The Dicyclopentadienyllanthanide Chlorides

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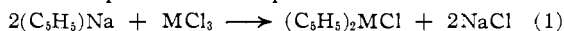
The dicyclopentadienyllanthanide chlorides of Sm, Gd, Dy, Ho, Er, Yb and Lu have been prepared by treating the respective trichlorides with two equivalents of cyclopentadienylsodium in tetrahydrofuran. These derivatives were also prepared by treating the tricyclopentadienyllanthanides with the corresponding lanthanide trichlorides. Similar complexes of the lower lanthanides La, Ce, Pr and Nd could not be prepared. Magnetic susceptibility measurements, coupled with the chemical properties of the complexes, indicate that ionic type forces bond the cyclopentadienyl rings to the central lanthanide which is formally in a tripositive state. The chloride ion in the complexes can be displaced with other anions which in some cases enables the preparation of the corresponding amide, methoxide, phenoxide and acylate derivatives.

The absence of organo complexes of the lanthanide series comparable in quantity to the wide variety of derivatives prepared with the transition metals indicates the lack of similar type bonding forces in the series. The only organolanthanide complexes approaching those in the transition metal series were reported by Birmingham and Wilkinson[2], who isolated a number of tricyclopentadienyllanthanides. These authors considered their complexes as being held together by essentially localized ionic type interactions between a central tripositive lanthanide cation and the surrounding cyclopentadienyl anions. The reported physical and chemical properties strongly support such bonding, as opposed to delocalized bonding involving π-electrons of the rings which is so widespread in the cyclopentadienyl derivatives of the transition metals.[3]

In an attempt to expand the organolanthanide field we have prepared a novel class of complexes, the dicyclopentadienyllanthanide chlorides, of the elements from samarium to lutetium. The chemical and physical properties of these complexes are quite similar to those of the tricyclopentadienyllanthanides and the bonding involved is also believed to be essentially ionic.

The dicyclopentadienyllanthanide chlorides can be prepared by treating the trichlorides with two equivalents of cyclopentadienylsodium in tetrahydrofuran at room temperature. This mode of preparation and the lanthanide derivatives that have been prepared are illustrated in eq. 1. The compounds

$$2(C_5H_5)Na + MCl_3 \longrightarrow (C_5H_5)_2MCl + 2NaCl \quad (1)$$
$$M = Sm, Gd, Dy, Ho, Er, Yb, Lu$$

were all isolated by sublimation of the reaction residues at 150–250° (10^{-5} mm.) with yields in the order of 50 to 60%. Di-(methylcyclopentadienyl)-lanthanide chlorides of gadolinium, erbium and ytterbium were also prepared in this manner, although they were sublimed at somewhat lower temperatures. A summary of the elemental analysis of these complexes is shown in Table I.

Under nitrogen or vacuum the above lanthanide derivatives are stable indefinitely. In air, however, they decompose in a matter of minutes. The dicyclopentadienyl chlorides are soluble in tetrahydrofuran, but are insoluble in hydrocarbons and carbon disulfide and are readily decomposed with protolytic solvents. The methylcyclopentadienyls are somewhat more soluble in tetrahydrofuran, benzene and carbon disulfide and are even slightly soluble in petroleum ether. They are also readily decomposed with protolytic solvents. A summary of some physical properties of the complexes is listed in Table II.

Ebulliometric molecular weight determinations on the di-(methylcyclopentadienyl)-lanthanide chlorides

(1) To whom all inquiries should be forwarded.

(2) J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956).

(3) F. A. Cotton, "Progress in Inorganic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1959.

TABLE I

ANALYSIS OF DICYCLOPENTADIENYLLANTHANIDE CHLORIDES [C_5H_5]$_2$MCl

	Calcd.				Found			
Metal	C	H	Cl	M	C	H	Cl	M
Sm	38.0	3.19	11.2	47.6	39.0	3.28	11.0	47.3
Gd	37.2	3.12	11.0	48.7	36.7	3.17	10.6	49.5
Dy	36.6	3.08	10.8	49.5	36.8	3.11	10.8	48.7
Ho	36.3	3.06	10.7	49.9	36.3	3.13	10.8	50.0
Er	36.1	3.03	10.7	50.2	36.3	3.10	10.5	49.7
Yb	35.5	2.95	10.5	51.1	34.8	3.04	10.5	49.2
Lu	35.3	3.00	10.4	51.3	35.9	3.20	10.5	51.5

