Interaction between alkali metal aromatic ketone radical anions and the chlorides of lithium and magnesium in solution. A case of a carbon–carbon bond strengthening through complex formation

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The interaction between lithium, sodium and potassium salts with the pre-formed radical anions of benzophenone, 2-methylbenzophenone, 2,4,6-trimethylbenzophenone or fluorenone, and lithium or magnesium chlorides has been studied by nuclear magnetic resonance spectroscopy. The interaction between the radical anions and the metal salt depends on both the anion and the countercation and is stronger with magnesium chloride than with lithium chloride. Interaction leads either to the establishment of equilibria (lithium chloride) or to the formation of diamagnetic complexes in solution with rather well defined stoichiometry (magnesium chloride). Sodium 2-methylbenzophenone radical anion, unlike sodium benzophenone radical anion, is soluble and paramagnetic in tetrahydrofuran (THF). The highly hindered 2,4,6-trimethylbenzophenone radical anion exhibits a very weak interaction with magnesium chloride. It appears to exist in solution either as a very loose aggregate or as a monomeric entity. It is concluded that complexation between unhindered aromatic ketone radical anions with magnesium chloride causes a C–C bond strengthening in the incipient pinacolate dianion moiety within the radical anion cluster. On the basis of the above information, the success of the *Gomberg–Bachmann pinacol synthesis* by reducing aromatic ketones with Mg–MgI_2, can now be understood.

Introduction

There is continued interest in the chemistry of stable radical anions, both in solution and in the solid state. One of the reasons for this is that radical anions may be good candidates for the development of new materials with technologically interesting and useful magnetic or electric properties.[1] Physicochemical studies can also provide a better understanding of the nature of the bonding in the radical anion–countercation pair. Crystalline state studies, for example, have revealed that heavier alkali metal ions exhibit multiple hapticity with the anion of the aromatic molecule.[2] This information is crucial for an appreciation of the covalency between a radical anion and a heavier alkali metal.[3] Magnesium can also exhibit similar coordination behaviour.[4] Complexes of the fluorenone radical anion have been generated by reduction of the ketone by metallic or low-valent samarium and other lanthanide compounds and their crystal structures have been determined. These have shown that the stability of the ketyl species with respect to the formation of the corresponding pinacolate depends markedly on the metal environment, the ketyls being especially favoured by the presence of sterically demanding ligands and a strongly coordinating solvent such as hexamethylphosphoric triamide (HMPA).[5] Metal complexes of radical anions, particularly those of nitrogen-based ligands, have also been extensively studied by Kaim and co-workers.[6] It should be noted that the generation of these complexes is based on a ligand-centred reduction process[7] rather than complexation with pre-formed radical anions, as reported in the present work. The mechanism of the protonation of alkali metal aromatic ketone radical anions has been elucidated as has also the mechanism of the base-catalysed decomposition of benzopinacol.[8] Another recent study, relevant to the potential materials applications of radical anions, has examined the effect of polyoxyethylene solvents on the ionic conductivity of sodium aromatic hydrocarbon radical anions.[9] In the field of organic chemistry, the scope of the synthetic utility of aromatic hydrocarbon radical anions has been further widened,[10] while the theoretical and mechanistic aspects of reactions between radical anions and alkyl halides and other organic compounds continues to be the subject of intense scrutiny.[11]

One might hope that, by forming complexes between radical anions and non-reducible metal salts, one could form composite materials with technologically useful magnetic or electro-optic properties. In our first study, using ^{6,7}Li hydrocarbon radical anions and ^{6,7}LiCl, it became possible to acquire a better understanding about the dynamic processes involving anions, cations and solvent molecules.[12] A major conclusion of that work was that the countercation should not be considered as an integral part of the radical anion. We reasoned that, in order to facilitate complex formation between a radical anion and a non-reducible metal salt, we should move to radical anions possessing electronegative atoms and the aromatic ketone radical anions appeared to be the best choice. An earlier report from this laboratory concerned the solubilisation of aromatic hydrocarbon radical anions in hydrocarbon media containing lithium 2-ethoxyethoxide.[13] The same work also reported the interaction between alkali metal benzophenone and fluorenone radical anions with magnesium 2-ethoxyethoxide in THF leading to disappearance of paramagnetism, but the question of the origin of this phenomenon was not addressed. In this work we have employed NMR spectroscopy for magnetochemical measurements,[14] and we report the results of the interaction of tetrahydrofuran (THF) solutions of the lithium, sodium (where applicable) and potassium salts of the radical anions of benzophenone, 2-methylbenzophenone, 2,4,6-trimethylbenzophenone and fluorenone with the chlorides of lithium and magnesium.

