Evidence for a concentration dependent $^{6(7)}$Li NMR contact shift in tetrahydrofuran solutions of lithium naphthalene radical anion and the effect of added $^{6(7)}$LiCl

Maria Micha-Screttas,* George A. Heropoulos and Barry R. Steele

Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation,
Athens 116 35, Greece

Received (in Cambridge) 26th January 1999, Accepted 26th April 1999

The paramagnetic nuclear magnetic resonance shifts for $^{6(7)}$Li in tetrahydrofuran solutions of lithium biphenyl, naphthalene, phenanthrene, anthracene and *trans*-stilbene radical anions have been measured as a function of the radical anion concentration. The shift *vs.* concentration relationships are linear except in the case of naphthalene. Both the observed molar shifts, $\delta_{\mathrm{obs}}[^{6(7)}\mathrm{Li}]$, and the corresponding contact shifts, δ_c, are equal for the two isotopes. The paramagnetic shifts observed for THF solutions of $^{6(7)}$Li naphthalene radical anion increase with increasing dilution resulting in a non-linear shift *vs.* concentration relationship. This relationship becomes linear in the presence of $^{6(7)}$LiCl. A qualitative interpretation is proposed based on dynamic processes involving lithium cation exchange. The relevance of these results to $\mathrm{S_{RN}1}$ reactions is noted.

Introduction

Lithium-6 and lithium-7 nuclear magnetic resonance spectroscopy has been used fairly extensively in recent years for studying the structure of organic derivatives of lithium.[1] There is, however, a scarcity of reports on the application of the method to the investigation of paramagnetic organic compounds. Stable radical anions, with their unpaired electron and a negative charge, can function as sensitive probes for the investigation of solution structure. This is because the unpaired electron of the radical anion interacts with the magnetic nuclei of the lattice as well as with its broader environment. Using NMR spectroscopy it is possible to measure very weak interactions which are beyond the capabilities of present-day EPR spectrometers. For example, it can be readily shown that for protons a hyperfine splitting constant (hfsc) of 0.1 mT corresponds to an NMR contact shift of 72 ppm at 36 °C. In a previous study from this laboratory the fluorenone radical anion has been employed as a spin label in conjunction with ^{31}P NMR spectroscopy for probing interactions of alkali metal ions with certain phosphorus ligands.[2] Even weaker hyperfine interactions have been measured between alkali metal fluorenone radical anions and naphthalene from observations of the ^{13}C NMR shifts of the aromatic hydrocarbon.[3] Radical anions of aromatic hydrocarbons induce paramagnetic ^{1}H and ^{13}C NMR shifts to the hydrogen and carbon nuclei of the solvent, tetrahydrofuran. These shifts are linearly related to the concentration of the radical anion, thus indicating the absence of equilibria involving diamagnetic or paramagnetic aggregates in this solvent.[4] Solvent and countercations are of paramount importance and, for a given anion radical, are the factors which determine the ion-pairing situation both in solution[5] and in the crystalline state.[6,7] It has been stated that X-ray studies of radical anions may be correlated to results from solution studies and "provide insight into ion-pairing in solution".[6] Indeed, in contact ion pairs, factors such as the hapticity of the cation–anion pair can only be revealed by studies in the crystalline state.[6,7]