ANALYSIS OF DI-(METHYLCYCLOPENTADIENYL)-LANTHANIDE CHLORIDES [C_6H_7]$_2$MCl

	C	H	Cl	M	C	H	Cl	M
Gd	41.07	4.02	10.1	44.8	41.3	4.02	9.87	44.5
Er	39.9	3.91	9.82	46.3	40.3	3.86	10.0	46.2
Yb	39.3	3.85	9.68	47.2	39.5	3.92	10.1	46.9

TABLE II

PROPERTIES OF THE DICYCLOPENTADIENYLLANTHANIDE CHLORIDES (C_5H_5)$_2$MCl

Metal	Color	Thermal properties (under N$_2$)	Molecular weight Found	Molecular weight Calcd.
Sm	Yellow	No. m.p. progressive dec. from 200°	..	..
Gd	Colorless	No m.p. progressive dec. from 140°	375^a	323
Dy	Yellow	M.p. 343–346° with sl. dec.	..	..
Ho	Yellow-orange	M.p. 340–343° with dec.	..	..
Er	Pink	No. m.p. progressive dec. from 200°	340^a	333
Yb	Orange-red	No m.p. progressive dec. from 240°	353^a	339

(C_6H_7)$_2$MCl (METHYLCYCLOPENTADIENYLS)

Metal	Color	Thermal properties	Molecular weight Found	Molecular weight Calcd.
Gd	Colorless	M.p. 188–197°	394^a 746^b	351
Er	Pink	M.p. 119–122°	759^b	361
Yb	Red	M.p. 115–120°	395^a 757^b	368

^{a} Ebulliometric in tetrahydrofuran. ^{b} Ebulliometric in benzene.

show that they are dimeric in benzene but monomeric in tetrahydrofuran. This dimeric nature indicates that the chloride ion partakes in bridge type bonding as illustrated in structure I.

I, M = Gd, Er, Yb
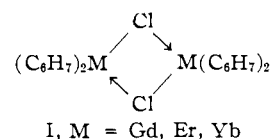
Such bonding must be relatively weak since tetrahydrofuran is a sufficiently strong base to dissociate the dimer through solvation and thus render it monomeric in this medium. Since the dicyclopentadienyllanthanide chlorides do not possess sufficient solubility in benzene or other non-polar media a similar molecular weight behavior could not be demonstrated. However, it could

be reasonably assumed that they would be dimeric in non-polar systems due to a similar involvement of the chloride ions in bridge type bonding.

Support for the viewpoint that the cyclopentadienyl groups in the dicyclopentadienyllanthanide chlorides are bonded by simple localized ionic type interactions is based on the physical and chemical properties of the complexes. The cyclopentadienyl ring is quite reactive in a manner characteristic of the ionically bonded cyclopentadienylmagnesium Grignard. All the complexes react instantaneously with protolytic solvents to liberate cyclopentadiene, and, in the case of dicyclopentadienylerbium chloride, treatment with ferrous chloride produces ferrocene in excellent yield. The insolubility of the unsubstituted cyclopentadienyl derivatives in non-polar solvents and the relatively low volatility and high melting points similarly suggest ionic type bonding. Evidence in support of the absence of any type of bonding which would induce spin coupling of electrons in the 4f levels of the lanthanides is provided by magnetic susceptibility measurements.[4] The experimental effective magnetic moments for all of the dicyclopentadienyllanthanide chlorides were determined using the Curie–Weiss law and are listed in Table III. A comparison of the experimental μ_{eff} with the

TABLE III

MAGNETIC DATA FOR SOME DICYCLOPENTADIENYLLANTHANIDE CHLORIDES

Compound	Temp., °K.	χ_{Mol}^{Corr} $\times 10^{6a}$	Δ, °C.	Exptl. μ_{eff}	Theor. μ_{eff}^{b}	Oxidation state of metal
Er(C$_5$H$_5$)$_2$Cl	300	36480	29	9.79	9.8	+3
	195	53600				
Yb(C$_5$H$_5$)$_2$Cl	301	7141	108	4.81	4.5	+3
	195	9644				
Gd(C$_5$H$_5$)$_2$Cl	301	24610	98	8.86	7.94	+3
	195	33533				
Lu(C$_5$H$_5$)$_2$Cl	300	−13	..	0	0	+3
Ho(C$_5$H$_5$)$_2$Cl	300	43110	10	10.3	10.4	+3
	195	65200				
Dy(C$_5$H$_5$)$_2$Cl	300	45000	11	10.6	10.6	+3
	195	52891				
Sm(C$_5$H$_5$)$_2$Cl	300	1068	0^c	1.62	1.65	+3
			50	1.74		
			100	1.94		
	195	1145				

^{a} Includes correction of −116 × 10^{-6} for 2 C$_5$H$_5^-$ rings and 1 Cl$^-$. ^{b} Values from P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 142; see also J. M. Birmingham and G. Wilkinson, J. Am. Chem. Soc., 78, 42 (1956). ^{c} These values of Δ were assumed for the samarium compound, the true value being uncertain because Δ varies for samarium.

theoretical μ_{eff} for lanthanides in the tripositive state strongly suggests that the central lanthanide in our derivatives is in such an oxidation state with no disruption of the inner 4f levels.

