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Phosphorus-31 contact shifts as a measure of weak ligand affinities. Interaction between alkali metal fluorenone radical anions and certain phosphorus(III or V) ligands

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ABSTRACT: The nuclear magnetic resonance shifts, δ_{obs}, induced to ^{31}P in Ph_3P, $(MeO)_3P$ and $(MeO)_3PO$ by alkali metal fluorenone radical anions in tetrahydrofuran solutions were measured. These parameters, which depend significantly on the cation for a given ligand, and also on the ligand for a given cation, were used to extract the corresponding ^{31}P contact shifts, $\delta_c(M)$. The latter parameters are proposed as a measure of the ligand affinity of a given phosphorus compound for a particular alkali metal. Trimethyl phosphate exhibits the greatest affinity for the lithium cation. The magnitudes of $\delta_c(M)$ imply some covalency between the cation and the radical anion and the 'paradox' of a heavier alkali metal such as potassium being covalently bonded to fluorenone radical anion has been explained. The transferability of the reported ligand affinities of Li^+, Na^+ and K^+ is discussed. © John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{31}P NMR; contact shifts; fluorenone radical anions; trimethyl phosphate; ligand affinities

INTRODUCTION

Solutions of radical anions in a solvent such as tetrahydrofuran (THF) induce a paramagnetic shift on the magnetic nuclei of the solvent. The shift is linearly related to the concentration of the paramagnetic solute, and this permits the determination of the paramagnetic shift per mole of the paramagnetic solute. This shift, the so called molar paramagnetic solvent NMR shift, is referred to a certain resonance due to a given magnetic nucleus of the solvent molecule and it is a characteristic parameter for a particular anion–cation–solvent combination at a given temperature.[1] The observed shift, δ_{obs}, is composed of two parts[2], [Eqn (1)], one of which, δ_{bulk}, is constant for all radical anions, or any paramagnetic solute with one unpaired spin, and is due to macroscopic interactions.

$$\delta_{obs} = \delta_{bulk} + (\pm\delta_c) \tag{1}$$

The bulk shift, sometimes also referred to as the susceptibility shift, is expressed by the combined Dickinson[3] and Langevin equation, [Eqn (2)], the derivation of which is due to de Boer and McLean.[4]

$$\delta_{bulk} = (-2\pi/3)10^3(N\beta_e^2/kT)C \tag{2}$$

$$\delta_{bulk} = (4\pi/3)10^3(N\beta_e^2/kT)C \tag{2a}$$

where N = Avogadro's number, β_e = Bohr magneton, k = Boltzmann's constant, T = absolute temperature and C = concentration.

Equation (2) holds for instruments in which the effective magnetic field is normal to the long axis of the sample, as is the case in a continuous-wave NMR instrument. For a present-day instrument with a superconducting magnet, in which the effective magnetic field is parallel to the long axis of the sample, the bulk shift should be given by Eqn (2a).[5] Thus, from Eqn (2a) we calculate the macroscopic shift to be 5.238 ppm mol^{-1} at 300 K for a solute with one unpaired electron. The second term, the so-called contact shift, δ_c, arises from hyperfine interactions, i.e. spin density transfer from the paramagnetic molecule to the magnetic nuclei of its 'environment', and may be positive or negative.[6] It is expressed by

$$\delta_c = -A_i(\gamma_e/\gamma_N)[g\beta S(S+1)]/3kT \tag{3}$$

where A_i is the corresponding hyperfine splitting constant γ_e = magnetogyric ratio, γ_N = nuclear magnetogyric ratio (for the nucleus which experiences the contact shift), g = Landé g-factor, β = Bohr magneton and S = resultant spin (=$n/2$; n = number of unpaired electrons).