Aromatic hydrocarbon radical anions have found considerable application in synthetic chemistry and especially for the preparation of active metals[8] and in reactions involving cleavage of carbon-to-heteroatom bonds where they act either as deprotecting agents[9] or as homogeneous sources of lithium metal for the formation of C–Li bonds.[10] In those cases where the heteroatom is a halogen, lithium halide is a by-product. Moreover, aromatic substitution by the $\mathrm{S_{RN}1}$ mechanism involves radical anionic intermediates.[11] It is of interest, therefore, to be able to examine the effect of additives such as lithium halides on the structure of the radical anion solutions. Another even more important reason for studying the interaction between radical ions and metal derivatives, such as salts is the possibility of generating materials with useful magnetic or electric properties.[6,12] In this work we report the behaviour of $^{6(7)}$Li paramagnetic NMR shifts as a function of the concentration of the radical anions of biphenyl, naphthalene, phenanthrene, anthracene and *trans*-stilbene. Furthermore, we also report on the effect of added $^{6(7)}$LiCl on the structure of lithium naphthalene radical anion in THF. We have also studied the effect of added ^{7}LiCl to solutions of ^{6}Li phenanthrene and anthracene radical anion. It is appropriate, perhaps, at this point to mention also a related paper by Takeshita and Hirota which reports, *inter alia*, the case of sodium 2,2′-bipyridyl radical anion in dimethoxyethane which exhibits concentration dependent ^{23}Na splittings.[13] This is interpreted as arising from an equilibrium between ion pairs and ion clusters. An early report by Hirota and Weissman[14] deals with the rate of exchange between sodium xanthone radical anion and sodium iodide in dimethoxyethane. The authors report a bimolecular rate constant at 25 °C of the order of 10^8 M s^{-1} for the exchange between sodium ions associated with the radical anion and sodium iodide.

Results

Radical anions of biphenyl, naphthalene, phenanthrene, anthracene and *trans*-stilbene were prepared by the reaction of stoichiometric amounts of the aromatic hydrocarbon and ^{6}Li or ^{7}Li chips in 20 mmol quantities and in concentrations of *ca.* 1 M. This method differs markedly from that using alkali metal mirrors in contact with solutions of the hydrocarbons.[13,15] Our method leads to solutions devoid of either any significant excess of the hydrocarbon or any over-reduction product. The small uncertainty in the amount of lithium introduced by the surface

Table 1 Molar paramagnetic $^{6(7)}$Li NMR shifts (ppm mol^{-1}) for some aromatic hydrocarbon radical anions and the corresponding contact shifts (ppm mol^{-1}) in THF at 300 K

Entry	Radical anion	$\delta_{obs}(^7Li)$	$\delta_{obs}(^6Li)$	$\delta_c(^7Li)$	$\delta_c(^6Li)$
1	Biphenyl	7.59	7.88	1.18	1.32
2	Phenanthrene	9.93	9.77	2.35	2.27
3	Anthracene	6.45	6.28	0.60	0.52
4	Stilbene	5.45	5.23	0.10	−0.02

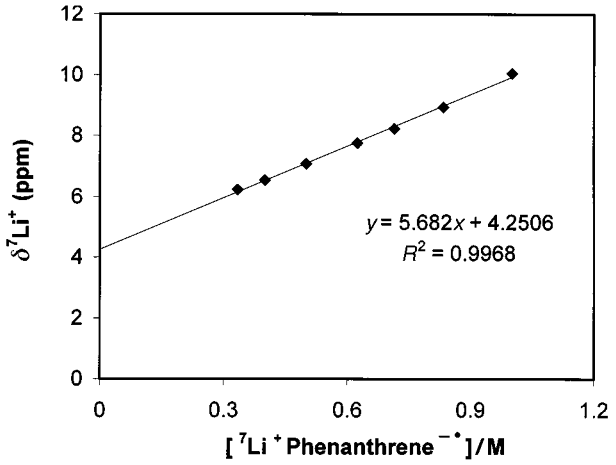


Fig. 1 Observed ^{7}Li NMR shift in solution of $^7Li^+$ (phenanthrene)$^{-•}$ in THF as a function of concentration.