In addition to the direct synthesis of the dicyclopentadienyllanthanide halides as illustrated in eq. 1 they can also be prepared by methods utilizing the tricyclopentadienyllanthanides. Thus, treatment of a lanthanide trichloride in tetrahydrofuran with its respective tricyclopentadienyl derivative yields the desired complex, as shown in eq. 2, in good yield for all the lanthanides studied.

$$2(C_5H_5)_3M + MCl_3 \longrightarrow 3(C_5H_5)_2MCl \qquad (2)$$
M = Sm, Gd, Dy, Ho, Er, Yb
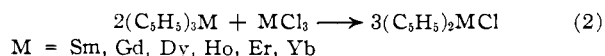
The reaction involves a simple redistribution of anions and lends additional proof of the ionic nature of the cyclopentadienyl–lanthanide bond. Free halogens and the anhydrous hydrogen halides react with equivalent quantities of the tricyclopentadienyllanthanides to

yield the monohalogen derivatives. Dicyclopentadienylytterbium chloride was prepared in good yields by treating tricyclopentadienylytterbium with hydrogen chloride in tetrahydrofuran, and an equivalent of iodine will react with tricyclopentadienylerbium to yield dicyclopentadienylerbium iodide. These reactions illustrate a number of approaches that can be utilized in synthesizing not only the monohalogen derivatives but, with the proper choice of acids, halogens and lanthanide salts of a wide variety of other dicyclopentadienyllanthanide complexes.

Despite the fact that the dicyclopentadienyllanthanide chlorides of the higher lanthanides from samarium to lutetium can be readily prepared, all attempts to prepare similar derivatives of the lower lanthanides neodymium, praseodymium, cerium and lanthanum have failed. The approach as illustrated in eq. 1 was completely inadequate and in the case of lanthanum, cerium and praseodymium only traces of the corresponding tricyclopentadienyllanthanide could be detected. Neodymium, however, yielded a material which appeared to be a mixture of the desired compound, dicyclopentadienylneodymium chloride, and tricyclopentadienylneodymium. This mixture could not be resolved by either fractional recrystallization or sublimation. Identical results were obtained when an attempt was made to redistribute the anions between the tricyclopentadienyls and the respective trichlorides as illustrated in eq. 2. Treatment of the lower tricyclopentadienyllanthanides with free halogens or anhydrous hydrogen chloride, techniques that were successful in the case of erbium and ytterbium, also failed to yield the desired products. From the results thus far accumulated, samarium is the lowest lanthanide that will yield a dicyclopentadienyl chloride with our reaction schemes. Neodymium exhibits transition-like properties and yields a mixture of unresolved products whereas praseodymium, cerium and lanthanum simply do not form dicyclopentadienyl chlorides. The exact reason for this behavior in the lanthanide series is unknown to us but it could broadly be attributed to the lanthanide contraction.[5] If so, our data are a remarkable illustration of the influences of small changes in ionic radii, coupled with an increase in atomic number, upon the accessibility of the dicyclopentadienyllanthanide chlorides.

The chloride ion in the dicyclopentadienyllanthanide chlorides can be readily displaced with a variety of other anions. Treatment of some of the complexes at room temperature in tetrahydrofuran with sodium methoxide, sodium amide and the sodium carboxylates yields the corresponding substitution products as illustrated in eq. 3. Some of the properties and elemental

$$NaY + (C_5H_5)_2MCl \longrightarrow (C_5H_5)_2MY + NaCl \qquad (3)$$
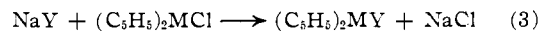
analyses of a series of derivatives prepared in this manner are illustrated in Table IV. Although the metal analyses are consistently low as shown in the table, the carbon and hydrogen contents are in complete accord with the proposed products.