It should be noted that the contact shift is a constant, i.e. independent of the concentration, provided that the nucleus undergoing the shift is an integral part of the paramagnetic molecule. In the case of rapidly exchanging solvent molecules in the coordination sphere of the cation, however, as happens with alkali metal aromatic

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compound radical anions, the contact shift depends linearly on the concentration of the paramagnetic molecule in solution. In such a case, one has to consider contact shifts referred to a 1 M solution of the paramagnetic compound.[1,2]

It thus becomes evident that the contact shift, where operable, is the factor that determines the 'individuality' of the molar paramagnetic solvent NMR shifts. It has been concluded[7] that hyperfine interactions, i.e. spin density transfer from the anion to the magnetic nuclei of the solvent, take place through the mediation of the cation. Since spin density transfer takes place through covalent bonds,[8] a necessary condition for hyperfine interactions between a radical anion and a solvent or any other molecule is for the said molecule to be found for some time in the coordination sphere of, and to be covalently bonded to, the cation. In the case of THF solvent, there is a rapid exchange between the THF molecules in the coordination sphere of the cation and the bulk solvent on the NMR time-scale and hence all solvent molecules receive an average spin density,[7] [Eqn (4)], where S* and S are, bulk and 'coordinated' solvent molecules, respectively.

$$A^{-\bullet}M^{+}(S)_n + nS^* \rightleftharpoons A^{-\bullet}M^{+}(S^*)_n + nS \qquad (4)$$

In the case where S and S* are different molecules, a competition for coordination sites sets in. It can be readily understood that, when S and S* are different, complete displacement of S by S* in the coordination sphere of M^+ should be expected only in the extreme case where the affinity of the cation for S* is much greater than that for S. In all other cases mixed solvation should be expected. The former situation seems to occur in the case of addition of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to lithium benzophenone radical anion[1] or tetraethylene glycol dimethyl ether to sodium coronene or triphenylene radical anions.[9] The latter situation obtains in cases where 'poor' cosolvents are added to solutions of radical anions, where cation-dependent phenomena may take place. For example, on adding increments of triethylamine to potassium naphthalene radical anion in THF, an abrupt disproportionation takes place when the solvent system reaches a certain composition.[2]

Hence we reasoned that, by adding a phosphorus compound such as triphenylphosphine (TPP) or trimethyl phosphite (TMP) to an alkali metal aromatic radical anion in THF, we should be able to see, and even measure, the ability of the phosphorus ligands to compete against THF for sites in the coordination sphere of the cation. Namely, one could take ^{31}P contact shifts, if any, as a measure of the affinity between the phosphorus compound and the cation under consideration. Janzen and Zhang[10] have already shown that ^{31}P is a very sensitive nucleus for probing hyperfine interactions. They synthesized the phosphorus-containing spin trap 2-(diethylphosphono)-5,5-dimethyl-1-pyrroline *N*-oxide, which forms spin adducts which, in the ESR spectra, exhibit ^{31}P hyperfine splitting constants markedly larger than the corresponding nitrogen values. Of course, one has to consider also the possible reaction between the radical anion and the phosphorus compounds. This reaction leads to the cleavage of phosphorus–carbon or oxygen–carbon bonds,[11] so we chose to work with the less reactive alkali metal fluorenone radical anions which appear to be unreactive toward the aforementioned phosphorus compounds.

It is appropriate here to mention the recently reported[12] complexes of sodium fluorenone radical anions with hexamethylphosphoric triamide (HMPTA) with one and two HMPTA molecules per sodium cation. Lithium halides have also been reported to form hygroscopic products with tribenzyl phosphate.[13] Other phosphorus ligands which have been reported to form complexes with certain alkali metal halides include $Ph_2P(O)CH_2P(O)Ph_2$,[14] $(EtO)_2P(O)CH_2C(O)R$ (R = Me, Ph) and $Ph_2P(O)CH_2C(O)Ph$.[15]

RESULTS

Increments of a 1 M solution of triphenylphosphine in THF were added to a THF solution of lithium fluo-

Table 1. Paramagnetic ^{31}P shift measurements for the interaction between triphenylphosphine, trimethyl phosphite or trimethyl phosphate and alkali metal fluorenone radical anions in tetrahydrofuran at 300 K

