Aluminium–Olefinic Double Bond Interaction in Alkenylaluminium Compounds

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ORGANOMETALLIC compounds which contain an olefinic double bond have aroused some interest in relation to intramolecular interaction between metal atoms and π-electrons.[1,2] This Communication describes spectroscopic evidence for an intramolecular aluminium atom–π-electron interaction in 4-alkenylaluminium compounds. It is well known that trialkylaluminium adds to α-olefins. The first step of this reaction is presumably an interaction between a vacant orbital of the aluminium atom and the π-electrons of the olefin, though this has never been confirmed experimentally.

Alkenylaluminium compounds were prepared by reaction of di-isobutylaluminium hydride with diolefins, $CH_2{=}CH{\cdot}[CH_2]_m{\cdot}CH{=}CH{\cdot}CH_3$ (m = 1, 3, 4) and $CH_2{=}CH{\cdot}CH_2{\cdot}CH{=}CH_2$, at 55°. Di-isobutylaluminium hydride added to the terminal double bonds to give selectively the corresponding alkenylaluminium compounds. Reaction

TABLE 1

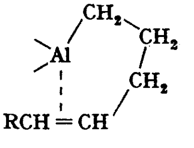
Infrared-spectral data of alkenyldi-isobutylaluminiums and diolefins

	Internal C=C bond (cm.$^{-1}$)	
	$\nu_{C=C}$	δ_{CH}
$CG_3{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH_2$ (*cis*)	1657	708
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_3\ Bu^i_2Al$ (*cis*)	1635	738
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_3\ Bu^i_2Al{\cdot}OEt_2$ (*cis*)	1658	—
$CH_3{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH_2$ (*trans*)	—	965
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_3\ Bu^i_2$ (*trans*)	1646	1003
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_3\ Bu^i_2Al{\cdot}OEt_2$ (*trans*)	—	966
$CH_2{=}CH{\cdot}CH_2{\cdot}CH{=}CH_2$[a]	1641	913; 996
$CH_2{=}CH{\cdot}[CH_2]_3\ Bu^i_2Al$[a]	1618	—
$CH_2{=}CH{\cdot}[CH_2]_3\ Bu^i_2Al{\cdot}OEt_2$[a]	1641	—
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_3{\cdot}CH{=}CH_2$ (*trans*)	—	967
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_5\ Bu^i_2Al$ (*trans*)	—	966
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_5\ Bu^i_2Al{\cdot}OEt_2$ (*trans*)	—	965
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_4CH{=}CH_2$ (*trans*)	—	965
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_6\ Bu^i_2Al$ (*trans*)	—	965

[a] Absorptions due to a terminal C=C bond.

of di-isobutylaluminium hydride with penta-1,4-diene (molar ratio, 1:3) afforded a mixture of pent-4-enyldi-isobutylaluminium (76%) and pentamethylenebis(di-isobutylaluminium) (24%).

Infrared absorptions due to the C=C bonds of the alkenylaluminium compounds were compared with those of the starting diolefins (Table 1). The CH=CH deformation frequencies of *trans*-oct-6-enyl- and *trans*-non-7-enyl-di-isobutylaluminium had the same values as those of the internal C=C bonds of the starting diolefins. However, those of *cis*- and *trans*-hex-4-enyldi-isobutylaluminium were shifted to higher wave-numbers (by 30—38 cm.$^{-1}$) as compared with the corresponding frequencies of the starting diolefins. The C=C stretching frequencies of *cis*-hex-4-enyl- and pent-4-enyl-di-isobutylaluminium appeared at lower wave-numbers by 22—23 cm.$^{-1}$. These specific frequency shifts in the alk-4-enyldi-isobutylaluminium can be explained by assuming intramolecular complex formation between the aluminium atom and the C=C bonds, which is sterically favoured. These frequency shifts are in accord with the results reported for Ag$^+$–olefin complexes.[4] Molecular-weight measurement on *cis*-hex-4-enyldi-isobutylaluminium (cryoscopy in benzene) showed that it was monomeric, which indicates that the interaction is intramolecular.



(I)

Dilution of *cis*-hex-4-enyldi-isobutylaluminium with n-heptane or benzene (4—10 mole %) showed no effect on the frequencies.

Addition of a Lewis acid to alk-4-enyldi-isobutylaluminiums would destroy the intramolecular interaction. The infrared spectra of the etherates of these compounds showed no frequency shifts, as expected.

Additional evidence for the aluminium–π-electron interaction in alk-4-enyldi-isobutylaluminium was obtained from an n.m.r. study (Table 2). The olefinic protons of the structure (I) will be less shielded, and consequently are expected to appear at a lower field. In fact, the olefinic protons of *trans*-hex-4-enyldi-isobutylaluminium appeared at a lower field by 0·30 p.p.m. than those of *trans*-oct-6-enyl and *trans*-non-7-enyl derivatives. The high-field shift (by 0·15 p.p.m.) of the methylene protons of the isobutyl groups of *trans*-hex-4-enyldi-isobutylaluminium seems to be due to the increase of electron density at the aluminium atom due to complex formation.

TABLE 2

N.m.r.-spectral data of alkenyldi-isobutylaluminiums

$RAlBu^i_2$	Chemical shift (p.p.m.)[a]		
		Bu^i	
R	CH=CH	CH_3	CH_2
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_3$ (*trans*)	1·53	6·25	7·10
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_5$ (*trans*)	1·84	6·23	6·95
$CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_6$ (*trans*)	1·83	6·23	6·95

[a] Referred to benzene.

Reaction of di-isobutylaluminium hydride with hepta-1,5-diene afforded cyclic products, *i.e.*, (1-cyclpentylethyl)di-isobutylaluminium and ethylidenecyclopentane.[5]

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