Li salt but, in contrast to 1^{2-}, CIP for the Na salt.

In a related flash-photolysis study, Levin and Szwarc determined the kinetics of the comproportionation of neutral tetracene (Te) and Te^{2-} to $Te^{-\bullet}$ in THF (eq 3).[30] In contrast to

$$Te^{2-}/2M^+ + Te \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Te^{-\bullet}/M^+ \qquad k_1: \ Li > Na < K < Cs \tag{3}$$
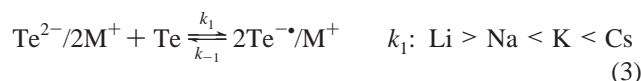
the endothermicity of the first step of eq 1, the comproportionation in eq 3 is highly exothermic and k_1 approaches the value for a diffusion-controlled process. Nevertheless, small differences in k_1 were observed in the order $Na \leq Li \approx K \leq Cs$. In addition, $Te^{2-}/2Na^+$ and $Te^{-\bullet}/Na^+$ in benzene with added THF were shown to exist as THF-solvated CIPs and SSIPs, respectively, while their interconversion was determined to occur through a transition state that is *partially desolvated* relative to the radical anion, i.e., it is a *CIP transition state*.[31]

Note that the ion pairing in the CIP transition state in eq 3 differs from that in the SSIP transition state proposed by us for $1^{2-}/2Na^+$ in eq 1. This can be explained by the transition structure depicted for eq 3 by Levin and Szwarc,[30] where a partially or fully desolvated cation has been proposed to facilitate *inter*molecular CT between two tetracenes aligned face-to-face (3, $Te^{-\bullet}$, M^+, $Te^{-\bullet}M^+(S)_n$). Such a geometry is not possible for *intra*molecular CT in $1^{2-}/2Na^+$. Consequently, the migrating Na^+ in the latter case maintains maximum solvent coordination in the transition state by transferring as an SSIP.

A flash-photolysis study of the disproportionation reaction of alkali metal salts of COT^{2-} in 2-MTHF (eq 4)[32] gave results similar to those for tetracene. The comproportionation rate constants (k_{-1}) were not determined, but the relative values of

$$2COT^{-\bullet}/M^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$COT^{2-}/2M^+ + COT \qquad k_1: \ Li < Na < K < Rb \tag{4}$$
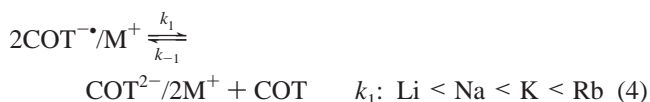
k_1 ($Li < Na < K < Rb$) are consistent with an activated complex where a partially desolvated alkali metal cation serves as a bridging group between two COT rings. This is analogous to the TS proposed[30] for the Na, K, and Cs in salts of tetracene in

eq 3 and further supports the idea that an alkali metal can play the role of an electron conduit between two electrophiles.[33]

The study most directly related to the present one is that of charge transfer in dicyclooctatetraenyldimethylsilane dianion (4^{2-}) in THF (eq 5), where the rate constant for CT follows the

$$2M^+/COT^{2-}\!-\!SiMe_2\!-\!COT \ (4^{2-})\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$COT\!-\!SiMe_2\!-\!COT^{2-}/2M^+ \qquad k_1: \ Na < K < Li \tag{5}$$

order $Na < K < Li$.[3c] The value of δ_{av} ^{13}C for the dianion ring in 4^{2-} in THF at ca. 25 °C is 89.4, 88.6, and 92.2 for the Li, Na, and K salts, respectively. These follow the same order as does 1^{2-} but the values for 4^{2-} are increasingly upfield of those for 1^{2-} in the order $K < Na < Li$, suggesting that the ion pairs are tighter in 4^{2-} than in 1^{2-}. However, comparisons between different dianions are more complex than comparisons between different alkali metal cations in combination with a specific dianion, and the "tightness" of 1^{2-} vs 4^{2-} will therefore not be discussed in detail.

