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DIALKYLCYCLOPENTADIENYL DERIVATIVES OF GROUP IIIB ELEMENTS; PREPARATION AND VIBRATION SPECTRAL ANALYSIS

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Summary

The preparation of dialkyl-aluminium, -gallium, and -indium cyclopentadienyls, R_2MCp, is described. For the diethyl derivatives, a detailed analysis of the IR and Raman spectra in both solid and liquid phase clearly rules out a σ-bonded structure. *pentahapto* (h^5) Cyclopentadiene—metal bonding can be established for the diethylaluminium cyclopentadienyl ether adduct; for the uncomplexed compounds, spectral evidence points towards h^2/h^3 bonding.

Introduction

Following the synthesis of diethyl(cyclopentadienyl)aluminium by Giannini and Cesca in 1961 [1], several compounds of the type R_2MCp (M = Group IIIB element, Cp = cyclopentadienyl) have been reported. A crystal structure determination has been carried out on $InCp_3$ (X-ray diffraction at —100°C) [2] and $(CH_3)_2AlCp$ has been studied in both the gaseous phase [3] and solid state [4], but the IR, Raman, and ^{13}C NMR spectral properties of Group IIIB Cp derivatives have not previously been investigated in detail.

For cyclopentadienyl compounds of alkali and earth-alkali metals, ionic or ferrocene-type structures have been reported [5,6]; on the other hand, rapidly fluctuating σ-type carbon—metal bonds have been established for Group IVB cyclopentadienyls [7]. This left open the question of where the Group IIIB derivatives would fit into the wide spectrum of cyclopentadienyl bonding. Along with a reinvestigation of the aluminium compounds, we have therefore synthesized the diethyl Cp derivatives of gallium and indium [8] and studied their vibration spectral behaviour in order to gain some insight into the structure of carbon—metal bonding in these compounds, especially in the liquid state and in solution.

The results of a concurrent ^{13}C investigation of these and other Main Group metal cyclopentadienyl derivatives are reported in an accompanying paper [9].

Methods of preparation

Various routes have been used to make cyclopentadienyl derivatives of Group IIIB elements.

(*a*) Reaction of an organometallic Group III halide with sodium or potassium cyclopentadienide (eq. 1) usually gives the cyclopentadienyl derivatives in satisfactory yield [1,8].

$$R_2M\text{—}Hal + Na(Li,K)Cp \rightarrow R_2MCp + Na(Li,K)Hal \qquad (1)$$

$(R = CH_3, C_2H_5; M = Al, Ga, In; Hal = Cl, Br)$

In this procedure, by far the best solvent is cyclohexane, which does not form donor—acceptor complexes with the product. If the reaction is carried out in benzene or toluene, on the other hand, the solvent cannot be totally removed and is readily detected in the NMR spectrum of the product even after several purifications.

In special cases, the reaction of alkylmetal dichlorides with alkali cyclopentadienide gives the corresponding dialkyl compounds by a transalkylation process [8].

$$(C_2H_5)AlCl_2 + NaCp\ (excess) \rightarrow (C_2H_5)_2AlCp \qquad (2)$$
$$(CH_3)GaCl_2 + NaCp\ (excess) \rightarrow (CH_3)_2GaCp \qquad (3)$$

Methylaluminium dichloride, however, yields the dicyclopentadienyl derivative $(CH_3)AlCp_2$ in a straightforward halogen—alkyl exchange [8].

(*b*) For preparation of thallium and indium cyclopentadienyl derivatives, direct metallation of the diene according to eq. 4 is satisfactory [4,5].

$$R_3M + C_5H_6 \rightarrow R_2M(C_5H_5) + R\text{—}H \qquad (4)$$

However, we were unable to prepare the analogous gallium compounds by this method (other authors have recently reported a similar failure [10]); in the aluminium series, only the n-butyl homologue could be obtained in this way [11].

(*c*) The reaction of cyclopentadiene with a dimethylaminoorganometallic compound has been reported in which the amine ligand is replaced by Cp (eq. 5).

$$(CH_3)_2N\text{—}MR_2 + C_5H_6 \rightarrow (C_5H_5)MR_2 + (CH_3)_2NH \qquad (5)$$

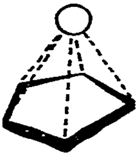
This method, which has so far been used only for $(CH_3)_2InCp$ [10], looks promising for the preparation of the gallium homologues also [12].

