The Interaction of Main Group Metals with CC Double Bonds. Molecular Orbital Calculations on the Model Complexes $H_2Zn \cdot C_2H_4$ and $H_2Mg \cdot C_2H_4$

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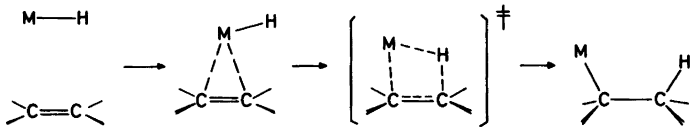
When an alkene is inserted into a main-group metal-to-hydrogen (or metal-to-carbon) bond, the reaction is believed to proceed *via* the formation of a weakly bonded and short lived complex where the CC π-electrons are coordinated to the metal.[1,2] The CC double bond and the M–H (or M–C) bond are then broken, while the new M–C and C–H bonds are formed in a concerted four-center reaction:[2]



To the best of our knowledge, no such main-group metal alkene complex has been isolated. However, after Cliver and coworkers had found evidence for *intra*molecular metal/CC double bond interactions in the ^1H NMR spectrum of dipent-4-enylzinc,[3] we carried out gas electron diffraction (GED) investigations of both dipent-4-enyl- and dibut-3-enyl-zinc. In both molecules we found the prevalent, if not exclusive, conformation to be one in which the hydrocarbon chains were coiled back in such a manner as to bring the π-electrons in the CC double bonds into the immediate vicinity of the metal atom.[4]

We now report the results of *ab initio* molecular orbital calculations on the model systems H_2Zn/C_2H_4 and H_2Mg/C_2H_4.

Calculations. The geometries of the dihydrides, of ethylene and of the π-complexes were optimized at the self-consistent-field (SCF) level of *ab initio* molecular orbital theory using the conjugategradient technique implemented in the GAUSSIAN-82 computer program.[5]

The π-complexes were assumed to have C_{2v} symmetry with coplanar H_2MC_2 fragments as indicated in Fig. 1.

For the zinc compounds we used a (5,1) basis set contracted to ⟨2,1⟩ for H, a (9,5,1) set contracted to ⟨4,2,1⟩ for C,[6] and a (12,8,5) set contracted to ⟨8,6,4⟩ for zinc.[7]

For the magnesium compounds we used the 6–31G** basis throughout.[8] In order to assess the importance of correlation effects, we carried out third order Møller-Plesset perturbation theory calculations[9] on the magnesium compounds.

Results and discussion. The potential energy curve for the complex $ZnH_2 \cdot C_2H_4$ obtained from the SCF calculations has a very shallow- and hence very wide – minimum (D_e=5.0 kJ

Table 1. Dissociation energies (D_e) and M–C bond distances (R_e) in the π-complexes $ZnH_2 \cdot C_2H_4$, $MgH_2 \cdot C_2H_4$ and $AlH_3 \cdot C_2H_4$.

M	D_e/kJ mol^{-1}	R_e(M–C)/pm
Zn	5.0	340
Mg	22	290
Al[a]	36	270

[a] Ref. 2.

0302-4377/85 $2.50

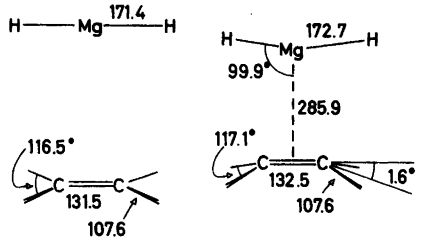


Fig. 1. Optimized geometries for MgH_2, C_2H_4 and $MgH_2 \cdot C_2H_4$. Bond distances are given in pm.

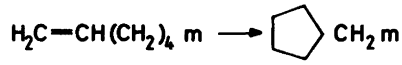
mol^{-1}) with equilibrium M–C distances of about 340 pm. The GED investigation of dibut-3-ezylzinc yielded a Zn···C(4) distance in the prevalent, coiled back conformation of 315(6) pm, and the metal/CC double bond interaction was estimated to be about $-\Delta G°=4.5$ kJ mol^{-1}. In gaseous dipent-4-enylzinc the distance from the metal atom to the nearest of the two unsaturated carbon atoms is Zn–C(4)=300(8) pm, and the interaction energy was estimated as $-\Delta G^c=6$ kJ mol^{-1} or greater: on the whole we consider the agreement between calculations and experiments satisfactory.

SCF calculations on the $MgH_2 \cdot C_2H_4$ complex yielded a dissociation energy of 22 kJ mol^{-1} and equilibrium Mg–C bond distances of about 290 pm. Inclusion of correlation energies increased the dissociation energy to 29 kJ mol^{-1}. This decreases to 25 kJ mol^{-1} when 6–31G** zero-point vibrational energies are included.

We are not aware of any experimental information on Mg alkene complexes, but it is well known that monomeric dialkylmagnesium complexes are better electron acceptors than dialkylzinc compounds.

In Fig. 1, we present the optimized geometries of MgH_2, C_2H_4 and the π-complex. The formation of the weak complex leads to very small geometry changes in both donor and acceptor. The optimal Zn–H distance in ZnH_2 is 156.5 pm. As expected, the formation of the π-complex $ZnH_2 \cdot C_2H_4$ leads to even smaller geometry changes in both donor and acceptor than for the Mg complex.

We have previously published the results of similar calculations on the complex $AlH_3 \cdot C_2H_4$ which indicate that the dissociation energy is $D_e=36$ kJ mol^{-1}.[2] This result is in good agreement with the estimate (based on the different associative behaviour of tripentyl- and tripent-4-enylaluminium [11,12]) that the interaction energy is at least 30 kJ mol^{-1}.[2]



These calculations suggest that the stability of the metal/alkene complexes decreases in the order Al>Mg>Zn. Oliver and coworkers have investigated the intramolecular cyclization of metal hexenylcompounds $m=\frac{1}{3}$ Al, $\frac{1}{2}$ Mg or $\frac{1}{2}$ Zn.[3] They find that the ease of cyclization follows the same order: Al>Mg>Zn. It does not seem unreasonable to assume that the strength of the M/CC double bond interaction in the complexes reflects the strength of the partial M–C bonds formed in the activated complex.

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Received December 17, 1984.