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COMPLEXES OF DIALKYLALKENYLALUMINIUM COMPOUNDS

K.B. STAROWIEYSKI

Institute of Organic Chemistry and Technology, Technical University (Politechnika), 00-662 Warsaw (Poland)

C. BANDLOW and K. HAAGE

Central Institute of Organic Chemistry, Academy of Sciences of the German Democratic Republic, Berlin-Adlershof (G.D.R.)

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Summary

Complexes of two dialkylalkenylaluminium compounds with organic donors were investigated. It was found that stable complexes are formed only with strong donors, but not with very weak ones like anisole, because of the strong donor properties of the alkenyl group. The donors with reactive bonds as in RC≡N undergo rearrangement reactions after several hours.

Dialkylalkenylaluminium compounds were synthesized first by Wilke and Müller from trialkylaluminium and acetylene [1]. We repeated the synthesis of $Et_2AlCH{=}CHEt$ (I) according to this procedure and obtained a new compound $i\text{-}Bu_2AlCH{=}CH\text{-}i\text{-}Bu$ (II). We have found that I is dimeric in agreement with Wilke but II is monomeric in diluted benzene solution.

There is a difference in the stability of compounds bridged by n-alkyl and alkenyl groups. The heat of complex formation with organic donors is lower for I than for Et_3Al (III) (e.g. with Et_2O it is 7.5 kcal/mol and 11 kcal/mol respectively) [2,3]. The ν(C≡N) value in complexes of I and III with benzonitrile [4] is the same, which indicates similar acidity of the aluminium center. These data show that the heat of complex formation is lower with I because of the stronger bridging bond which has to be broken. Zweifel and Clark [2] explained the high stability (compared with R_3Al) of the bridge, by two effects; (1) overlap of the carbon sp^2 orbitals of the vinyl groups with the sp^3 orbitals of the aluminium atom and (2) additional overlap of the carbon—carbon π-orbital of the vinyl group with the non-bonding orbitals of the aluminium atom, but not by an increase in acceptor ability of aluminium owing to the presence of the alkenyl substituent.

In this work we investigated compounds I and II and their complexes with

TABLE 1

MOLECULAR WEIGHTS, IR ν(C=C) BANDS, AND CHEMICAL SHIFTS OF THE VINYL PROTONS OF $Et_2AlCH{=}CHEt$, $i\text{-}Bu_2AlCH{=}CH\text{-}i\text{-}Bu$ AND THEIR 1 : 1 COMPLEXES WITH ORGANIC DONORS. IR, 3—5% IN HEPTANE; PMR, 10—20% IN CYCLOHEXANE (LOW TEMP. IN CYCLOPENTANE) AND MOLECULAR WEIGHT, 1% SOLUTION IN BENZENE

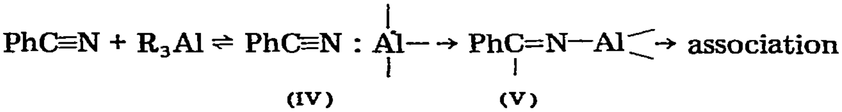
Complex	$Et_2AlCH{=}CHEt$					$i\text{-}Bu_2AlCH{=}CH\text{-}i\text{-}Bu$			
	Mol. wt. found (calcd.)	ν(C=C)	Chemical shift (τ)			Mol. wt. found (calcd.)	ν(C=C)	Chemical shift (τ)	
			EtCH=	(M) [a]	=CH—Al (D) [b]			i-BuCH= (M)	=CH—Al (D)
uncomplexed	284 (280) [c]	1557	2,24		4.42	244 (224) [d]	1556	2,13	4,22
				−76°C	4.43 [f]				
Et_2O	167 (214) [c]	1586	3,53		4.45 [f]	230 (298) [e]	1585	3,47	4,30
				−76°C	4.44 [f]				
Pyridine	221 (219) [c]	1584	3,50		4.35	298 (303) [e]	1583	3.40	4,10
PhCN	300 (343) [c]	1586	3,60		4.35	226 (327) [e]	1586	3.50	4,17
PhOMe	135 (248) [c]	1557	not observed		4.41	175 (332) [d]	1558	not observed	4,25
				−76°C	4.41				
Et_3N	not investigated	1578	3,61		4.46	not investigated	1590	3,52	4.40

[a] (M), multiplet. [b] (D), doublet $J \approx 15$ Hz. [c] For dimer. [d] For monomer. [e] For 1 : 1 complex. [f] Doublet of doublets $J \approx 15$ Hz, $J \approx 5$ Hz.

various organic donors. The degree of association, IR ν(C=C) band position and chemical shifts of olefinic protons in uncomplexed and complexed I and II are collected in Table 1.

