The Effects of Substituents and Solvents on the Structure of Fluorenyl and Cyclopentadienyl Salts

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The electronic spectra of 9-(ω-methoxyalkyl) and 9-(ω-dimethylaminoalkyl)fluorenyl salts of alkali cations were measured in ethereal solvents. The relative amounts of the contract ion pairs connected with the 9-substituents (R) decreased in this order: $R=(CH_3)_2N\text{-}(CH_2)_2\text{-}>CH_3O\text{-}(CH_2)_2\text{-}>CH_3O\text{-}(CH_2)_3\text{-}>(CH_3)_2N\text{-}(CH_2)_3\text{-}\gg CH_3O\text{-}(CH_2)_4\text{-}\approx n\text{-}C_4H_9\text{-}$. This behavior was explained in terms of the formation of an intramolecular association between the hetero atoms in the substituents and the counter ions; such an association favored the formation of the contact ion pair. The interaction of magnesium fluorenide and cyclopentadienide with hexamethylphosphoramide (HMPA) was studied by means of NMR spectroscopy in ether or tetrahydrofuran. The fluorenide changed from a covalent type to a solvent-separated ion pair by the coordination of three HMPA with the magnesium. The cyclopentadienide was proposed to change from a contact ion pair to a solvent-separated ion pair by means of two-step process in which the cyclopentadienyl ions became successively separated from the magnesium ion.

It is well-known that donor solvents interact with organometallic compounds of alkali or alkaline earth metals and affect the structure or reactivity of the compounds.[1] For example, Hogen-Esch and Smid have reported that alkali fluorenides exist as two kinds of ion pairs—contact and solvent-separated ion pairs in ethereal solvents.[2] In previous papers,[3–5] it was shown that the reactivity of organo-magnesium compounds increased markedly in the presence of hexamethylphosphoramide (HMPA). Such phenomena can be explained in terms of the coordination of donor solvents with the metals of organometallic compounds. In this paper, the electronic spectra of 9-substituted fluorenyl salts of alkali cations, in which the substituents can interact with the cations, were measured in ethereal solvents in order to investigate the nature of the intramolecular association. The interaction of magnesium fluorenide and cyclopentadienide with HMPA was also studied by NMR spectroscopy.

The study of such interaction will be useful in accounting for the behavior of the anionic polymerization initiated with organometallic compounds of alkali or alkaline earth metals.

Experimental

Reagents. Six 9-substituted fluorenes were prepared by the reaction of fluorenylsodium with the corresponding alkyl halides[6,9] or by the base-catalyzed alkylation of fluorene with alcohols[7,8]: *n*-butyl-[8] (bp 127 °C/0.6 mmHg), 2-methoxyethyl-(bp 143 °C/0.5 mmHg. Found: C, 85.08; H, 7.44%. Calcd for $C_{16}H_{16}O$: C, 85.71; H, 7.14%), 3-methoxypropyl- (bp 135 °C/0.2 mmHg. Found: C, 84.90; H, 7.62%. Calcd for $C_{17}H_{18}O$: C, 85.71; H, 7.56%), 4-methoxybutyl- (bp 169 °C/1.5 mmHg. Found: C,85.00; H, 7.99%. Calcd for $C_{18}H_{20}O$: C, 85.71; H, 7.94%), 2-dimethylaminoethyl-[9] (bp 137 °C/0.5 mmHg), 3-dimethylaminopropyl-fluorene[9] (bp 154 °C/0.5 mmHg). The structure of these fluorenes was also confirmed by means of NMR spectroscopy. The tetrahydrofuran (THF), dimethoxyethane (DME), and *n*-hexane were refluxed and distilled over metallic sodium under a nitrogen atomosphere. The HMPA was refluxed and distilled over calcium hydride *in vacuo*.