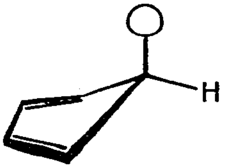
Physical properties

The physical characteristics of the aluminium, gallium, indium as well as of the thallium cyclopentadienyl derivatives have been described in preliminary communications [8,13]. The importance of very careful molecular weight determinations for these compounds must be emphasized once more. To rigorously exclude any possibility of donor—acceptor complex formation with the solvent, we have re-determined the mol.-weight of $(C_2H_5)_2GaCp$ in cyclohexane at various concentrations. The degree of association was found to be 1.4—1.7, i.e. somewhat higher than in benzene solutions [8].

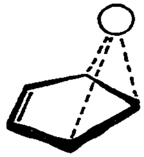
Vibrational spectra

Three different model structures may be envisaged for organometal derivatives of cyclopentadiene; a symmetrical π-complex with a *pentahapto* (h^5) Cp ring (I), a σ-bonded type (II) incorporating a *monohapto* (h^1) cyclopentadienyl moiety, and an asymmetric complex containing *di-* or *trihapto* (h^2/h^3) Cp rings (III).


(I) h^5-type



(II) h^1-type


(III) h^2/h^3-type

Compounds with a purely ionic structure, M^+Cp^-, may be classified as a sub-species (Ia) of the *pentahapto* type I, derivatives with fluctuating carbon—metal bonds as a sub-species of the *monohapto* group II. For differentiation between the basic structures I, II, and III for a given compound, decisive evidence is provided by vibration spectroscopy.

Fritz has shown in a series of papers [14] that cyclopentadienylmetal derivatives may unequivocally be assigned one of the three basic structures, I, II, or III, by examination of their IR and Raman spectral properties. The general validity of his approach has recently been confirmed by the work of Harrison and Healy [15] and of Aleksanyan and his group [16].

For compounds with *pentahapto* cyclopentadienyl moieties having local C_{5v} symmetry for the C_5-ring, all three C—H stretching vibrations which are theoretically possible are expected to give rise to absorptions at frequencies greater than 3000 cm^{-1}. The line of highest energy, belonging to the totally symmetrical C—H vibration and classified as A_1, is found around 3100 cm^{-1} and appears with high intensity in the Raman spectra, and low intensity in the IR. The E_1 and E_2 bands are usually spaced rather closely; definite assignment is nevertheless usually possible since only the E_1 absorption can be observed in the IR.

Since in ionic cyclopentadienides interaction between the metal ion and the ring is very weak, the Cp ring assumes D_{5h} symmetry. Theory again demands three stretching bands above 3000 cm^{-1} thus rendering this spectral region unsuitable for differentiation between structures I and Ia. A clear distinction between the spectra of compounds with *pentahapto* Cp groups of partial symmetry C_{5v} and D_{5h}, respectively, is expected, though, in the C—C(ring) stretching region (1000—1600 cm^{-1}). The main emphasis here must be placed on the ring pulsation mode; while giving an extremely strong Raman line, it is of very low IR intensity for C_{5v} rings and totally IR-inactive for D_{5h} rings. At least in the case of π- and centrally σ-bonded Cp ligands, the frequency of the pulsation band remains almost constant at 1120 cm^{-1} (C_{5v}) and 1000 cm^{-1} (D_{5h}), respectively [17,18].

Compounds containing monohapto cyclopentadienyl groups (local symmetry C_s), on the other hand, are expected to give rise to five or six C—H stretching vibrations, at least one of which should absorb below 3000 cm^{-1}. A vibration equivalent to ring pulsation is no longer possible; instead, there are several distinct C—C stretching modes, of which the one of highest frequency lies between 1500 and 1600 cm^{-1}.

Additional to C—H and C—C stretching bands, the region of certain C—H deformation modes may be utilized for further characterization of the various structural types. These δ and γ C—H deformation modes appear between 600 and 750 cm^{-1} for the C_5H_5 anion; for h^5-rings with local C_{5v} symmetry, they are expected at 700—850 cm^{-1}, and for *monohapto* rings at 750—900 cm^{-1}. The IR bands from these transitions are usually very strong, with the complementary Raman lines having only low intensity.

