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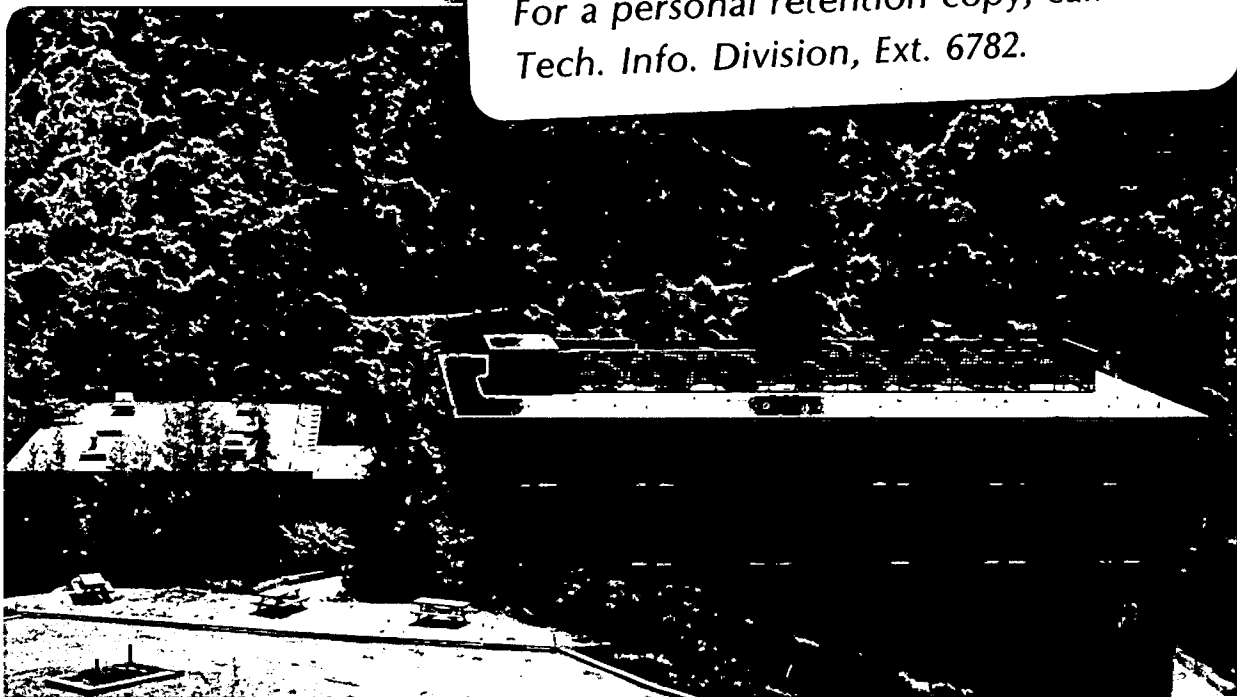
HIGH SPIN ELECTRONIC STATES OF THE EXPERIMENTALLY  
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Mark A. Vincent, Yasunori Yoshioka,  
and Henry F. Schaefer III

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HIGH SPIN ELECTRONIC STATES OF THE EXPERIMENTALLY  
OBSERVED MOLECULAR IONS  $\text{MnCH}_2^+$  and  $\text{CrCH}_2^+$

Mark A. Vincent,  
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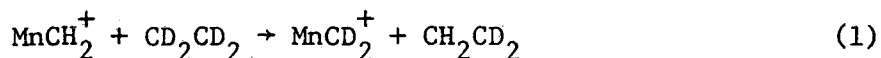
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Abstract

The  ${}^7B_1$  electronic state of  $\text{MnCH}_2^+$  and  ${}^6B_1$  state of  $\text{CrCH}_2^+$  have been investigated using nonempirical molecular electronic structure theory. Large gaussian basis sets were used in conjunction with explicitly correlated wave functions. Equilibrium geometries were predicted at the self-consistent-field level of theory, yielding for  $\text{MnCH}_2^+$   $r_e(\text{Mn-C}) = 2.076 \text{ \AA}$ ,  $\theta_e(\text{HCH}) = 114.5^\circ$  and for  $\text{CrCH}_2^+$   $r_e(\text{Cr-C}) = 2.064 \text{ \AA}$ ,  $\theta_e(\text{HCH}) = 113.5^\circ$ . The  $\text{M}^+-\text{CH}_2$  bond dissociation energies for these high spin electronic states are significantly less than the ground state bond energies deduced from laboratory measurements by Beauchamp and co-workers.