The substituted fluorenyl salts of lithium, sodium, and potassium ions were prepared by the reaction of the corresponding fluorenes with *n*-butyllithium, sodium hydride or amide, and metallic potassium respectively. The magnesium fluorenide was prepared by the reaction of fluorene with diethylmagnesium in the presence of HMPA.[4] The dicyclopentadienylmagnesium was prepared from magnesium turnings and cyclopentadiene at about 500 °C.[10]

Spectroscopic Measurements. The samples for spectral measurements were prepared under a nitrogen atmosphere. The electronic spectra of the fluorenyl salts were recorded at room temperature by means of a Shimadzu UV-200 spectrophotometer, using 0.2-cm optical cells provided with a 0.18-cm spacer. The NMR spectra of the organo-magnesium-HMPA systems were taken on a JNM C-60H spectrometer, using benzene or tetramethylsilane as the internal standard.

Results and Discussion

Electronic Spectra of 9-Substituted Fluorenyl Salts of Alkali Cations. Figures 1 and 2 show the spectra of 9-substituted fluorenyllithiums in THF at room temperature. The peaks near 360 and 380 nm could be assigned to contact and solvent-separated ion pairs

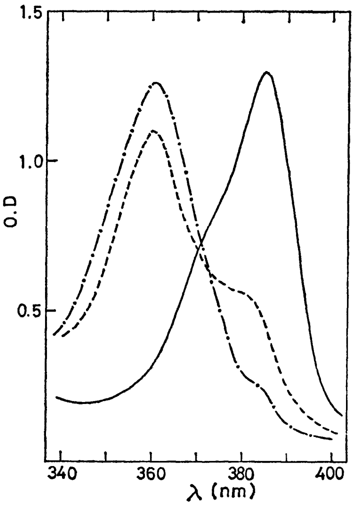


Fig. 1. Electronic spectra of 9-substituted fluorenyllithiums in THF at room temperature.
(——): 9-(*n*-butyl)fluorenyllithium,
(----): 9-(2-methoxyethyl)fluorenyllithium,
(·—·): 9-(2-dimethylaminoethyl)fluorenyllithium.

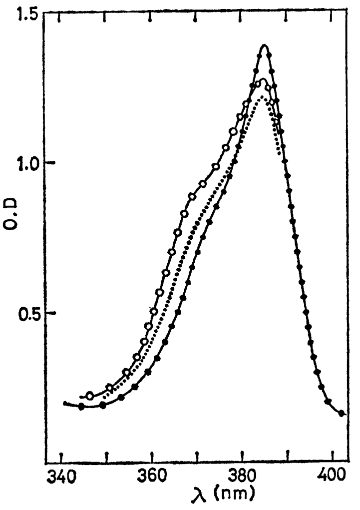


Fig. 2. Electronic spectra of 9-substituted fluorenyllithiums in THF at room temperature.
(-●-): 9-(4-methoxybutyl)fluorenyllithium,
(-○-): 9-(3-methoxypropyl)fluorenyllithium,
(……): 9-(3-dimethylaminopropyl)fluorenyllithium.

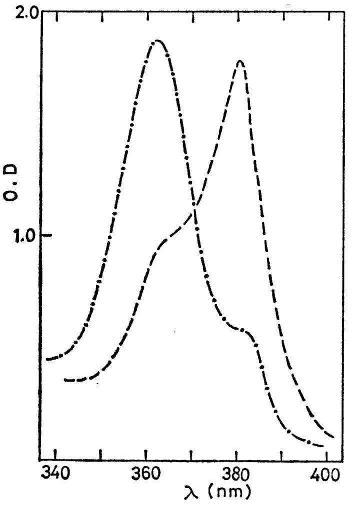
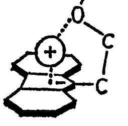


Fig. 3. Electronic spectra of 9-substituted fluorenyllithiums in DME at room temperature.
(----): 9-(2-methoxyethyl)fluorenyllithium,
(·—·): 9-(2-dimethylaminoethyl)fluorenyllithium.