$(CH_3)_2AlCp$ has been shown by electron diffraction in the gas phase, where it is strictly monomeric, to contain a *di-* or possibly a *tri-hapto* Cp ring (basic structure III) [3]. An h^2 ring has likewise been established by X-ray diffraction for solid $TiCp_3$ [19]. In both these compounds, though, the *polyhapto* (h^2/h^3) rings have approximately fivefold symmetry; thus, their normal mode frequencies are expected to be quite similar to those of true h^5 rings. Since the effective symmetry of such a ring is lowered to C_s by the presence of the metal atom, more modes will be IR and Raman active; consequently, the spectra will contain more lines than in the case of h^5 Cp moieties.

We are not aware of any spectroscopic investigation of compounds containing h^2/h^3 rings. By using the general arguments set out above, it should be possible, to assign one of the basic structures I—III to the cyclopentadienyl derivatives of Group IIIB metals on the basis of their vibrational behaviour. As the degree of association of these compounds varies from 1.3 to 1.7, depending upon concentration and solvent, the presence of oligomeric species must be taken into account, and we shall at first discuss the vibrational data of the strictly monomeric diethylaluminium cyclopentadiene diethyletherate, $(C_2H_5)_2AlCp \cdot O(C_2H_5)_2$.

Both the IR and Raman spectrum of the liquid ether adduct exhibit numerous bands; apart from the dominant skeletal vibrations of the diethylaluminium moiety, however, only those frequencies are listed in Table 1 which are relevant to the structural discussion. Three lines appear in the C—H stretching region, all above 3000 cm^{-1}. A very intense Raman absorption at 1112 cm^{-1}, with an extremely weak matching IR band, can be unequivocally assigned to the C_5 ring pulsation. The group of lines with high intensity between 760 and 790 cm^{-1} mainly originates from the pronounced C—H deformational modes of the Cp ring superimposed, however, on the fundamental vibrations of the complexed ether molecule. This spectral evidence is compatible only with an h^5 cyclopentadienyl ring structure for the etherate (type I); there are no additional lines indicative of a symmetry lower than C_{5v}.

For a spectroscopic characterization of the ether-free compounds, the diethyl derivatives of both aluminium and gallium are the most suitable since they are very soluble, and as low melting compounds may also be subjected to polarized Raman analysis. In Table 2, the dominant absorption band frequencies of the IR and Raman spectra taken with molten $(C_2H_5)_2AlCp$ and $(C_2H_5)_2GaCp$ are listed

TABLE 1

MAJOR IR AND RAMAN SPECTRAL FREQUENCIES OF DIETHYLALUMINIUM CYCLOPENTADIENE—DIETHYL ETHERATE (ν (cm^{-1}), intensity [a])

IR	Raman	Assignment
3098vvw(sh)	3091s-m(p)	ν_s(CH)(a_1)
3078m		$\}\nu$(CH) (e_1)
	3065m-w(br)(dp)	(e_2)
1460s-m(br)	1455m(dp)	ν(C—C)(e_2) + δ_{as}(CH$_3$)(Al—C$_2$H$_5$)
1395s	1391m-w(dp)	ν(C—C)(e_1) + δ(CH$_2$)(Al—C$_2$H$_5$)
1195s-m	1190s-m(p)	δ_s(CH$_2$)(Al—C$_2$H$_5$)
1113vw	1112vs(p)	ring-breathing (c_1)
1076vvw	1073w(dp)	δ(CH$\perp$)(e_2)
1039s	1045m-w(p)	ν(C—O—C)($\leftarrow$O(C$_2$H$_5$)$_2$)
995s	998m(dp)	δ(CH$\|$)(e_1) + ν(C—C)(Al—C$_2$H$_5$)
955m	955m-w(p)	ν_s(C—C)(Al—C$_2$H$_5$)
895s-m	891w(dp)	δ(ring)(e_1?)
784 vs(br)	779m-w(sh)(dp)	$\}\delta$(CH$\perp$)(a_1 + e_1) + ν(C—C)($\leftarrow$O(C$_2$H$_5$)$_2$)
768	765m(p)	
635vs	632m(dp)	ν_{as}(AlC$_2$) + ρ(CH$_2$)(Al—C$_2$H$_5$)
538m	536s(p)	ν_s(AlC$_2$)