Entry	Cation	Ligand	δ_{obs} (ppm mol^{-1})	δ_c (ppm mol^{-1})	δ_c(Li) : δ_c(Na) : δ_c(K)
1	Li	Ph_3P	6.472	+0.617	
2	Na	Ph_3P	7.766	+1.264	1:2.05:2.50
3	K	Ph_3P	8.319	+1.541	
4	Li	$(MeO)_3P$	6.502	+0.632	
5	Na	$(MeO)_3P$	10.344	+2.553	1:4.04:8.20
6	K	$(MeO)_3P$	15.599	+5.181	
7	Li	$(MeO)_3PO$	15.249[a]	+5.001	
8	Na	$(MeO)_3PO$	9.353	+2.058	1:0.41:1.15
9	K	$(MeO)_3PO$	16.752	+5.757	

[a] Estimated from the linear part of the experimental curve, Fig. 2.

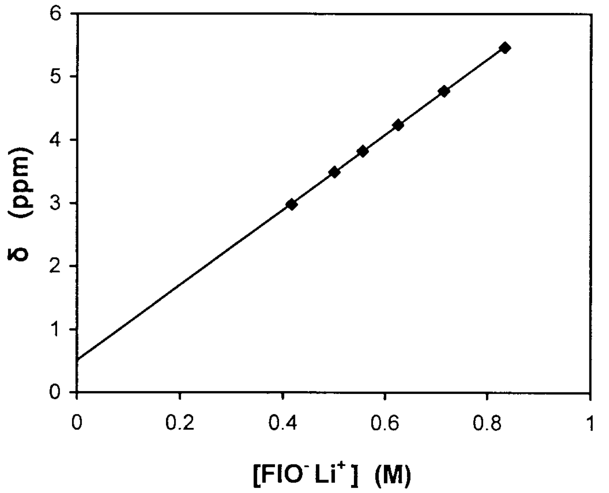

Figure 1. Shift induced to ^{31}P of triphenylphosphine by lithium fluorenone radical anion as a function of the concentration of the radical anion.

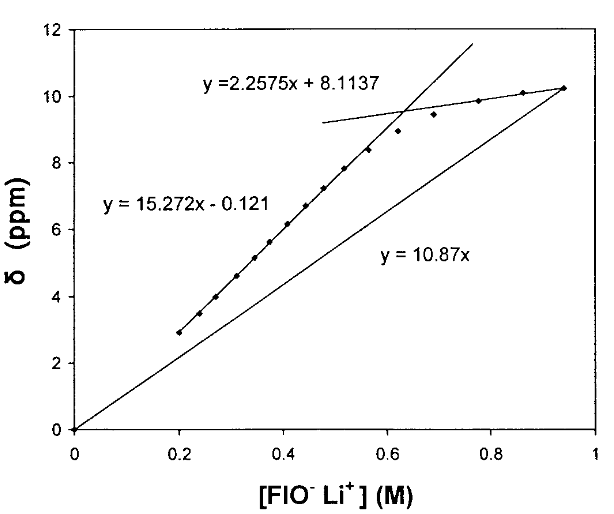

Figure 2. Shift induced to ^{31}P of trimethyl phosphate as in Fig. 1.

renone radical anion and the ^{31}P shift was recorded. The shift was referred to the ^{31}P resonance of the phosphorus compound in the absence of the paramagnetic solute. It is of importance to note that, in the presence of the radical anion, a single phosphorus resonance was observed. By plotting the observed shift against the corresponding formal concentration of the fluorenone radical anion, the linear relationship shown in Fig. 1 was obtained. Similar linear plots were obtained for sodium and potassium fluorenone radical anions, but the slopes of the straight lines exhibited a marked dependence on the cation, leading to different molar δ_{obs} values ranging from *ca.* 6.5 to 8.3 ppm mol^{-1}, (Table 1, entries 1–3). The data for trimethyl phosphite were obtained in a similar manner and the plots of shift versus concentration were also linear. The corresponding molar δ_{obs} values in this case are between 6.5 and 15.6 ppm mol^{-1} (Table 1, entries 4–6).

