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Bonding in Cationic MCH_2^+ (M = K–La, Hf–Rn): A Theoretical Study on Periodic Trends

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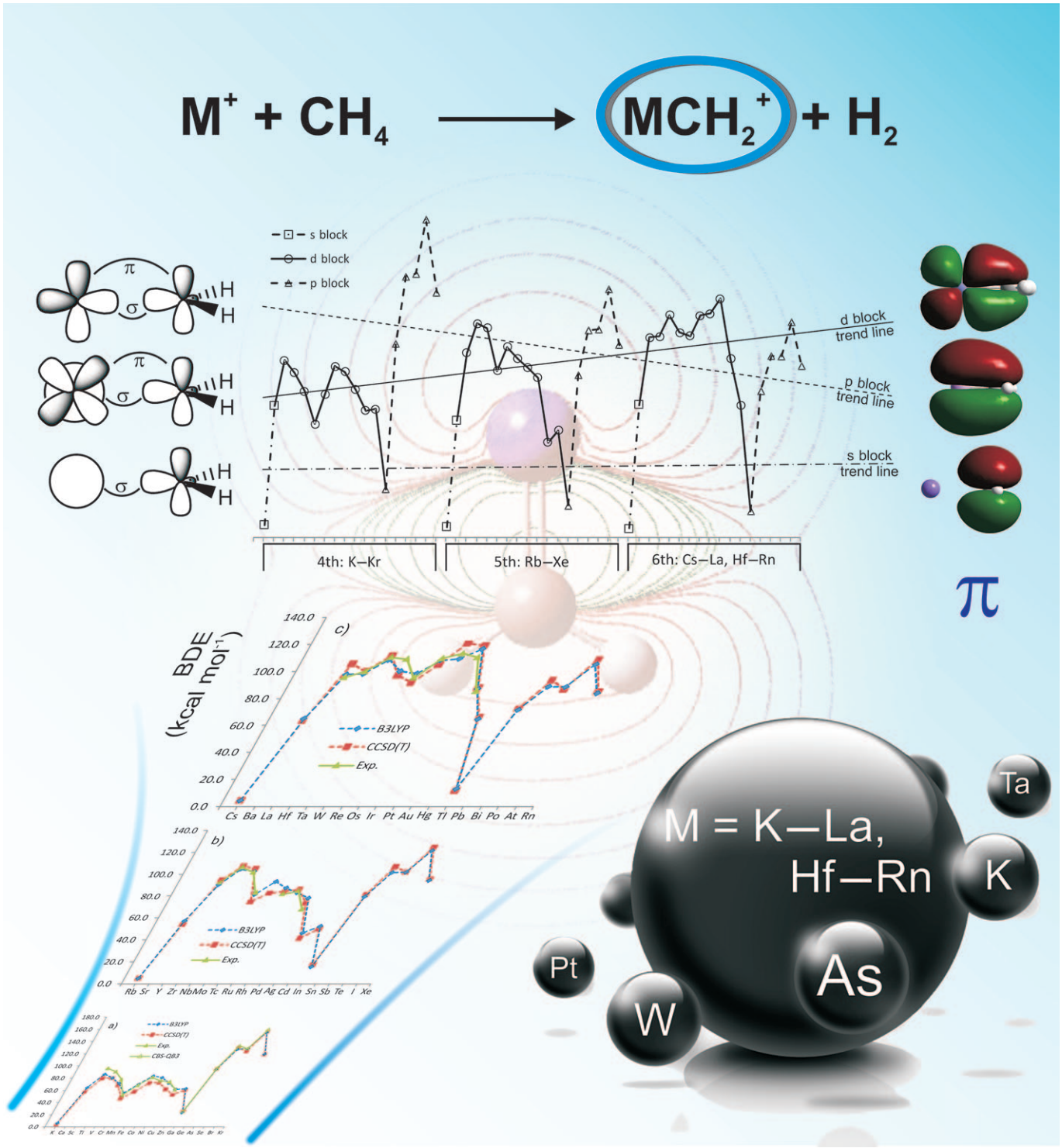
In memory of Björn O. Roos



Abstract: DFT and CCSD(T) calculations have been performed to investigate the bonding situation of 54 cationic methylene complexes, MCH_2^+ (M = K–La, Hf–Rn). A comparison of the computed results with experimentally and CBS-QB3-derived data demonstrates the reliability of B3LYP/def2-QZVP with regard to the bond dissociation energies. Further, the bonding character of the MCH_2^+ complexes is revealed by geometrical and molecular-orbital (MO) analysis. The comparison of the periodic trends within the s-, p-, and d-block MCH_2^+ carbenes shows a pattern different for main-group versus transition-metal complexes. By combining this work with the recently reported trends for the f-block lanthanide carbenes MCH_2^+, a systematic and comprehensive overview can be obtained.