respectively, by analogy with the results obtained by Chan and Smid.¹¹⁾ The methoxyethyl and dimethylaminoethyl derivatives were found to yield higher fractions of contact ion pairs, while the other derivatives gave much higher fractions of solvent-separated ion pairs. Figure 3 shows the spectra of the methoxyethyl and dimethylaminoethyl derivatives with the lithium counter-ion in DME at room temperature. The former was predominantly present as a solvent-separated ion pair, while the latter was predominantly present as a contact ion pair. In a *n*-hexane–THF (1 : 1) mixture, the methoxypropyl derivative gave a higher fraction of a contact ion pair, while the *n*-butyl, methoxybutyl, and dimethylaminopropyl derivatives gave higher fractions of solvent-separated ion pairs. Consequently, the relative amounts of the contact ion pairs of the lithium salts due to the 9-substituents (R) decreased in the following order: $R=(CH_3)_2N\text{-}(CH_2)_2\text{-} > CH_3O\text{-}(CH_2)_2\text{-} > CH_3O\text{-}(CH_2)_3\text{-} > (CH_3)_2N\text{-}(CH_2)_3\text{-} \gg CH_3O\text{-}(CH_2)_4\text{-} \approx n\text{-}C_4H_9\text{-}$. A similar order was observed for the sodium and potassium salts.

Such an effect of substituents suggests that a special interaction between the counter ions and the oxygen or nitrogen of the substituents may take place because of the favorable position of the hetero atoms with respect to the cations. In the case of the methoxyethyl and dimethylaminoethyl derivatives, the hetero atom exists at a position where a five-membered ring can be formed by the intramolecular coordination of the atom with the counter ion. For example, the structure of a contact ion pair for the methoxyethyl derivative could be represented as in Formula (I): In this formula, the counter ion was assumed to be located over the aromatic ring, by analogy with the results on fluorenyllithium in THF.¹²⁾ In contrast, the X-ray analysis of fluorenyllithium as a tertiary amine complex has shown the lithium ion to be located above the plane, but outside the perimeter of the ring.¹³⁾ The intramolecular association as is shown in Formula (I) is, in any event, considered to take place easily and to favor the formation of a contact ion pair.



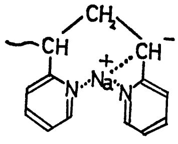
(I)

The observed order also shows that the formation of a contact ion pair becomes easier with a decrease in the size (n) of a ring, which is formed by intramolecular association— *i.e.*, in the order of $n=5>6>7$. Kuhn and Wires¹⁴⁾ have measured the equilibrium constant for the equilibrium between intramolecularly hydrogen bonded conformations and nonbonded conformations in the monomethyl ethers of ethylene glycol, propane-1,3-diol, and butane-1,4-diol: the constant became smaller with an increase in the number of carbon atoms between two oxygen atoms. The observed order for the fluorenyl salts is in good agreement with this order. This finding supports the presence of an intramolecular association such as has been described above.

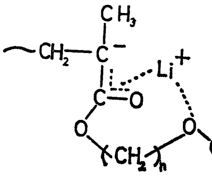
The coordinating power of aliphatic nitrogen donors is generally stronger than that of aliphatic oxygen donors.¹⁵⁾ The difference between the dimethylaminoethyl and methoxyethyl derivatives, therefore, can be explained in terms of that in the coordinating power of the hetero atoms. However, the dimethylaminopropyl derivative gave fewer contact ion pairs than the methoxypropyl one. The formation of an intramolecular bonding must result in conformational changes, and thereby increase the repulsive interactions among atoms, groups, and bonds in the ring formed. Such interactions, which reduce the formation of a contact ion pair, may be stronger in the former derivative, which has two methyl groups, than in the latter, which has only one.

All the salts yielded higher fractions of solvent-separated ion pairs in ethereal solvents containing a small amount of HMPA. This fact suggests that the solvating power of HMPA is stronger than the intramolecular coordinating power of the hetero atoms.