Increments of a 1 M solution of trimethyl phosphate were added to a solution of lithium fluorenone radical anion and the corresponding ^{31}P resonances were recorded to give a plot of shift versus concentration of the radical anion which is not linear (Fig. 2). Only in the region of concentration below *ca.* 0.6 M does the relationship become linear. In contrast to the case with lithium, the shifts induced to ^{31}P by sodium and potassium fluorenone radical anion are very nearly linearly related to the concentration of the radical anion. From these linear relations and the linear part of the curve in Fig. 2, the molar δ_{obs} values were obtained and are summarized in Table 1, entries 7–9. The latter values range from *ca.* 9.4 to 16.8 ppm mol^{-1}.

DISCUSSION

Separating the contact shift

The molar δ_{obs} values in Table 1 for all the cases studied for a given phosphorus compound exhibit a more or less a pronounced dependence on the cation. One then might decide to use these parameters as a measure of the strength of interaction between the phosphorus compound and the anion–cation pair. Given, however, that the parameter δ_{obs} also includes the susceptibility shift, it appeared to us that it would be better to consider as a measure of the strength of interaction the component of δ_{obs} which is due to hyperfine interactions, i.e. the corresponding contact shift δ_c. The reason for this is that the contact shifts reflect the spin density transfer from the paramagnetic solute to the magnetic nuclei of the phosphorus ligand and, in order for this to occur, it is necessary for the ligand to be found for some time at least in the coordination sphere of the cation.[7] In order to extract the parameter δ_c from the experimental data using Eqn (1), it was necessary to examine whether Eqn (1) holds for measurements with an instrument in which the effective magnetic field is parallel to the long axis of the sample, such as the instrument used in this investigation. By measuring the molar paramagnetic solvent shift of sodium fluorenone radical anion with an instrument with a superconducting magnet and comparing it with the published molar shift[1] which was measured with a continuous-wave instrument, we concluded that δ_c is given by Eqn (5). (We measured the observed solvent shift of $FlO^{\bullet-}Na^+$ in THF at 35 °C with an instrument with a superconducting magnet, $\delta_{obs} = 5.40$ ppm mol^{-1}, $\delta_{bulk} = 5.10$ ppm mol^{-1} [from Eqn (2a)]; difference $5.40 - 5.10 = 0.30$ ppm mol^{-1} {cf $\delta_{obs} = 2.70$ ppm mol^{-1} (from Ref. 1), $\delta_{bulk} = 2.55$ ppm mol^{-1} [from Eqn (2)]; difference $2.70 - 2.55 = 0.15$ ppm mol^{-1}}.)

$$\delta_c = 0.5(\delta_{obs} - \delta_{bulk}) \qquad (5)$$

Another question that arises is whether the susceptibility shift is indeed independent of the nucleus. If so, we can insert in Eqn (5) the value of δ_{bulk} calculated from Eqn (2a) and obtain the desired parameter δ_c. In order to verify that the susceptibility shift does not depend on the nucleus, we sought a paramagnetic compound which could induce susceptibility-only shifts to the magnetic nuclei of the THF solvent and of the phosphorus ligands. Chromium(III) acetylacetonate [Cr(acac)$_3$]

seemed very nearly to fulfil this requirement. Indeed, in $Cr(acac)_3$ the acetylacetonate chelate ligands are rigidly coordinated to the central metal and this, together with the known substitution inertness of Cr(III) coordination complexes, makes ligand displacement by either THF or triphenylphosphine molecules impossible, thus precluding the transfer of spin density from the paramagnetic center to the magnetic nuclei of THF and triphenylphosphine. $Cr(acac)_3$ possesses three unpaired electrons and, in order to calculate the theoretical susceptibility shift induced by a solute with a resultant spin 3/2, we used Eqn (6), which expresses the susceptibility shift for a solute with any number of unpaired electrons.

$$\delta_{\text{bulk}} = (4\pi/9) \times 10^3 (N\beta_e^2/kT)[4S(S+1)]C \qquad (6)$$

We then measured the shifts induced to ^{13}C resonances of THF in solutions of $Cr(acac)_3$ and to ^{31}P resonance of triphenylphosphine, as a function of the concentration of the paramagnetic solute. The results are given in Fig. 3. It can be seen that both the ^{13}C and ^{31}P shifts follow the same linear relationship. More specifically, $Cr(acac)_3$ induces a shift of 25.96 ppm mol^{-1} to both ^{13}C resonances of THF and of 25.72 ppm mol^{-1} to ^{31}P of TPP. These numbers agree to within 99.1 and 98.2% with the theoretical (susceptibility-only) shift, 26.19 ppm mol^{-1}, calculated from Eqn (6). We conclude that the macroscopic or susceptibility shift does not depend on the type of the nucleus and therefore we can use Eqn (5) in order to extract the contact shift by measuring the molar paramagnetic ^{31}P shift. The δ_c values thus derived are summarized in Table 1.

