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Preliminary communication

Conjugative interactions between carbon and aluminum in vinylalane dimers

G. ZWEIFEL and G.M. CLARK
Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)

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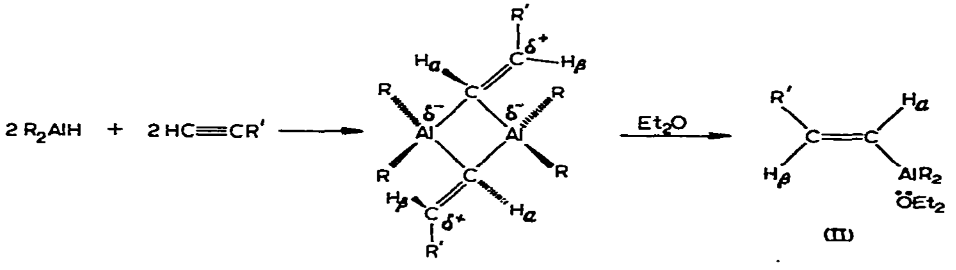
We have recently proposed[1] that the structures of vinylaluminum dimers in hydrocarbon solvents may be represented by the model suggested by Visser and Oliver[2] for vinylgallium dimers. In this model, primary bonding is attributed to overlap of carbon *sp*^{2} orbitals of the vinyl groups with the *sp*^{3} orbitals of the metal atoms to form two three-centered bridging bonds. In addition, the vinyl bridge is stabilized by conjugative overlap of the carbon–carbon π-orbital of the vinyl group with the non-bonding orbitals of the metal. Both of these types of orbitals possess symmetry appropriate to overlap with each other.

We have now examined the 60-MHz proton magnetic resonance (PMR) spectra of a number of alkenyldialkylalanes and dienyldialkylalanes in hydrocarbon and other solvents, and find that the spectra obtained provide evidence for conjugation interaction in vinylalane dimers[★].

The hydroalumination of 1-alkynes with diisobutylaluminum hydride (R_2AlH) in hydrocarbon solvents leads, via a stereospecific *cis*-addition of the Al–H bond to the triple bond, to the corresponding *trans*-1-alken-1-yldiisobutylalane dimers (I)[3]. The salient feature of the PMR data obtained for the various substituted vinylalane dimers (Table 1) is the low field position of the β-proton absorption, pointing to a displacement of electron density from the carbon–carbon π-system toward aluminum.



(I)

(II)

[★] The low frequency of the intense C=C stretching vibration (~ 1550 cm^{-1}) of vinylalanes, attributed to the polarizing influence of aluminum[3], also indicates conjugation of the vinyl π-system with aluminum. This band is shifted ~ 30 cm^{-1} to higher frequency upon coordination of aluminum with ether. (The H_α undergoes a small shift which is consistent with the decreased electronegativity of aluminum upon coordination[3].)

TABLE 1

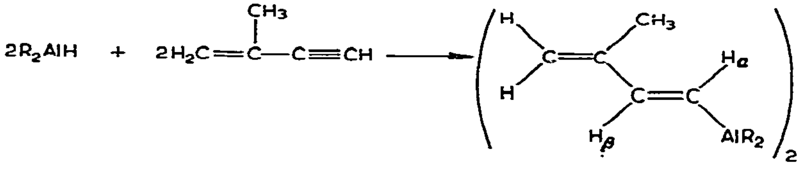
CHEMICAL SHIFTS OF VINYL PROTONS OF VINYLALANE DIMERS AND VINYLALANE ETHERATES $R_2AlCH{=}CHR'$ (R = isobutyl)

R′	*Vinyl proton chemical shifts*[a]					
	H_α[b]		H_β[b]		*Other H*	
	Dimer	*Etherate*	*Dimer*	*Etherate*	*Dimer*	*Etherate*
n-butyl	5.75	5.73	7.42	6.03		
cyclohexyl	5.78	5.68	7.37	5.96		
t-butyl	5.73	5.67	7.39	6.96		
phenyl	6.6	*c*	8.1	*c*		
isopropenyl	5.88	6.10	7.77	6.76	5.31[d] 5.41[d]	4.83[d]
1-cyclohexenyl	5.68	5.92	7.64	6.62	6.12[e]	5.56[e]

[a]Chemical shifts in ppm (δ) downfield from internal TMS; in all cases the expected spin multiplicities were observed. [b]$R_2AlCH_\alpha{=}CH_\beta R'$; $J_{trans\ \alpha,\beta} = 20-21$ Hz. [c]Obscured by phenyl proton resonance signals at δ7.1–7.9 ppm. [d]Terminal methylene protons. [e]Ring vinyl proton.

Conjugation should be inhibited or severely diminished in ether solvents by conversion of the dimer into the corresponding etherate (II). Indeed, the Hβ absorption is shifted upfield by ca. 1.3 ppm upon treatment of the vinylalanes contained in octane solvent with ether, indicating an electron shift from aluminum to the β-carbon[4].

