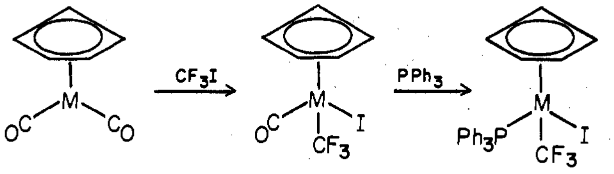
Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

Reactions of π-Cyclopentadienyliodotrifluoromethyltriphenylphosphine-Metal Complexes (M = Co, Rh, Ir) with Grignard Reagents

Sylvia A. Gardner and Marvin D. Rausch*

Received July 11, 1973

In connection with our current research program concerning the formation and properties of new σ-bonded organotransition metal complexes, we have recently studied the reactions of π-cyclopentadienylmetal complexes of types **2** and **3** with Grignard reagents. Complexes **2a** and **2b** have previously been prepared *via* an oxidative addition reaction between the appropriate π-cyclopentadienyldicarbonylmetal complex **1a** and **1b** and trifluoromethyl iodide.[1,2] Using these reactions as a model, the iridium analog **2c** has also been prepared. Unfortunately, all attempts thus far to methylate each of the three complexes **2a-c** using methylmagnesium iodide or chloride have failed, and no identifiable reaction products have been obtained.



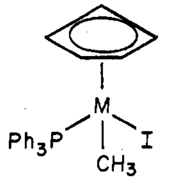
1a, M = Co
b, M = Rh
c, M = Ir

2a, M = Co
b, M = Rh
c, M = Ir

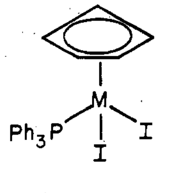
3a, M = Co
b, M = Rh
c, M = Ir

It is well known that strongly π-bonding ligands such as π-cyclopentadienyl and triphenylphosphine tend to stabilize σ-bonded organic ligands attached to the same transition metal atom. Complexes **2a-c** were therefore treated with triphenylphosphine which resulted in each case in displacement of the carbonyl ligand. In this manner, complexes **3a-c** were prepared in yields of 86, 96, and 49%, respectively. Complexes **3a-c** were then caused to react with methylmagnesium iodide, and the products obtained from each reaction were separated by column chromatography on alumina under nitrogen.

The cobalt product, formulated as complex **4**, was identified by comparison with an authentic sample of **4** prepared by the method of Yamazaki and Hagihara.[3] Complex **4** contains a methyl resonance in its nmr spectrum with a coupling constant of 7.8 Hz, corresponding to spin-spin interaction caused by the phosphorus atom. Both diiodide products **6** and **7** obtained in these reactions were also identified *vs.* authentic samples of the rhodium[4] and iridium[5] compounds. The formation of the monomethyl rhodium complex **5** was verified by nmr, ir, and elemental analysis, as well as by a melting point comparison.[6] The methyl group in the nmr spectrum of **5** appears as a quartet, due to splitting by both the phosphorus and rhodium atoms.



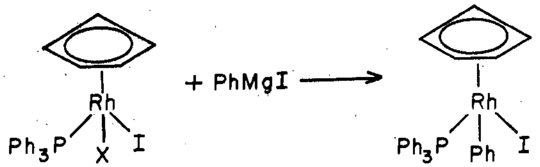
4, M = Co
5, M = Rh



6, R = Rh
7, R = Ir

It is surprising to note that the trifluoromethyl group, and not the iodide group, is displaced in this series of reactions. Several authors[7,8] have discussed the relative electronegativity of the perfluoroalkyl group, and the value for the trifluoromethyl group is generally considered to fall between that of chlorine and fluorine on the Pauling scale. The trifluoromethyl ligand is thus generally regarded as a pseudohalogen, and its behavior in the above series of reactions can perhaps be rationalized in this manner.

In a further attempt to prepare a compound containing two different σ-bonded organic ligands on the same metal, the monophenyl rhodium complex **8** was prepared either by the reaction of phenylmagnesium iodide with **6** or *via* reaction of this Grignard reagent with **3b**.



6, X = I
3b, X = CF_3

8

In this latter reaction, substitution of the trifluoromethyl group instead of the iodide group is again observed, and the organorhodium diiodide **6** was also isolated. Subsequent attempts to methylate **8** with methylmagnesium iodide have not yet been successful.