Keywords: bond energy · carbenes · density functional calculations · main group elements · periodic trends

Introduction

Methylene complexes, especially those with transition metals, have been implicated as crucial intermediates in numerous important catalytic reactions. Understanding of both the bonding and the reactivity of naked MCH_2^+ sheds light on mechanistic aspects of catalytic processes in which these simple complexes are involved. One of the most relevant examples concerns the stoichiometric activation of methane by bare transition-metal cations M^+,[1] as show in Equation (1), which represents a combination of Equations (2) and (3).

$$M^+ + CH_4 \rightarrow MCH_2^+ + H_2 \quad \Delta E_1 \tag{1}$$

$$CH_4 \rightarrow CH_2 + H_2 \quad \Delta E_2 \tag{2}$$

$$M^+ + CH_2 \rightarrow MCH_2^+ \quad \Delta E_3 = -BDE(M{-}CH_2^+) \tag{3}$$

Given the fact that ΔE_2 is constant, the reaction energy (ΔE_1) for various M^+ is thus solely determined by the bond dissociation energy (BDE) of the resulting $M{-}CH_2$ bond in MCH_2^+. To achieve thermal activation of methane, the BDE of the $M{-}CH_2$ bond in MCH_2^+ has to exceed ΔE_2. Experimental[2] and theoretical[3] studies aimed at determining the bond strengths of transition-metal methylene complexes MCH_2^+ have been performed extensively.

Recently, in a slightly different context, methane activation by main-group element oxides, for example, MgO^+,[4] $[(Al_2O_3)_x]^+$,[5] SO_2^+,[6] and $P_4O_{10}^+$,[7] revealed the unexpected potential of main-group elements. In fact, even atomic As^+ was found to dehydrogenate methane ([Eq. (1)]) at room temperature.[8] However, in contrast to the transition-metal complexes, there is a lack of measured BDEs of the $M{-}CH_2$ bond in MCH_2^+ for main-group elements. Here, we report a systematic theoretical study of the cationic complexes MCH_2^+ (M = K–La, Hf–Rn). Lanthanides have been excluded because their carbene complexes have been recently analyzed comprehensively by Roos and Pyykkö.[9] We provide energetic and structural data and, in addition, present a comparison of the periodic trends for the s-, d-, and p-elements.

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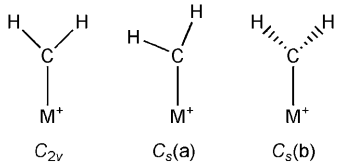
Computational Details

The calculations were performed by using the Gaussian 03 package.[10] Geometries were optimized at the unrestricted B3LYP level of theory[11] using the def2-QZVP basis sets.[12] Frequencies were computed for all optimized structures with the same method to verify the nature of the stationary points and to obtain the zero-point energy corrections. Single-point energy calculations on the DFT optimized geometries were performed at the CCSD(T)/def2-QZVP level of theory. Because of the lack of experimental data, highly accurate CBS-QB3[13] calculations were performed for the complexes MCH_2^+ (M = Ga–Br), and they were then employed as references to verify the B3LYP and CCSD(T) findings.

Similar to the transition-metal complexes, for the main-group elements the carbene structures MCH_2^+ are more stable than their isomeric forms $HMCH^+$ or H_2MC^+.[14] To ensure that the global minima were located, symmetry factors were carefully examined by using different symmetric and asymmetric starting geometries. The geometry optimizations converged to three point groups as shown in Scheme 1. Different spin states have been taken into account and only the ground states of M^+ and MCH_2^+ are presented. Note that in some cases there are low-lying states that are very close to the ground state. However, such near-degenerate states do not affect the calculation of BDE.