Of particular interest are the effects of coordination with ether on the PMR spectra of dienylalanes. The vinyl region of the PMR spectra of the product mixture resulting from hydroalumination of isopropenylacetylene in octane to give (III) exhibits the Hβ absorption as a doublet at δ7.77 ppm. The terminal methylene protons absorb at δ5.31 and δ5.41 ppm*. The spectrum of the corresponding etherate, obtained by adding a two-fold excess of ether to the alane contained in octane solution, shows the Hβ and terminal methylene absorptions at δ6.76 and δ4.83, respectively, clearly demonstrating the large upfield shift of the Hβ absorption, and also an appreciable upfield shift of the terminal



(III)

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*Other peaks in the δ4.8–6.0 ppm region are due to unreacted starting enyne, and to a mixed vinyl–alkynyl bridged dimer, formed because some metalation (~ 15%) occurs during the hydroalumination.

methylene proton absorptions, upon complexation of the alane with ether. Because of the *trans* orientation about the double bond adjacent to aluminum it seems improbable that any direct interaction of the terminal methylene protons with the metal can occur. Also, appreciable interaction of the terminal methylene protons with the alkyl groups bonded to the metal appears improbable.

Similar results were obtained for the dienylalane dimer IV. In Fig. 1 are summarized chemical shifts of the vinyl protons of IV and its etherate V, and of the related non-dimeric borane (VI)[5] and silane (VII)[★,6].

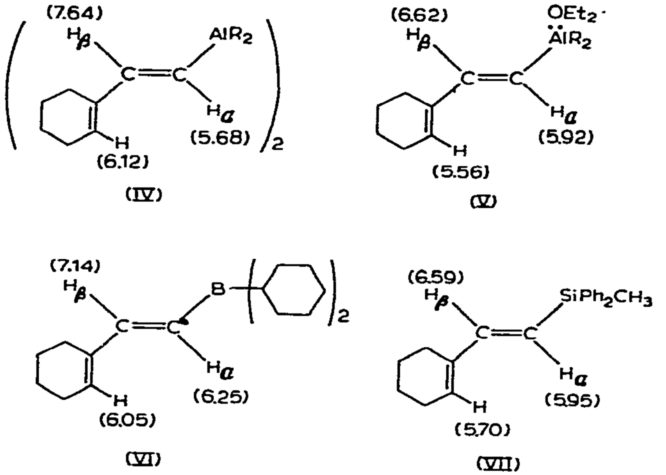

Fig. 1. Vinyl proton chemical shifts in ppm downfield from internal TMS for some dienyl organometallics.

In comparing the alane dimer IV and the monomeric borane VI, in which vinyl-boron conjugation is known to occur, it is noted that the ring vinyl protons have quite similar chemical shifts. The H_α proton of the borane is at a low field position relative to that of the alane, in keeping with the greater electronegativity of boron. The low field position of the absorption due to H_β in IV relative to that in VI is possibly caused by differing interactions of the β proton with the alkyl groups bonded to the metal[★★].

A striking similarity is observed between the chemical shifts of the vinyl protons of the dienylalane etherate V and the dienylsilane VII. Since p_π–p_π interactions are not possible in VII[7] the correspondence of the two spectra shows again that such interactions in the alane etherate are at least strongly diminished relative to those in the alane dimer. The

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[★] We thank Professor Sommer for permission to use this data.

[★★] Approach to a planar geometry, necessary for maximum conjugation in the monomeric borane, would lead to appreciable interaction of the β-vinyl proton with the protons on the cyclohexyl rings. Models show that considerably less interaction of the H_β proton with the isobutyl moieties of the alane dimer would be expected.

appreciable upfield shifts in the ring vinyl proton absorptions (and the Hβ proton) of the silane and alane etherate relative to those of the borane and of the alane dimer also suggest conjugation in the latter pair of compounds, and thus provides support for use of the Visser—Oliver model for vinylalane dimers. The "exceptional stability"[8] of the vinyl bridge in vinylalane dimers may thus result from the conjugative bonding of the π-orbital of the vinyl group with the non-bonding orbitals of aluminum.

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REFERENCES

1 G.M. Clark and G. Zweifel, *J. Amer. Chem. Soc.*, 93 (1971) 527.
2 H.D. Visser and J.P. Oliver, *J. Amer. Chem. Soc.*, 90 (1968) 3597.
3 G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, 629 (1960) 222.
4 T. Takeshita and W.E. Frankle, *Tetrahedron Lett.*, (1968) 5913.
5 G. Zweifel, G.M. Clark, and N.L. Polston, *J. Amer. Chem. Soc.*, 93 (1971) 3395.
6 C. Golino and L.H. Sommer, unpublished results.
7 H. Bock and H. Seidl, *J. Amer. Chem. Soc.*, 90 (1968) 5694.
8 R. Köster and P. Binger, *Advan. Inorg. Chem. Radiochem.*, 5 (1965) 274, 277.