Results

a) Benzophenone radical anion

On addition of increments of a standard solution of LiCl in

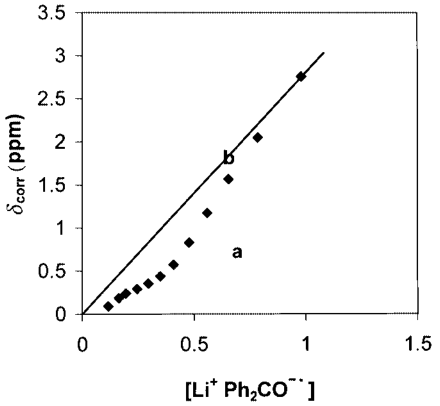

Fig. 1 Observed ^{1}H NMR shift for the α-proton of THF for dilution of THF solution of Li^+ $Ph_2CO^{-•}$ by (a) LiCl solution in THF (b) neat THF.

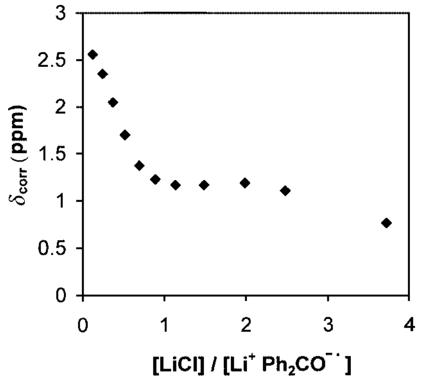

Fig. 2 Magnetic titration of THF solution of Li^+ $Ph_2CO^{-•}$ against THF solution of LiCl.

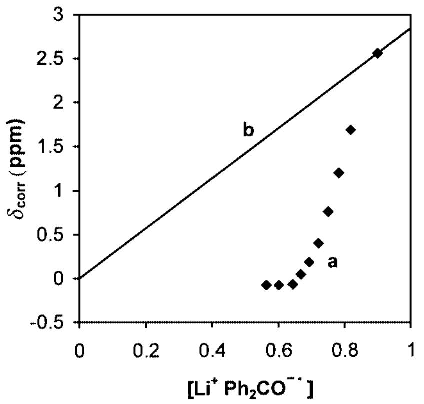

Fig. 3 Observed ^{1}H NMR shift for the α-proton of THF for dilution of THF solution of Li^+ $Ph_2CO^{-•}$ by (a) $MgCl_2$ solution in THF (b) neat THF.

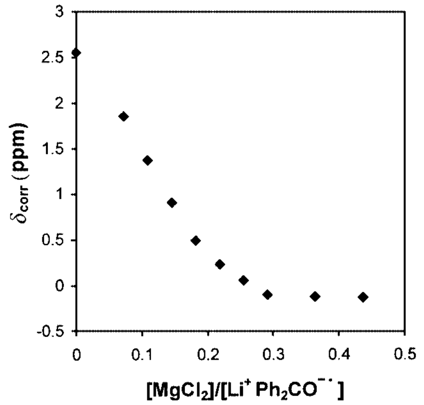

Fig. 4 Magnetic titration of THF solution of Li^+ $Ph_2CO^{-•}$ against THF solution of $MgCl_2$.

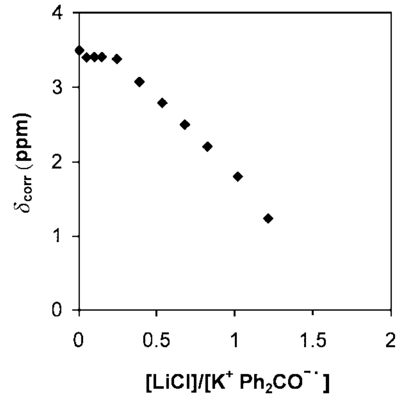

Fig. 5 Magnetic titration of THF solution of K^+ $Ph_2CO^{-•}$ against THF solution of LiCl.