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During the past two years Beauchamp and co-workers<sup>1-3</sup> have prepared a number of primitive, gas-phase transition metal-methylene molecular ions, of the general form  $MCH_2^+$ . For the manganese carbene  $MnCH_2^+$ , it was demonstrated that reaction with olefins yields products expected from a metathesis reaction,<sup>4</sup> for example



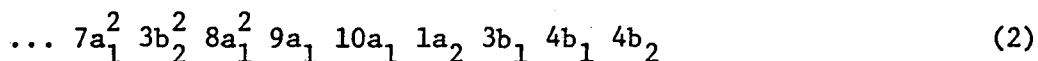
It was also possible from these studies to obtain the first experimentally determined metal-carbene bond dissociation energies, namely  $D(Cr^+-CH_2) = 65 \pm 7$  kcal,  $D(Mn^+-CH_2) = 96 \pm 4$ ,  $D(Co^+-CH_2) = 85 \pm 7$  kcal, and  $D(Ni^+-CH_2) = 86 \pm 6$  kcal.<sup>3</sup> Finally, Stevens and Beauchamp<sup>1</sup> noted that such strong metal-carbene bonds are a desirable feature of practical olefin metathesis catalysts, avoiding low turnover numbers resulting from consumption of carbene intermediates.

Nearly five years ago, we completed a detailed theoretical study<sup>5</sup> of the neutral metal-carbene system  $MnCH_2$ . In this case, the Mn-C bond energy was predicted to be in the range 33-55 kcal, with the most complete theoretical treatment<sup>6</sup> yielding 35 kcal. The fact that this neutral binding energy is only about half the  $96 \pm 4$  kcal observed for the cation  $MnCH_2^+$  is not surprising, since the doubly-occupied 4s orbital of the Mn atom ( $4s^2 3d^5$ ) inhibits the formation of strong chemical bonds.<sup>7</sup>

In the same theoretical study,<sup>5</sup> three electronic states of the cation  $MnCH_2^+$  were considered very briefly at the self-consistent-field (SCF) level of theory. However, using assumed geometrical structures, none of these states appeared to be strongly bound, and little confidence

was placed in the positive ion results. In light of Beauchamp's experimental determination of such a large Mn-CH<sub>2</sub> bond energy for the positive ion,<sup>1,3</sup> an explicit theoretical study of this system seems very much in order.

Of the three MnCH<sub>2</sub><sup>+</sup> electronic states considered previously,<sup>5</sup> the <sup>7</sup>B<sub>1</sub> state was predicted to lie lowest. This state arises from the electron configuration



A qualitative discussion of the MnCH<sub>2</sub> orbitals is given elsewhere,<sup>5</sup> and those of the cation are similar.<sup>8</sup> Here it need only be noted that the <sup>7</sup>B<sub>1</sub> state involves a single bond between the Mn<sup>+</sup> 4s orbital and the singly-occupied 3a<sub>1</sub> orbital (this is the lone pair or σ orbital of singlet CH<sub>2</sub>) of triplet methylene.

A large basis set of contracted gaussian functions was used in this research. For the Mn atom, the Wachters' basis<sup>9</sup> was augmented by two 4p-like functions (α = 0.21, 0.082) and one spatially extended d function (α = 0.1054).<sup>10</sup> A flexible contraction was chosen,<sup>11</sup> yielding a final basis designated Mn(14s 11p 6d/10s 8p 3d). For the CH<sub>2</sub> fragment, a standard triple zeta plus polarization basis,<sup>12</sup> designated C(9s 5p 1d/5s 3p 1d), H(5s 1p/3s 1p) was used, with polarization function exponents α<sub>d</sub>(C) = 0.75, α<sub>p</sub>(H) = 1.0.

At the SCF level of theory, the geometrical structures of <sup>7</sup>B<sub>1</sub> MnCH<sub>2</sub><sup>+</sup> and the analogous state (<sup>6</sup>B<sub>1</sub>) of CrCH<sub>2</sub><sup>+</sup> were optimized and are seen in Figure 1. The HCH bond angles are somewhat closer to the 102.4° value known<sup>13</sup> for singlet CH<sub>2</sub> than to the 133° triplet methylene

value,<sup>14</sup> while the C-H distances are comparable to those observed adjacent to C=C double bonds.<sup>15</sup> The predicted Mn-C distance of 2.08 Å is significantly longer than observed<sup>16,17</sup> Mn=C bonds ( $\sim 1.95$  Å), supporting the qualitative notion that we are dealing with a single bond in  ${}^7B_1$  MnCH<sub>2</sub><sup>+</sup>. However, in his 1972 review, Fischer<sup>17</sup> notes that Cr=C distances fall in the range 2.00 to 2.15 Å, and the predicted CrC distance of 2.06 Å certainly lies within this band. Nevertheless, our analysis of the CrCH<sub>2</sub><sup>+</sup> electronic wave function leaves little doubt that it possesses a Cr-C single bond.