Scheme 1.

Results and Discussion

Accuracy: In Figure 1, a comparison between calculated and experimentally derived BDEs is presented. The BDE values together with structural information are listed in Tables 1–3. The BDEs calculated at both B3LYP and CCSD(T) are consistent with the available experimental data. The mean abso-

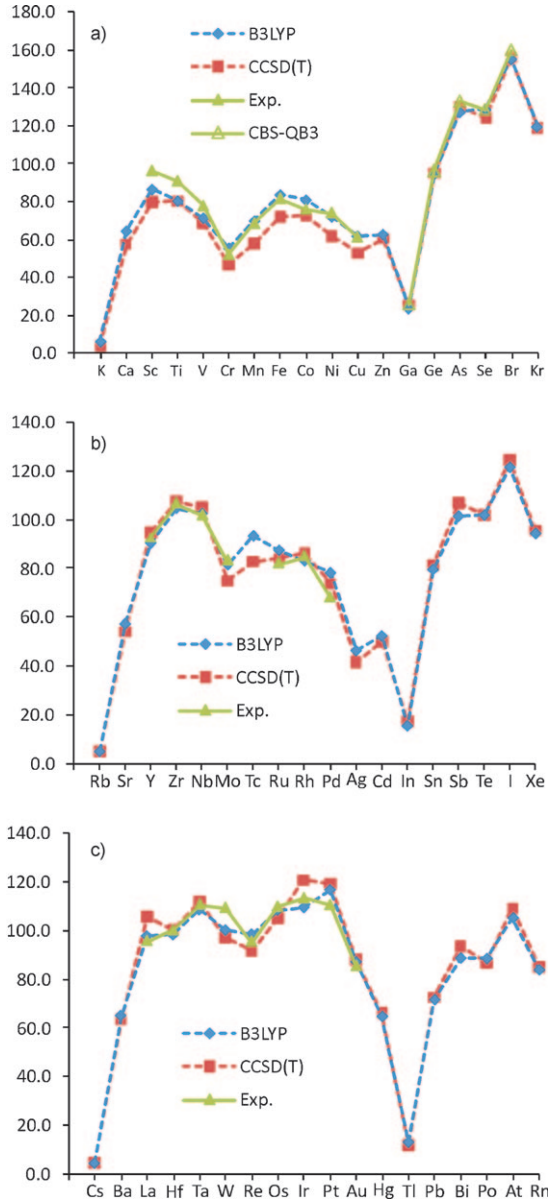


Figure 1. Bond dissociation energies (in kcal mol^{-1}) for a) the 4th row complexes MCH_2^+ (M = K–Kr); b) the 5th row complexes MCH_2^+ (M = Rb–Xe); c) the 6th row complexes MCH_2^+ (M = Cs–La, Hf–Rn).

lute errors (MAEs) at the B3LYP level are 4.5, 3.2, and 3.6 kcal mol^{-1} for the for MCH_2^+ complexes of the 4th, 5th, and 6th row transition metals. The corresponding MAEs at the CCSD(T) level are 9.5, 2.6, and 5.7 kcal mol^{-1}. Owing to the lack of experimental values for p-block elements, the BDEs for M–CH_2^+ (M = Ga–Br), calculated with the highly accurate CBS-QB3 method, were employed as a reference for the B3LYP and CCSD(T) data. The excellent agreement justifies the use of these two latter methods for the main-group elements as well. The errors for the 6th row elements are similar to that derived for the 4th and 5th row counterparts, demonstrating that relativistic effects[15] are well described by the def2-QZVP basis set (with the corresponding effective core potentials).[12a,b] Although CCSD(T) performed better in determining the BDEs of the 5th row transition-metal complexes MCH_2^+, the performance of B3LYP is rather good for all elements of the three rows (overall MAE = 3.8 kcal mol^{-1}) and also gives smaller maximum errors than CCSD(T). Therefore, we use the B3LYP results for the following discussion.