THF to a solution of lithium benzophenone radical anion and recording the α-proton resonance of THF, we observe a rather rapid decrease of the paramagnetism of the solution (line **a** in Fig. 1). In the same Figure, line **b** represents the dilution curve, *i.e.*, the shift *vs.* concentration relationship obtained by diluting with neat THF. By plotting the results in the form of a magnetic titration, *i.e.*, shift (corrected for dilution) *versus* ratio of [LiCl]/[$LiPh_2CO$], we obtained the plot shown in Fig. 2. This reveals that there is a well-defined break at a ratio of 1 : 1 and that also there is residual paramagnetism at the equivalence point. A less well-defined equilibrium appears to be established at a ratio of 2 : 1 while beyond this point the titration curve approaches linearity.

From the residual paramagnetism and the known molar paramagnetic solvent shift for $LiPh_2CO$, we calculate that at the first equilibrium *ca.* 13% of the radical anion remains uncomplexed. A similar experiment was carried out using $MgCl_2$. In Fig. 3, lines **a** and **b** respectively refer to the addition of increments of a THF solution of magnesium chloride to lithium benzophenone radical anion and dilution with THF, while the corresponding magnetic titration curve with magnesium chloride is shown in Fig. 4. Here the equivalence point occurs at a ratio for [$MgCl_2$]/[$LiPh_2CO$] of 1 : 4. It is also significant to note that, in this case, we observed complete disappearance of the paramagnetism as well as a change of the blue colour of the solution to a faint bluish-purple. Acidification of the solution at this stage gave benzopinacol almost exclusively. In another experiment, instead of acidifying we added an excess of methyl iodide and stirred the solution at room temperature for three days. In this case we isolated benzophenone. The potassium salt of benzophenone radical anion is also soluble in THF and the titration results with LiCl–KPh_2CO are given in Fig. 5. The almost linear curve suggests that, in this case, we have a rather weak interaction between the paramagnetic molecule and lithium chloride. In other words, the titration curve resembles a dilution curve. The analogous titration against magnesium chloride, however, is similar to that observed for $LiPh_2CO$ and exhibits an equivalence point at a ratio [$MgCl_2$]/[KPh_2CO] of 1 : 4 (Fig. 6) and again with complete disappearance of paramagnetism.

b) 2-Methylbenzophenone radical anion

Fig. 7 shows the magnetic titration curve of lithium 2-methylbenzophenone radical anion against lithium chloride, with rather ill-defined equivalence points. Lithium 2-methylbenzophenone radical anion titrated against $MgCl_2$, Fig. 8, showed a break at 1 : 2 stoichiometry, with complete disappearance of paramagnetism at the equivalence point. Unlike benzophenone, 2-methylbenzophenone also forms a THF soluble radical anion

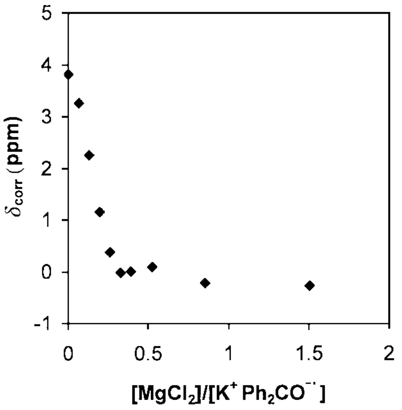

Fig. 6 Magnetic titration of THF solution of K^+ $Ph_2CO^{-\bullet}$ against THF solution of $MgCl_2$.

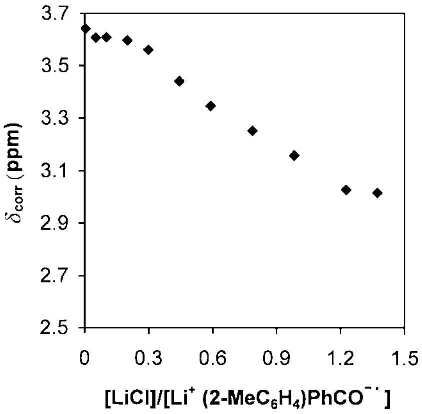

Fig. 7 Magnetic titration of THF solution of Li^+ (2-methylbenzophenone)$^{-\bullet}$ against THF solution of LiCl.