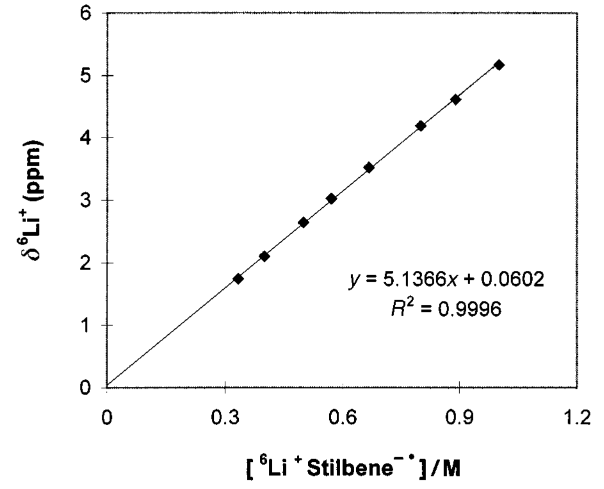


Fig. 2 Observed ^{6}Li NMR shift in solution of $^6Li^+$ (*trans*-stilbene)$^{-•}$ in THF as a function of concentration.

nitrides is minimised by the relatively large amount of radical anion prepared. The lithium resonances were recorded for solutions of various concentrations prepared by dilution of the original concentrated solution. The plots of the shift, δ, of either lithium isotope *versus* concentration were linear for all the radical anions apart from that of naphthalene (Fig. 1, 2). The molar paramagnetic lithium NMR shifts calculated from the linear relationships are presented in Table 1.

The plot obtained for lithium naphthalene radical anion (LiNap) is shown in Fig. 3. When the dilution was performed by incremental addition of THF solutions of $^{6(7)}$LiCl to solutions of $^{6(7)}$Li naphthalene radical anion, the shift *vs.* concentration relationship became linear (Fig. 4). This latter experiment was carried out in six variations depending on the isotopes used and the nucleus measured. One signal was observed in all cases. The experiments are summarised in Table 2 together with the values for δ_{obs} measured from the linear relationships.

Table 2 Molar paramagnetic $^{6(7)}$Li NMR shifts from combinations of $^{6(7)}$LiNap and $^{6(7)}$LiCl in THF

Isotope used to prepare radical anion solution	Lithium chloride added	Lithium isotope measured	δ_{obs}/ppm mol^{-1}
^{7}Li	^{6}LiCl	^{6}Li	18.85
^{7}Li	^{6}LiCl	^{7}Li	18.57
^{6}Li	^{7}LiCl	^{7}Li	18.87
^{6}Li	^{6}LiCl	^{6}Li	19.15
^{7}Li	^{7}LiCl	^{7}Li	18.02
^{6}Li	^{7}LiCl	^{6}Li	19.32

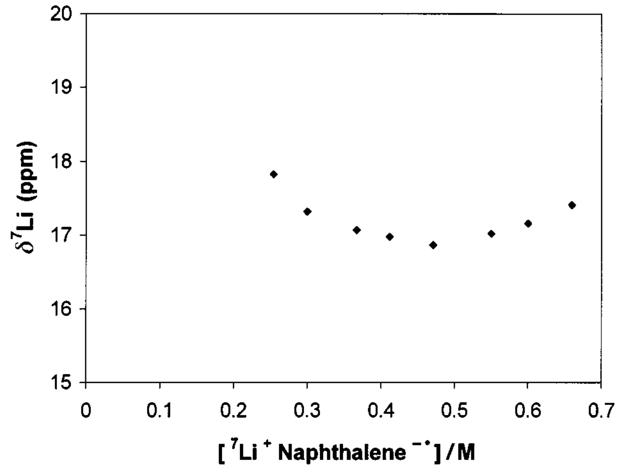


Fig. 3 Observed ^{7}Li NMR shift in solution of $^7Li^+$ (naphthalene)$^{-•}$ in THF as a function of concentration.