Experimental Section

All operations including column chromatography were carried out under nitrogen using Schlenk tube techniques. Hexane and benzene were distilled under nitrogen from calcium hydride before use, while ethyl ether was predried over calcium chloride and then distilled from sodium-benzophenone radical. Tetrahydrofuran was predried over potassium hydroxide and then distilled from sodium-naphthalene radical immediately before use. π-Cyclopentadienylcarbonyliodotrifluoromethylcobalt (**2a**) and π-cyclopentadienylcarbonyliodotrifluoromethylrhodium (**2b**) were prepared in pressure tubes in yields of 51 and 50% using a slight modification of the published procedures.[1,2] Nmr spectra were recorded on a Varian A-60 instrument, and ir spectra were taken on a Beckman IR-10. Melting points were all taken under nitrogen and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Mass.

Preparation of π-Cyclopentadienylcarbonyliodotrifluoromethyliridium (2c). π-Cyclopentadienyldicarbonyliridium (**1c**) (3.13 g, 10 mmol) was mixed with 5 ml of benzene in a thick-walled pressure tube (3 × 20 cm) which had been flushed with nitrogen. The tube was cooled to −78° and *ca.* 3 ml of trifluoromethyl iodide was added. The tube was capped and allowed to stand at room temperature for 48 hr. The reaction tube was then cooled to −78°, uncapped, and evacuated to remove the excess solvent. The residue was sublimed at 125° (10^{-4} mm) to yield 1.9 g (40%) of orange crystals of **2c**, mp 195-197°. *Anal.* Calcd for $C_7H_5F_3IIrO$: C, 17.47; H, 1.05; F,

---

[1] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 3593 (1961).

[2] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

[3] H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **21**, 431 (1970).

[4] A. Kasahara, Y. Izumi, and K. Tanaka, *Bull. Chem. Soc. Jap.*, **40**, 699 (1967).

[5] W. A. G. Graham and A. J. Oliver, *Inorg. Chem.*, **9**, 2653 (1970).

[6] W. A. G. Graham and A. J. Oliver, *Inorg. Chem.*, **10**, 1165 (1971).

[7] H. C. Clark, *Advan. Fluorine Chem.*, **3**, 19 (1963).

[8] J. J. Lagowski, *Quart. Rev., Chem. Soc.*, **8**, 233 (1959).

11.84; I, 26.37; Ir, 39.94; O, 3.32. Found: C, 17.58; H, 0.97; F, 11.90; I, 26.40; Ir, 40.01; O, 3.32.

Preparation of π-Cyclopentadienyliodotrifluoromethyltriphenylphosphinecobalt (3a). A solution of π-cyclopentadienylcarbonyliodotrifluoromethylcobalt (**2a**) (1.25 g, 3.6 mmol) in 50 ml of methylene chloride was treated dropwise with a solution of triphenylphosphine (1.05 g, 4 mmol) in 15 ml of methylene chloride. Immediate gas evolution occurred and the solution turned from yellow-green to brown. The reaction mixture was stirred at room temperature for 24 hr, filtered, and mixed with 25 ml of hexane. The volume of the solution was reduced to *ca.* $^1/_3$ and the brown crystals that formed were filtered, washed well with hexane, and dried under vacuum to produce 1.7 g (86%) of **3a.** An analytical sample was prepared by recrystallization from benzene–hexane, mp 200–201°. *Anal.* Calcd for $C_{24}H_{20}CoF_3IP$: C, 49.51; H, 3.46; Co, 10.12; F, 9.79; I, 21.80; P, 5.32. Found: C, 49.60; H, 3.50; Co, 10.15; F, 9.82; I, 21.72; P, 5.35. The ir spectrum (KBr) exhibited the following major peaks: 1480 (w), 1430 (m), 1080–940 (s), 850–810 (s), 740 (m), 690 cm^{-1} (m). The nmr spectrum ($CDCl_3$) consisted of a singlet at τ 4.96 (π-C_5H_5) and a multiplet at τ 2.1–2.8 (C_6H_5), intensity 1:3.