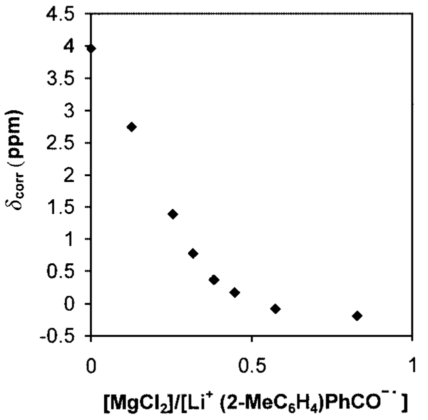

Fig. 8 Magnetic titration of THF solution of Li^+ (2-methylbenzophenone)$^{-\bullet}$ against THF solution of $MgCl_2$.

with sodium as the countercation. Titration of this radical anion against $MgCl_2$, Fig. 9, revealed an equivalence point at approximately 0.5 : 1 or 1 : 2, but in this case some paramagnetism remained. There is also a notable concavity in the curve in Fig. 9, at low $[MgCl_2]/[Na(2\text{-}MeC_6H_4)PhCO]$ ratios. The magnetic titration curve of potassium 2-methylbenzophenone radical anion and magnesium chloride is shown in Fig. 10. In this case we observe that there is a rather uncertain break-point close to 0.5 : 1 or 1 : 2.

c) 2,4,6-Trimethylbenzophenone radical anion

Titration of a solution of lithium 2,4,6-trimethylbenzophenone radical anion with magnesium chloride gave the relationship shown in Fig. 11. Similar titration curves were obtained with

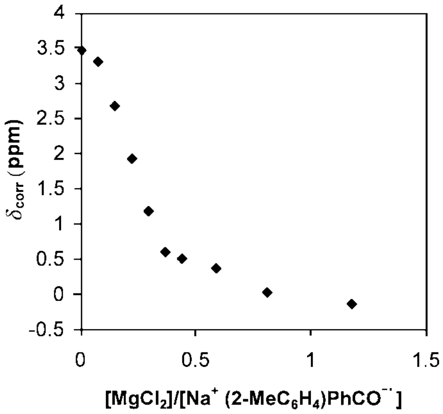

Fig. 9 Magnetic titration of THF solution of Na^+ (2-methylbenzophenone)$^{-\bullet}$ against THF solution of $MgCl_2$.

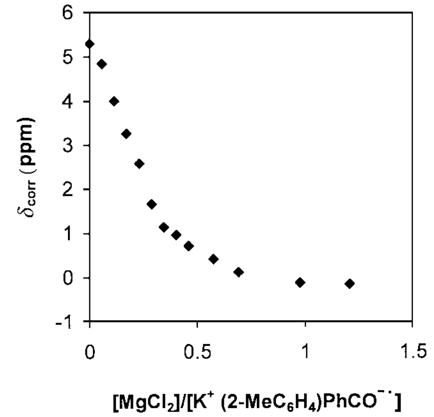

Fig. 10 Magnetic titration of THF solution of K^+ (2-methylbenzophenone)$^{-\bullet}$ against THF solution of $MgCl_2$.

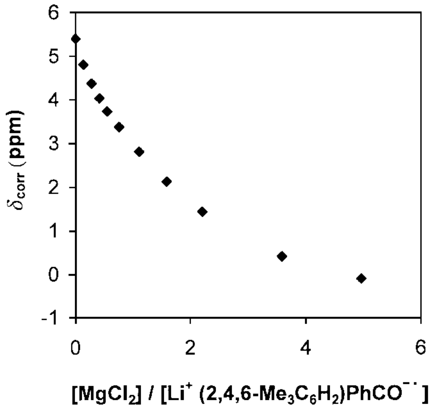

Fig. 11 Magnetic titration of THF solution of Li^+ (2,4,6-trimethylbenzophenone)$^{-\bullet}$ against THF solution of $MgCl_2$.

sodium and potassium 2,4,6-trimethylbenzophenone radical anions.

