The Organoaluminum Bond: Single vs. Multiple Bonding

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Although Lewis dot structures would lead to the expectation of an AlC double bond in $AlCH_2$, Fox, Ray, Rubesin, and Schaefer III found strong evidence for a single bond from high accuracy ab initio calculations. These calculations have been extended by generating ab initio wave functions for $AlCH_2$, BCH_2, $HAlCH_2$, and $HBCH_2$ and making comparisons between them. The ground and first excited states of $AlCH_2$ are found to be single bonded: BCH_2 and $HBCH_2$ possess double bonds; $HAlCH_2$ is intermediate. The origin of these results has been investigated by analysis of orbital compositions, charge density difference maps, and energies. Considerable insight has been gained into the long-standing problem of multiple vs. single bonding in the second and third rows of the periodic table. Our results also suggest that control of Al substituent electronegativity can impose AlC bond order changes from 1 to 2.

Introduction

This paper is an extension of the recent important study by Fox, Ray, Rubesin, and Schaefer[1] on the organometallic model compounds $AlCH_3$, $AlCH_2$, and AlCH. The molecule $AlCH_2$ is of particular note because its dissociation energy, dipole moment, and bond length in the ground state is more representative of the Lewis dot structure, :Al—$\dot{C}H_2$, than the expected double bonded structure, ·Al=CH_2. Thus, Schaefer et al. found the optimized Al—C bond length in $AlCH_2$ (using a double-ζ basis set) to be 1.989 Å while a value of 2.013 Å was obtained for $AlCH_3$. Dissociation energies (using a double-ζ plus polarization basis and a two reference state CI) were 77.4 kcal/mol (Al—CH_2) and 67.8 kcal/mol (Al—CH_3).

One reason for special interest in these species is the long-standing question of multiple bonding between atoms of the second and third rows. In this respect we investigate some aspects of the Al—C bonding in $AlCH_2$ by comparative calculations on $AlCH_2$, $HAlCH_2$ and their boron analogues BCH_2 and $HBCH_2$.

Method

Energy-optimized geometries of $AlCH_2$, BCH_2, $HAlCH_2$, and $HBCH_2$ were determined ab initio by using the STO-3G basis set[2] in GAUSSIAN 70[3] (see Figure 1) with the force relaxation scheme of Pulay.[4] For reference, STO-3G optimized geometries of HAl, HB, and CH_2 are also reported (Figure 1). All open-shell SCF calculations were performed by using UHF wave functions, and closed-shells were calculated RHF.

In general, STO-3G level calculations have been found to give reliable geometries and our energy-optimized Al—C bond length in $^2B_1$ $AlCH_2$ (1.948 Å) compares well with the value calculated by Schaefer et al. (1.989 Å). We also find that our ground-state energy level ordering ($^2B_1$: $1a_1^2$, $1b_2^2$, $2a_1^2$, $1b_1$, $3a_1^2$) agrees with Schaefer's larger basis set. This substantial agreement supports the belief that the STO-3G basis set is adequate for explaining the qualitative nature of the bonding and characterizing the essential differences between the molecules in this study.

$AlCH_2$ and BCH_2. Energy Levels. Insight into why Al—C is a single bond in $AlCH_2$ can be gained from the one-electron energy levels of $AlCH_2$ (ground-state $^2B_1$) and its fragments ^2P Al and $^3B_1$ CH_2 (Figure 2a and Table I). Several features should be noted.

First, the orbital ordering shows a singly occupied $1b_1$ in $AlCH_2$ falling below the double occupied $3a_1$. This arises from the reduction in electron–electron repulsion upon removing one electron from the closed-shell species $AlCH_2^-$. Removal of an electron from the $1b_1$ results in a large stabilization of the remaining $1b_1$ electron and a smaller stabilization of the $3a_1$ electrons. This difference is accentuated by the large spatial separation of the $1b_1$ and $3a_1$ orbitals (the $1b_1$ is primarily a perpendicular p orbital on carbon while the $3a_1$ is a largely s lone pair on Al). A lesser effect is the differential stabilization of the α orbitals as a result of removing a $1b_1$ β electron. As shown, this splitting is greatest for those orbitals nearest the $1b_1$ β "hole" (i.e., $1a_1$). The reverse of this argument can be applied to the removal of a single electron from the $3a_1^\beta$ orbital. In this case, the remaining $3a_1^\alpha$ orbital would be expected to fall below the double-occupied $1b_1$ orbitals again because of the reduction in electron–electron repulsion. This in fact happens in BCH_2 (Figure 2b and Table I), leading to a $^2A_1$ ground state. The $1b_1$ itself mixes with the p_x of B where it did not in Al.