A wide variation in properties is exhibited by the above substitution products. The methoxide and amide derivatives resemble the parent chlorides in that they are very reactive both hydrolytically and oxidatively and decompose in a matter of minutes when exposed to air. Their solubility properties are also comparable to the parent chlorides although, in contrast, the methoxy derivative possesses fairly good solubility in benzene and carbon disulfide. They can be sublimed at 160–200° (10^{-5} mm.) in a manner comparable to

(4) We are indebted to Mr. William Bos and Professor Stanley Kirschner, Wayne State University, for the magnetic susceptibility measurements.

(5) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 1, Oxford University Press, London, 1950, p. 445.

TABLE IV

SUBSTITUTION PRODUCTS OF THE DICYCLOPENTADIENYLLANTHANIDE CHLORIDES

$(C_5H_5)_2MCl + NaY \longrightarrow (C_5H_5)_2MY + NaCl$

M	Y	Yield, %	Color	M.p., °C.	Analyses, %					
					Calcd.			Found		
					C	H	M	C	H	M
Er	$-O\overset{O}{\overset{\|}{C}}CH_3$	45	Pink	331–335 d.	40.4	3.68	46.9	41.1	3.77	45.5
Yb	$-O\overset{O}{\overset{\|}{C}}CH_3$	65	Orange	325–329 d.	39.8	3.62	47.8	40.0	3.75	45.6
Gd[a]	$-O\overset{O}{\overset{\|}{C}}CH_3$	65	White	207–209	44.9	4.58	42.0	45.1	4.61	41.3
Er[a]	$-O\overset{O}{\overset{\|}{C}}CH_3$	55	Pink	199–201	43.7	4.46	43.5	43.8	4.42	44.2
Yb	$-O\overset{O}{\overset{\|}{C}}C_6H_5$	54	Orange	350–375 d.	48.1	3.56	40.8	48.9	3.64	38.4
Er	$O-\overset{O}{\overset{\|}{C}}H$	27	Pink	Dec. >270	38.6	3.24	48.8	39.0	3.33	49.5
Dy	$-OCH_3$	5	Yellow	Dec. >235	40.8	4.05	50.9	41.2	4.35	48.7
Er	$-OCH_3$	52	Pink	236–240	40.2	3.99	50.9	40.0	4.25	50.0
Yb	$-OCH_3$	60	Orange	290–305	39.5	3.92	51.8	39.4	4.01	49.8
Er	$-NH_2$	33	Pink	330–334	38.3	3.86		38.6	3.95	
Yb	$-OC_6H_5$	64	Red	382–386	48.5	3.82	43.7	48.8	3.91	41.4

[a] Substitution carried out on the di-(methylcyclopentadienyl)-lanthanide chlorides $(C_6H_7)_2MCl$.

the chlorides. Dicyclopentadienylytterbium phenoxide, which in volatility is comparable to the respective chloride, is somewhat soluble in tetrahydrofuran but is completely insoluble in benzene and carbon disulfide. In contrast to the chloride, this derivative is strikingly stable oxidatively and can be exposed to air for a number of days without much change. The carboxylate derivatives, formate, acetate and benzoate, also exhibit marked stability to air oxidation relative to the parent chlorides. All the complexes are, however, unstable hydrolytically, much in the same way as a Grignard reagent. The carboxylates possess somewhat similar solubilities; the formate derivative is soluble in tetrahydrofuran and is only slightly soluble in benzene whereas the acetates and benzoates exhibit less solubility in these solvents.

The molecular weight of di-(methylcyclopentadienyl-erbium acetate was found to be 811 in boiling benzene (monomer = 385). This indicates that the complex exists as a dimer in this solvent. The most probable structure for the dimer would involve the acetate ion as a bridging group as illustrated in structure II.

CH₃ structure II.
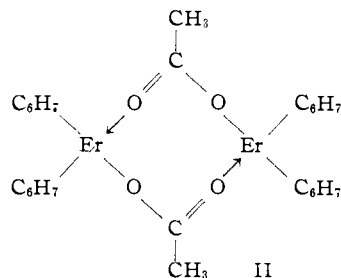
An unequivocal proof of the bridge nature of the acetate ion will require a complete X-ray diffraction study on the solid. Although molecular weight studies on the unsubstituted dicyclopentadienyllanthanide acetate, benzoate and formate derivatives were not made due to their low solubility in benzene, it can be reasonably assumed that they would also exist as dimers in this solvent. Their marked stability relative to the parent chlorides is probably a result of the chelating effect displayed by the acetate ion which in turn stabilizes the ring metal bond.