d) Fluorenone radical anion

Lithium fluorenone radical anion (LiFlO) and lithium chloride gave the titration curve shown in Fig. 12. Noticeable breaks are seen at [LiCl]/[LiFlO] ratios of 1 : 1 and 2 : 1, whereas at higher ratios the shift *vs.* [LiCl]/[LiFlO] relationship becomes linear. For sodium fluorenone radical anion and LiCl, the magnetic titration curve is shown in Fig. 13. The differences in Fig. 12 and 13 are worthy of comment. In the former there is a concavity in the initial stages, whereas in the latter a convexity is observed. Again, breaks at 1 : 1 and 2 : 1 are also evident in the case of the sodium fluorenone radical anion. The corresponding titration curve for potassium fluorenone radical anion and

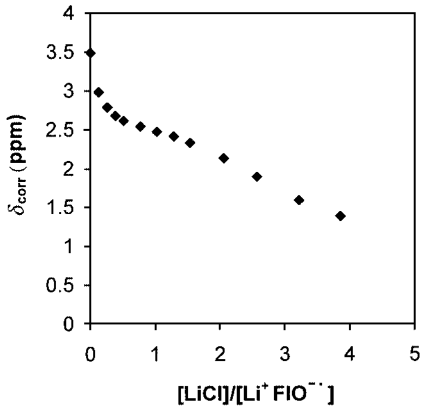

Fig. 12 Magnetic titration of THF solution of Li^+ (fluorenone)$^{-•}$ against THF solution of LiCl.

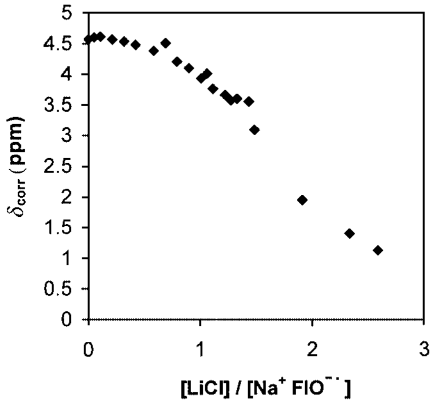

Fig. 13 Magnetic titration of THF solution of Na^+ (fluorenone)$^{-•}$ against THF solution of LiCl.

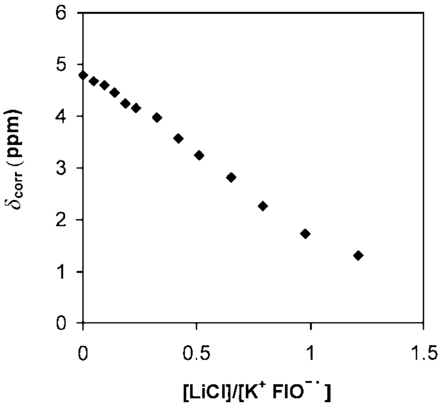

Fig. 14 Magnetic titration of THF solution of K^+ (fluorenone)$^{-•}$ against THF solution of LiCl.

lithium chloride (Fig. 14) deviates very little from linearity. It should also be noted that addition of lithium chloride to lithium, sodium and potassium fluorenone radical anions did not cause complete disappearance of paramagnetism. The titrations of lithium, sodium or potassium fluorenone radical anions against magnesium chloride all gave equivalence points at a ratio of $[MgCl_2]/[MFlO]$ equal to 1:2 (*e.g.* Fig. 15), with complete disappearance of paramagnetism at the equivalence point.

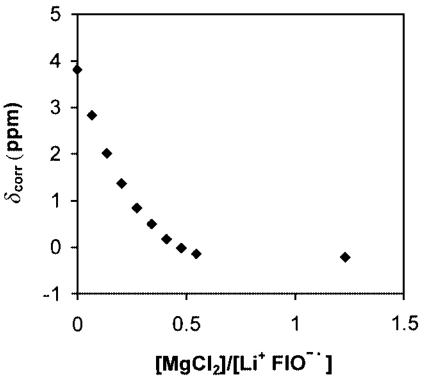

Fig. 15 Magnetic titration of THF solution of Li^+ (fluorenone)$^{-•}$ against THF solution of $MgCl_2$.