[a] Band intensities are signified by the following symbols: s, strong; m, medium; w, weak; v, very; (sh), shoulder; (br), broad; (p), polarized; (dp), depolarized.

along with the proposed assignments. We have likewise analyzed the solid state spectra of $(CH_3)_2AlCp$ [4] and $(CH_3)_2GaCp$ as well as those of $(C_2H_5)_2GaCp$ and $(C_2H_5)_2InCp$ [8,12]. Apart from the fundamental vibrations of the C—M—C skeleton, the spectra of all these compounds are quite similar, the liquid film traces of both diethyl-aluminium and -gallium cyclopentadienyl being almost identical. Marked differences appear, though, in comparison with the spectrum of the etherate discussed above. Of these, the increased number of Raman lines in the cyclopentadienyl C—H stretching region above 3000 cm^{-1} is most striking. There are four lines for the molten state, and five for the solid state spectra; additionally, one might guess at further C—H valence bands below 3000 cm^{-1} but obscured by C—H stretching bands of the alkyl groups. According to the general criteria discussed above, these Raman data indicate that the local symmetry of the Cp ring is in fact lower than C_{5v}. Since there is no equivalent number of C—H absorptions in the IR spectra, and since the other two "characteristic regions" do not meet the conditions set out for h^1-bonded rings, *monohapto* cyclopentadienyl ligands cannot be present in either the Al or the Ga compound in the liquid or solid phase. Rather, as the spectra of both products incorporate all major absorptions of the etherate, with only insignificant frequency shifts and intensity changes, the cyclopentadienyl bonding in the ether-free compounds must be close to that in the etherate.

For cyclopentadienyl derivatives uncomplexed by R_2O, association becomes more and more likely when going from dilute solution to the molten and then to the solid state. Since the melt almost certainly consists of a mixture of monomeric and associated species incorporating cyclopentadienyl ligands in a bridging position between two metal atoms [4,8,12], straightforward spectral assignment is not possible. However, the Raman spectra of dilute solutions in which the monomer must be the predominant species still differ from the spec-

TABLE 2

MAJOR IR AND RAMAN SPECTRAL FREQUENCIES OF DIETHYLALUMINIUM- AND DIETHYL-GALLIUM CYCLOPENTADIENYL (liquid capillary film, ν (cm^{-1}), intensity [a])

$(C_2H_5)_2Al(C_5H_5)$		$(C_2H_5)_2Ga(C_5H_5)$		Assignment
IR	Raman	IR	Raman	
3110vw(sh)	3105s-m(p)	3106vw(sh)	3100s(p)	ν_s(CH)(Cp)
3080 3075 }m	3086m-w(br)(dp)	3078 3069 }m	3080m-w(dp)	ν(CH)(Cp)
	3040w(br)(dp)		3048w(br)(dp)	
	3019w(p^*) [b]		3035vw(br)(dp)	
1463 1456 }s-m	1468m(dp)	1458s-m(br)	1470m(dp)	ν(C—C)(Cp) + $\delta_{as}(CH_3)(M—C_2H_5)$
	1455(sh)(dp)		1458(sh)(dp)	
1360vw(sh)	1353m(p^*) [b]	1361vw(sh)	1362m(p^*) [b]	ν(C—C)(Cp)
1194m	1192s(p)	1191m-w	1195s(p)	$\delta_s(CH_2)(M—C_2H_5)$
1112w	1113vs(p)	1110vw	1112vs(p)	ring-breathing
1075m-w	1075(sh)(dp)	1072w	1080(sh)(dp)	δ(CH)(Cp)
1060m-w(br)	1067s-m(p)	1051m-w	1064s-m(p)	δ(CH)(Cp) + ν_s(C—C)(oligomer?)
988s(br)	988m-w(br)(dp)	1000s	1003m-w(br)(dp)	δ(CH)(Cp) + $\nu(C—C)(M—C_2H_5)$
		983m		
961m	958m-w(p)	961m	968m-w(p)	$\nu(C—C)(M—C_2H_5)$
840m-w	842m-w(sh)(dp)	833m	838(sh)(dp)	δ(C—C)(Cp)
	825m(dp)		824m(dp)	
786vs	788vw(p)	798vs	794vw(p)	δ(CH)(Cp)
755s-m	756vw(dp)	750s	749vw(dp)	
630vs(br)	642m-w(dp)	655vs(br)	634vw(br)(dp)	$\rho(CH_2)(M—C_2H_5) + \nu_{as}(AlC_2)$
		561s	560m-w(dp)	$\nu_{as}(GaC_2)$
537m	533vs(p)	510s-m	512vvs(p)	
	433m-w(p)		355w(p)	ν(M—Cp) (monomer + oligomer), δ_s(M—C—C), $\delta_s(MC_2)$
375s-m		325s-m		
	345m(br)(dp)		295s-m(p)	
310m(br)		285m(br)		
			258m-w(p)	