Triphenylphosphine

The parameters δ_c in the case of triphenylphosphine increase from lithium to sodium to potassium. It should be stressed that the molar δ_{obs} which have been used to extract the contact shifts are devoid of any contributions due to aromatic solvent-induced shifts (ASIS). [We measured the ^{31}P shift in solutions of TPP in THF, in the absence of a paramagnetic solute, as a function of the concentration of TPP in order to check for any aromatic solvent-induced shift (ASIS) contributions to the observed shift. The ASIS contribution was found to be almost zero. Hence the smaller contact shift observed in the case of TPP, as compared with that of TMP, is real.] The above trend parallels the corresponding increase in the ionic radius of the three metals and it is opposite to what one should expect on the basis of electrostatic considerations. The coordinating ability of triphenylphosphine to lithium, sodium and potassium cations may perhaps be rationalized by considering the relative hardness of the interacting species.[16] A molecule such as triphenylphosphine with extensive conjugation, besides functioning as a Lewis base, could also behave as a π base. This means that there could be more than one mode of coordination between the TPP molecule and the alkali metal cations, namely either through the lone pair of the phosphorus atom of TPP or through the π-cloud of the aromatic system. Whatever the mode of interaction might be, the effect is rather weak. The small δ_c values certainly reflect the small spin density which is transferred from the paramagnetic molecule to the ^{31}P nucleus. It therefore appears reasonable to assume that TPP forms a weak complex, probably an encounter or collision complex, with the radical anion–cation, which exists in both the dissolved and the crystalline state as a solvated oligomeric cluster.[12] The factor then that differentiates the δ_c(M) parameters for a given ligand should be the fraction of the solvent molecule displaced by the phosphorus compound in the coordination sphere of one cation in the cluster per unit time or, in other words, the time of residence (i.e. the correlation time) of the ligand in the coordination sphere of the cation in the cluster. The observation of single resonances for both the solvent and the phosphorus compound implies a dynamic process in which there is a rapid exchange between complexed and uncomplexed solvent and added ligand molecules. This situation may be represented by Eqn (7), assuming that the alkali metal fluorenone radical anions form a tetrameric cluster in solution, as does the sodium fluorenone radical anion–HMPT complex in the crystalline state.[12]

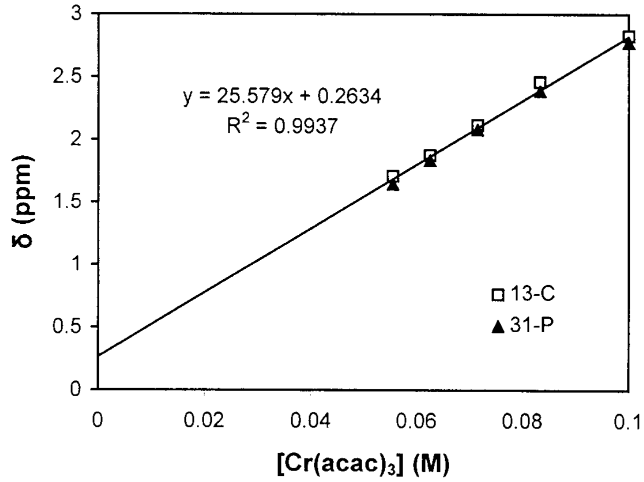

Figure 3. Shift induced to the ^{13}C resonances of THF (triangles) and to ^{31}P resonance of triphenylphosphine (circles) as a function of the concentration of chromium(III) acetylacetonate.