Although the formation and isolation of dicyclopentadienyllanthanide acetates from the corresponding chlorides appears to be general with our presently employed techniques, differences between members in the lanthanide series have been observed with other reaction systems. Thus, dicyclopentadienylerbium formate is readily formed in the manner depicted in eq. 3 and is isolated by sublimation of the dry reaction mixture; however, the formates of gadolinium and ytterbium cannot be isolated as well defined products with the same procedure. Similarly, dicyclopentadienylerbium amide can be formed by substitution, but the amides of gadolinium and ytterbium cannot be isolated. This lack of generality for the preparation of similar types of complexes with each of the lanthanides demonstrates the differences in chemical properties between the members of the series. These examples are most likely related to differences in thermal stability of the complexes, and if suitable alternative isolation procedures other than sublimation at high temperatures are employed the products of reaction may be isolated. This is borne out in the preparation of dicyclopentadienylytterbium formate which, as mentioned, cannot be isolated by sublimation of the dry reaction mixture prepared in accordance with eq. 3. The complex can be prepared with an alternative procedure by treating tricyclopentadienylytterbium with formic acid as shown in eq. 4 and isolating it by crystallization. In view of this result it is probable that the amide derivatives of gadolinium and ytterbium will be readily accessible by

$$(C_5H_5)_3Yb + HO\overset{O}{\overset{\|}{C}}H \xrightarrow{THF} (C_5H_5)_2YbO\overset{O}{\overset{\|}{C}}H + C_5H_6 \quad (4)$$
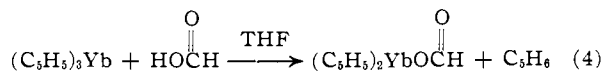
a suitable modification of the preparative or isolation methods.

Experimental

All manipulations were performed under an atmosphere of prepurified nitrogen and the anhydrous solvents utilized were always freshly distilled and protected from the atmosphere. The anhydrous lanthanide chlorides were prepared from the commercially available hydrates by treatment with thionyl chloride.[6] Cyclopentadienylsodium and methylcyclopentadienylsodium were prepared by treating the freshly distilled monomers with sodium dispersion in tetrahydrofuran.

(6) Inorg. Syntheses. 5, 153 (1957).

The dicyclopentadienyllanthanide chlorides were prepared by utilizing two general methods. Procedure A involved treatment of the anhydrous trichlorides with two equivalents of cyclopentadienylsodium and, where the methylcyclopentadienyl derivative was sought, methylcyclopentadienylsodium was employed. In procedure B, the tricyclopentadienyllanthanides were treated with the respective trichlorides. Since the procedures are common to all the investigated lanthanides, only the examples with lutetium and holmium are described. All melting points are uncorrected and were taken under nitrogen in sealed capillaries.

Molecular Weight Determinations.—Molecular weight values in benzene were determined by employing the standard differential ebulliometric techniques with high purity benzene. The determinations in tetrahydrofuran were made with the aid of anthracene as an internal standard in order to compensate for trace impurities in this solvent.

Preparation of Dicyclopentadienyllutetium Chloride (Procedure A).—A solution of cyclopentadienylsodium (0.048 mole) was added to a dispersion of 7.4 g. (0.026 mole) of anhydrous lutetium trichloride in 100 ml. of tetrahydrofuran. The resulting pale orange suspension was stirred overnight at room temperature and the solvent was then removed under vacuum leaving a yellow residue. Sublimation of this residue at 170–240° (10⁻⁵ mm.) yielded 6.3 g. (72%) of pale greenish-white crystals, m.p. 318–320°. The major infrared absorption peaks occurred at 3300, 1625, 1440, 1350, 1010 and 890 cm.⁻¹. All the dicyclopentadienyllanthanide chlorides studied possessed identical infrared spectra.

Preparation of Dicyclopentadienylholmium Chloride (Procedure B).—To a solution of 1.5 g. (0.0042 mole) of tricyclopentadienylholmium in 100 ml. of tetrahydrofuran 1.14 g. (0.0042 mole) of holmium trichloride was added with stirring. The resulting yellow-orange solution was allowed to stir for 2 days at room temperature. The solvent was then removed at reduced pressure and the resulting orange-brown residue was sublimed at 210° (10⁻⁵ mm.) for 5 hours. The yield of pale yellow crystals of dicyclopentadienylholmium chloride was 0.7 g. (50%), m.p. 340–342°.