Preparation of π-Cyclopentadienyliodotrifluoromethyltriphenylphosphinerhodium (3b). Complex **3b** was obtained as orange-red crystals (96%) from a reaction between equimolar amounts of π-cyclopentadienylcarbonyliodotrifluoromethylrhodium (**2b**) and triphenylphosphine in a manner similar to the preparation of complex **3a.** An analytical sample was prepared by recrystallization from benzene–hexane, mp 266–267°. *Anal.* Calcd for $C_{24}H_{20}F_3IPRh$: C, 46.05; H, 3.22; F, 9.10; I, 20.27; Rh, 16.44; P, 4.95. Found: C, 45.85; H, 3.04; F, 9.00; I, 20.57; Rh, 16.40; P, 4.90. The ir spectrum (KBr) exhibited the following major bands: 1480 (w), 1435 (m), 1090–960 (s), 830–810 (m), 745 (m), 690 cm^{-1} (m). The nmr spectrum ($CDCl_3$) consisted of a doublet at τ 4.65 (π-C_5H_5, $J_{P-H} = 1.7$ Hz) and a multiplet at τ 2.2–2.8 (C_6H_5), intensity 1:3.

Preparation of π-Cyclopentadienyliodotrifluoromethyltriphenylphosphineiridium (3c). Complex **3c** was obtained as yellow crystals (49%) from a reaction between equimolar amounts of π-cyclopentadienylcarbonyliodotrifluoromethyliridium (**2c**) and triphenylphosphine in a manner similar to the preparation of complex **3a.** An analytical sample of **3c** was prepared by recrystallization of the product from benzene–hexane, mp 226–227°. *Anal.* Calcd for $C_{24}H_{20}F_3IIrP$: C, 40.29; H, 2.82; F, 7.96; I, 17.74; Ir, 26.86; P, 4.33. Found: C, 40.26; H, 2.93; F, 7.90; I, 17.47; Ir, 27.00; P, 4.30. The ir spectrum (KBr) showed the following major bands: 1480 (w), 1430 (m), 1190–1050 (s), 860–810 (m), 745 (m), 690 cm^{-1} (m). The nmr spectrum ($CDCl_3$) consisted of a doublet at τ 4.60 (π-C_5H_5, $J_{P-H} = 1.3$ Hz) and a multiplet at τ 2.3–2.8 (C_6H_5), intensity 1:3.

Reaction of π-Cyclopentadienyliodotrifluoromethyltriphenylphosphinecobalt (3a) and Methylmagnesium Iodide. A solution of methylmagnesium iodide in 10 ml of ethyl ether [prepared from 0.292 g of Mg (12 mmol) and 1.7 g of methyl iodide (12 mmol)] was added dropwise to a solution of **3a** (2.33 g, 4 mmol) in 75 ml of benzene in a flask which had previously been flamed out under vacuum and flushed with nitrogen. The solution was stirred at room temperature for 2 hr and then chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with benzene removed a brown band from the column which was evaporated to dryness and recrystallized from benzene–hexane, yielding 0.14 g of brown crystals identified as π-cyclopentadienyliodomethyltriphenylphosphinecobalt (**4**), mp 107–108° (reported[3] 112°). *Anal.* Calcd for $C_{24}H_{23}CoIP$: C, 54.57; H, 4.39; Co, 11.16; I, 24.02; P, 5.86. Found: C, 54.99; H, 4.22; Co, 11.17; I, 25.10; P, 5.19. The nmr spectrum ($CDCl_3$) consisted of a doublet at τ 8.21 (CH_3, $J_{P-H} = 7.8$ Hz), a singlet at τ 5.18 (π-C_5H_5), and a multiplet at τ 2.1–3.0 (C_6H_5), intensity 3:5:15.

Reaction of π-Cyclopentadienyliodotrifluoromethyltriphenylphosphinerhodium (3b) and Methylmagnesium Iodide. A solution of methylmagnesium iodide in 20 ml of ethyl ether [prepared from 0.58 g of Mg (24 mmol) and 3.4 g of methyl iodide (24 mmol)] was added dropwise to a solution of **3b** (5.0 g, 8 mmol) in 150 ml of benzene in a flask which had previously been flamed out under nitrogen and flushed with nitrogen. The reaction mixture was stirred at room temperature for 24 hr and then chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with benzene removed a red band from the column which was evaporated to dryness. The residue was recrystallized twice from benzene–hexane, yielding 0.83 g (20%) of red crystals of π-cyclopentadienyliodomethyltriphenylphosphinerhodium (**5**), mp 173–174° (reported[6] 174°). *Anal.* Calcd for $C_{24}H_{23}IPRh$: C, 50.38; H, 4.05; I, 22.18; P, 5.41; Rh, 17.98. Found: C, 51.14; H, 4.16; I, 22.00; P, 4.76; Rh, 17.70. The nmr spectrum consisted of a quartet at τ 8.62 (CH_3, $J_{P-H} = 6.2$ Hz, $J_{Rh-H} = 2.5$ Hz), a quartet at τ 4.95 (π-C_5H_5, $J_{P-H} = 1.8$ Hz, $J_{Rh-H} = 0.4$ Hz), and a multiplet at τ 2.3–2.8 (C_6H_5), intensity 3:5:15.