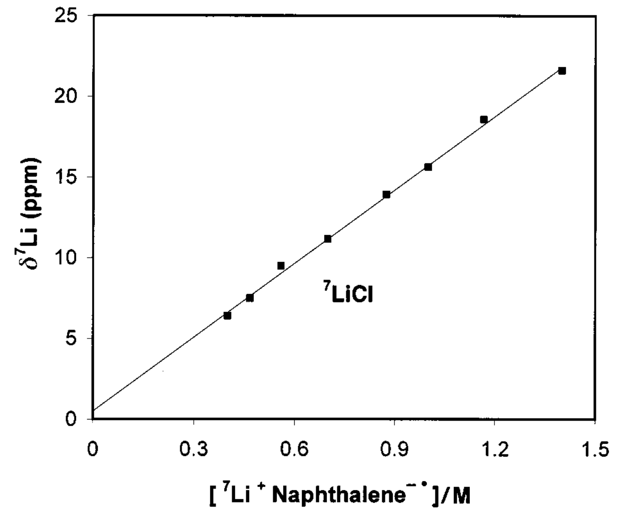


Fig. 4 Relationship $\delta_{obs}(^7Li)$ *vs.* [$^7Li^+$ (naphthalene)$^{-•}$] in THF in the presence of ^{7}LiCl.

Dilution of a solution of ^{6}Li phenanthrene and anthracene radical anions with a solution of ^{7}LiCl in THF gave linear $\delta(^7Li)$ *vs.* radical anion concentration plots, from which values for $\delta_{obs}(^7Li)$ of 9.72 and 6.32 ppm mol^{-1} were obtained.

The paramagnetic shifts induced by chromium(III) acetylacetonate in $^{6(7)}$Li nuclei were measured in THF solutions of LiCl as a check for the validity for these nuclei of the formula for the bulk paramagnetic shift.[2] The molar paramagnetic shifts of 26.47 and 26.21 ppm mol^{-1} observed at 300 K for ^{6}Li and ^{7}Li respectively agree very closely with the theoretical value of 26.19 ppm mol^{-1}.

Discussion

The molar paramagnetic lithium isotope shift parameters, δ_{obs},

Table 3 Paramagnetic NMR ^{7}Li shifts (ppm), normalised shifts (ppm mol^{-1}), and contact shifts (ppm mol^{-1}) in ^{7}Li naphthalene radical anion solution at various concentrations

Concentration	Shift	Normalised shift	Contact shift
0.660	17.406	26.37	10.57
0.600	17.159	28.60	11.68
0.550	17.017	30.94	12.85
0.471	16.868	35.81	15.29
0.412	16.977	41.21	17.98
0.367	17.069	46.51	20.64
0.300	17.320	57.73	26.25
0.254	17.820	70.16	32.46

for biphenyl, phenanthrene, anthracene and stilbene, listed in Table 1, indicate that they depend markedly on the nature of the anion whereas, for a given anion, the values for the lithium isotopes are equal within experimental error. The observed shift is composed of two parts—one is due to macroscopic interactions which are responsible for the so-called susceptibility shift, while the other is due to hyperfine interactions which give rise to the contact shift. The contact shifts, δ_c, listed in Table 1, have been extracted from δ_{obs} parameters and the calculated at 300 K value of the susceptibility shift using eqn. (1).[2]

$$\delta_c = 0.5(\delta_{obs} - 5.238) \text{ ppm mol}^{-1} \qquad (1)$$

For biphenyl, phenanthrene and anthracene, the contact shifts are very small, suggesting that these radical anions exist in THF in the form of loose ion pairs. On the other hand, from the absence of any observed contact shift in the case of the lithium stilbene radical anion, we conclude that the cation and anion are solvent-separated.

Lithium naphthalene radical anion

The interpretation of the curvature observed in the case of the shift *versus* concentration relationship for $^{6(7)}$Li naphthalene radical anion is more challenging. It could be attributed to a concentration dependent structure for the lithium naphthalene radical anion. An equilibrium involving diamagnetic and paramagnetic aggregates, for example, could explain a situation such as in Fig. 3. However, the fact that the paramagnetic NMR solvent shifts are linear with respect to the concentration precludes the occurrence of aggregation or the involvement of diamagnetic–paramagnetic equilibria. We also note that the hydrocarbon radical anions, unlike the bipyridyl[13] radical anion or the fluorenone radical anion,[16] lack electronegative atoms which would promote cluster formation. The curvature should therefore be attributed to some other effect and, since the susceptibility shift varies linearly with the concentration, we are led to assign it to the hyperfine component of the shift. If this is the case, then we are forced to conclude that the observed contact shift is concentration dependent in this system. Furthermore, we deduce that this shift *increases* with decreasing concentration. This becomes more evident if we consider the normalised with respect to the concentration shifts, summarised in Table 3.