Reaction of Tricyclopentadienylytterbium with Hydrogen Chloride.—A green solution of 1.41 g. (0.0038 mole) of tricyclopentadienylytterbium in 75 ml. of tetrahydrofuran was treated with 25 ml. of tetrahydrofuran containing 0.0038 mole of hydrogen chloride. The addition was carried out at room temperature with rapid stirring over a period of 45 minutes. Stirring of the clear orange reaction mixture was continued overnight and the solvent was then removed at reduced pressure. Sublimation of the orange residue at 220° (10⁻⁵ mm.) yielded 0.9 g. (70%) of red crystalline dicyclopentadienylytterbium chloride.

Reaction of Tricyclopentadienylerbium with Iodine.—To a cloudy orange solution of tricyclopentadienyl erbium, 2.06 g. (0.0057 mole) in 100 ml. of tetrahydrofuran, was added a solution of 0.82 g. (0.0032 mole) of iodine in 60 ml. of tetrahydrofuran. The addition was carried out over a period of 75 minutes at room temperature with rapid stirring which was continued for an additional 2 hours. The solvent was then removed under reduced pressure and the residue was sublimed at 150–250° (10⁻⁵ mm.) to yield 1.4 g. (58.3%) of pink crystalline dicyclopentadienylerbium iodide.

Anal. Calcd. for C₁₀H₁₀ErI: C, 28.30, H, 2.37; Er, 39.4; I, 29.9. Found: C, 28.9; H, 2.50; Er, 39.1; I, 29.8.

This material was soluble in tetrahydrofuran and acetone, somewhat soluble in benzene but insoluble in low boiling petroleum ether. Sealed in a tube under nitrogen the material turned gray-brown in the region of 250° and melted at 270°.

Treatment of the tricyclopentadienyls of lanthanum, praseodymium and neodymium under the above conditions failed to yield the desired mono-iodo product.

The Preparation of Dicyclopentadienylerbium Methoxide.—Sodium methoxide (0.22 g., 0.004 mole) was added to dicyclopentadienylerbium chloride (1.35 g., 0.0041 mole) dissolved in 100 ml. of tetrahydrofuran. The mixture was allowed to stir at room temperature overnight and then it was refluxed for 5 hours. Removal of solvent under reduced pressure yielded an orange-brown residue which was sublimed at 160–290° (10⁻⁵ mm.). The sublimate, a light pink solid, was isolated in a yield of 0.7 g. (52%), m.p. 236–240°.

The dicyclopentadienyl methoxides of dysprosium and ytterbium were prepared in an identical manner with yields and analysis indicated in Table IV. All of the methoxide derivatives possess similar infrared absorption spectra in carbon disulfide with absorptions at 1035, 1012 and 972 cm.⁻¹ (strong); 2935, 2810 and 1250 cm.⁻¹ (medium); and at 1640, 831 and 712 cm.⁻¹ (weak). The derivatives all exhibited solubility in tetrahydrofuran, benzene and carbon disulfide.

The Preparation of Dicyclopentadienylytterbium Acetate.—To a clear red–orange solution of dicyclopentadienylytterbium

chloride (24 g., 0.0071 mole) in 100 ml. of tetrahydrofuran was added 0.6 g. (0.0073 mole) of anhydrous sodium acetate. The resulting finely divided orange suspension was stirred overnight and then refluxed for 3.5 hours. Removal of solvent under vacuum yielded a yellow residue which was sublimed at 160–250° (10⁻⁵ mm.). This yielded 1.65 g. (65%) of orange sublimate, m.p. 325–329° dec. This complex was quite stable in air since after an exposure of 48 hours it still possessed a m.p. of 323–330° and an identical infrared spectrum to the unexposed material. The major infrared absorption peaks (KBr pellet) were at 1575, 1450, 1400, 1340, 1015 and 960 cm.⁻¹.

Dicyclopentadienylerbium acetate, di-(methylcyclopentadienylerbium)-acetate and di-(methylcyclopentadienyl)-gadolinium acetate were prepared from the respective chlorides in a similar manner.

The Preparation of Dicyclopentadienylytterbium Benzoate.—To a clear red-orange solution of 1.9 g. (0.0056 mole) of (C₂H₅)₂-YbCl in 100 ml. of tetrahydrofuran was added 0.81 g. (0.0056 mole) of sodium benzoate. The red-orange suspension was stirred for a total of 65 hours at room temperature followed by 3 hours at reflux temperature. The solvent was removed at reduced pressure from the bright orange suspension and the residue was sublimed at 280° (10⁻⁵ mm.) to yield 1.33 g. (54%) of orange sublimate. Resublimation at 270° (10⁻⁴ mm.) yielded 1.0 g. of orange product. A melting point determination indicated gradual darkening at about 350° with a melting-decomposition range of 375–380° giving a black melt; considerable effervescence was observed during melting. An air-exposed sample exhibited an identical melting behavior. The material was only very slightly soluble in THF and benzene.