Geometry: For most of the MCH_2^+ species the calculations converge into the C_{2v} point group, except those of the early transition-metal complexes MCH_2^+ (M = Sc, Ti, Y, Zr, Nb, La, Hf, and Ta) which adopt C_s(a) symmetry; the MCH_2^+ species (M = group 12 and 18) prefer the C_s(b) form (see Scheme 1). The calculated M–C bond lengths, $d_{(M-C)}$, are mostly in line with the covalent radii proposed by Pyykkö and co-workers.[16] Only for the group 1 complexes are the M–C bonds much longer than expected for a typical M–C single bond, indicating that no significant covalent bonding interaction exists. For the M–C bonds (M = group 12, 13, 14, and 18), the $d_{(M-C)}$ data for complexes with elements suggest a single bond,[16b] whereas the $d_{(M-C)}$ for the remaining carbenes agree very well with those expected for a double bond.[16c,d] No indication for triple-bond character was found.[16a]

The rather small ∡MCH angles of the early transition-metal complexes MCH_2^+ in C_s(a) geometry reveal the existence of agostic interactions.[17] The structure and electron density of $ScCH_2^+$, chosen as a representative, is shown in Figure 2. Such interactions, which are related to the empty

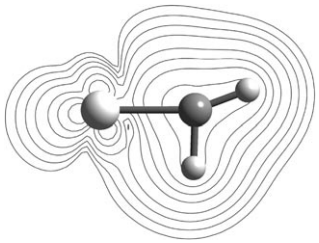


Figure 2. Structure and electron density of $ScCH_2^+$ exhibiting an α-agostic interaction.

valence orbitals on the metal, have been analyzed in detail by Roos, Pyykkö, and co-workers.[9,18] The α-hydrogen interaction was also found to be significant in metal–silicon multiple bonds owing to their electron deficiency.[19] One imaginary frequency, which corresponds to the in-plane twist of the CH_2 group, was found in the C_{2v} symmetry of all C_s(a) MCH_2^+ species. The relative energies for these C_{2v} transition states vary over the range 0.3–12.4 kcal mol^{-1}, implying that the agostic interactions are not very strong.

For both the far-left and far-right elements of a row, that is, the alkali-metal and the rare-gas species MCH_2^+, the ∡HCH amounts to around 133°, which is close to that in the free triplet CH_2 radical (ground state $^3B_1$). MCH_2^+ complexes with group 12 and group 18 elements adopt a C_s(b)

Table 1. Geometries and BDEs for the 4th row complexes MCH_2^+ (M = K–Kr).

	State	Structure			BDE [kcal mol^{-1}]		
		$d_{(M-C)}$ [Å]	∡MCH [°]	∡HCH [°]	B3LYP	CCSD(T)	Exptl
KCH_2^+	$^3B_1$	3.078	111.5	137.1	6.2	3.9	–
$CaCH_2^+$	$^2B_1$	2.211	125.6	108.7	64.5	57.2	–
$ScCH_2^+$	$^1A'$	1.839	88.2	112.4	86.5	79.8	96.1 ± 5.5[a]
$TiCH_2^+$	$^2A'$	1.801	87.6	113.8	80.4	80.1	90.8 ± 2.2[a]
VCH_2^+	$^3B_1$	1.882	123.3	113.4	71.4	68.6	77.7 ± 1.4[a]
$CrCH_2^+$	$^4B_1$	1.865	121.7	116.5	55.5	46.7	51.9 ± 1.0[a]
$MnCH_2^+$	$^5B_1$	1.891	122.5	114.9	69.8	57.8	68.4 ± 2.2[a]
$FeCH_2^+$	$^4B_2$	1.851	122.7	114.7	83.6	71.6	81.5 ± 1.0[a]
$CoCH_2^+$	$^3A_1$	1.827	123.5	113.0	80.9	72.4	75.8 ± 1.2[a]
$NiCH_2^+$	$^2A_1$	1.811	123.7	112.7	72.1	61.8	73.8 ± 1.8[b]
$CuCH_2^+$	$^1A_1$	1.858	124.3	111.3	61.9	52.6	61.2 ± 1.2[a]
$ZnCH_2^+$	$^2A'$	1.933	116.1	123.9	62.7	60.3	–
$GaCH_2^+$	$^3B_1$	2.014	117.1	125.8	23.7	25.1	25.4[c]
$GeCH_2^+$	$^2B_1$	1.915	123.0	114.0	94.6	94.8	96.5[c]
$AsCH_2^+$	$^1A_1$	1.731	122.4	115.2	127.3	129.8	132.6[c]
$SeCH_2^+$	$^2B_2$	1.734	120.8	118.4	128.7	124.2	128.4[c]
$BrCH_2^+$	$^1A_1$	1.750	119.4	121.3	155.2	155.8	159.4[c]
$KrCH_2^+$	$^2A'$	2.018	107.1	132.5	119.6	118.6	–

[a] Reference [2f]. [b] Reference [2g]. [c] Calculated with CBS-QB3, not included in MAE calculation.

