was carried out as described above for bis(η^5-pentamethylcyclopentadienyl)titanium dibromide, by using 0.21 g (0.64 mmol) of (η^5-pentamethylcyclopentadienyl)(η^5-cyclopentadienyl)titanium dichloride, 0.77 mL (0.77 mmol) of 1.0 M boron tribromide in methylene chloride, and 15 mL of methylene chloride. The product was recrystallized from methylene chloride/hexane to give 0.15 g (58% yield) of the desired dibromide as black crystals: mp 250–252 °C; ^{1}H NMR ($CDCl_3$) δ 6.37 (5 H, s), 2.12 (15 H, s); exact mass m/e 405.9417 (calcd m/e 405.9410). Anal. Calcd for $C_{15}H_{20}Br_2Ti$: C, 44.15; H, 4.94. Found: C, 44.14; H, 4.99.

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Registry No. Cp_2TiF_2, 309-89-7; $CpCp^*TiF_2$, 38496-78-5; $Cp^*_2TiF_2$, 87050-22-4; Cp_2TiCl_2, 1271-19-8; Cp_2TiBr_2, 1293-73-8; $CpCp^*TiCl_2$, 38496-87-6; $CpCp^*TiBr_2$, 87050-23-5; $Cp^*_2TiCl_2$, 11136-36-0; $Cp^*_2TiBr_2$, 87050-24-6.

Orientation and Structure of (η^5-Cyclopentadienyl)rhenium and -manganese Tricarbonyl Complexes Dissolved in Liquid Crystal Solvents

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The anomalous ratios of the direct dipole coupling constants obtained from the proton NMR spectra of oriented solutions of (η^5-cyclopentadienyl)manganese tricarbonyl dissolved in two different nematic liquid crystal solvents are also found for the analogous rhenium compound. For a solvent in which the orientation of the solutes is parallel to the liquid crystal axis, the ratios of the direct dipole coupling constants are temperature dependent. The orientation in a phenylcyclohexyl-type solvent is perpendicular to the liquid crystal axis and independent of temperature. The effects are attributed to an exchange between two sites, parallel and perpendicular to the liquid crystal axis.

The proton NMR spectra of oriented (η^5-cyclopentadienyl)manganese(I) tricarbonyl, $CpMn(CO)_3$, dissolved in nematic liquid crystal solvents have been reported by several different groups.[1-4] The ratio of the two different direct dipole coupling constants (or of the interproton distance) in a regular pentagonal ring structure should be independent of the actual carbon–carbon and carbon–hydrogen bond lengths, but all the investigations have shown that deviations occur from the expected value of 4.236, or 4.216 if vibrationally corrected.[5] Since there is currently some theoretical interest in the conformations of organometallic complexes[6,7] and in the implications that distortions of the cyclopentadienyl ring have with regard to the bonding of this ligand,[7-10] we have investigated the oriented NMR spectrum of the analogous rhenium complex, $CpRe(CO)_3$. Two different solvents were used: a nematic mixture (EK X-11643) from Eastman Kodak with a nematic range of 12–100 °C and a cyanophenylcyclohexyl (PCH) mixture, Merck 1132, temperature range −6 to +70 °C. As a consequence of the results we have also reexamined the manganese compound.

Results and Discussion

The results of the spectral analyses are given in Table I, where the errors are derived from the probable errors of the D_{ij} values given by the LAOCOON3 fit. Similar results were obtained for both the rhenium and manganese complexes. (The rhenium complex, $CpRe(CO)_3$, was prepared as previously described;[8] the manganese compound was a generous gift from Ethyl Corp. Solute concentrations are approximately 5% by weight of $CpMn(CO)_3$ and 1.5% of $CpRe(CO)_3$. Proton NMR spectra were obtained for the manganese complex in M1132 using a Bruker WH90 and the others on a Varian HR200. Spectra were analyzed by using a version of LAOCOON3 modified for oriented spectra. The indirect coupling constants were taken to be ^3J = 2.7 Hz and ^4J = 1.48 Hz, the averages of the values obtained when these parameters were allowed to vary in the initial analyses.) In the PCH solvent, the dipole coupling constants were found to be negative, and therefore the orientation of the solvent molecule must be perpendicular to the liquid crystal axis. The ratio, D_{12}/D_{13}, is much lower than that found for the EK solvent and reported in the literature for other solvents.[1-4] This implies that a greater distortion of the cyclopentadienyl ring occurs for this solvent mixture. However, the ratio appears to be independent of temperature whereas, in the EK solvent, it decreased with increasing temperature.