The Preparation of Dicyclopentadienylerbium Formate.—Anhydrous sodium formate (0.69 g., 0.01 mole) was added to a solution of dicyclopentadienylerbium chloride (2.9 g., 0.009 mole) in 150 ml. of tetrahydrofuran. This reaction mixture was stirred overnight at room temperature and then for 6.5 hours under reflux followed by an additional overnight stirring at room temperature. The tetrahydrofuran was then completely removed under vacuum and the residue was sublimed at 165–250° (10⁻⁵ mm.). The sublimed product was isolated in a yield of 0.8 g. (27%) as an orange-pink solid which did not exhibit a melting point up to 300°. Some effervescence was observed in the region of 270°. Dicyclopentadienylerbium formate was found to be soluble in tetrahydrofuran and insoluble in benzene, carbon tetrachloride and carbon disulfide.

Preparation of Dicyclopentadienylytterbium Formate by Reaction of Tricyclopentadienylytterbium with Formic Acid.—To a deep green solution of 3.22 g. (0.00874 mole) of tricyclopentadienylytterbium in 100 ml. of tetrahydrofuran was added dropwise a solution of 0.40 g. (0.00874 mole) of formic acid in 25 ml. of tetrahydrofuran. The resulting clear orange solution was stirred 1 hour followed by solvent removal under vacuum down to approximately one-fifth the original volume. The remaining solution was allowed to cool in a Dry Ice–acetone-bath overnight from which 0.7 g. (23%) of a bright orange powder was isolated. This material was soluble in tetrahydrofuran; slightly soluble in benzene and insoluble in petroleum ether. In an attempted melting point determination, it gradually turned brown over 250° and was almost black above 350°. No melting was observed up to 400°. Major infrared absorption peaks were observed at 1575, 1360, 1285 and 1010 cm.⁻¹.

The Preparation of Dicyclopentadienylerbium Amide.—Sodium amide (0.68 g., 0.017 mole) was added with stirring to a clear pink solution of dicyclopentadienylerbium chloride (2.87 g., 0.0086 mole) in 150 ml. of tetrahydrofuran. The reaction mixture was allowed to stir at room temperature for 54 hours. After solvent removal under vacuum the residue was sublimed at 150–245° (10⁻⁵ mm.). The sublimed product was isolated as a pink solid, m.p. 330–334°, with a yield of 0.9 g. (33.3%). Dicyclopentadienylerbium amide was soluble in tetrahydrofuran and acetone, slightly soluble in benzene, and insoluble in petroleum ether. It is very unstable in air and decomposes in a matter of minutes.

The Preparation of Dicyclopentadienylytterbium Phenoxide.—To a clear orange-red solution of 1.9 g. (0.0056 mole) of (C₅H₅)₂-YbCl in 100 ml. of THF was added 0.68 g. (0.006 mole) of sodium phenoxide. The resulting orange-yellow suspension was refluxed for 2 hours and, after stirring overnight, the solvent was removed at reduced pressure giving an orange residue. This was sublimed at 275° (10⁻⁴ mm.) yielding 1.4 g. (64%) of red-orange sublimate, m.p. 382–386°. It was slightly soluble in tetrahydrofuran and insoluble in benzene, ether, pyridine, carbon disulfide and acetone. The compound was quite stable in air and only showed signs of decomposition after 7 days exposure. An infrared spectrum of 7-day exposed material was essentially the same as that of the protected sample.

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Molecular Orbitals in B₅H₉ and B₁₀H₁₆[1]

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A linear combination of atomic orbitals study of the seven boron framework atomic orbitals and the six boron framework electrons of B₅H₉ yields three bonding molecular orbitals. The energy of the highest filled molecular orbital (M.O.) is -11.0 e.v., which compares favorably with the observed ionization energy of 10.8 e.v. The population matrix yields a formal charge of $-0.87e$ on the apex boron atom and of $+0.22e$ on each basal boron, the order of which agrees with the experimental. These charges yield a dipole moment of 4.6 D. When account is taken of the hydridic nature of the bridge hydrogens and the apex terminal hydrogen, the dipole moment becomes 1.8 D, compared with the experimental value of 2.13 D. A similar study of the 16 boron framework atomic orbitals and 14 framework electrons of B₁₀H₁₆ yields seven bonding M.O.'s, an energy of -10.2 e.v. for the highest filled M.O., a charge of $-0.86e$ on each apex boron and a charge of $+0.22e$ on each basal boron. Comparison of the electron population matrices of the two molecules shows that only single bond character may be attached to the boron–boron bond between the two halves of B₁₀H₁₆ even though enough properly oriented atomic orbitals are available for the formation of a triple bond.