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[a] For the band intensity symbols, see *footnote a*, Table 1. [b] *Partially depolarized bands.*

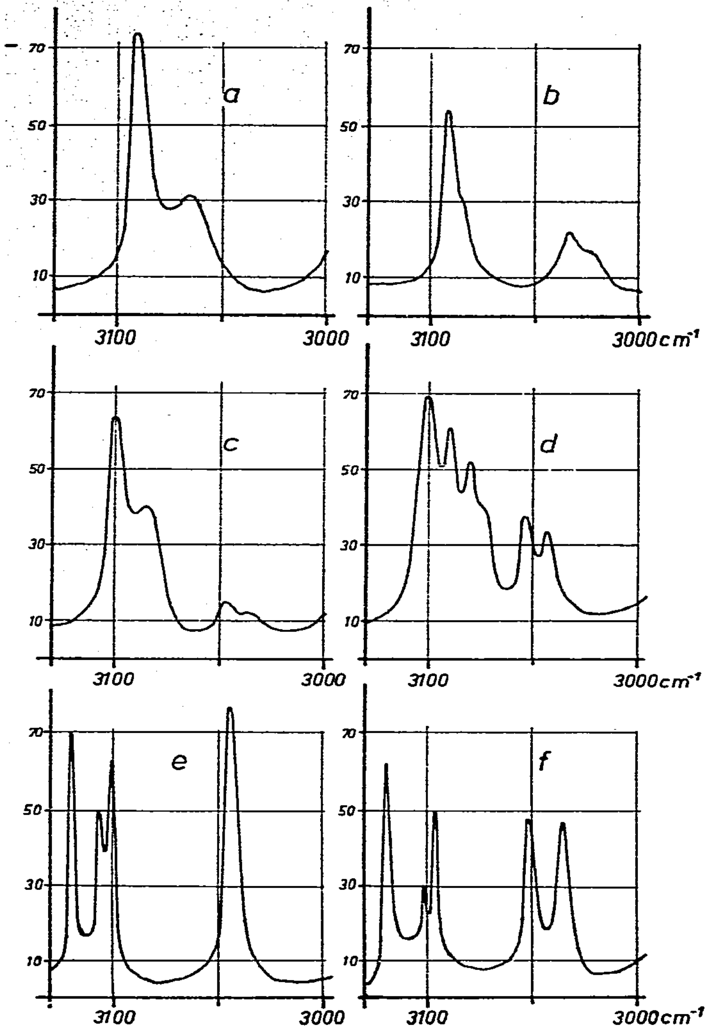

Fig. 1. C—H stretching region of the Raman spectra of dialkylaluminium and dialkylgallium cyclopentadienyls in both liquid and solid phase: (a) $(C_2H_5)_2AlCp \cdot O(C_2H_5)_2$, liquid phase; (b) $(C_2H_5)_2AlCp$, liquid phase; (c) $(C_2H_5)_2GaCp$, liquid phase; (d) $(C_2H_5)_2GaCp$, solid phase; (e) $(CH_3)_2AlCp$, solid phase; (f) $(CH_3)_2GaCp$, solid phase.

trum of the etherate, thus indicating that the monomer may contain cyclopentadienyl rings with local symmetry lower than C_{5v}. Spectral traces illustrating the changes observed in Raman spectra between liquid (melt) and solid phase are given in Fig. 1.