The downfield shift in $4^{2-}/2Li^+$ of δ_{av} ^{13}C for the dianion ring relative to $4^{2-}/2Na^+$ indicates a contribution from SSIPs in the Li salt. The >3 kcal mol smaller value of $\Delta G^{\ddagger}_{CT}$ in the Li salt can also be attributed, at least in part, to a contribution of SSIPs (and/or looser CIPs) in the transition state for Li relative to Na. This parallels the SSIP transition state proposed for CT in $1^{2-}/2Li^+$.

Although the ion pairing in the CT transition state in 1^{2-} is similar to that of 4^{2-} for the Li and K salts, it apparently differs for the Na salt. In contrast to $1^{2-}/2Na^+$, $4^{2-}/2Na^+$ undergoes CT more slowly than the corresponding K salt. This suggests an SSIP TS for $1^{2-}/2Na^+$ and a CIP TS for $4^{2-}/2Na^+$, and can be rationalized on the basis of (a) greater delocalization of charge in the CT transition state of 1^{2-} (which favors SSIPs) and (b) a TS structure for $4^{2-}/2Na^+$ that adopts an angled face-to-face conformation (5) in which the migrating Na^+ is coordinated to both COT rings simultaneously.

5
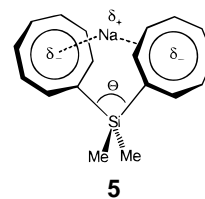
HF/3-21G$^{(*)}$ calculations have indicated that θ (see 5) decreases from 109° in 4 to 104.5° in $4^{2-}/2Na^+$.[3c] Structure 5 is analogous to the transition structure postulated for CT in tetracene (3)[30] where the two Te molecules are oriented face-to-face.

The ion pairing found or postulated for the foregoing five disodium salts during comproportionation is summarized in Table 5. Note that only the disodium salts of COT and 4 share the same ion pairing in the starting material, transition state, and intermediate or product. Of particular interest is the observation that only $1^{2-}/2Na^+$ gives evidence of reacting via SSIPs. *This can be attributed primarily to the difficulty of this salt forming an intramolecular face-to-face transition structure.* In contrast, K, Rb, and Cs can bridge the two rings in the TS owing to their larger size and "looser" CIP structure, and to the fact that their smaller solvation energies make for less competition from SSIP transition structures.

(29) (a) Levin, G.; Claesson, S.; Szwarc, M. *J. Am. Chem. Soc.* **1972**, *94*, 8672. (b) Lundgren, B.; Levin, G.; Claesson, S.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 262.
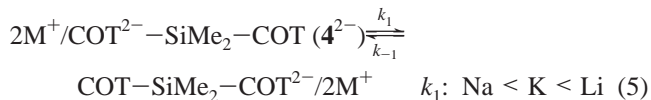
(30) Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1976**, *98*, 4211.

(31) (a) Pola, J.; Levin, G.; Szwarc, M. *J. Phys. Chem.* **1976**, *80*, 1690. (b) Szwarc, M. *Pure Appl. Chem.* **1979**, *51*, 1049. (c) Szwarc, M. *Acta Chem. Scand.* **1997**, *51*, 529.

(32) van Willigen, H. *J. Am. Chem. Soc.* **1972**, *94*, 7966.

(33) Sheppard, J. C.; Wahl, A. C. *J. Am. Chem. Soc.* **1957**, *79*, 1020.

Charge Transfer in the Bicyclooctatetraenyl Dianion

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Table 5. Ion Pairing in Intra- or Intermolcular Charge-Transfer Reactions of Various Disodium Salts in THF ($A^{2-}/2Na^+ + A \rightarrow 2(A^-/Na^+)$)

A	A^{2-}	transition state[a]	A^-/A^-	ref
1	CIP/CIP	SSIP	CIP/CIP	b, c
$Ph_2C{=}CPh_2$	CIP/CIP	CIP	SSIP/SSIP	d
Tetracene	SSIP/CIP	CIP	SSIP/SSIP	e
COT	CIP/CIP	CIP[f]	CIP/CIP	g
4	CIP/CIP	CIP	CIP/CIP	c, h

[a] Ion pairing of the cation being transferred. [b] This work. [c] The ion pairing in A^-/A^- is assumed to be as in $COT^{-\bullet}/Na^+$ (ref 35). [d] Reference 29. [e] References 30 and 31. [f] In 2-MTHF. [g] References 16, 32 and 35. [h] Reference 3c.