The second striking feature of the orbital level diagram for $AlCH_2$ (Figure 2a) is the destabilization of the "methylene" orbitals, namely, the $1a_1$, $1b_2$, $2a_1$, and $1b_1$ orbitals. This destabilization is countered by a large drop in the energy of the single Al p electron and the formation of the Al—C single bond (primarily the $2a_1$ orbital). Because of the sizeable electronegativity difference between Al and C, the methylene-like orbitals gain charge (destabilization) while Al loses charge (stabilization). That $AlCH_2$ should behave in this fashion can be seen in a third feature of the orbital level diagram—the single occupied orbitals of methylene ($2a_1$ and $1b_1$) fall below the doubly occupied Al 3s. Thus there is a mismatch of orbital energies. The 3s orbitals are not well suited for mixing with the methylene orbitals, but the 3p orbitals are much worse: in essence, the p's do not contribute greatly to the bonding. Instead, the lone p electron of Al will occupy the "s-like" $2a_1$ bonding orbital and the 3s electrons will become the $3a_1$ "s-like" lone pair. This can be formally likened to a charge-transfer process (to the $2a_1$ of methylene) followed by the formation of a coordinate-covalent bond to Al.[5]

(1) Fox, D. J.; Ray, D.; Rubesin, P. C.; Schaefer, H. F., III, *J. Chem. Phys.* **1980**, *73*, 3246.
(2) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
(3) Hehre, W. H.; Ditchfield, R.; Pople, J. A.; Latham, W.; Newton, M. D. GAUSSIAN 70, *QCPE* **1973**, *No. 236*.
(4) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.
(5) Because of the formation of a coordinate covalent bond in the ground state the dipole moment is much smaller than might be expected on the basis of a simple charge-transfer process. A charge transfer to the $1b_1$ methylene orbital (leading to the $^2A_1$ excited state) does not permit the formation of the covalent coordinate bond and results in a higher dipole moment. (Schaefer reports a dipole moment of 3.15 D for the $^2A_1$ state and 0.74 D for the $^2B_1$ ground state.)

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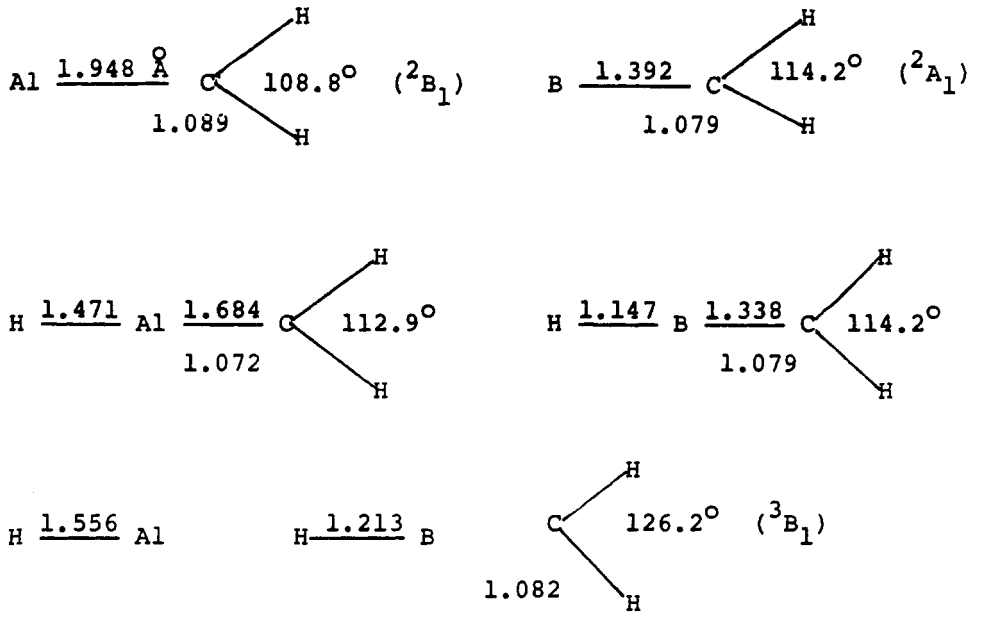

Figure 1. Optimized geometrical parameters (STO-3G) for $AlCH_2$, BCH_2, $HAlCH_2$, $HBCH_2$, HAl, HB, and CH_2.