Such an intramolecular solvation has also been proposed to account for the behavior of the anionic polymerizations of 2-vinylpyridine[16)] and ω-methoxyalkyl methacrylate.[17)]



(II)



(III)

In the case of 2-vinylpyridine, (II), the nitrogens of both the ultimate and penultimate units have been considered to contribute to the coordination of the counter cation. Such a penultimate unit effect seems reasonable in view of the similarity of structure between (II) and 9-(3-dimethylaminopropyl)fluorenyl salt, in which six-membered rings formed by intramolecular coordination.

Ito *et al.*[17)] have proposed that, in the case of the methacrylate, (III), the interaction of the methoxy oxygen in the substituent (R′) with the counter ion decreases with an increase in the number of carbon atoms between the oxygen and ester oxygen, so that the syndiotacticities of the polymers obtained in toluene increase in this order: $R'=CH_3O\text{-}(CH_2)_2\text{-}>CH_3O(CH_2)_3\text{-}>CH_3O\text{-}(CH_2)_4\text{-}$. This order is in agreement with that of the ease of formation of contact ion pairs for 9-(ω-methoxyalkyl)fluorenyl salts. Therefore, it is reasonable that the intramolecular association shown as Formula (III) is present in the propagation step of the anionic polymerization of these methacrylates.

Intraction of Magnesium Fluorenide with HMPA. Figure 4 shows the NMR spectrum of the magnesium fluorenide prepared by the reaction of fluorene with equimolar quantities of diethylmagnesium (Et_2Mg) at $[HMPA]/[Et_2Mg]=3$. This spectrum indicates that the fluorenide consists of equimolar amounts of fluorenyl and ethyl groups. The chemical shift of methylene protons, δ_{CH_2}, in the fluorenide was -1.10, while the δ_{CH_2} for Et_2Mg was -0.88 at $[HMPA]/[Et_2Mg]=3$.[4)] This fact indicates that the diamagnetic anisotropy induced by the aromatic ring strongly shields the ethyl protones. The fluorenyl part of the NMR spectrum of the fluorenide was similar to that of fluorenyllithium in THF.[18,19)] Consequently, the metalation results in the formation of ethylfluorenylmagnesium (Fl^-Mg^+Et) as follows:

$$\text{Fluorene}+Et_2Mg \xrightarrow{\text{HMPA}} Fl^-Mg^+Et+\text{Ethane}$$

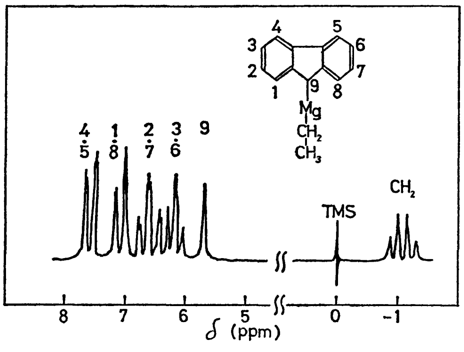


Fig. 4. NMR spectrum of magnesium fluorenide.
Solvent: ether, $[HMPA]/[Mg]=3$.
Peaks of ether, HMPA, and methyl group in Fl^-Mg^+-Et are not written in the figure.

The chemical shifts of the ethyl and fluorenyl ring protons for Fl^-Mg^+Et changed as is shown in Fig. 5 on the addition of Et_2Mg to the fluorenide solution. The chemical shift of the 9-proton for the fluorenide, δ_9, changed markedly with the molar ratio of HMPA to magnesium, [HMPA]/[Mg]. This fact indicates that the nature of the carbon–magnesium bond of the fluorenide is highly dependent on the [HMPA]/[Mg] ratio. The chemical shifts of the 9-proton for alkali fluorenides are between ∼5.8 and ∼6.0, and they are not appreciably affected by the variation in the counter ion and the solvent.[18,19)] This behavior must correspond to the fact that the carbon–alkali bonds of alkali fluorenides are essentially ionic.[1d)] On the other hand, the large shift in δ_9 (from ∼4.9 to ∼5.8) suggests that the carbon–magnesium bond of the magnesium fluorenide is essentially covalent in the absence of HMPA (see below) and that the bond changes to an ionic type in the presence of HMPA. The charge formed on the 9-carbon delocalizes over the aromatic ring; hence, the peaks due to the ring protons and 9-proton must shift upfield and downfield respectively. The fact that the values of δ_9 become approximately constant at $[HMPA]/[Mg]\geq\sim 3$ suggests that the ionic species are formed by the coordination of three HMPA molecules to the magnesium. Figure 6 shows the variation in the chemical shift of the methyl protons for HMPA with the [HMPA]/[Mg] ratio. The chemical shift was approximately constant (∼2.0) at $[HMPA]/[Mg]<\sim 3$, and then it