At the SCF level of theory the high-spin states of MnCH<sub>2</sub><sup>+</sup> and CrCH<sub>2</sub><sup>+</sup> are bound by only 9.1 kcal and -0.3 kcal, respectively, relative to separated M<sup>+</sup> + CH<sub>2</sub>. Therefore it was deemed imperative to explicitly consider the effects of electron correlation.<sup>18</sup> For both molecules, configuration interaction (CI) was carried out including single and double excitations. With the ten core SCF orbitals (M 1s, 2s, 2p, 3s, 3p; C 1s) doubly occupied, this amounts to 22,288 configurations for  ${}^7B_1$  MnCH<sub>2</sub><sup>+</sup> and 18,379 for  ${}^6B_1$  CrCH<sub>2</sub><sup>+</sup>.

The CI Mn<sup>+</sup>-CH<sub>2</sub> bond dissociation energy is predicted to be 36.0 kcal, or 40.8 kcal when the Davidson correction<sup>19</sup> for unlinked clusters is appended. These results assumed the MnCH<sub>2</sub><sup>+</sup> and triplet CH<sub>2</sub> equilibrium geometries obtained at the SCF level of theory. Similarly the Cr<sup>+</sup>-CH<sub>2</sub> bond energy is predicted to be 18.3 kcal (CI) and 22.3 kcal (Davidson corrected). Even allowing for errors of as much as 20 kcal,<sup>20</sup> it seems likely that the experiments of Beauchamp<sup>1-3</sup> do not determine the bond energies of these high spin electronic states of MnCH<sub>2</sub><sup>+</sup> and CrCH<sub>2</sub><sup>+</sup>.

Seemingly the simplest harmonious explanation of the different theoretical and experimental bond energies for  $\text{MnCH}_2^+$  and  $\text{CrCH}_2^+$  would be that the experimental results refer to a low-spin state. Stevens and Beauchamp<sup>21</sup> have indeed suggested that the ground state of  $\text{MnCH}_2^+$  is a  $^5\text{B}_1$  electronic state. Qualitatively this would appear reasonable, since this state allows a second Mn-C bond, between the  $3d_{yz}$  (molecule lies in xz plane) orbital of  $\text{Mn}^+$  and the methylene  $1b_1$  (or  $p$ )<sup>22</sup> orbital. However, at the Hartree-Fock and single and double excitation CI levels of theory,  $^5\text{B}_1$   $\text{MnCH}_2^+$  lies above the  $^7\text{B}_1$  state studied in detail here. Unfortunately, our results in this regard are not conclusive, since the  $^5\text{B}_1$  state is poorly described by a single electron configuration and could conceivably have the sort of collective electronic structure recently demonstrated<sup>23,24</sup> for the diatomic molecules  $\text{Cr}_2$  and  $\text{Mo}_2$ . Further theoretical studies of the low-spin states of  $\text{MnCH}_2^+$  and  $\text{CrCH}_2^+$  are certainly in order.

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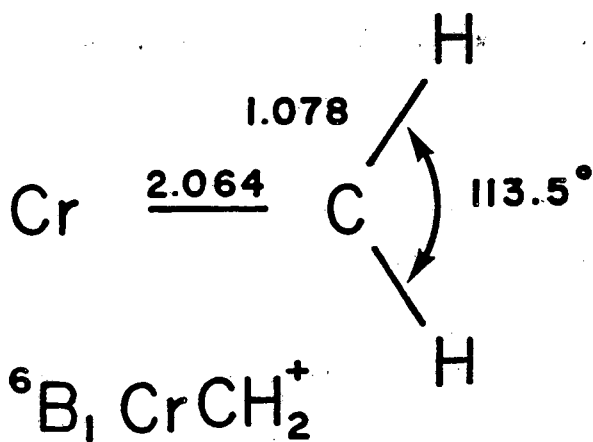
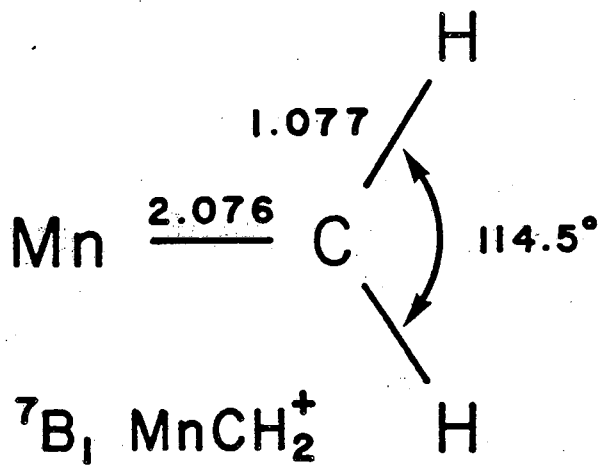


Figure Caption. Predicted equilibrium geometries for the high spin electronic states of  $\text{MnCH}_2^+$  and  $\text{CrCH}_2^+$ . The SCF energies obtained for these minima are -1188.56336 and -1082.04347 hartrees, respectively.

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