To eliminate effects due to possible ring fluctuations which have been established even for the solid state [20], IR spectra were also run at −160°C but the IR spectra were temperature invariant.

Conclusions

By the vibration spectral evidence detailed above, the Cp ring of diethylaluminium cyclopentadiene etherate was unequivocally established to be h^5-

bonded, with the metal atom on the fivefold axis of the ring. Such a true π-complex structure has been demonstrated previously (by various spectroscopic methods and crystal structure analysis) only for transition metal derivatives; but their vibrational spectra cannot be compared directly with those of our compounds. Main Group element complexes of this type, on the other hand, have so far only been studied in crystalline state where these molecules are invariably oligomeric or polymeric. It is thus not possible to state whether the small discrepancies between the cyclopentadiene partial spectra of the ether adduct and those of established π-complexes are to attributed to the different central atom (Main Group vs. transition metal) or to a slightly different type of central (h^5) bonding.

As shown by mol.-weight determinations in both cyclohexane and benzene, the ether-free compounds are associated even in dilute solution; in the aggregates, two MR_2 moieties are interconnected by one Cp group. Similar results have been obtained for $InCp_3$: in crystalline $InCp_3$ [2], each In atom is surrounded by two terminal *monohapto* cyclopentadienyls and by two bridging Cp rings with approximately fivefold symmetry. Since the contact to the two indiums is from C(1) and C(3), respectively, the local symmetry of the bridging cyclopentadienyl rings is lowered to C_2. By replacing the terminal *monohapto* Cp moieties of $InCp_3$ with alkyl groups, a reasonable model may be obtained for solid R_2MCp compounds which is in good agreement with the vibrational data.

The spectra of liquid Et_2AlCp and Et_2GaCp likewise show the presence of Cp rings with only approximately fivefold symmetry. Since these compounds are partly associated even in dilute hydrocarbon solution, the melts may safely be assumed to contain monomeric as well as associated species. The three or four Raman lines in the cyclopentadienyl stretching region therefore are no proof of Cp rings with local symmetry lower than C_{5v}. However, the spectra even of dilute solutions (with predominantly monomeric species) are still different from the spectrum of $Et_2AlCp \cdot OEt_2$, thus indicating that Cp ring symmetry in the monomer is probably somewhat lower than C_{5v}. This agrees well with the results of an electron diffraction study of (monomeric) Me_2AlCp in the gas phase where an h^3 ring has been found [3].

Experimental

The starting materials, i.e. LiCp, NaCp, KCp, and the alkyl halides of the Group IIIB elements, were prepared as described in the literature. All reactions were carried out under dry nitrogen.

The preparations of aluminium cyclopentadienyl derivatives have been described previously [8].

R_2GaCp: A solution of 18.45 g (0.113 mol) Et_2GaCl or 15.28 g (0.113 mol) Me_2GaCl, respectively, in 40 ml cyclohexane was added dropwise with vigorous stirring to a suspension of 10.0 g (0.113 mol) NaCp in 40 ml cyclohexane. To ensure complete reaction, the mixture was stirred for 2 h at 70—75°C. The hot mixture was then filtered, and the solvent stripped off. Crude yield 10.5 g Et_2GaCp (45%) and 4 g Me_2GaCp (20—30%), respectively. Both products were purified by either distillation or sublimation; melting and boiling points and elemental analyses have already been reported [8].

R_2InCp: Because of the low solubility of the dialkylindium halides, the reaction was carried out by mixing a suspension of 10.0 g (0.113 mol) NaCp in 100 ml cyclohexane with a suspension of 23.5 g Et_2InCl or 20.3 g Me_2InCl (0.113 mol in each case) in 150 ml cyclohexane. After evaporation of the solvent, the crude products were obtained in a 30—40% yield.

IR spectra were taken of either the neat liquids or of Nujol or Hostaflon mulls, pressed as capillary films between CsBr plates, and recorded on a Beckman IR 12 or a Perkin—Elmer PE 457 spectrometer. Raman spectra were measured on a PH O spectrometer of Coderg, Inc., employing the blue-green (4880 Å) line of an Ar laser for excitation.

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