Introduction

The recent discovery and elucidation[2] of the molecular structure of B₁₀H₁₆ disclosed a previously unknown boron hydride structural feature: two adjacent boron atoms without any hydrogen atoms attached to either boron. In all the other known boron hydride molecules and ions at least one hydrogen atom is attached to each boron atom. Since this boron–boron bond is unique, it is of interest to investigate its character, particularly since in B₁₀H₁₆ the boron atomic orbitals may be arranged in such a fashion as to suggest the possibility of a triple bond, even though the molecule as a whole is electron deficient.

When the structure of B₁₀H₁₆ was announced, we had already completed our investigation of the electronic structure of B₅H₉, which we carried out in order to confirm the general usefulness, with respect to the boron hydrides, of the method which we used to study[3,4] the electronic structure of B₁₀H₁₄. Since the structures of B₅H₉ and B₁₀H₁₆ are closely related it was not difficult to examine the electronic structure of B₁₀H₁₆ by the same means. For other theoretical treatments of B₅H₉ see references 5 and 6.

The purpose of this paper, then, is to report the results of our studies of the electronic structures of B₅-H₉ and B₁₀H₁₆ and to examine the character of the unique boron–boron bond in B₁₀H₁₆.

General Method.—We used the same linear combination of atomic orbitals method that we used for B₁₀H₁₄ in which the molecular orbital

$$\Psi_j = \Sigma_r c_{rj} \Phi_r$$

leads to the set of equations

$$(\alpha_{rr} - E)c_r + \Sigma_s'(\beta_{rs} - S_{rs} E)c_s = 0$$

where

$$\alpha_{rr} = \int \Phi_r H \Phi_r \, d\tau, \ \beta_{rs} = \int \Phi_r H \Phi_s \, d\tau \text{ and } S_{rs} = \int \Phi_r \Phi_s d\tau$$

With the assumption that the resonance integrals are proportional to the overlap integrals, $\beta_{rs} = KS_{rs}$, the equations become

$$(\alpha_{rr} - E)c_r + \Sigma'_s (K - E)S_{rs}c_s = 0 \quad (1)$$

The orbital Φ_r may be an atomic orbital on center r but more often it is a symmetry orbital, which is a linear combination of atomic orbitals on different centers. With the aid of group theory, the symmetry orbitals may be determined and the equations simplified according to the point group of the molecule. For our purposes hybrid orbitals on the boron atoms, as suggested by the atomic arrangements, are more suitable starting orbitals than pure 2s and 2p atomic orbitals. Thus the symmetry orbitals become linear combinations of hybrid orbitals which are in turn linear combinations of the boron 2s and 2p atomic orbitals.

In both B₅H₉ and B₁₀H₁₆ we neglected the boron 1s atomic orbitals and electrons and assumed that the 2s and 2p atomic orbitals are hybridized according to the arrangement of atoms around the boron in question. We assumed that each terminal hydrogen atom is bonded to a single boron atom by a two-electron, two-center bond and that each bridge hydrogen atom is bonded to two boron atoms by a two-electron, three-center bond.[5] This uses two electrons and two atomic orbitals for each terminal hydrogen and two electrons and three atomic orbitals for each bridge hydrogen. These orbitals and electrons were not considered further in the calculations except at the end where they were brought into the B₅H₉ dipole moment discussion.

We determined the symmetry orbitals, evaluated all the hybrid orbital overlap integrals using Slater orbitals, and then calculated the symmetry orbital normalization factors N_{rr} and the symmetry orbital overlap integrals S_{rs}. We evaluated the symmetry orbital coulomb integrals by writing them out in terms of atomic orbitals and by assuming the boron 2s and 2p coulomb integrals to be equal to the valence state ionization energies,[7] that is

$$\int \Phi_{2s} H \Phi_{2s} \, d\tau = -15.36 \text{ e.v. and } \int \Phi_{2p} H \Phi_{2p} \, d\tau = -8.63 \text{ e.v.}$$

We then solved eq. 1 several times on the IBM 7090 computer using a different value of K each time. We chose values of K between -10 and -25 e.v.

It should be remarked that the evaluation of overlap integrals between hybrid orbitals pointing in arbitrary directions is not as straightforward as the evaluation of overlap integrals for a diatomic molecule, for which tables[8,9] and computer programs[10] are readily available.

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