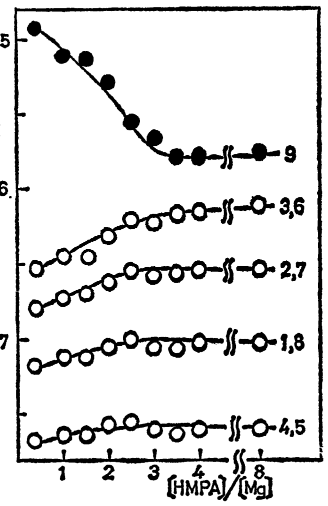


Fig. 5. Variation of chemical shifts for fluorenyl ring protons with [HMPA]/[Mg] ratio.
Numbers in the figure denote positions of the protons.

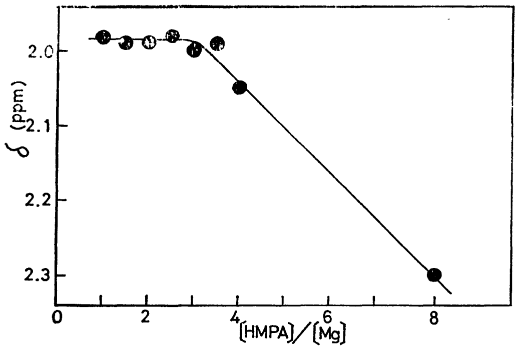


Fig. 6. Variation of chemical shift for HMPA with [HMPA]/[Mg] ratio.

shifted downfield with a further increase in the [HMPA]/[Mg] ratio, while the chemical shift for free HMPA was ~2.5. Those facts indicate that the diamagnetic anisotropy induced by the aromatic ring strongly shields the methyl protons of the HMPA coordinated with the magnesium; they also support the above concept of the formation of the ionic species.

This ionic species was confirmed to be a solvent-separated ion pair by a study of its electronic spectrum. However, the spectra of the magnesium fluorenide–HMPA systems, even at [HMPA]/[Mg]<3, had no peak near 340 nm, where the contact ion pair of the fluorenide is considered to have a characteristic peak by analogy with the results of barium and strontium fluorenides (347 and 344 nm respectively).[20,21] This finding suggests that magnesium fluorenide of a covalent type may change to a solvent-separated ion pair directly, not *via* a contact ion pair.

In the case of the interaction of HMPA with Et_2Mg, the species coordinated by two HMPA molecules was predominantly formed at [HMPA]/[Mg]>2, and the ionic species with the coordination of three HMPA was considered to be formed only slightly.[4] This behavior is in contrast to that in the case of the fluorenide. Such a difference can be explained in terms of that in the stabilities of the carbanions formed. That is to say, the fluorenyl anion, in which there is a resonance stabilization, must be formed more easily than the ethyl anion, in which there is no resonance stabilization.