$$(\text{FlO}^{\cdot}\text{—M})_4(\text{thf})_4 + \text{L} \rightleftharpoons (\text{FlO}^{\cdot}\text{—M})_4(\text{thf})_3\text{L} + \text{thf}$$

$$(\text{FlO}^{\cdot}\text{—M})_4(\text{thf})_3\text{L} + 3\text{thf}^* + \text{L}^*$$

$$\rightleftharpoons (\text{FlO}^{\cdot}\text{—M})_4(\text{thf}^*)_3\text{L}^* + 3\text{thf} + \text{L}$$

$$(\text{L} = \text{TPP, TMP}) \qquad (7)$$

Trimethyl phosphite

The molar contact shifts for trimethyl phosphite (TMP) follow the same trend as for TPP. However the δ_c values exhibit a more pronounced cation dependence than the corresponding values for TPP. This can be seen by comparing the values, normalized with respect to lithium, for Li, Na and K (see the last column in Table 1), namely $\delta_c(\mathrm{Li}):\delta_c(\mathrm{Na}):\delta_c(\mathrm{K}) = 1:2.0:2.5$ for TPP versus 1:4:8 for TMP. The data indicate that there is a pronounced preference of TMP for the heavier alkali metals. Trimethyl phosphite could possibly function as a Lewis base by donating the lone pair of the central heteroatom, i.e. the phosphorus atom or the lone pair of one of the oxygen atoms. If one considers the relative hardness of the alkali metals and the oxygen and phosphorus atoms, one is led to the conclusion that TMP could coordinate through phosphorus.

As far as the dynamic behavior of the system TMP–alkali metal fluorenone radical anions is concerned, one could propose an equation analogous to Eqn (7) for reasons which have already been explained.

Trimethyl phosphate

The relationship between ^{31}P shift and concentration in the system trimethyl phosphate (TMPO) and lithium fluorenone radical anion is not linear over the entire range of concentrations. This is in contrast to the 'normal' behavior of the systems sodium and potassium fluorenone radical anion–TMPO. Indeed, only the last two systems exhibited the usual linearity between ^{31}P shift and concentration of the paramagnetic solute. In this respect, the system TMPO–lithium appears to be unique. By comparing the normalized molar contact shift values $\delta_c(\mathrm{Li}):\delta_c(\mathrm{Na}):\delta_c(\mathrm{K}) = 1:0.4:1.2$ with the corresponding values for TPP and TMP (see Table 1), we can see that the trend in the case of TMPO is entirely different from that observed with the other two ligands. Trimethyl phosphate appears to interact with lithium fluorenone radical anion much more strongly than does TPP or TMP. Trimethyl phosphate can coordinate only through the oxygen, most probably the one in the P=O group.[12,14,15] The experimental curve of ^{31}P shift versus concentration (Fig. 2), exhibits a break at *ca.* 0.64 M, at which the corresponding observed shift is *ca.* 9.7 ppm. Beyond this point the relationship becomes linear. If the TMPO added to the lithium fluorenone radical anion were simply functioning as a diluent, the ^{31}P shift versus concentration should be linear with a slope or a δ_{obs} of 10.87 ppm mol^{-1}. From the linear part of the experimental curve we calculate a δ_{obs} of 15.25 ppm mol^{-1}. Therefore, the structural changes caused by the addition of TMPO result in a substantial increase in the ^{31}P contact shift. Alternatively, this increase can be seen by considering the first few points in the high concentration region where, despite the dilution, the shift remained almost unchanged. This type of behavior is closely analogous to the lithium benzophenone radical anion–TMEDA system.[1] The 'stoichiometry' of interaction between TMPO and lithium fluorenone radical anion could be estimated from the experimental data. By plotting the data in the form of a magnetic titration (Fig. 4), we can obtain an estimate of the 'equivalence,' $[\mathrm{TMPO}]/[\mathrm{FlO}^{\bullet -}\mathrm{Li}^+]$, equal to *ca.* 0.8:1. This result probably indicates that there could be interacting up to three TMPO molecules per four lithium atoms. Trimethyl phosphate is the oxygen analogue of HMPTA, which with sodium fluorenone radical anion forms two different crystalline products, a dimer and a tetramer with two HMPTA molecules per sodium atom in the dimer and one HMPTA molecule per sodium atom in the tetramer.[12]