Discussion

a) Benzophenone radical anion

It appears to us that a reliable criterion for the interaction between an alkali metal benzophenone radical anion and lithium or magnesium chloride, and, for that matter, any other "ligand", would be the deviation of the shift *vs.* concentration curve from that of the linear dilution plot. Thus, just by comparing Figs. 1 and 3, we can conclude that lithium benzophenone radical anion interacts more strongly with magnesium chloride than with lithium chloride. In a more quantitative way, the strength of the interaction between a radical anion–cation pair and a metal salt can be expressed by the initial slope of the shift *vs.* concentration relationship (*e.g.* Fig. 1). Indeed, the initial slope expresses the initial rate of the decrease of paramagnetism caused by the addition of the salt. Thus, for example, in the case of lithium benzophenone radical anion the initial slope is 3.57 ppm mol^{-1} for LiCl compared with 10.37 ppm mol^{-1} for $MgCl_2$. The magnetic titration curve, Fig. 2, indicates that a rather marked change occurs once one equivalent of LiCl is added to one equivalent of the radical anion and that on adding a second equivalent a second species is formed with $[LiCl]/[LiPh_2CO] = 2:1$. The latter species appears to retain its integrity beyond this point, as is borne out by the linear part of the titration curve at ratios higher than 2:1. Given that lithium benzophenone radical anion exists in the form of oligomers, most probably tetramers, the equilibria can be written as in eqn. (1).

$$4Li_2Cl_2 + (LiPh_2CO)_4 \rightleftharpoons (LiCl,LiPh_2CO)_4 + 2Li_2Cl_2 \rightleftharpoons [(LiCl)_2,LiPh_2CO]_4 \quad (1)$$

Judging from the residual paramagnetism, we conclude that equilibrium (1) is shifted to the right. Another consequence of the complexation between lithium benzophenone radical anion and lithium chloride is the marked decrease in paramagnetism, a phenomenon that awaits an answer. The interpretation we offer as more probable is that complexation makes the $Ph_2(OLi)C(OLi)Ph_2$ moiety in the oligomeric structure tighter to resemble a pinacolate dianion. Along the same line of reasoning, the magnetic titration curve in Fig. 4 suggests that strong complexation occurs between lithium benzophenone radical anion and $MgCl_2$ with the formation of $[MgCl_2(LiPh_2CO)_4]$. The diamagnetic character of the complex indicates that complexation results in complete spin-pairing within the complex. This might be effected either by pinacolate formation or by disproportionation to a dianion and the free ketone. The fact that on acidification of the complex we obtained benzopinacol as the sole product suggests that spin-pairing occurs *via* pinacolate formation.[15] Therefore, a better representation of the diamagnetic complex should be $\{MgCl_2[Ph_2C(OLi)–C(OLi)Ph_2]_2\}$. Bearing in mind that even the monoanion of benzopinacol undergoes facile C–C bond fission,[8] the above mentioned converse phenomenon of spin pairing accompanied by C–C bond formation constitutes, to the best of our knowledge, the first report of a recognised strengthening of a weak C–C bond by complex formation (eqn. (2)).

$$2Ph_2CO^{\cdot -}Li^+ \xrightarrow{\text{complexation}} \text{“}Ph_2C(OLi)\text{–}C(OLi)Ph_2\text{”} \quad (2)$$

Potassium benzophenone radical anion appears to interact rather weakly with lithium chloride. The titration curve does not permit the estimation of any equivalence point. Judging from the small convexity of the shift *vs.* concentration relationship, we conclude that the interaction leads to some loosening of the potassium benzophenone radical anion oligomer. The interaction between magnesium chloride and potassium benzophenone radical anion is strong, leading to the formation of a diamagnetic complex, most probably of the composition $[MgCl_2(KPh_2CO)_4]$.

b) 2-Methylbenzophenone radical anion

Lithium 2-methylbenzophenone radical anion interacts rather weakly with lithium chloride. A comparison of the magnetic titration curve with that for lithium benzophenone radical anion seems to suggest the establishment of equilibria between lithium 2-methylbenzophenone radical anion and lithium chloride. It seems that weak complexation occurs with two different stoichiometries, namely 1:2 and 1:1. Most of the paramagnetism remains unchanged, which is indicative of a weak interaction between lithium chloride and the radical anion and of an equilibrium shifted toward the free species. Unlike lithium chloride, magnesium chloride appears to interact strongly with lithium 2-methylbenzophenone radical anion. We notice that the equivalence point in this case is 1:2, compared with that of 1:4 for the unsubstituted benzophenone. It appears reasonable, therefore, to attribute this rather marked difference to the different degree of association between the lithium 2-methylbenzophenone radical anion moieties, namely dimers as opposed to tetramers. If this is the case, the difference can be understood in terms of steric constraints imposed by the 2-methyl group which either does not allow the formation of the cubane-like structure of the tetramer,[2a] or makes it loose enough for it to undergo facile dissociation to dimers.