Interaction of Dicyclopentadienylmagnesium with HMPA. The NMR spectrum of dicyclopentadienylmagnesium (Cp_2Mg) had a singlet peak in THF. The shape of the spectrum, however, varied upon the addition of HMPA to the Cp_2Mg solution (Fig. 7). The signal due to Cp_2Mg shifted upfield with an increase in the [HMPA]/[Mg] ratio when the ratio was less than ~1.5. A second peak began to appear at a lower field at [HMPA]/[Mg]=~2. The upfield peak shifted upfield with a further increase in the [HMPA]/[Mg] ratio, while the intensity of the peak decreased at the same time. In contrast, the intensity of the downfield peak increased and came to be almost equal to that of the upfield peak at [HMPA]/[Mg]=~3. The peaks gradually overlapped with a further increase in the HMPA concentration, and broadened at [HMPA]/[Mg]=~6. At [HMPA]/[Mg]>6, the spectrum had again a singlet peak, one between the previous peaks. The width of this peak decreased with an increase in the [HMPA]/[Mg] ratio. A similar phenomenon was observed for the variation in the spectrum with an increase in the temperature at a constant [HMPA]/[Mg] ratio. Figure 8 shows the variation in the spectrum at [HMPA]/[Mg]=3.3. These results indicate that, in the Cp_2Mg–HMPA system, several species coexist at equilibrium, one which is dependent on the [HMPA]/[Mg] ratio and the temperature.

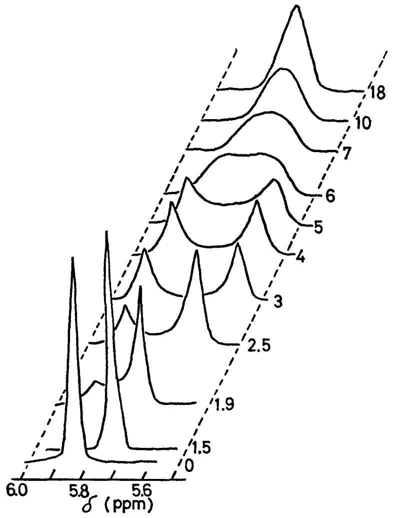


Fig. 7. Variation of NMR spectrum of Cp_2Mg with [HMPA]/[Mg] ratio.
Solvent: THF, Temp.: 22 °C.
Numbers in the figure denote values of [HMPA]/[Mg] ratio.

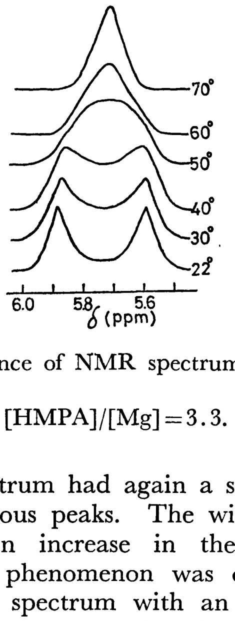


Fig. 8. Dependence of NMR spectrum of Cp_2Mg on temperature.
Solvent: THF, [HMPA]/[Mg]=3.3.

When Cp_2Mg and HMPA were mixed in ether at [HMPA]/[Mg]<~2.5, the solution separated into two layers. The spectrum of the lower portion of the solution had peaks for ether and two kinds of peaks for Cp_2Mg and HMPA (Fig. 9). The downfield peaks were assigned to free species of Cp_2Mg and HMPA, in comparison with the spectra of separate solutions of Cp_2Mg and HMPA. The upfield peaks of Cp_2Mg was found to shift upfield gradually with an increase in the HMPA concentration. The upfield peaks, therefore, were assigned to coordinated species