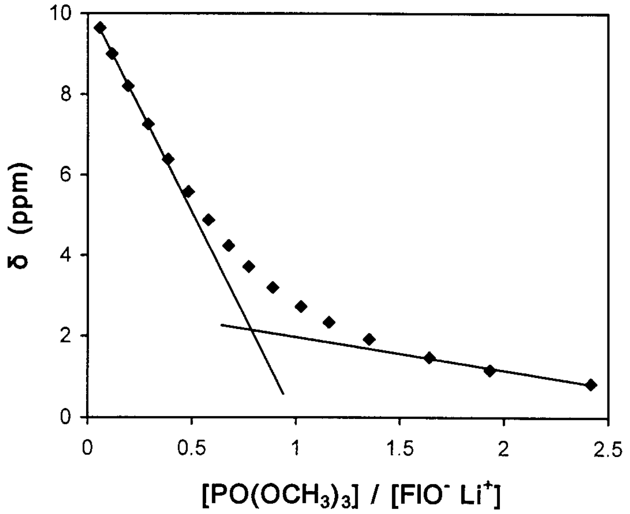

Figure 4. The data of Fig. 2 plotted in the form of a magnetic titration, i.e. ^{31}P shift, corrected for dilution, versus the ratio of the concentrations of trimethyl phosphate and lithium fluorenone radical anion.

Assuming that lithium fluorenone radical anion exists in solution in the form of a tetramer, we interpret the curve in Fig. 2 as follows. On adding TMPO to the system there is a gradual displacement of the coordinated THF molecules in the cluster by TMPO. Once a cluster is formed with three TMPO molecules, it retains its integrity on average by rapidly exchanging TMPO and THF ligands with uncomplexed ones [Eqn (8)].

$$\begin{aligned}&(\mathrm{FlO}^{\bullet}\text{—}\mathrm{M})_4(\mathrm{thf})_4 + 3\mathrm{L} \rightleftharpoons (\mathrm{FlO}^{\bullet}\text{—}\mathrm{M})_4\mathrm{L}_3(\mathrm{thf}) + 3\mathrm{thf}\\ &(\mathrm{FlO}^{\bullet}\text{—}\mathrm{M})_4\mathrm{L}_3(\mathrm{thf}) + 3\mathrm{L}^* + \mathrm{thf}^*\\ &\qquad \rightleftharpoons (\mathrm{FlO}^{\bullet}\text{—}\mathrm{M})_4\mathrm{L}^*_3(\mathrm{thf}^*) + 3\mathrm{L} + \mathrm{thf}\\ &\qquad\qquad\qquad (\mathrm{L} = \mathrm{TMPO}) \quad (8)\end{aligned}$$

Covalency

The parameters δ_c listed in Table 1, entries 1–9, may be related to the corresponding ^{31}P hyperfine splitting constants through Eqn (3), and ultimately to the corresponding spin density at the phosphorus nucleus.[6] It is important, then, to understand the mechanism by which the phosphorus nucleus receives spin density. If we denote the paramagnetic species for simplicity as $(\mathrm{FlO}^{\bullet})$—M, TMPO should be coordinated with metal through the oxygen, $(\mathrm{FlO}^{\bullet})\text{—M—O=P(OMe)}_3$. Therefore, the phosphorus atom of TMPO, although located three bonds away from the paramagnetic center, still receives some spin density from that center. Usually spin density is transferred through covalent bonds.[17] It is instructive to refer to the recently reported crystal structure[12] of the tetrameric sodium fluorenone radical