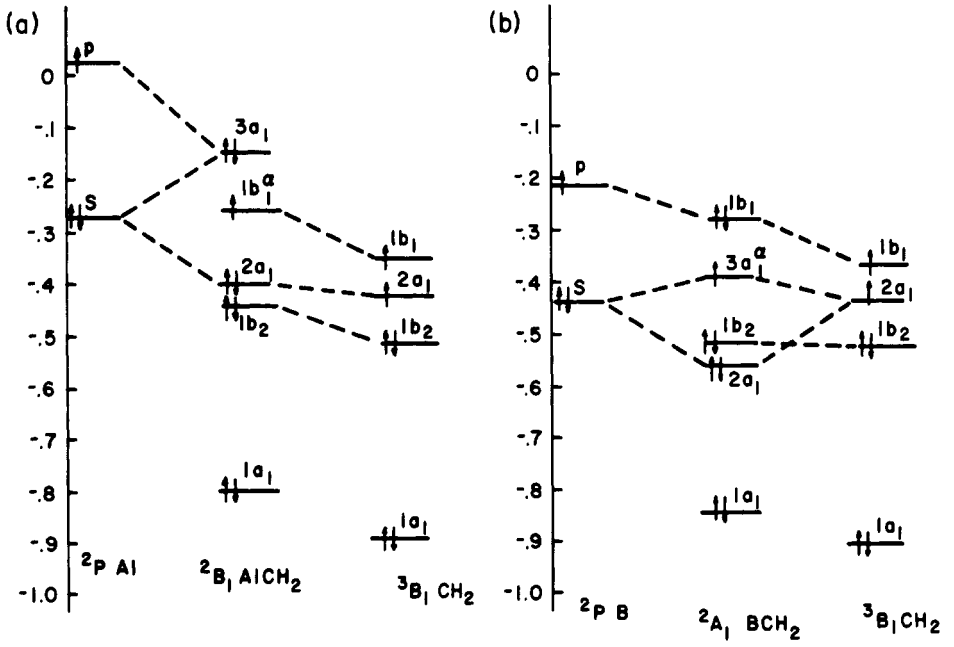

Figure 2. One-electron energy levels for α orbitals in (a) $AlCH_2$ and (b) BCH_2. All energies are in hartrees.

Table I. Molecular Orbital Energy Eigenvalues[a]

$AlCH_2$			BCH_2			$HAlCH_2$		$HBCH_2$	
	α	β		α	β				
$3a_1$	−0.1553	−0.1393	$1b_1$	−0.2635	−0.3012	$1b_1$	−0.1350	$1b_1$	−0.2739
$1b_1$	−0.2681		$3a_1$	−0.3744		$3a_1$	−0.3286	$3a_1$	−0.4950
$2a_1$	−0.4038	−0.3371	$1b_2$	−0.5041	−0.5129	$1b_2$	−0.4229	$1b_2$	−0.5148
$1b_2$	−0.4460	−0.4304	$2a_1$	−0.5506	−0.4960	$2a_1$	−0.4790	$2a_1$	−0.5928
$1a_1$	−0.8079	−0.7033	$1a_1$	−0.8259	−0.8672	$1a_1$	−0.7390	$1a_1$	−0.8623

[a] Energies are in hartrees.

For BCH_2 there is a strong stabilization of the $2a_1$ orbital upon formation of the B—C single bond consistent with the small difference in energy between the CH_2 $2a_1$ orbital and the B 2s orbital. The $3a_1$ orbital, made up from out-of-phase CH_2 and boron contributions, is stabilized by mixing with the unoccupied p_z orbital on B. This is possible for BCH_2 because the boron levels lie much closer to the CH_2 levels. The degree of charge transfer is much less in BCH_2 also. Thus there is only a slight destabilization of the $1a_1$ methylene-like orbital while the $1b_2$ orbital is essentially unchanged. In summary, the most important feature of Figure 2 is the stabilization of the 2s and 2p B orbitals relative to Al. The p orbitals are low enough to participate in the bonding leading to s,p mixing in the a_1 orbitals and π formation in the $1b_1$ orbitals of BCH_2.

Lewis Structures. In spite of modern advances in bonding theory, Lewis dot structures remain a remarkably powerful aid in guiding qualitative thinking.[6] It is

Table II. π orbital ($1b_1$) Mulliken Populations for M = Al and B

	M (%)	C (%)
$AlCH_2$	0.1142 (11)	0.9649 (89)
BCH_2	0.8877 (44)	1.1096 (56)
$HAlCH_2$	0.5673 (28)	1.4855 (72)
$HBCH_2$	0.8396 (42)	1.1603 (58)

therefore important to explore cases where a breakdown in the Lewis representation occurs, to make connection between Lewis structures and the quantum calculations, and to establish criteria that can help anticipate such cases. In contrast to the expected double bond in $AlCH_2$, the actual $^2B_1$ ground state is best pictured as :Al—$\dot{C}H_2$. This structure is entirely compatible with its Al—C bond length, Al—C dissociation energy, and small dipole moment (0.74 D). The $^2A_1$ state, now the first excited state instead of the expected ground state, contains an AlC double bond as one of the resonance contributors