The normalised shifts, which actually correspond to molar shifts at the specified concentrations, can be inserted into eqn. (1) and the corresponding contact shift values extracted, 4th column, Table 3.

The trend of increasing contact shift values with increasing dilution could be explained if the ion-pair becomes tighter and the covalency increases as the concentration decreases, but we find this counterintuitive and difficult to understand. A reasonable explanation arose as a result of a series of experiments which examined the effect of added lithium chloride. At this point, however, it could be appropriate to note that the counterion of naphthalene radical anion, and perhaps of any aromatic hydrocarbon radical anion, should not be considered as an integral part of the paramagnetic molecule. This then is the justification for expressing the contact shifts in ppm mol^{-1} rather than in ppm, as they should be expressed if the nucleus were an integral part of the paramagnetic molecule, and therefore independent of the concentration.

The effect of added lithium-6(7) chloride

As described in the Results section above, we performed all the possible combinations of $^{6(7)}$Li NMR experiments for $^{6(7)}$Li lithium naphthalene radical anion in THF diluted by THF solutions of $^{6(7)}$LiCl. In all cases only one NMR signal was observed and the shift *versus* concentration plots were linear. The molar shifts obtained from these plots agreed to within 5% or less of the mean value. The implication is that the lithium associated with the radical anion becomes indistinguishable from the lithium of the added chloride and that the addition of LiCl lifts the conditions responsible for the curvature observed in Fig. 3. Given that LiCl in THF is a dimer,[17] the exchange may be represented as in eqn. (2).

$$\begin{aligned} {}^7\text{Li}^+ [\text{C}_{10}\text{H}_8]^{-\bullet} + {}^6\text{Li}_2\text{Cl}_2 &\rightleftharpoons {}^6\text{Li}^+ [\text{C}_{10}\text{H}_8]^{-\bullet} + {}^7\text{Li}^6\text{LiCl}_2 \\ {}^6\text{Li}^+ [\text{C}_{10}\text{H}_8]^{-\bullet} + {}^7\text{Li}_2\text{Cl}_2 &\rightleftharpoons {}^7\text{Li}^+ [\text{C}_{10}\text{H}_8]^{-\bullet} + {}^7\text{Li}^6\text{LiCl}_2 \quad (2) \end{aligned}$$

The exchange may take place within an aggregate such as $[\text{Li}_3\text{Cl}_2]^+$ $[\text{C}_{10}\text{H}_8]^{-\bullet}$. The conclusion that there is a rapid exchange on the NMR timescale between the lithium associated with the radical anion and that from the added lithium chloride is further strengthened by the observation that the ^{7}Li shifts measured after addition of ^{7}LiCl to ^{6}Li phenanthrene or anthracene radical anion led to molar values of 9.72 and 6.32 ppm mol^{-1}, respectively. These values agree to within 2% of those obtained with ^{7}Li phenanthrene or anthracene radical anion, entries 2 and 3, Table 1.

We may now speculate on the origin of the curvature in Fig. 3. For the lithium biphenyl, phenanthrene, *trans*-stilbene and anthracene radical anions, where there is a linear shift *vs.* concentration relationship, we assume that there is a dynamic exchange of lithium cations between identical sites [eqn. (3)]. This is also exemplified by the linearity of the solvent shift *vs.* concentration relationships for radical anion solutions where all the solvent molecules experience an average of the bulk and hyperfine paramagnetic effects.[18]