There is now both theoretical and experimental evidence that the carbon–carbon bonds in the cyclopentadienyl ligand are not of equal length. The results of the crystallographic structure study of the manganese tricarbonyl

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Table I. Direct Dipole Coupling Constants and Ratios for the Cyclopentadienyl Complexes of Rhenium and Manganese Tricarbonyl

	solv	temp, K	D_{12}, Hz	D_{13}, Hz	D_{12}/D_{13}
$CpRe(CO)_3$	EK	279	783.66	188.42	4.159 ± 0.005
		293	691.87	167.11	4.140 ± 0.006
		311	540.51	131.03	4.125 ± 0.005
		323	415.29	101.17	4.105 ± 0.005
		353	231.69	57.04	4.062 ± 0.009
	M1132	279	−358.69	−90.83	3.949 ± 0.019
		293	−331.30	−83.79	3.954 ± 0.009
		311	−272.59	−68.83	3.960 ± 0.005
		323	−197.65	−49.89	3.961 ± 0.009
$CpMn(CO)_3$	EK	279	589.65	142.66	4.133 ± 0.004
		293	519.23	125.88	4.132 ± 0.008
		311	402.23	97.61	4.121 ± 0.005
	M1132	275	−338.08	−84.67	3.993 ± 0.004
		301	−257.78	−64.53	3.995 ± 0.004
		324	−153.78	−38.63	3.981 ± 0.008

complex[8] have received some recent theoretical support[7] which indicated that C–C bonds eclipsed by a carbonyl should be long and those in a trans conformation should be short. A simple resolution of this, and similar questions, is complicated by the low barriers to rotation of the Cp ligand since the internal barrier is essentially zero and that in the solid, ~7 kJ mol^{-1}, is determined by intermolecular contacts.[10] In the free molecule the inherent distortion of the ring will be averaged on the time scale of NMR experiments and the customary corrections for the effects of vibrational motion would not account for the actual experimental ratios. Thus the value of the dipolar coupling constant ratio of 4.216 is not appropriate in the case of the tricarbonyl complexes. If the ring bond lengths and angles determined in the X-ray study are used, with a C–H distance of 1.09 Å, then the ratio of the averaged cubes of the distances is 4.174. This value does depend upon the C–H distance. Molecular deformations in anisotropic solvents are well-known and can be considered as arising from either solvent-induced changes in the molecular structure or from vibration–reorientation interactions.[11-15] In the present cases, when the solute molecule is oriented with its symmetry axis parallel to the liquid crystal axis the in-plane vibrations of the ring should not be affected, since cylindrical symmetry is maintained. Distortions due to the solvent must arise from interactions with the out-of-plane vibrations. For a perpendicular orientation, as found for the PCH solvent, the forces on the ring are no longer cylindrically symmetric and in-plane deformations are now possible, leading to a much wider discrepancy in the dipolar coupling constant ratio. Thus a solvent-induced change in molecular structure might account for additional changes in the distance ratios, but not for the temperature dependence.

Apparent variations of molecular structure with temperature have been reported, for instance, for acetylene[16] and various methyl derivatives[17,18] in nematic solvents and have been attributed to an exchange between different orientational sites. We assume that the solute molecule can occupy one of two orientations, either parallel or perpendicular to the liquid crystal axis. The dipolar coupling constants are averaged not only over the internal motions but also over the change in molecular geometry, since the structure is probably different in the two sites, as discussed above. Therefore we consider the ratios of the two experimental dipole coupling constants. The observed ratio is assumed to be a population weighted average over the limiting values for the two sites, and from the temperature dependence of the ratio it is possible to determine approximately the enthalpy difference between them. For parallel orientation a ratio of 4.174 is assumed. This is an arbitrary choice since the actual value cannot be determined. For the perpendicular orientation, the experimentally determined ratios in the M1132 solvent of 3.960 and 3.990 are assumed for the Re and Mn complexes, respectively. The population of the parallel site is given by

$$p = (R_{\text{obsd}} - R_{\text{perp}})/(R_{\text{para}} - R_{\text{perp}})$$

and from the temperature dependence of this function, enthalpy differences were estimated to be 7 and 3 kJ mol^{-1} for the rhenium and manganese compounds, respectively. This treatment is qualitative and the enthalpy values approximate, since the limiting values of the ratios are not known accurately. However, the possibility that an orientational exchange process occurs means that useful quantitative structural information cannot be derived from the direct dipole coupling constants.

An investigation of the polarized infrared spectra of solutions in the EK and PCH solvents, homogeneously aligned on rubbed NaCl plates, gave no useful information on the possible deformations of the Cp ligand since the ring vibrational frequencies were obscured by solvent absorptions.[19] However, in both solvents the strong carbonyl stretching modes, in the 2000 cm^{-1} region, were clearly observed for both compounds. Two vibrations, with symmetries a_1 and e, should occur, with perpendicular and parallel polarization, respectively, for the PCH case and the converse for the EK solvent. The observed dichroism of the a_1 mode in all cases is consistent with these predictions. In the EK spectra of both complexes, the e mode displayed perpendicular polarization as expected but was split into two components while, in the PCH case, it exhibited a splitting into a perpendicular and a parallel component at higher and lower wavenumbers, respectively. These observations of a loss of the degeneracy of the e mode clearly indicate a reduction in the symmetry of the

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$CpMn(CO)_3$ and $CpRe(CO)_3$ solutes in both liquid crystals.