The magnetic titration curve of sodium 2-methylbenzophenone radical anion exhibits some peculiarities compared to that for the lithium salt. The convexity of the titration curve in the region of the low magnesium chloride-radical anion concentration ratios implies that addition of magnesium chloride *initially* causes an increase of paramagnetism and this could be attributed to a loosening of the oligomeric structure of the radical anion. However, when the ratio $[MgCl_2]/[Na(2\text{-}MeC_6H_4)PhCO]$ approaches 1:2 a marked reduction of paramagnetism takes place. Here it may be significant that sodium benzophenone radical anion is insoluble and almost diamagnetic in THF, most probably due to high degree of association of the radical anion moiety. The steric requirements of the 2-methyl group result in a lower degree of association and thus the solubility and the paramagnetic character of the sodium 2-methylbenzophenone radical anion in THF can be understood.

Potassium 2-methylbenzophenone radical anion seems to behave in an analogous manner to that of the lithium or sodium salts. A complex with the constitution $MgCl_2[K(2\text{-}MeC_6H_4)PhCO]_2$ can be deduced from the titration curve.

c) 2,4,6-Trimethylbenzophenone radical anion

Lithium, sodium and potassium 2,4,6-trimethylbenzophenone radical anions and magnesium chloride interact rather weakly. The interaction between the radical anions and magnesium chloride does not result in the disappearance of paramagnetism. Thus the inflection points in the titration curves are ill defined. This behaviour can be understood on the basis of the steric effects of the two 2-and 6-methyl groups in the 2,4,6-trimethylphenyl group, which do not permit formation of a pinacolate dianion. The radical anion of 2,4,6-trimethylbenzophenone may exist in solution in the form of either very loose dimers or as a monomeric entity.

d) Fluorenone radical anion

Lithium fluorenone radical anion and lithium chloride interact by establishing equilibria with [LiCl]/[LiFlO] at ratios of 1:1 and 1:2. Complexation appears to make the oligomeric structure of the radical anion tighter, hence the diminishing of paramagnetism caused by the addition of LiCl. In contrast, addition of one equivalent of lithium chloride to sodium fluorenone radical anion causes a loosening of the oligomeric structure of the radical anion as evidenced by an increase in paramagnetism (convex line, Fig. 13). Lithium chloride in excess of this stoichiometry causes a tightening of the oligomeric structure of sodium fluorenone radical anion.

The interaction between potassium fluorenone radical anion and lithium chloride is rather weak. Some loosening in the oligomer of potassium fluorenone radical anion is evidenced from the small convexity of the titration curve.

Magnesium chloride and lithium, sodium and potassium fluorenone radical anions interact and appear to form diamagnetic complexes of the composition $[(MgCl_2)_2(MFlO)_4]$.

e) General remarks

The disappearance of paramagnetism upon the addition of magnesium chloride to alkali metal “unhindered” aromatic ketone radical anions brings to mind the diamagnetic character of, for example, magnesium benzophenone radical anion in THF. It therefore appears of interest to examine whether the observed disappearance of paramagnetism at the equivalence point arises from the displacement of the alkali metal by magnesium. If this is the case, we should expect a $[MgCl_2]/[MPh_2CO]$ ratio equal to 1:1 or 1:2, depending on whether the alkali metal ions are displaced by either Mg^{2+} or by $MgCl^+$. This, however, does not agree with the experimental ratio of 1:4. An alternative interpretation is that the disappearance of paramagnetism is due to complexation and this is further supported by the observation that addition of lithium chloride causes a decrease in paramagnetism. In the latter case, a simple exchange between *e.g.* lithium chloride and lithium benzophenone radical anion would result in no change. In the case of *e.g.* lithium fluorenone radical anion the ratio $[MgCl_2]/[LiFlO]$ is equal to 1:2, and this could explain the disappearance of paramagnetism by displacement of lithium by magnesium in the fluorenone radical anion cluster. However, we feel that the observed decrease in paramagnetism for the LiCl–lithium fluorenone radical anion system lends support to the view that, even in the $MgCl_2$–lithium fluorenone radical anion system, the disappearance of paramagnetism is due to complexation-induced tightening of the “pinacolate dianion” moieties in the radical anion cluster. The experimentally determined ratio of 1:4 suggests that there may be high coordination of the magnesium in the cluster. It is known that magnesium compounds can exhibit 6- or even higher coordination while high-hapticity coordination to unsaturated molecules is also well-documented.[4]