$$\cdot Al{=}CH_2 \leftrightarrow \cdot Al^+{-}\ddot{C}H_2^-$$

We can estimate the dissociation energy of the $^2A_1$ state and compare it to that of the $^2B_1$ ground state in order to ascertain which of the above resonance contributors has the largest weight. The $^2A_1$ separates at infinity to ^2P Al + $^1A_1$ CH_2 which was been recently determined to be 10.9 kcal/mol higher[7] than the ^2P Al plus $^3B_1$ CH_2 separation of the $^2B_1$ ground state. Combining this value with the 22.9 kcal/mol $^2A_1$ - $^2B_1$ energy difference obtained from the double ζ with polarization plus CI calculation of Schaefer et al.[1] yields a $^2A_1$ dissociation energy of 65.4 kcal/mol, a smaller value than that of $^2B_1$ $AlCH_2$ or Al—CH_3. This line of reasoning points to the $\cdot Al^+$—$\ddot{C}H_2^-$ Lewis structure as a strong contributor (in spite of its six bonding electrons compared to eight in the double-bonding structure), and this assignment is supported by the 3.14 D dipole moment computed for the $^2A_1$. On the other hand, the internuclear separation is 1.802 Å, only 5% greater than the double bond length predicted form the average single-to-double bond length ratio generally observed.[6] As in the $^2B_1$ ground state, the origin of the reduced bond strength is mismatch in orbital energies between Al and methylene, in this case the Al p_x with $1b_1$ in CH_2. (Schaefer et al.[1] found a similarly weak bond with an extremely short (1.668 Å) AlC length in $^1\Sigma^+$ AlCH.) For BCH_2 the single structure, $\cdot B{=}CH_2$, is an adequate representation; the ionic structure can be eliminated by the usual arguments of formal charges (plus fewer bonding electrons).

As shown by the orbital energy levels discussed later, addition of hydrogen to BCH_2 leads to the expected Lewis dot structure H—B=CH_2. Addition of H to $AlCH_2$, on the other hand, shortens the AlC bond length by exactly that ratio expected in going from a single to a double bond. Nevertheless the AlC bond retains considerable ionic character and the two resonance contributors analogous to those for $^2A_1$ $AlCH_2$ are also those which must be considered here. As in that case, the bond strength is less, and the bond more polar, than that suggested by its length and associated Lewis structure, but there is considerably more double-bond character in $HAlCH_2$ than in $^2A_1$ $AlCH_2$.

(6) DeKock, R. L.; Gray, H. B. "Chemical Structure and Bonding", Benjamin/Cummings: New York, 1980. Huheey, J. E. "Inorganic Chemistry"; Harper and Row: New York, 1978. Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Philadelphia, Pa., 1977.

(7) Bauschlicher, C. W.; Shavitt, I. *J. Am. Chem. Soc.* **1978**, *100*, 739. As discussed in this article, there is one experimental measurement that suggests a $^3B_1$ - $^1A_1$ separation of 19.5 kcal/mol, but the resulting binding energy of $^2A_1$ $AlCH_2$ would still be less than that of its $^2B_1$ ground state.

The ability of a singly occupied orbital of intermediate electronegativity (like H) to significantly modify the aluminum carbon bond suggests the large range of organoaluminum compounds potentially available. It also suggests that a highly electronegative substituent should produce a full AlC double bond.

Orbital Composition. The molecular orbital shapes[8] (Figure 3a) further elucidate the bonding in $AlCH_2$. Because of the large differences in orbital energies between the aluminum and methylene, the lowest orbitals ($1a_1$ and $1b_2$) are essentially unchanged from their parent methylene orbitals. The $2a_1$ orbital consists largely of the methylene $2a_1$ with a small out-of-phase Al s contribution and can be interpreted as a coordinate covalent bond (recall that in the parent CH_2 orbitals, the $2a_1$ is only singly occupied). The singly occupied $1b_1$ is almost entirely localized on the carbon atom, thereby excluding the formation of even a partial π bond. Finally, the doubly occupied $3a_1$ shows a lone pair directed away from the Al—C bond and has a high degree of s character consistent with the poor energetics of the Al p orbitals. The directionality of the lone pair is obtained by an out-of-phase mixing with the methylene $2a_1$ orbital. The region of positive polarity enclosing the aluminum nuclei is primarily due to the radial node of the 3s orbital.

The bonding in BCH_2 stands in sharp contrast to that in $AlCH_2$. The B—C bond is unequivocally a double bond as shown by the shortening of the BC bond distance from 1.558 Å in BCH_3 to 1.392 Å in BCH_2 and by the shape of the $1b_1$ π orbital (Figure 3b). A comparison of the p_x Mulliken populations (Table I) displays a well-shared density between boron and carbon (44% on boron) while the singly occupied $1b_1$ in $AlCH_2$ is 89% on the carbon. The $1a_1$ orbitals in BCH_2 largely retain their CH_2 character, stabilized by a weak in-phase interaction with a B sp orbital. The $2a_1$ orbitals form the B—C σ bond from an in-phase combination of the CH_2 $2a_1$ and the boron s and p_z orbitals. The $2a_1^\alpha$ orbital is stabilized relative to the $2a_1^\beta$ orbital (because of the Fermi hole arising from the singly occupied $3a_1^\alpha$ orbital) and has more 2s character than the $2a_1^\beta$. The $1b_2$ orbitals are virtually unchanged from the CH_2 fragment. The singly occupied $3a_1$ consists of an sp hybrid on boron directed away from the CH_2 and a smaller contribution from the $2a_1$ CH_2 orbital in-phase with the tail of the B sp hybrid. Finally, the doubly occupied $1b_1$ is a pair of π spin orbitals with the α orbital polarized toward the boron (toward the Fermi hole) and the β orbital polarized toward carbon. The net polarization (as shown in Table I) is toward carbon.