Further elution of the column with ethyl ether removed a red band. After evaporation to dryness, the residue was recrystallized from benzene–hexane to yield 0.15 g (2.7%) of π-cyclopentadienyltriphenylphosphinerhodium diiodide (**6**), mp 245–250° (reported[4] dec >260°). *Anal.* Calcd for $C_{23}H_{20}I_2PRh$: C, 40.38; H, 2.95; I, 37.10; P, 4.53; Rh, 15.04. Found: C, 40.43; H, 3.06; I, 37.18; P, 4.55; Rh, 15.00. The nmr spectrum ($CDCl_3$) consisted of a doublet at τ 4.58 (π-C_5H_5, $J_{P-H} = 2.0$ Hz) and a multiplet at τ 2.2–2.8 (C_6H_5).

Reaction of π-Cyclopentadienyliodotrifluoromethyltriphenylphosphineiridium (3c) with Methylmagnesium Iodide. A solution of methylmagnesium iodide in 10 ml of ethyl ether [prepared from 0.29 g (12 mmol) of Mg and 1.7 g (12 mmol) of methyl iodide] was added dropwise to a solution of **3c** (2.86 g, 4 mmol) in 75 ml of benzene. The reaction flask had previously been flamed out under vacuum and flushed with dry nitrogen. The solution was stirred at room temperature for 4 hr and then chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane.

Elution with benzene removed a yellow band from the column which was evaporated to dryness, dissolved in a small amount of benzene, and placed on two preparative tlc plates. After one elution of the plates with benzene, the major yellow-orange band was removed, extracted with ethyl ether, and filtered. The filtrate was evaporated to dryness and recrystallized from benzene–hexane, yielding 10 mg of an unidentified orange solid. The following major peaks were observed in the mass spectrum of the product: m/e 722–724, 645–648, 544–546, 517–520, 431–439, 277, 262, and 183. The ir spectrum contained the following bands: 1480 (w), 1430 (m), 1185 (w), 990 (m), 840–800 (m), 745 (m), and 690 cm^{-1} (s). The nmr spectrum ($CDCl_3$) consisted of two multiplets at τ 5.1–5.4 (π-C_5H_5) and 2.2–3.1 (C_6H_5).

Further elution of the column with 1:1 benzene–ether removed an orange band. The solution was evaporated to dryness and the residue recrystallized from benzene–hexane, yielding 0.26 g of red π-cyclopentadienyltriphenylphosphineiridium diiodide (**7**), mp 289–290° (reported[5] 290°). *Anal.* Calcd for $C_{23}H_{20}I_2IrP$: C, 35.72; H, 2.61; I, 32.82; Ir, 24.85; P, 4.00. Found: C, 36.23; H, 2.58; I, 33.00; Ir, 24.60; P, 3.88. The nmr spectrum ($CDCl_3$) consisted of a doublet at τ 4.60 (π-C_5H_5, $J_{P-H} = 1.4$ Hz) and a multiplet at τ 2.2–2.8 (C_6H_5), intensity 1:3.

Preparation of π-Cyclopentadienyliodophenyltriphenylphosphinerhodium (8). Method A. A solution of phenylmagnesium iodide in 15 ml of ethyl ether [prepared from 1.02 g (5 mmol) of iodobenzene and 0.12 g (5 mmol) of Mg] was added dropwise to a solution of π-cyclopentadienyltriphenylphosphinerhodium diiodide (**6**) (2.74 g, 4 mmol) in 400 ml of 1:1 THF–ethyl ether. The reaction flask had previously been flamed out under vacuum and flushed with nitrogen. The mixture was heated at reflux for 24 hr, evaporated to dryness, and mixed with 200 ml of benzene. The benzene solution was chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with benzene removed an orange-red band from the column which was reduced to dryness and recrystallized from benzene–hexane to yield 0.61 g (24%) of red π-cyclopentadienyliodophenyltriphenylphosphinerhodium (**8**), mp 154–155°. *Anal.* Calcd for $C_{29}H_{25}IPRh$: C, 54.91; H, 3.97; I, 20.01; P, 4.88; Rh, 16.22. Found: C, 54.84; H, 4.01; I, 19.97; P, 4.80; Rh, 16.20. The ir spectrum (KBr) contained the following major bands: 1555 (m), 1475–1465 (m), 1425 (m), 1085 (m), 1010 (m), 825 (m), 800 (m), 730 (s), 690 cm^{-1} (s). The nmr spectrum ($CDCl_3$) consisted of a quartet at τ 4.62 (π-C_5H_5, $J_{P-H} = 1.9$ Hz, $J_{Rh-H} = 0.4$ Hz) and a multiplet at τ 2.5–2.9 (C_6H_5), intensity 1:4.