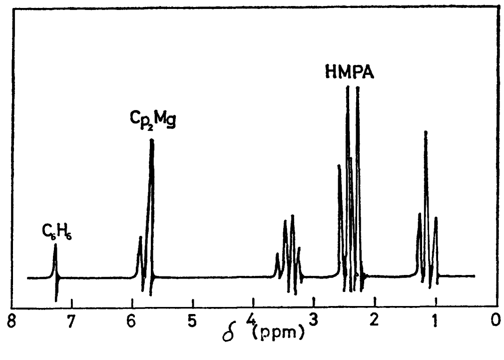
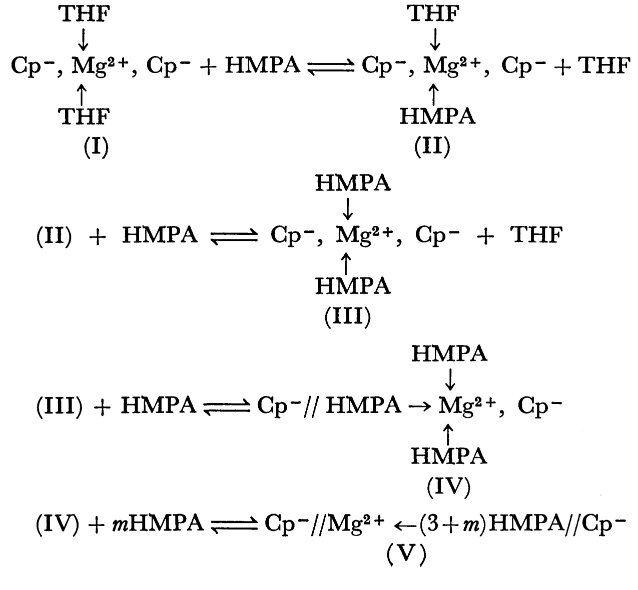


Fig. 9. NMR spectrum of Cp_2Mg in the presence of HMPA in ether.

of Cp_2Mg and HMPA. The unmber of HMPA molecules coordinated with magnesium was estimated from the intensity ratio of the upfield peaks of Cp_2Mg and HMPA; the number was $\sim$1.6 when Cp_2Mg and HMPA were mixed at $[\text{HMPA}]/[\text{Mg}]=2$. This fact indicates that the upfield peak of Cp_2Mg is due to the Cp_2Mg coordinated with one or two HMPA molecules. When Cp_2Mg and HMPA were mixed in ether at $5>[\text{HMPA}]/[\text{Hg}]>\sim2.5$, an ether-insoluble product was obtained. The precipitate, which was filtered, washed with ether, and dried under a vacuum, was found by acid-base titration to be a complex with the formula of $Cp_2Mg\cdot(\text{HMPA})_{3.0-3.1}$. The NMR spectrum of this precipitate (THF-soluble) in THF had two kinds of peaks for Cp_2Mg, and the intensities were almost equal. This spectrum, moreover, was almost the same as that of the Cp_2Mg–HMPA mixture prepared directly in THF at $[\text{HMPA}]/[\text{Mg}]=\sim3$ (see Fig. 7). This finding suggests that the evolution of two peaks for Cp_2Mg in a THF–HMPA mixture is also due to the coordination of three HMPA molecules with the magnesium.

Consequently, the spectral change in the presence of HMPA is most likely to be due to the structural change in the Cp_2Mg ion pair, since Cp_2Mg has been considered to be an ion triplet in THF.[22] The change in the contact ion pair to the solvent-separated ion pair could be accounted for by the following scheme:



$$\underset{\text{(I)}}{\mathrm{Cp^-},\ \underset{\underset{\text{THF}}{\uparrow}}{\overset{\overset{\text{THF}}{\downarrow}}{\mathrm{Mg^{2+}}}},\ \mathrm{Cp^-}} + \text{HMPA} \rightleftharpoons \underset{\text{(II)}}{\mathrm{Cp^-},\ \underset{\underset{\text{HMPA}}{\uparrow}}{\overset{\overset{\text{THF}}{\downarrow}}{\mathrm{Mg^{2+}}}},\ \mathrm{Cp^-}} + \text{THF}$$

$$\text{(II)} + \text{HMPA} \rightleftharpoons \underset{\text{(III)}}{\mathrm{Cp^-},\ \underset{\underset{\text{HMPA}}{\uparrow}}{\overset{\overset{\text{HMPA}}{\downarrow}}{\mathrm{Mg^{2+}}}},\ \mathrm{Cp^-}} + \text{THF}$$

