

Disproportionation of Cyclopentadienyldialkylaluminiums in Presence of Lewis Base

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Summary The disproportionation of cyclopentadienyldialkylaluminum-THF adducts in benzene solution has been studied by n.m.r., and the products have been identified.

STABLE Lewis-base adducts of trialkylaluminiums and dialkylaluminum halides have been known for quite some time. In 1961 Giannini¹ reported that cyclopentadienyldiethylaluminum formed a stable, distillable 1:1 adduct with ether. No n.m.r. data on such adducts are available. In view of the observed non-rigidity of aluminum-cyclopentadienyl structures² it seemed of great interest to examine the n.m.r. of a simple, monomeric complex like $R_2AlC_5H_5, \kappa B$ (B = Lewis Base). I have found that these complexes are not stable at ambient temperature and

disproportionate. This was unexpected in view of ref. 1 and in view of the relatively large thermal stability of cyclopentadienyldialkylaluminiums.³

When attempting to prepare the above 1:1 adducts, in all cases a mixture of products was found which has the n.m.r. spectrum shown in the Figure.

The spectrum shows two singlets for the ring protons (6 c./sec. separation) and three singlets for methyls attached to the aluminum. Subsequently I have identified the species present by comparison of the chemical shift of the observed signals with those of known compounds, by addition of known compounds, and by integration of the various proton signals. Singlets A and D belong to $Me_2AlC_5H_5, \kappa THF$, C belongs to $AlMe_3, \kappa THF$, B and E belong to $MeAl(C_5H_5)_2, \kappa THF$ (see also Table).

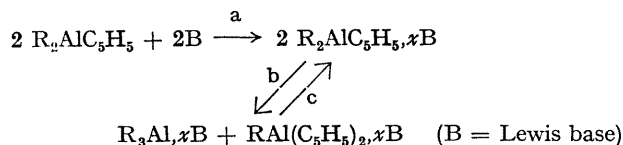
The results indicate that the initially formed adduct $R_2AlC_5H_5, \pi B$ is unstable at ambient temperature in solution

1H n.m.r. data (60 Mc./sec) for 0.25M solutions in C_6H_6 or C_6D_6

Compound	Chemical shift (c./sec.) from internal cyclopentane	
	$Al-C_5H_5$	$Al-CH_3$
$AlMe_3, \pi THF$ 1:1	—	-116
$Me_2AlC_5H_5, \pi THF$ 1:1 ^a	—	—
Peak A	+336	—
Peak B	+330	—
Peak C	—	-116
Peak D	—	-130
Peak E	—	-144

^a Product obtained by adding at ambient temperature a dilute solution of THF to $Me_2AlC_5H_5$ in benzene (1:1 molar ratio). All spectra obtained at room temperature. Shifts upfield from cyclopentane negative; shifts downfield positive sign.

and partially (ca. 25%) disproportionates to the trialkylaluminum adduct and the alkylaluminum biscyclopentadienyl adduct:



Further evidence for the disproportionation is obtained upon fractional distillation of the reaction products *in vacuo* at temperatures below 100° (R = Me). Because of its lower boiling point the trimethylaluminum adduct distills first and can easily be identified. The existence of an equilibrium (b and c) was indicated in the following experiment. Upon addition of some trimethylaluminum-THF 1:1 complex to the disproportionation product of the equation not only does signal C increase but signals B and E decrease simultaneously. This means that the reverse reaction (c) occurs according to the mass law.

The biscyclopentadienylmethylaluminum-THF adduct which is formed in these reactions could not be isolated in pure form. It is not stable at ambient temperature with or without solvent, as indicated by the formation of coloured precipitates after several days. This type of complex has not been reported in the literature.

Subsequently I investigated whether or not the cyclopentadienyldialkylaluminum-THF adduct can be prepared at low temperature *without* undergoing disproportionation. Dilute THF was added in a 2:1 ratio† to cyclopentadienyldimethylaluminum at -40° in [2H_8]toluene. The 1H n.m.r. spectra were then recorded at -40°, -17°, -5°, and at ambient temperature. At -40° the adduct is formed *without* disproportionation as shown by the n.m.r. spectrum which contains only *one* singlet for the ring protons and *one* singlet for the methyl groups attached to the aluminium. Upon warming to -17° no change in the n.m.r. spectrum occurs, whereas at -5° a

very small amount of disproportionation is observed. However, when warming to ambient temperature a large amount of disproportionation occurs comparable to the preparation at ambient temperature. Currently we are studying the effect of temperature on the disproportionation equilibrium.

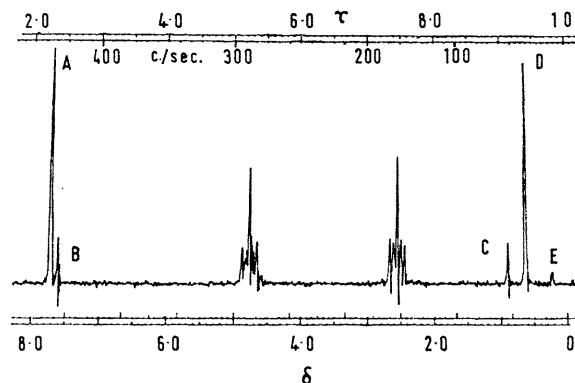


FIGURE. 1H n.m.r. spectrum of the reaction mixture (ambient temperature) from $Me_2AlC_5H_5 + 2THF$ in $C_6H_6-C_6D_6$. 60 Mc./sec.

This disproportionation reaction is general for other cyclopentadienyls (e.g. R = Bu¹) and methylcyclopentadienyls, or when using other bases than THF (e.g. dioxan, diethyl ether *etc.*). If a Lewis base is used as solvent, only one signal is observed for the two different types of ring protons A and B (see n.m.r. spectrum). This would indicate a rapid intermolecular exchange of cyclopentadienyl groups between the mono- and the bis-cyclopentadienyl compounds. The three different signals for the different types of methylaluminum groups appear in polar as well as in Lewis-base solvents, indicating that methyl group exchange at ambient temperature is not occurring or is slow on the n.m.r. time scale. This is not surprising, as the formation of methyl bridges is not favoured under these conditions. However, upon heating to 100° all three methyl signals coalesce reversibly.

I have found that the monomeric cyclopentadienyldimethylaluminum-THF adduct prepared at -40° shows only one signal for the ring proton—similarly to the free monomeric and dimeric dialkylaluminum cyclopentadienyls.² This means that the complex formation with THF does not significantly decrease the rate of rearrangement of the cyclopentadienyl ring. Possibly the use of a different type of Lewis base in conjunction with a methyl-substituted cyclopentadienyl might result in a substantial change that can be analysed by n.m.r.

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† Using a 2:1 ratio was generally preferred in order to make sure that no free, uncomplexed alkylaluminum was present. There is no difference in principle in the results whether using a 1:1 or 2:1 ratio.

¹ U. Giannini and S. Cesca, *Gazetta*, 1961, **91**, 597.

² W. R. Kroll and W. Naegele, *Chem. Comm.*, 1969, 246.

³ W. R. Kroll, *Trans. New York Acad. Sci.*, 1965, **27**, 337.