Charge Density Difference Plots. The large differences in the bonding between $AlCH_2$ and BCH_2 is further illustrated in the charge density difference plots shown in Figure 4. These plots were generated from the total density minus the density of a spherically averaged Al (or B) atom (^2P ground state) and the density of the CH_2 biradical. This choice of reference fragments corresponds to that used in the MO splitting diagram, and the resultant plot shows the change in electron density upon formation of the bond. Both density plots are presented as two half planes through the C_{2v} axis. The *xz* plane contains the hydrogen atoms; the *yz* plane bisects the HCH angle.

The charge density difference plot for BCH_2 shows a large concentration of density in the *yz* plane at the expense of density in the *xz* plane. This shift is associated with the formation of the B—C π bond. (Since the reference density is based on spherically averaged boron

(8) Jorgensen, W. L. *QCPE* **1977**, *No.* 340.

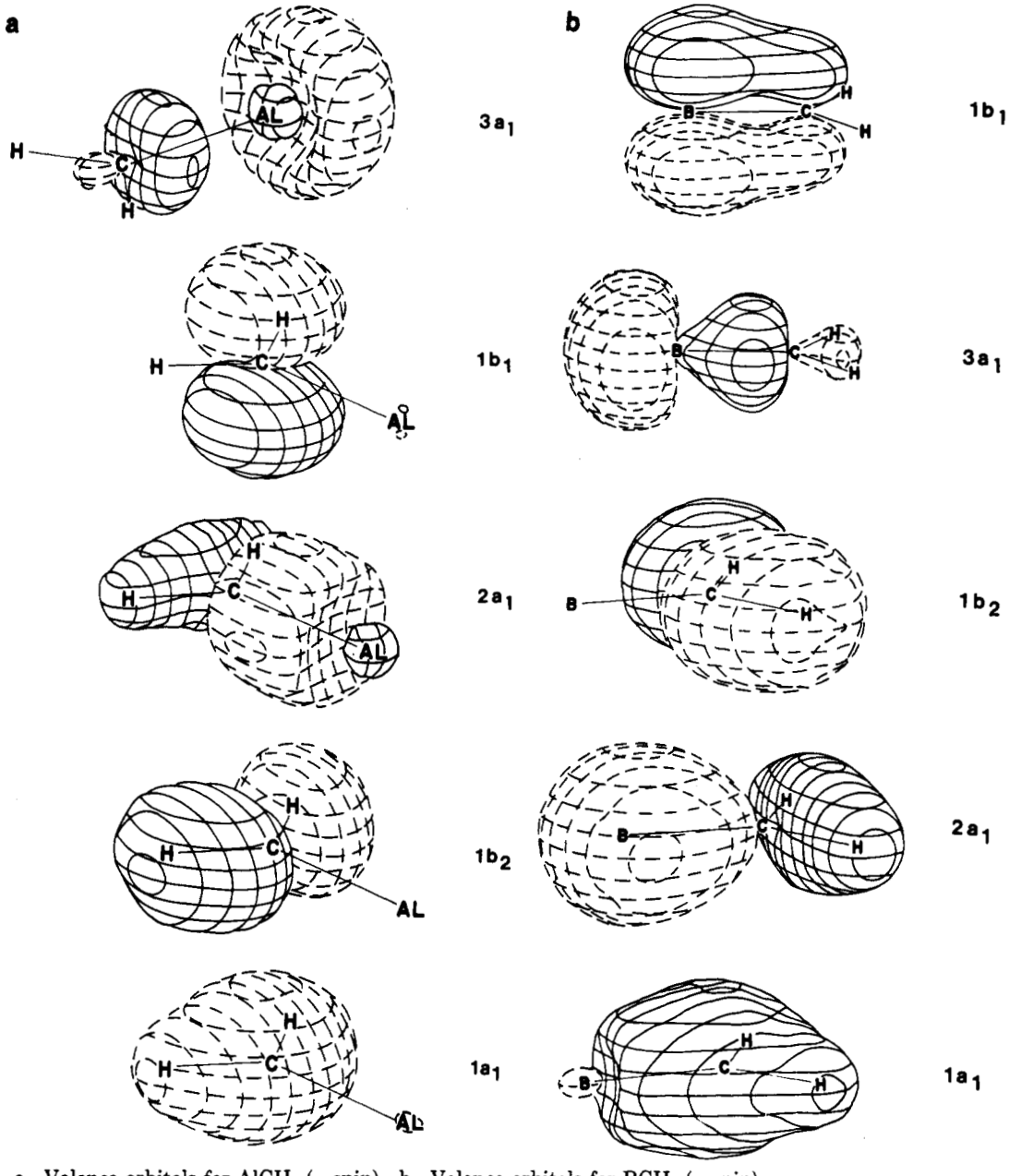

Figure 3. a. Valence orbitals for $AlCH_2$ (α spin). b. Valence orbitals for BCH_2 (α spin).

density, this shift reflects the orientation of the lone 2p electron of boron along the y axis.) There is also a large gain in charge along the B—C bond associated with the formation of the σ bond. The shape of this region, especially in the xz plane, is indicative of the covalent nature of the bond: both atoms contribute electrons to the region. Finally, there is a slight loss of density around the hydrogen atoms (relative to CH_2) and a gain in the region between them consistent with the increase in the HCH angle.