Table 2. Geometries and BDEs for the 5th row complexes MCH_2^+ (M = Rb–Xe).

	State	Structure			BDE [kcal mol^{-1}]		
		$d_{(M-C)}$ [Å]	∡MCH [°]	∡HCH [°]	B3LYP	CCSD(T)	Exptl
$RbCH_2^+$	$^3B_1$	3.298	111.7	136.6	5.0	5.1	–
$SrCH_2^+$	$^2B_1$	2.366	126.0	108.0	57.2	54.1	–
YCH_2^+	$^1A'$	1.974	88.6	110.6	90.2	94.5	92.7 ± 3.1[a]
$ZrCH_2^+$	$^2A'$	1.888	84.5	112.8	104.5	107.3	106.5 ± 1.6[b]
$NbCH_2^+$	$^3A'$	1.824	80.7	114.0	102.3	104.7	102.3 ± 2.2[a]
$MoCH_2^+$	$^4B_1$	1.870	121.9	116.2	81.4	74.8	82.3 ± 2.3[c]
$TcCH_2^+$	$^5B_1$	1.874	122.2	115.5	93.1	82.7	83 ± 5[d,e]
$RuCH_2^+$	$^2A_2$	1.791	120.8	118.4	87.2	84.0	82.2 ± 1.2[a]
$RhCH_2^+$	$^1A_1$	1.752	119.2	121.6	83.0	86.0	85.1 ± 1.9[a]
$PdCH_2^+$	$^2A_1$	1.854	121.7	116.6	78.0	73.6	68.1 ± 1.2[a]
$AgCH_2^+$	$^1A_1$	2.063	124.5	111.1	46.3	41.5	$>25.6 \pm 1.0$[e,f]
$CdCH_2^+$	$^2A'$	2.119	114.6	124.2	52.3	50.0	–
$InCH_2^+$	$^3B_1$	2.279	115.4	129.1	15.5	17.1	–
$SnCH_2^+$	$^2B_1$	2.118	123.2	113.5	79.3	81.3	–
$SbCH_2^+$	$^1A_1$	1.939	122.6	114.9	101.2	106.9	–
$TeCH_2^+$	$^2B_2$	1.941	121.1	117.7	101.6	102.0	–
ICH_2^+	$^1A_1$	1.944	119.9	120.2	121.2	124.4	–
$XeCH_2^+$	$^2A'$	2.139	110.2	130.3	94.1	95.4	–

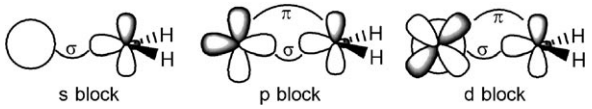
[a] Reference [2f]. [b] Reference [2e].; [c] Reference [2h]. [d] Reference [3a], theoretical. [e] Not included in Figure 1 and MAE calculation. [f] Reference [2b], lower limits.

geometry, in which the four atoms are no longer confined to the same plane.[20] Again, their C_{2v} structures exhibit one imaginary frequency, which corresponds to an inversion process. The electronic energies of the C_{2v} transition-state structure is only slightly, <1 kcal mol^{-1}, higher than those of the C_s(b) minimum structure. Including ZPE corrections, the C_{2v} structures are even lower in energy than their C_s(b) counterparts. Optimization with the BP86 functional reproduces the same situation in that the energies of the C_{2v} species and the C_s(b) structures are almost degenerate. Therefore, a clear-cut assignment in which the C_{2v} and C_s(b) structures correspond to the transition state and to the minimum does not seem possible for the time being.

Molecular orbitals: In addition to the apparent geometric information, more insight can be derived from a molecular orbital (MO) analysis. Because the $^3B_1$ ground state of the methylene group CH_2 has one electron in a σ orbital and one in a π orbital (Scheme 2), M^+ must possess two electrons of the same symmetry to achieve a M=CH_2^+ covalent double bond.