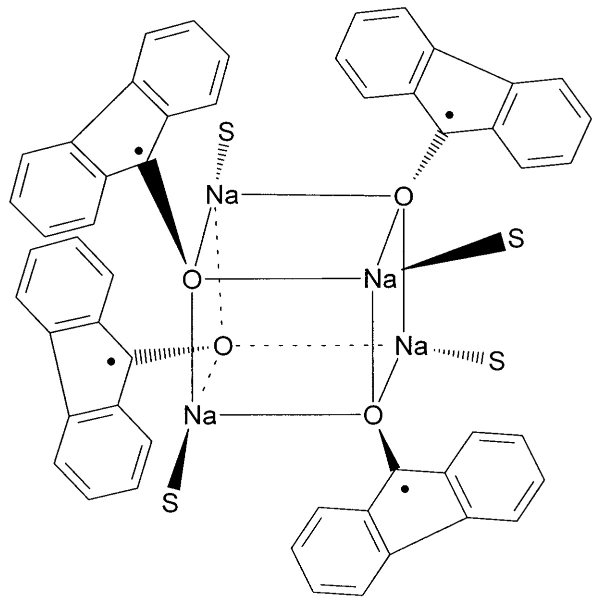

Figure 5. Structure of the sodium fluorenone radical anion tetramer (see Ref. 12).

anion–HMPTA complex (Fig. 5) (S = HMPTA). The complex possesses an Na_4O_4 distorted cubane core in which each ketyl oxygen is bonded to three sodiums and each sodium to three ketyl oxygens. The fourth coordination site on the metal is occupied by the HMPTA ligand. It can be readily understood that, even in the case when one of the three bonds of the alkali metal and the ketyl oxygens is purely ionic, the metal can still receive spin density through the other two bonds. Hence the paradox of a heavier alkali metal such as potassium being covalently bonded to fluorenone radical anion can be explained.

Transferability

A question that has to be answered is whether δ_c, which is proposed as a measure of the ligand affinity, could be transferable to other alkali metal ionic compounds. This question seems to have a positive answer in the case of the TMPO ligand. Indeed, the paper by Clark and Todd,[13] which reports complexes of lithium halides with tribenzyl phosphate, could provide a justification for this. Reasons for the possible non-transferability, in some cases, of the ligand affinities derived by the method described in this work, are that (i) the ligand affinity might be dependent on the reference anion and (ii) fluorenone radical anions in solution exist in the form of paramagnetic clusters, with a degree of clustering that may be counterion dependent.[18]

CONCLUSIONS

The alkali metal fluorenone radical anions are unreactive toward triphenylphosphine, trimethyl phosphite and trimethyl phosphate. This allowed the employment of the fluorenone radical anion as a 'spin label' for measuring the ligand affinities of these phosphorus compounds for alkali metal cations, by measuring the phosphorus-31 contact shifts of a given ligand for lithium, sodium and potassium cations. The δ_c(M) for TPP and TMP parameters are interpreted as reflecting the average residence time of the ligand in the coordination sphere of one metal in the ketyl cluster (Fig. 5), and their magnitudes seem to parallel the corresponding ionic radii. In the case of $FlO^{\bullet -}Li^{+}$–TMPO up to three TMPO molecules replace THF in the coordination sphere of three lithiums in the ketyl cluster and the resulting species retains its integrity by exchanging rapidly the three coordinated TMPO molecules and one THF molecule with uncomplexed ones.

EXPERIMENTAL

A Bruker AC 300 MHz instrument operating at a probe temperature of *ca.* 300 K was employed for ^{31}P shift measurements. Tetrahydrofuran was doubly distilled under argon from lithium aluminium hydride, shortly before use. The phosphorus compounds were commercial products 98% pure or better, and were purified further by recrystallization (TPP) or distillation (TMP and TMPO). Chromium(III) acetylacetonate was also a commercial product and was used as received. Lithium, sodium and potassium fluorenone radical anion were prepared as described previously[1] in 20 mmol quantities and at concentrations of *ca.* 1 M in tetrahydrofuran solvent. The concentration was measured by titration of a hydrolysed aliquot for total alkalinity, confirming the previously determined molar paramagnetic solvent shifts.[1] Samples for NMR measurements were prepared as described.[1] Standard solutions were handled with microsyringes. Increments of 1 M solution in THF of the phosphorus compound were added gradually to the radical anion solution and the ^{31}P resonance was recorded after each addition. The observed shift was referred to the ^{31}P resonance in the absence of the paramagnetic solute.

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