The corresponding plot for $AlCH_2$ shows a large loss in both the xz and yz planes in the region associated with the Al $3p_x$ and $3p_y$ orbitals and in the region along the Al—C bond nearest the aluminum. There is a large gain along the z axis both between the Al and C and in the Al lone pair region. The latter is due to the strong polarization of charge away from the Al as indicated in the $3a_1$ molecular orbital. The shape of the charge gain between the atoms is significantly different than in the boron case. Here the pattern is dominated by the gain of charge in the methylene $2a_1$ region and not by a sharing of charge. The pattern is essentially that of an ionic bond. (The smallness of the dipole moment is understandable: the dipole arising from the ionic bond is reduced by the polarization of the Al 3s electrons and by the small spatial separation of the component charges—which in turn is due to the hybridization of the carbon.) Also unlike the density in BCH_2 there is a region of large charge gain near the hydrogen atoms. This is another indication of the net gain on CH_2 by charge transfer from the aluminum. It is interesting that except for this region, the charge density difference plot has virtually pure σ symmetry.

$HAlCH_2$ and $HBCH_2$. To examine the effect of additional ligands on aluminum and boron, we have also carried out calculations for $HAlCH_2$ and $HBCH_2$[9] (geometries given in Figure 1). The AlC bond length in $HAlCH_2$ showed a considerable shortening relative to $AlCH_2$ (0.264 Å) while the BC bond length in $HBCH_2$ shortened only 0.054 Å compared to that of BCH_2. This is indicative of the formation of at least a partial aluminum carbon double bond.[10] Since the $3a_1$ orbital of $AlCH_2$ is doubly occupied,

(9) Previously reported: Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402.

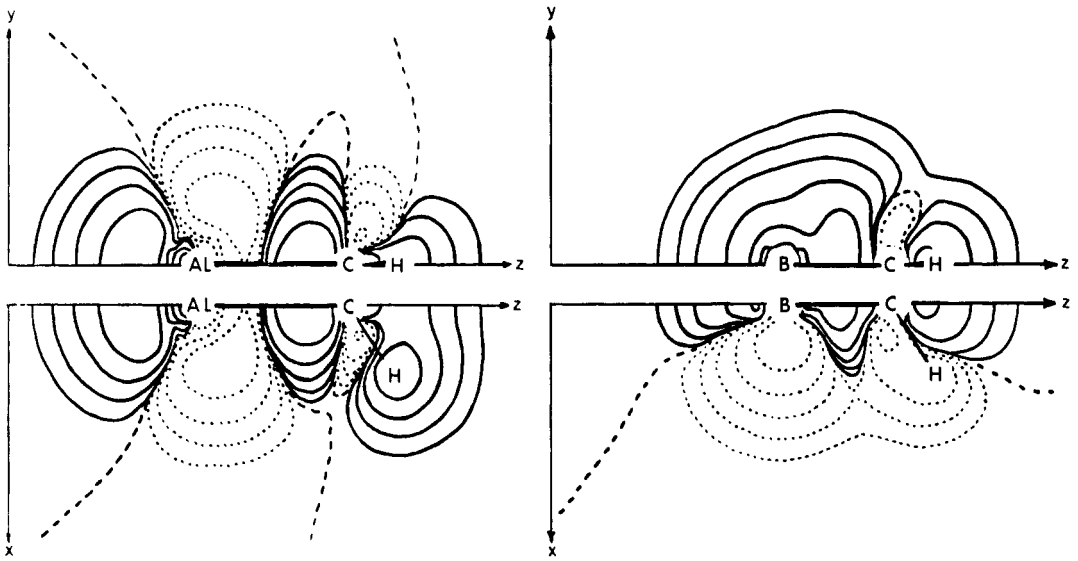

Figure 4. Charge density difference maps, $AlCH_2$ (left), BCH_2 (right). Total charge density minus spherical Al (B) minus CH_2 diradical in plane of molecule (*xz*) and the perpendicular plane (*yz*): solid lines, gain relative to separated fragments; dotted lines, loss; dashed lines, zero contour. Lowest gain (loss) contour is 0.000 316 e^-/a_0^3; successive contours increase by $10^{1/2}$.