Another important point which deserves some discussion concerns the steric phenomena observed in this work. In comparing the radical anions of benzophenone and fluorenone, it is of interest to ask why the two radical anions form complexes with magnesium chloride with different stoichiometries, *i.e.*, 1:4 *versus* 1:2. It seems reasonable to attribute this difference to the different steric requirements of eight freely rotating phenyl groups in the tetrameric cluster, and the four planar and heavier fluoren-9-yl groups in the cubane-like structure[2a] of the fluorenone radical anion. It appears that the four fluoren-9-yl groups allow room for a second $MgCl_2$ while the eight phenyl groups do not. Another comparison, which has been already made (see paragraph b), is the possibility of preparing concentrated solutions of sodium 2-methylbenzophenone radical anion in THF, whereas it is not possible to do so for sodium benzophenone radical anion. Thus an important piece of evidence which seems to emerge from the present work is the effect that the alkyl groups may have on the degree of aggregation of aromatic ketone radical anions in solution.

Lastly the present work might explain the success of the method of preparing aromatic pinacols by reducing the corresponding ketones with Mg–MgI_2, the so-called *Gomberg–Bachmann pinacol synthesis*.[16]

Conclusion

Interaction between alkali metal aromatic ketone radical anions and the chlorides of lithium and magnesium leads to either diminishing or complete disappearance of paramagnetism. Magnetic titration studies revealed that the interaction in most cases is stoichiometric and leads either to the establishment of equilibria or to the formation of diamagnetic products with rather well defined stoichiometry or composition. In the latter case, stoichiometry appears to reflect the degree of association of the radical anion moiety in solution. Clustering of the radical anion in solution and complex formation between the radical anions and non-reducible salts are markedly dependent on steric factors.

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 fluoren-9-ylpotassium shortly before use. LiCl was a commercial product and was dried by heating under vacuum for several hours. $MgCl_2$ was prepared from magnesium and 1,2-dichloroethane in THF, as described in a previous publication.[17] An almost saturated solution of $MgCl_2$ in THF was approximately 0.66 M. Radical anion solutions were prepared and standardised as described previously.[14] Samples for NMR measurements were prepared as described in a previous publication.[14] Standard solutions were handled with microsyringes.

Acid hydrolysis of the diamagnetic $LiPh_2CO$–$MgCl_2$ complex

To a solution of 20 mmol of lithium benzophenone radical anion, prepared from 3.8 g of benzophenone, 0.140 g lithium chips and 18 ml of anhydrous THF, were added 10 mmol of $MgCl_2$, as a standard solution. The bluish-purple solution formed was acidified with 6 M hydrochloric acid. Solvent was removed under vacuum and the product was taken up in dichloromethane, the organic layer was washed with water, dried over anhydrous sodium sulfate and evaporated to dryness to yield a white solid (3.6 g) which exhibited a mp 168–70 °C. After one recrystallisation from hexane–toluene the mp was 182–185 °C (benzopinacol, lit.[18] mp 182–183 °C). The ^1H and ^{13}C NMR spectra were consistent with those of authentic benzopinacol.

Reaction of the diamagnetic $LiPh_2CO$–$MgCl_2$ complex with methyl iodide

To a solution of the diamagnetic title complex, prepared as described in the previous paragraph, was added methyl iodide, 4 ml, and the resulting mixture was stirred at room temperature for 72 hours. The mixture was hydrolysed with a dilute solution of ammonium chloride, and the product was taken up in dichloromethane. Evaporation of the extraction solvent left a viscous liquid which by GC–MS was identified as benzophenone. NMR analysis confirmed the GC–MS results and indicated the absence of any $Ph_2C(Me)OH$.

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