Method B. A solution of phenylmagnesium iodide in 15 ml of ethyl ether [prepared from 0.36 g (15 mmol) of Mg and 3.03 g (15 mmol) of iodobenzene] was added dropwise to a solution of π-cyclopentadienyliodotrifluoromethyltriphenylphosphinerhodium (**3b**) (3.13 g, 5 mmol) in 350 ml of benzene. The reaction flask had previously been flamed out under vacuum and flushed with nitrogen. The reaction mixture was stirred at room temperature for 24 hr and then chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane.

Benzene elution removed a red-orange band from the column. The red solution was evaporated to dryness and recrystallized from benzene–hexane to yield 0.20 g (6.3%) of π-cyclopentadienyliodophenyltriphenylphosphinerhodium (**8**).

Further elution of the column with ethyl ether removed a second red-brown band. The solution was evaporated to dryness and recrystallized from benzene-hexane to yield 0.05 g (1.5%) of π-cyclopentadienyltriphenylphosphinerhodium diiodide (**6**).

Acknowledgment. The authors are grateful to the National Science Foundation for a grant in support of this research program and to Professor Howard Clark for helpful assistance.

Registry No. **2c**, 50276-27-2; **3a**, 50276-28-3; **3b**, 50276-29-4; **3c**, 50430-95-0; **4**, 12203-93-9; **5**, 34922-92-4; **6**, 12131-90-7; **7**, 32660-88-1; **8**, 50276-32-9; **1c**, 12192-96-0; **2a**, 12078-24-9; **2b**, 12078-27-2; PPh_3, 603-35-0.

Contribution from the Instituto de Quimica,
Universidade de Sao Paulo, Sao Paulo, Brazil

Studies of Membrane Processes. II. Participation of the Dimethyltin Ion in an Electrical Double Layer

L. W. Reeves,*[1] M. Suzuki, A. S. Tracey, and J. A. Vanin

Received August 9, 1973

In two recent communications[2] from this laboratory, we have shown that the structure of complex ions can be investigated in lyotropic nematic phases. The thermotropic nematic phases, which are generally useful media for ordering molecular solutes, are not suitable for ionic compounds because of their general organic nature. Lyotropic nematic phases on the other hand[3-7] are much more sensitive to molecular solutes and undergo transitions to isotropic or lamellar phases at relatively low concentrations of solute. The study of small oriented solute molecules by nuclear magnetic resonance (nmr) spectroscopy is well established[8] and leads in general to structural data in terms of internuclear distance ratios. While X-ray and neutron diffraction have been the only useful tools to determine the structures of ions so far, it is evident that the nmr method of oriented ionic species becomes available and has the advantage that the nuclear positions in ionic structure are determined in an aqueous environment.[2] This report is the first determination of relative atomic positions in an aqueous ion. The dimethyltin ion reported here requires either a ^{13}C nmr spectrum or sensitivity enhancement of the proton spectrum of the ^{13}C-containing ions to determine relative positions of all atoms. Since we are not equipped for this work, the structural information is limited to proton and tin positions.

The thermotropic phase imposes orientation on solute molecules from the uniaxial and parallel alignment to the magnetic field of the molecular tumbling in the nematic solvent. The nature of the lyotropic middle nematic soap phase is quite different. The optic axis of superlattice structures of cylindrical arrangements is perpendicular to the magnetic field in highly and homogeneously aligned samples.[9] The cylinders are composed of hydrophobic hydrocarbon chains in the interior with ionic head groups at the interface and an aqueous counterion environment filling the interior space between varied packing of the cylinders.[10] The complex ion which achieves orientation in the phase does so in an exchange process in the interface region of the oriented electrical double layer. The proposed exchange process in the interstitial water of the nematic phase and with the electrical double-layer interface can be regarded chemically as somewhat analogous to ion-pair formation at the interface and a free-ion environment in the water. The fact that the negative detergent counterions are highly ordered results in transfers of this order to the positive ion during the lifetime in the double layer.