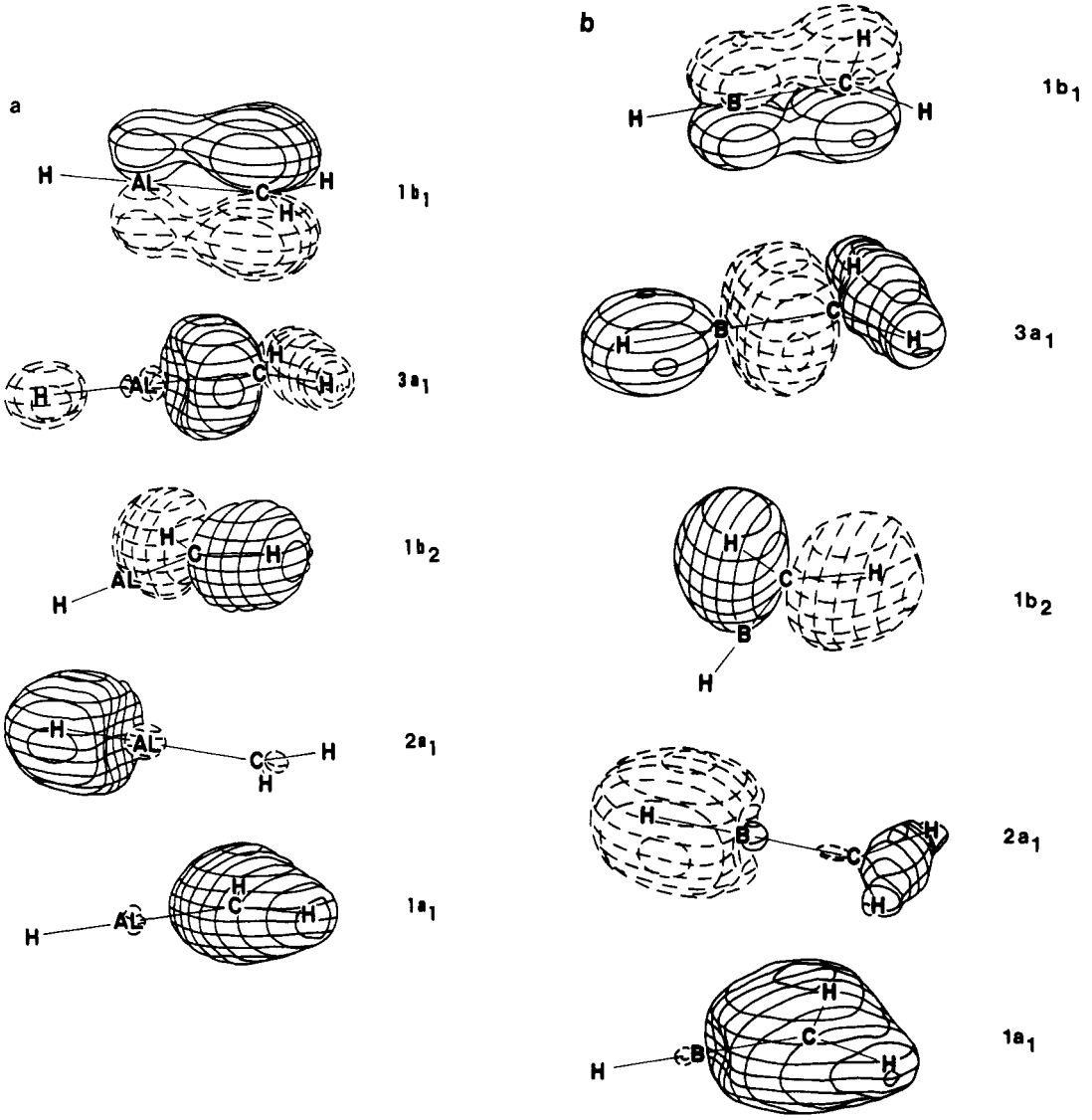

Figure 5. a. Valence orbitals for $HAlCH_2$. b. Valence orbitals for $HBCH_2$.

it is easiest to view the formation of $HAlCH_2$ as a protonation of the Al lone pair followed by the addition of an electron to the LUMO $1b_1^\beta$ orbital. The orbitals in $HAlCH_2$ and $HBCH_2$ are compared in parts a and b, re-

spectively, of Figure 5. The principal effect of the hydrogen is stabilization of the $3a_1$ orbital and withdrawal of charge from the aluminum. The charge withdrawal has two effects. First, it stabilizes the 3s Al orbitals by increasing the positive charge on Al, thus allowing them to participate more fully in bonding. Secondly, it greatly reduces the electron–electron repulsion between the $2a_1$ and the $3a_1$ orbitals. Both effects will tend to reduce the Al—C bond length. A shorter bond length also increases the Al $3p_x$—C $2p_x$ overlap leading to additional stabilization of the $1b_1$ orbital. We note, however, that the relative Mulliken population of the $1b_1$ orbital on the Al is only 28% (11% in $AlCH_2$) and thus remains highly polarized.

(10) As suggested by a reviewer, a thermodynamic measure of the degree of XC double bonding in these compounds as well as $AlCH_2$ and BCH_2 might be obtained by considering isodesmic reactions of the form

$$HXCH_2 + XH_n \rightarrow XCH_2 + XH_{n+1} \quad (1)$$

$$XH_2 + XH_n \rightarrow XH + XH_{n+1} \quad X = B, Al;\ n = 0, 1, 2 \quad (2)$$

In the table below we give heats of reaction for these two reactions with the same basis set employed throughout our study.