Despite differences in association of I and II the ν(C=C) IR bands of both compounds have the same value and the chemical shifts of the protons of $\geq$AlCH=CHR are very similar. This indicates only a small influence of bridging on the electronic environment of aluminium and on the double bond in the alkenyl group. There are big changes in the IR ν(C=C) frequency as well as in the chemical shift of the RCH= proton, when complexes with a strong base are formed. These are caused by a large increase in electron density on the aluminium atom. The changes of ν(C=C) towards higher frequencies (of about 30 cm^{-1}) and of the olefinic protons upfield (about 1.4 ppm) are in agreement with the decreasing acceptor properties of aluminium. Nearly the same frequencies for the IR band of the double bond and similar chemical shifts of the olefinic protons in all complexes indicate similar electron distribution in the carbon—carbon double bond.

The stability of the complexes is related to the donor ability and the reactivity of the used bases. The strong but unreactive donors like pyridine form 1 : 1 complexes with I and II as indicated by the results of molecular weight measurements. Benzonitrile (with a reactive triple bond) is also a strong electron donor [4]. Some trialkylaluminium compounds undergo, after complexation, alkylation or reduction reactions forming derivatives of aldoimine or ketimine. These products have a very strong tendency towards association with any organoaluminium compound (eq. 1).



$$PhC{\equiv}N + R_3Al \rightleftharpoons \underset{(IV)}{PhC{\equiv}N : \overset{|}{\underset{|}{Al}}-} \rightarrow \underset{(V)}{Ph\underset{|}{C}{=}N{-}Al\lessdot} \rightarrow \text{association} \qquad (1)$$

The IR spectrum obtained after several hours of preparation of a 1 : 1 complex with I shows the presence of rearrangement products. A broad weak band of ν(C=N) at 1638 cm^{-1}, which appears to increase in intensity with time, indicates slow formation of V. Also the disappearance of the strong ν(C≡N) band (2278 cm^{-1}), after 5 hours of heating at 50°C, indicates reaction 1. In the latter spectrum one can see the appearance of a medium ν(C≡N) band at 2235 cm^{-1} due to free benzonitrile, which was hardly visible in the spectrum recorded before heating. This suggests dissociation of PhCN : Al(CH=CHEt)Et_2 because of usage of I in the formation of a mixed dimer with the rearrangement product V, similar to that proposed by Jeffery [5]. A 1 : 1 mixture of benzonitrile and II has a much lower molecular weight than calculated (the complex of I has a higher molecular weight than calculated). This is explained by the presence of isobutylene, formed in the rearrangement reaction [6], which was found in large amounts in the reaction mixture. The IR spectra of complexed II obtained after preparation (similar to that of I) reveals three bands: a strong band at 1638 cm^{-1}, a medium band at 2235 cm^{-1} and a very strong band at 2278 cm^{-1}. This pattern of bands shows that reaction 1 proceeds faster for II than for I. It was observed earlier, in agreement with our results, that whereas PhCN : Et_3Al is reasonably stable, PhCN : Al(i-Bu)$_3$ undergoes rapid rearrangement and no complex was observed at room temperature.

One can expect that weaker unreactive donors like ethers form complexes in equilibrium with the substrates. This was observed in the case of Et_3Al and anisole [7] but not for Et_3Al and Et_2O. Wilke [2] stated that from the mixture of ether with I it is possible to distill off the ether. This indicates the presence of a visible dissociation in solution. Molecular weight measurements of both complexes of I and II with ether agree with the existence of the equilibrium shown in eq. 2.

$$R_2AlCH{=}CHR + Et_2O \rightleftharpoons R_2(RCH{=}CH)Al : OEt_2 \qquad (2)$$

We have at present no explanation for the existence of only one ν(C=C) band at 1585 cm^{-1} in the complex but not at 1556 cm^{-1} in the free compound. The presence of only one doublet of the Al—C$\underline{H}$= proton in PMR spectra, even at —70°C can be explained by the shift of equilibrium 2 towards complex formation. The splitting of both peaks of the doublet of I at τ 4.4 ppm into doublets of nearly the same intensity at —70°C and of complexation with ether, even at ambient temperatures, is an open question.

Anisole does not form a complex with either I or II. It is still a problem why the R—C$\underline{H}$= peak disappears in this mixture, The shape of the aromatic proton peaks of anisole (5 protons) and of its mixture with I and II is the same, so a tentative explanation of the presence at this position of R—C$\underline{H}$— (1 proton) is hardly possible.

References

1 G. Wilke and H. Müller, Ann. Chem., 618 (1960) 222.
2 G. Zweifel and G.M. Clark, J. Organometal. Chem., 39 (1972) C33.
3 E. Bonitz, Chem. Ber., 88 (1955) 742.
4 K. Starowieyski and S. Pasynkiewicz, Rocz. Chem., 40 (1966) 47.
5 E.A. Jeffery and T. Mole, Australian J. Chem., 23 (1970) 715.
6 J.E. Lloyd and K. Wade, J. Chem. Soc., (1965) 2662.
7 K.B. Starowieyski, unpublished results.