Experimental Section

Spectra were recorded with both a Perkin-Elmer R10 spectrometer at 33.3° and 60 MHz and a Varian T-60 with probe temperature 33.0°. Dimethyltin decyl sulfate was synthesized by ion-exchange methods from sodium decyl sulfate. Dowex 50 H^+ (13 ml) was washed with a dilute aqueous solution (5.5 g/100 ml of water) of dimethyltin dichloride until the eluent was neutral. The column was then washed with 200 ml of water. Sodium decyl sulfate solution (2.6 g/50 ml of water) was then slowly passed down the column followed by 100 ml of distilled water. The eluted solution was evaporated to dryness in a vacuum desiccator. The product was used without further purification to avoid complexation of the dimethyltin ions with organic donor molecules.[11]

The composition of the middle soap phase was 40 wt % dimethyltin decyl sulfate, 50% D_2O, 4% sodium sulfate, and 6% decanol.[2] All nmr spectra were calibrated by the audio side band technique and measured on a frequency counter.

Results

A study of the spectrum of the dimethyltin ion in aqueous solutions was considered necessary because previous work shows the scalar spin-spin coupling $^2J_{H-Sn}$ to be solvent and concentration dependent.[11] Concentrations of dimethyltin dinitrate (prepared by ion exchange) were made up in water so as to cover the region of concentration of the ion in the aqueous part of the nematic phase (1.5-3.0 mol %). The values of J obtained for these solutions were as follows: 1.5 mol %, $J = 102.5 \pm 0.1$ Hz (weighted mean value of J for the tin-117 and tin-119 isotopes); 1.9 mol %, $J = 102.5 \pm 0.1$ Hz; 2.2 mol %, $J = 102.8 \pm 0.1$ Hz; 3.0 mol %, $J = 102.6 \pm 0.1$ Hz. Each determination is the result of eight calibrations of different spectra of each tin satellite. The values are satisfactorily independent of concentration. The environment of an isotropic aqueous solution is sufficiently different from the aqueous part of the nematic phase to warrant a further check on J. Isotropic concentrated micellar[10] solutions of dimethyltin decyl sulfate were prepared in water containing sodium sulfate but omitting the decanol to avoid mesophase formation. The proportions of compounds by weight were

---

* To whom correspondence should be addressed at the Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

(1) Visiting Professor, 1967-present. Research supported by the Banco Nacional de Desenvolvemento Economico (BNDE) and the Fundacao de Amparo a Pesquisa do Estado de Sao Paulo (FAPESP). Expenses provided under the agreement Conselho Nacional de Pesquisas (CNPq) of Brazil and the National Research Council of Canada (NRCC).

(2) (a) L. W. Reeves, J. Sanches de Cara, M. Suzuki, and A. S. Tracey, *Mol. Phys.*, **25**, 1481 (1973); (b) L. W. Reeves, A. S. Tracey, and M. M. Tracey, *J. Amer. Chem. Soc.*, **95**, 3799 (1973).

(3) L. W. Reeves, J. M. Riveros, R. A. Spragg, and J. A. Vanin, *Mol. Phys.*, **20**, 9 (1973).

(4) S. A. Barton, M. A. Raza, and L. W. Reeves, *J. Magn. Resonance*, **9**, 45 (1973).

(5) R. C. Long Jr., S. L. Baugheum, and J. H. Goldstein, *J. Magn. Resonance*, **7**, 253 (1972).

(6) P. J. Black, K. D. Lawson, and T. J. Flautt, *J. Chem. Phys.*, **50**, 542 (1969).

(7) R. C. Long Jr. and J. H. Goldstein, *J. Chem. Phys.*, **54**, 1563 (1971).

(8) P. Deihl and C. L. Khetrapal, "NMR–Basic Principles and Progress," Vol. 1, P. Deihl, E. Fluck, and R. Kosfeld, Ed., Springer-Verlag, New York, N. Y., 1969.

(9) D. M. Chen and L. W. Reeves, *J. Amer. Chem. Soc.*, **94**, 4384 (1972).

(10) G. H. Brown, J. W. Doane, and V. D. Neff, "A Review of the Structure and Physical Properties of Liquid Crystals," Chemical Rubber Co., Cleveland, Ohio, 1971.

(11) B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, **46**, 1399 (1968).