Figure 3 shows the MOs containing the p orbital of CH_2, which contributes to possible π bonding. KCH_2^+, $CaCH_2^+$, $ScCH_2^+$, $FeCH_2^+$, $ZnCH_2^+$, and $AsCH_2^+$ were chosen as representative examples.

Because K^+ has a rare-gas electronic configuration, there is no significant covalent bonding interaction between the ground state CH_2 and K^+ as shown in the HOMO. The HOMO−1 corresponds to the other single-occupied orbital of the triplet CH_2 moiety and contains almost no contribution from K^+. The singlet KCH_2^+ ($^1A_1$) lies 0.4 kcal mol^{-1} higher in energy than the ground state ($^3B_1$), indicating that the stabilization from the donation of the lone pair of singlet CH_2 to the empty orbital of K^+ is not enough to compensate the energy cost to promote triplet CH_2 to singlet CH_2. Therefore, K^+ and triplet CH_2 are held together more likely by mere electrostatic interaction. Having one s electron, Ca^+ can form a single bond with CH_2. In addition, a slight contribution of the empty d orbital of Ca^+ was found in its HOMO. For the transition metals M^+ (s^1d^{n-1} or d^n, $2<n<10$), a double bond can be obtained. In fact, a strong π overlap between the symmetry-matched orbitals exists in the HOMO of $ScCH_2^+$ and the HOMO−4 of $FeCH_2^+$. A similar trend was reported



Scheme 2.

Table 3. Geometries and BDEs for the 6th row complexes MCH_2^+ (M = Cs–La, Hf–Rn).

	State	Structure			BDE [kcal mol^{-1}]		
		$d_{(M-C)}$ [Å]	∠MCH [°]	∠HCH [°]	B3LYP	CCSD(T)	Exptl
$CsCH_2^+$	$^3B_1$	3.472	111.9	136.2	4.3	4.6	–
$BaCH_2^+$	$^2B_1$	2.492	126.4	107.2	65.0	63.6	–
$LaCH_2^+$	$^1A'$	2.101	91.4	111.5	97.7	105.8	95.8 ± 1.7[a]
$HfCH_2^+$	$^2A'$	1.894	88.4	112.7	98.2	100.0	100.8 ± 1.6[b]
$TaCH_2^+$	$^3A'$	1.841	82.6	113.7	108.6	112.0	110.9 ± 0.7[c]
WCH_2^+	$^4B_1$	1.882	122.8	114.3	100.1	97.1	109.3 ± 0.7[d]
$ReCH_2^+$	$^5B_1$	1.863	121.8	116.3	98.4	91.4	95.5 ± 1.4[e]
$OsCH_2^+$	$^4B_1$	1.827	121.0	118.0	108.3	104.9	109.9 ± 1[f]
$IrCH_2^+$	$^3B_2$	1.800	120.4	119.1	109.4	120.6	113.5 ± 0.7[g]
$PtCH_2^+$	$^2A_1$	1.816	120.7	118.8	116.7	119.0	110.7 ± 0.7[a]
$AuCH_2^+$	$^1A_1$	1.894	121.7	116.5	87.1	88.0	85.3 ± 1.6[h]
$HgCH_2^+$	$^2A'$	2.093	111.7	126.9	64.6	65.9	–
$TlCH_2^+$	$^1B_1$	2.820	126.7	106.6	12.9	11.9	–
$PbCH_2^+$	$^2B_1$	2.208	123.2	113.7	71.5	72.5	–
$BiCH_2^+$	$^1A_1$	2.031	122.3	115.4	88.7	93.3	–
$PoCH_2^+$	$^2B_2$	2.042	120.9	118.1	88.4	86.4	–
$AtCH_2^+$	$^1A_1$	2.043	119.9	120.2	105.2	109.0	–
$RnCH_2^+$	$^2A'$	2.226	110.4	129.4	83.8	84.8	–

[a] Reference [2f]. [b] Reference [2i]. [c] Reference [1j]. [d] Reference [1i]. [e] Reference [2f]. [f] Reference [1a]. [g] Reference [1h]. [h] Reference [2j].