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Registry No. $CpRe(CO)_3$, 12079-73-1; $CpMn(CO)_3$, 12079-65-1.

Ligand Exchange in Tetraalkylaluminate Ions: Catalysis by the Sodium Ion

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When $NaAlMe_4$ and $NaAlEt_4$ are combined in benzene solution containing HMPA, exchanges of alkyl groups occur resulting in a statistical distribution of alkylaluminate ions. Rates of exchange can be followed by ^{27}Al heteronuclear decoupled ^1H NMR, and pseudo-first-order rate constants are a function of HMPA to Na^+ mole ratio, decreasing to essentially zero in pure HMPA. The reactions are interpreted as occurring in contact ion pairs in which two aluminate anions occupy coordination sites on the same Na^+. A large decrease in exchange rate occurring at $HMPA{:}Na^+ = 2.5{:}1$ is proposed to be due to the formation of solvent-bridged species of stoichiometry $[2Na{\cdot}5HMPA]^{2+}$.

Mixed alkyl derivatives of the group 3 elements are of considerable interest for synthetic and other purposes.[1] While mixed alkylboranes are stable toward disproportionation under a variety of conditions,[1] trialkylaluminum derivatives are well-known to give rapid intermolecular alkyl group exchange. Mixed organoborates of types MBR_3R'[2] and MBR_3H[3] have been known for some time and are apparently perfectly stable. The situation with respect to mixed aluminates containing H and alkyl groups is less clear,[4,5] and mixed alkyl compounds of the type $MAlR_nR'_{4-n}$ are apparently unknown in pure form. A previous attempt to prepare such species in our laboratories by mixing an alkyllithium reagent and a trialkylaluminum in benzene resulted in a mixture containing $LiAlR_4$, $LiAlR_3R'$, $LiAlR_2R'_2$, $LiAlRR'_3$, and $LiAlR'_4$.[6]

Results and Discussion

Exchange Equilibria. Anticipating that exchange pathways available to $LiAlR_4$ salts would not necessarily be the same as those available to the Na analogues, we have investigated the exchange reactions occurring on mixing $NaAlMe_4$ and $NaAlEt_4$ in benzene in the presence of controlled amounts of HMPA or Me_2SO. Combining these components results in a two-liquid-phase system with all of the organometallic, and essentially all of the donor solvent, in the lower phase. Many properties of these two-phase mixtures have been described elsewhere.[7] In the lower phase, alkyl group exchange does take place, and the progress of the exchange can be followed by ^{27}Al heteronuclear decoupled ^1H NMR, as shown in Figure 1. The spectrum of the equilibrated mixture shows four methyl proton signals that are almost base line resolved at 100 MHz and that appear in 1:3:3:1 relative intensities when the salts are mixed in a 1:1 molar ratio. The distribution of Me groups among the four Me-containing species is thus a random one; i.e., $\Delta H°$ for eq 1 is 0, and $\Delta S°$ is determined only by the contribution of external symmetry numbers to the partition coefficients.[8]

$$3NaAlMe_4 + 3NaAlEt_4 \rightleftarrows 2NaAlMe_3Et + 2NaAlMe_2Et_2 + 2NaAlMeEt_3 \quad (1)$$

Exchange of hydrogen or alkyl groups in aluminate species has been observed by others. In some solvents a slow H–H or H–D exchange can be observed in the ^{27}Al NMR of solutions of $MAlH_4$ and $MAlD_4$.[9] Since there is considerable overlapping of the ^{27}Al signals, the proportions of $LiAlH_nD_{4-n}$ species present cannot be determined, but the inference is drawn that all five possibilities are formed when $LiAlH_4$ and $LiAlD_4$ are mixed in 1:1 ratio and that the final equilibrium distribution is random. In contrast, in exchanges observed between $MAlH_4$ and $MAlR_4$ in THF, catalyzed by AlR_3, the formation of mixed $MAlH_nR_{4-n}$ species does not follow a random pattern.[5] For instance, a 1:1 mixture of $NaAlH_4$ and $NaAlMe_4$ in THF at 66 °C (presumably with $AlMe_3$ catalysis) results in formation of $NaAlH_2Me_2$ exclusively, as indicated by the ^{27}Al NMR spectrum. The authors conclude that $MAlH_3R$

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