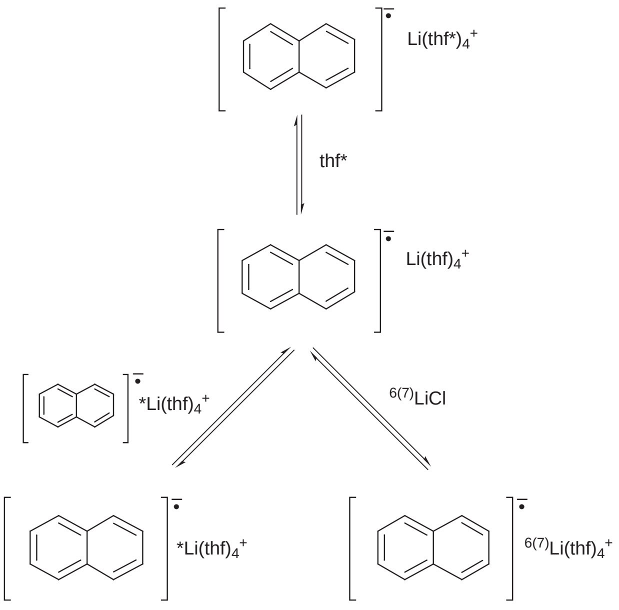
The less tight the ion pairs are, the more facile such a process would be. Judging from the very small contact shifts in the cases of the radical anions of biphenyl, phenanthrene and anthracene, we conclude that they exist in the form of loose ion pairs, while the lithium *trans*-stilbene radical anion, where no contact shift is observed, is presumed to be a solvent-separated ion pair. In contrast, lithium naphthalene radical anion exhibits a substantial contact shift which suggests considerable covalency between the anion and cation and thus tight ion-pairing. Such a situation would make cation exchange less favourable,[19] and we thus interpret the observed results as follows. At high concentrations there is a relatively rapid exchange of lithium cations such as in eqn. (3).

$$\text{A}^{-\bullet}\ \text{S}_n\text{Li}^+ + \mathbf{A}^{-\bullet}\mathbf{S}_n\mathbf{Li}^+ \rightleftharpoons \text{A}^{-\bullet}\text{S}_n\mathbf{Li}^+ + \mathbf{A}^{-\bullet}\mathbf{S}_n\text{Li}^+ \quad (3)$$

(A = aromatic hydrocarbon; S = solvent molecule)

Such a process would be concentration dependent, becoming less rapid at lower concentrations. Thus in dilute solutions the cation is correlated for an increasingly longer time with the anion, resulting in a situation where the lithium nucleus receives an increasing amount of spin density from the paramagnetic anion. This is manifested as a contact shift which increases in magnitude with increasing dilution.

The network of exchange equilibria which have been demonstrated to exist in solutions of alkali metal aromatic hydrocarbon radical anions is exemplified in Scheme 1 for lithium naphthalene radical anion. Thus the lithium countercation may exchange with another lithium from either a second lithium naphthalene species or from added lithium chloride, while the solvent in the coordination sphere of the lithium is in rapid equilibrium with the bulk solvent.



Scheme 1

It is felt that interactions such as that in eqn. (2) and Scheme 1 are of importance for understanding the elementary steps of nucleophilic reactions involving radical or radical anionic intermediates. For example, in the $S_{RN}1$ mechanism, we could have radical anion intermediates which would interact quite strongly with the salts which provide the nucleophile. We would thus expect a cation effect in these reactions. We could also expect the radical anion–metal salt interactions discussed in this work to provide the basis for synthetically useful chemistry.

Concluding remarks

The major conclusion derived from a broad range of experiments involving measurements of paramagnetic NMR $^{6(7)}$Li shifts in lithium aromatic hydrocarbon solutions in the absence or in the presence of $^{6(7)}$LiCl in THF, is that the counterion should not be considered to be an integral part of the paramagnetic anion. This then implies that contact shifts experienced by the positive ions are concentration dependent and therefore should be expressed in ppm mol^{-1} rather than in ppm. In addition, the interaction demonstrated between radical anions and a non-reducible metal salt could provide guidelines for investigating new chemistry aimed towards either synthetically useful reactions or new functional materials.