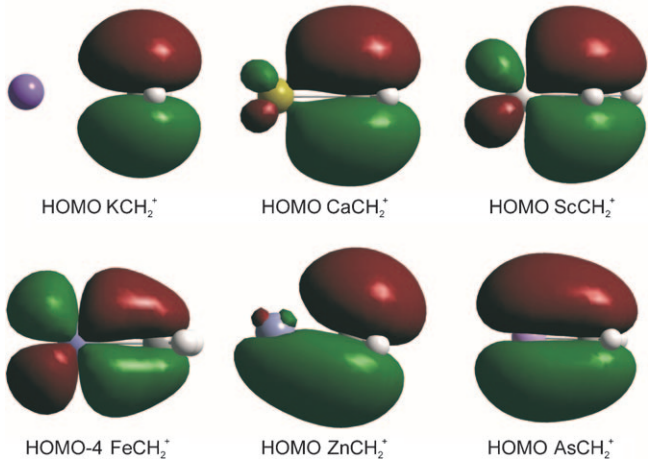


Figure 3. The selected MOs for KCH_2^+, $CaCH_2^+$, $ScCH_2^+$, $FeCH_2^+$, $ZnCH_2^+$, and $AsCH_2^+$.

recently for the transition-metal M=CH_2^+ and M=NH^+ systems.[21] The d orbital of Zn^+ (s^1d^{10}) is fully occupied, therefore, Zn^+ cannot form a double bond with CH_2. Rather, the CH_2 fragment bends out of the plane, thus avoiding the repulsion between its π orbital and the occupied d orbitals of Zn^+. In contrast to the transition-metal carbenes, the MCH_2^+ complexes containing p-block elements display yet another bonding scenario in which the p orbitals of M^+ offer a better overlap with CH_2.

BDE and periodic trend: The bonding pattern can be related to the BDEs. The predicted values for the s- and p-block carbenes MCH_2^+ are listed in Tables 1–3. The periodic trend of the BDEs is presented in Figure 4.

The negligible bonding between the group 1 cation M^+ (ns^0) and CH_2 results in a very low BDE of approximately 5 kcal mol^{-1}. Group 2 M^+ (ns^1) can only form a single bond with CH_2, and the BDE of this simple σ bond centers around 62 kcal mol^{-1}. Similar to the ionization energy of alkali metals M (ns^1), the BDEs of s-block carbenes MCH_2^+ remain unchanged along the three periods. The relationship of the BDE and the promotion energy for the d-block transition-metal carbene cations has been well established and have been studied extensively by many groups.[2a,3d,22] The same relation for the f-block lanthanide carbene cations was reported recently by Roos and Pyykkö.[9] Therefore, here we focus on the p-block elements. The bonding situation in p-block carbenes MCH_2^+ is relatively simple compared with those containing d- and f-block elements, which is due to the symmetry of the valence p orbitals of M^+ that perfectly match with the σ and π orbitals in CH_2 (Scheme 2). The question is how many valence p electrons and orbitals are available for a bonding with CH_2. The electronic ground state of the p-block element cations M^+ corresponds to ns^2p^x ($x = 0$–5 for group 13–-18). Owing to the lack of p electrons for group 13 M^+, a high promotion energy is needed to excite one ns electron to an np orbital. As a consequence, an extremely weak single bond results with BDEs of 23.7–12.9 kcal mol^{-1}. Group 14 M^+ (ns^2np^1) can form a single bond with CH_2 by its single p electron. Clearly, the energy gain by forming an additional π bond is not large enough to compensate for the promotion energy to prepare excited M^+ (ns^1np^2), and consequently M–CH_2^+ also remain as a single bond with BDE of 94.6–71.5 kcal mol^{-1}. Such a bond strength is comparable to those of the double bond in transition-metal carbenes, reflecting the better overlap of a p–p covalent bond. From group 15 to 17, M^+ has at least two valence p electrons, which are ready to be coupled with CH_2 and to form a σ bond and a π bond. The strongest BDEs for M=CH_2^+ double bonds are calculated to amount to 127.3, 128.7, and 155.2 kcal mol^{-1} for As, Se, and Br, respectively. Such high BDEs render the dehydrogenation of methane feasible. In contrast to the group 13 and group 14 M^+, which do not have enough p electrons to form a double bond with CH_2, the group 18 M^+ are lacking valence p orbitals to accommodate two electrons from CH_2. As a result, only single bonds are formed with BDEs of 119.6–83.8 kcal mol^{-1}. It should be mentioned that the BDE of M–CH_2^+ was calculated based on [Eq. (3)]. However, for cations with high electron affinities, that is, group 17 and 18, the MCH_2^+ complexes may prefer to dissociate into M + CH_2^+ with a lower threshold, as demonstrated by Schröder and co-workers for the rare-