ΔE_m, kcal/mol	reaction 1		reaction 2	
n	X = Al	X = B	X = Al	X = B
0	−66.0	+29.7	−142.5	−48.1
1	+76.5	+77.8	0.0	0.0
2	−177.3	−87.3	−253.8	−165.1

It is clear from the energies for the second reaction that bonding to either Al or B is very sensitive to the value of n. This variability makes it difficult to evaluate changes in the XC bonding from reaction 1. Although the trends are interesting and worthy of future study, the differences in spin multiplicity and coordination number make a detailed analysis at the minimal basis set level impractical.

Note Added in Proof. We have implicitly assumed the BC double bonded species, $B{=}CH_2$ and $HB{=}CH_2$, to be the expected and normally occurring reference compounds. However, BC double bonds have not, in fact, been observed (Onak, Thomas "Organoborane Chemistry"; Academic Press: New York, 1975; p 4). This fact undoubtedly derives from the relative stability of isomers with BC single bonds and therefore does not invalidate the BC double bonds we have calculated. It may actually enhance the value of our computational results because they elucidate the nature of a bond which has proved difficult to isolate experimentally.

Acknowledgment. We wish to thank the NIH (Grant GM 26462) for financial support.

Registry No. $AlCH_2$, 76392-50-2; BCH_2, 79435-75-9; $HAlCH_2$, 79435-76-0; $HBCH_2$, 56125-75-8.

The Molybdenum–Molybdenum Triple Bond. 11.[1] 1,1- and 1,2-Disubstituted Dimolybdenum Compounds of Formula $Mo_2X_2(CH_2SiMe_3)_4$ (M≡M). Observation of Rotation about the Triple Bond

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The preparation and characterization of a series of compounds of general formula $Mo_2X_2R_4$ (M≡M), where X = Br, Me, O-*i*-Pr, O-*t*-Bu, and NMe_2 and R = CH_2SiMe_3, are reported. The pattern of substitution may be 1,1-, $X_2RMo{\equiv}MoR_3$, or 1,2-, $XR_2Mo{\equiv}MoR_2X$, depending upon the nature of X and the preparative route. The 1,1- and 1,2-$Mo_2X_2R_4$ compounds do not isomerize, demonstrating the existence of a high kinetic barrier to R and X group transfer between molybdenum atoms. Alkyl group transfer may occur during the substitution reaction: 1,2-$Mo_2Br_2R_4$ and $LiNMe_2$ (2 equiv) yield 1,1-$Mo_2(NMe_2)_2R_4$, whereas 1,2-$Mo_2Br_2R_4$ and $HNMe_2$ yield 1,2-$Mo_2(NMe_2)_2R_4$. The formation of one isomer of $Mo_2(NMe_2)_2R_4$ must occur by kinetic control. Variable-temperature ^1H NMR spectra for 1,1- and 1,2-$Mo_2(NMe_2)_2R_4$ compounds provide the first observation of rotation about the Mo≡Mo bond. The energy barriers to rotation are reconcilable with steric restraints. By contrast, the barriers to rotations about Mo—N bonds in the 1,1- and 1,2-$Mo_2(NMe_2)_2R_4$ compounds are ΔG^* (kcal mol^{-1}) = 11.5 ± 0.5 and 15.0 ± 0.5, respectively, and the difference is correlated with electronic factors. The structure of 1,2-Mo_2(O-*t*-Bu)$_2R_4$, determined by a single-crystal X-ray diffraction study, revealed a staggered ethane-like (C_{2h}) *anti*-$Mo_2O_2C_4$ central skeleton with Mo—Mo = 2.209 (2) Å, Mo—O = 1.865 (8) Å, and Mo—C = 2.13 (1) and 2.14 (1) Å and internal angles Mo—Mo—O = 110.7 (3)° and Mo—Mo—C = 100.1 (5)° (averaged). Crystal data at −163 °C were a = 10.025 (3) Å, b = 18.473 (9) Å, c = 9.975 (5) Å, β = 102.03 (3)°, Z = 2, and d_{calcd} = 1.263 g cm^{-1} with space group $P2_1/n$. These new observations are discussed in the light of previous work.

Introduction

In the first paper of this series, the preparation and detailed characterization of $Mo_2(NMe_2)_6$ (M≡M) was reported.[2] This compound has since been the parent of an extensive family of others and affords an easy entry into the rich chemistry associated with the Mo≡Mo bond in Mo_2^{6+}-containing compounds.[3,4] Two views of the Mo_2-

(1) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P. *Inorg. Chem.* 1981, *20*, 2215.

(2) Chisholm, M. H.; Cotton, F. A.; Frenz, B. A.; Reichert, W. W.; Shive, L. W.; Stults, B. R. *J. Am. Chem. Soc.* 1976, *98*, 4469.

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