Experimental

The nuclear magnetic resonance spectra were recorded using a Bruker AC 300 MHz instrument operating at a probe temperature of *ca.* 300 K. Tetrahydrofuran was doubly distilled from 9-fluorenylpotassium shortly before use. ^{7}LiCl was a commercial product and was dried by heating under vacuum for several hours. Radical anion solutions were prepared and standardised as described previously.[4] The $^{6(7)}$Li resonances were referred to a 1 M solution of $^{6(7)}$LiCl in D_2O as external standard. Samples for NMR measurements were prepared as described in a previous publication.[20] Standard solutions were handled with microsyringes.

Preparation of ^{6}LiCl

Lithium-6 (1.5 g), cut into small chips, was added to 100 mL of argon-saturated distilled water under an atmosphere of argon. After complete dissolution of the metal, the solution was neutralised with concentrated hydrochloric acid. The resulting solution was evaporated to dryness under vacuum in a thin film evaporator and the residue dried *in vacuo* (0.02 mm Hg) at 250 °C for 20 h.

References

1 For a recent review, see H. Gunther, in *Advanced Applications of NMR to Organometallic Chemistry*, M. Gielen, R. Willem and B. Wrackmeyer, ed., Wiley, Chichester, 1996, ch. 9.
2 C. G. Screttas, G. A. Heropoulos, B. R. Steele and D. Bethell, *Magn. Reson. Chem.*, 1998, **36**, 656.
3 A. Behrendt, C. G. Screttas, D. Bethell, O. Schiemann and B. R. Steele, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2039.
4 C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1983, **48**, 153.
5 M. Szwarc and J. Jagur-Grodzinski, in *Ions and Ion Pairs in Organic Reactions*, M. Szwarc, ed., John Wiley and Sons, Inc., New York, 1974, vol. 2, ch. 1.
6 C. Näther, H. Bock, Z. Havlas and T. Hauck, *Organometallics*, 1998, **17**, 4707.
7 W. Jost, M. Adam, V. Enkelmann and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 878.
8 R. D. Rieke, *Acc. Chem. Res.*, 1977, **10**, 301.
9 R. L. Letsinger and J. L. Finnan, *J. Am. Chem. Soc.*, 1975, **97**, 7197.
10 C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1978, **43**, 1064.
11 J. F. Bunnett, *Acc. Chem. Res.*, 1978, **11**, 413.
12 For recent references see: A. Vlcek, Jr., F. Baumann, W. Kaim, F.-W. Grevels and F. Hartl, *J. Chem. Soc., Dalton Trans.*, 1998, 215; C. Näther, H. Bock, Z. Havlas and T. Hauck, *Organometallics*, 1998, **17**, 4707; C. D. Stevenson, A. L. Wilham and E. C. Brown, *J. Phys. Chem. A*, 1998, **102**, 2999; A. Klein, S. Hasenzahl and W. Kaim, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2573; S. Schmitt, M. Baumgarten, J. Simon and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1078; M. N. Bochkarev, I. L. Fedushkin, V. I. Nevodchikov, V. K. Cherkasov, H. Schumann, H. Hemling and R. Weimann, *J. Organomet. Chem.*, 1996, **524**, 125.
13 T. Takeshita and N. Hirota, *J. Chem. Phys.*, 1973, **58**, 3745.
14 N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, 1962, **86**, 2537.
15 B. M. P. Hendriks, G. W. Canters, C. Corvaja, J. W. M. de Boer and E. de Boer, *Mol. Phys.*, 1971, **20**, 193.
16 Z. Hou, A. Fujita, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1996, **118**, 2503.
17 M. K. Wong and A. I. Popov, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3615; H. J. Reich, J. P. Borst, R. R. Dykstra and D. P. Green, *J. Am. Chem. Soc.*, 1993, **115**, 8278.
18 C. G. Screttas and M. Micha-Screttas, *J. Phys. Chem.*, 1983, **87**, 3844.
19 N. Hirota, in *Radical Ions*, E. T. Kaiser and L. Kevan, ed., Interscience Publishers, New York, 1968, ch. 2.
20 C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1981, **46**, 993.

Paper 9/00705I