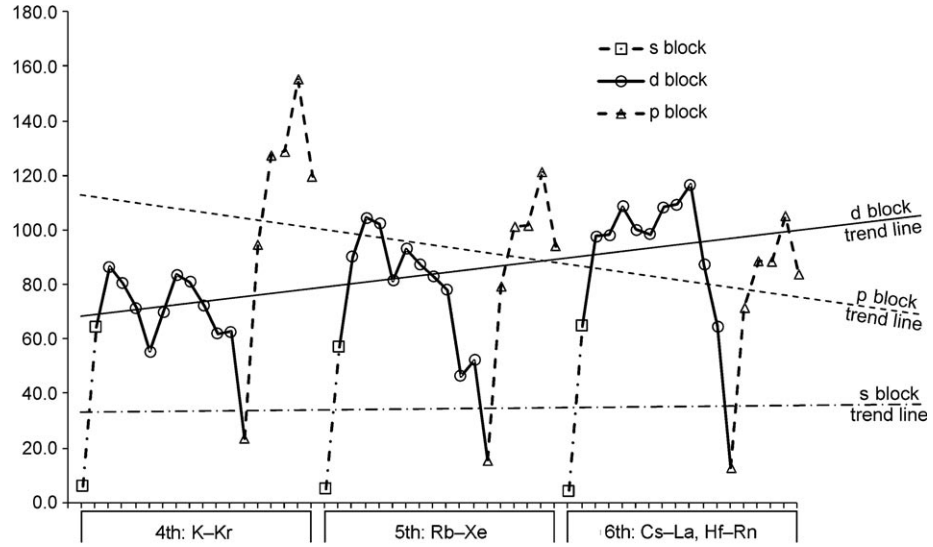


Figure 4. Periodic trends for the bond dissociation energy (in kcal mol^{-1}) of M–CH_2^+ (M = K–La, Hf–Rn) as calculated at B3LYP/def2-QZTV.

gas carbene cations.[23] The periodic trends of the BDEs of p-block MCH_2^+ seem to correlate well with other properties such as ionization energy and electronegativity: From top to bottom the BDEs decreases. Except for group 13, the promotion energy is not involved in the bonding of p-block MCH_2^+. Therefore, it is understandable that the BDEs decrease with increasing atomic radii.

Conclusion

Our computational survey on the MCH_2^+ complexes (M = K–La, Hf–Rn) can be summarized as follows:

1) The BDE(M–CH_2^+) of transition-metal complexes calculated at B3LYP/def2-QZVP agrees well with the available experimental data, with a MAE of 3.8 kcal mol^{-1}. This method enables us to predict a reasonable BDE-(M–CH_2^+) of the main-group element at low computational cost. Further calculations on similar systems such as MCH_3^+,[2f,24] MNH_n^+,[25] and MOH_n^+[2f,26] are indicated to test the performance of the methods employed in the present study.
2) Most of the MCH_2^+ complexes adopt C_{2v} symmetry structures, with the exception of C_s(a) for the early transition metals and C_s(b) for complexes with elements M^+ from group 13 and 18.
3) No significant covalent bonding between M^+ and CH_2 was found for group 1. M^+ of group 2, 12, 13, 14, and 18 form a single bond with CH_2, whereas the others form a double bond.
4) The valence p orbitals of the p-block element match the symmetry of triplet CH_2 perfectly. Thus, strong M=CH_2^+ bonds result for group 15–18 cations, which have 2–4 valence p electrons in the ground state. Promotion-energy aspects do not play a role in these three groups. Therefore, the BDEs of these p-block carbenes M=CH_2^+ decrease from the 4th row down to the 6th row in the periodic trend owing to the increasing atomic radii.

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