$$\text{(III)} + \text{HMPA} \rightleftharpoons \underset{\text{(IV)}}{\mathrm{Cp^-}/\!/\,\text{HMPA} \rightarrow \underset{\underset{\text{HMPA}}{\uparrow}}{\overset{\overset{\text{HMPA}}{\downarrow}}{\mathrm{Mg^{2+}}}},\ \mathrm{Cp^-}}$$

$$\text{(IV)} + m\text{HMPA} \rightleftharpoons \underset{\text{(V)}}{\mathrm{Cp^-}/\!/\mathrm{Mg^{2+}} \leftarrow (3+m)\text{HMPA}/\!/\mathrm{Cp^-}}$$

It is reasonable to assume that Cp_2Mg exists as monomeric Species (I) coordinated with two THF molecules in THF, since other Grignard reagents and dialkylmagnesium compounds have been found to be monomeric in THF, even at concentrations>1 M.[23] Species (I) and also Species (II), which is coordinated by one HMPA and one THF, coexist at equilibrium at $[\text{HMPA}]/[\text{Mg}]<1$. When the $[\text{HMPA}]/[\text{Mg}]$ ratio is between about unity and about two, Species (III), which is coordinated by two HMPA molecules, coexists with Species (II). The spectrum of Species (II) must have a singlet peak, since the two cyclopentadienyl rings of the species are equivalent. In the same manner, the spectrum of Species (III) must have a singlet peak different from that of Species (II) if the exchange between these species is slow. However, the fact that the chemical shift of Cp_2Mg changes continuously at $[\text{HMPA}]/[\text{Mg}]<\sim2$ suggests that the exchanges among Species (I), (II), and (III) are rapid at room temperature.

When the $[\text{HMPA}]/[\text{Mg}]$ ratio is more than about two, Species (IV) coexists with Species (III), and the former becomes a predominant species at $[\text{HMPA}]/[\text{Mg}]=\sim3$. Species (IV), which is coordinated with three HMPA molecules, was concluded, by a comparison with the results for the magnesium fluorenide–HMPA complex (see the above section), to be an asymmetrically solvent-separated ion pair in which one of the cyclopentadienyl rings is separated from the magnesium ion. The two rings of Species (IV) are nonidentical; hence, the spectrum must have two singlet peaks if the exchange between the two rings is slow. Actually the spectral behavior at $[\text{HMPA}]/[\text{Mg}]\geq3$ indicates that the exchange between the distinct rings is slow at room temperature on the NMR time scale, but becomes rapid with an increase in the temperature. On the basis of the spectral change with the $[\text{HMPA}]/[\text{Mg}]$ ratio, the upfield and downfield peaks of Cp_2Mg at $[\text{HMPA}]/[\text{Mg}]=\sim3$ were assigned to the contact and the separated cyclopentadienyl rings respectively.

When the $[\text{HMPA}]/[\text{Mg}]$ ratio is more than three, Species (IV) changes gradually to Species (V) by interaction with m molecules of HMPA. Species (V) is a symmetrically separated ion pair, in which two of the cyclopentadienyl rings are separated from the magnesium. This species has two identical rings; hence, the NMR spectrum must give a singlet peak. The spectral change at $[\text{HMPA}]/[\text{Mg}]>3$ can be explained by assuming that Species (V) is formed by the interaction of Species (IV) with three HMPA molecules; that is, the m in the equation is three. That is to say, the symmetrically separated ion pair of Cp_2Mg is formed by the interaction of Cp_2Mg with six HMPA molecules. Cp_2Mg was found to form a THF-insoluble complex with three octamethylpyrophosphoramide (OMPA) molecules. The coordination number of the magnesium ion is six since OMPA is a bidentate ligand. Magnesium perchlorate has also been reported to form a complex with three OMPA.[24] These results support the above concept. Such a two-step separation process has already reported in the case of fluorenylstrontium in THF when studied by electronic spectroscopy.[21)]

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