Scheme 1

$$\text{CIP/CIP} \xrightarrow{\sim\text{CIP}} \text{CIP-CIP} \xrightarrow{\sim\text{CIP}} \text{CIP/CIP}$$

Mechanisms of Charge Transfer. It is interesting to speculate on the stepwise mechanism by which $1^{2-}/2M^+$ undergoes charge transfer. Since the larger cations (M = K, Rb, Cs) all exist and react as CIPs, one can postulate a mechanism whereby a cation migrates across the π system between the two rings. The degree of solvation may change during this process, but the cation remains as a CIP throughout the transfer. This can be considered to be a short-range version of the "conducted tour" mechanism proposed many years ago by Cram.[34]

The mechanism for CIP transfer is described in shorthand form in Scheme 1, where a slash or a horizontal line indicates that the two cations are complexed to the same (dianion) ring or to two different monoanion rings, respectively, and the symbol "$\sim$" denotes the migration of a cation. We recognize the possibility that solvent molecules may be added to or removed from the solvation shell of the cation prior to or during migration.

The mechanism for CT in $1^{2-}/2Li^+$ can be represented as in Scheme 2, where S represents one or more solvent molecules. The difference between the upper and lower pathways is simply the difference between the nonmigrating Li being an SSIP or a CIP, respectively, during the transfer steps.

The mechanism for CT in the Na salt can be represented as

(34) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965; pp 101, 102, 105, 189, 190, 193.

Scheme 2
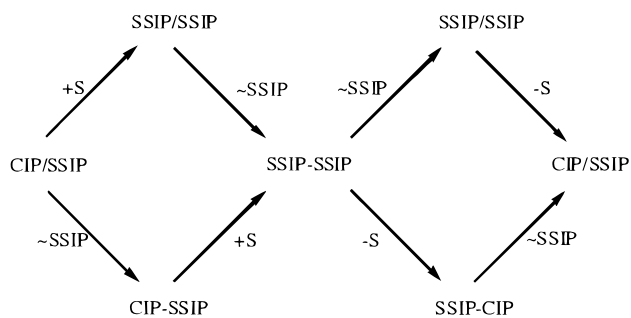
Scheme 3
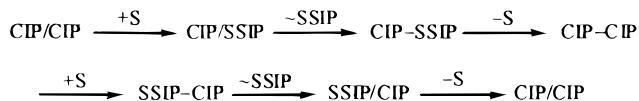
in Scheme 3. Here the intermediate di-monoanion (**2**) is represented as a diCIP because ESR evidence (hyperfine coupling of the Na with the COT ring) indicates CIPs in $COT^{-\bullet}/Na^+$.[35]

Finally, we note that Jedliński and co-workers have recently employed potasside anion–crown ether complexed potassium cation ion pairs (K^-,K^+/crown) for the reduction of styrene or α-methylstyrene.[36] One can conceive of transition structures for CT involving species such as K^0 or K^-. However, we consider these to be highly unlikely in the CT TS of 1^{2-} on energetic grounds, primarily because the requisite strong complexation of K^+ analogous to that in K^+/crown ether[37] cannot be achieved.

(35) (a) Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360. (b) Smentowski, F. J.; Stevenson, G. R. *J. Am. Chem. Soc.* **1967**, *89*, 5120.

(36) (a) Jedliński, Z.; Czech, A.; Janeczek, H.; Kowalczuk, M. *J. Am. Chem. Soc.* **1995**, *117*, 8678. (b) Szwarc, M.; Jedliński, Z.; Janeczek, H. *Macromolecules* **1997**, *30*, 4498. Jedliński, Z. *Acc. Chem. Res.* **1998**, *31*, 55.

(37) Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 327.