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A Model Transition Metal-Carbene System

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Abstract

The first transition metal-methylene species, $\text{Ta}(\text{C}_5\text{H}_5)_2 \text{CH}_2\text{CH}_2$, has recently been prepared and characterized by Schrock and coworkers. As a model for systems of this type, ab initio electronic structure theory has been applied to the MnCH_2 molecule. After experimentation with several types of basis sets, the following double zeta contracted gaussian basis was adopted: $\text{Mn}(12s \ 8p \ 4d/8s \ 6p \ 2d)$, $\text{C}(9s \ 5p/4s \ 2p)$, $\text{H}(4s/2s)$. However in some cases it was found necessary to add a set of more diffuse d functions to the above. Single-configuration self-consistent-field (SCF) potential curves are reported for electronic states dissociating to $\text{Mn}^+(4s3d^5 \ ^7S)$, $\text{Mn}(4s^2 3d^6 \ ^6S)$, $\text{Mn}(4s3d^6 \ ^6D)$ and $\text{Mn}(4s4p3d^5 \ ^8P)$ plus $^3B_1 \text{CH}_2$ and $^1A_1 \text{CH}_2$. The electronic ground state of MnCH_2 is of 8B_1 symmetry and for this state only a full geometry optimization was performed, yielding $r_e(\text{Mn-C}) = 2.16 \text{ \AA}$, $\theta_e(\text{HCH}) = 109^\circ$, and $r_e(\text{C-H}) = 1.09 \text{ \AA}$. In the SCF approximation $^8B_1 \text{MnCH}_2$ is bound by 33 kcal/mole relative to infinitely separated $^6S \text{Mn} + ^3B_1 \text{CH}_2$. The predicted dipole moment is +1.48 debye compared to those of isolated triplet and singlet methylene, -0.66 and -2.40 debye. The second low-lying strongly bound state is of 8A_1 symmetry, arising from $^6D \text{Mn} + ^3B_1 \text{CH}_2$. The predicted equilibrium geometry is $r_e(\text{Mn-C}) = 2.18 \text{ \AA}$, $\theta_e(\text{HCH}) = 142^\circ$, corresponding to a dissociation energy of 39 kcal. Several higher electronic states dissociating to singlet CH_2 are also predicted to be bound. The lowest bound state is of 6B_1 symmetry with $r_e(\text{Mn-C}) = 1.90 \text{ \AA}$, $\theta_e(\text{HCH}) = 108^\circ$, corresponding to a dissociation energy of 38 kcal/mole. The latter bond distance is reasonably close to the 1.95 and 1.96 $\text{\AA}$ values found for the two manganese

carbenes whose structures have been determined experimentally. The electronic structure of MnCH_2 is discussed in terms of Mulliken populations and orbital energies. The predicted methylene bond angles are readily understood in terms of a Walsh model. Allowing for the possibility of a) s^2d^n and sd^{n+1} metal atom ground states and b) singlet and triplet carbene electronic ground states, a rich spectrum of possible transition metal-carbene properties is predicted.

Introduction

Transition metal carbenes have been of special interest¹⁻⁵ to organometallic chemists since the synthesis of methoxymethylcarbene (pentacarbonyl) tungsten

by Fischer and Maasböl⁶ in 1964. In the intervening period much additional research on transition metal carbenes has been carried out by the Fischer group⁷. For example, they have demonstrated⁸ the conversion of the chromium analogue of (1) into an entire range of other complexes. Considerable practical interest in transition metal carbenes has arisen due to their role⁹ in olefin metathesis, the type of catalytically induced reaction wherein olefins undergo bond reorganization.¹⁰

Our own interest in the present subject was spurred by the synthesis and characterization by Schrock and coworkers¹¹ of $\text{Ta}(\text{C}_5\text{H}_5)_2 \text{CH}_3\text{CH}_2$, the first such transition metal complex incorporating nonsubstituted methylene (CH_2) as a ligand. The tantalum-carbon bond length was found to be 2.03 Å, consistent¹² with a $\text{Ta} = \text{CH}_2$ description. Of particular interest to carbene chemists is the methylene HCH angle, $107 \pm 9^\circ$, a result much closer to singlet methylene¹³ (102.4°) than to the $^3\text{B}_1$ ground state, which has a 134° equilibrium bond angle.¹⁴ The molecular structure of Guggenberger and Schrock¹¹ is given in Figure 1. Another interesting

Ta(C₅H₅)₂CH₂CH₃ feature, gleaned from ¹H NMR spectra, is the estimate that the barrier to rotation about the Ta = CH₂ bond is ≥ 21 kcal/mole.

In this paper we present an ab initio theoretical study¹⁵ of a simple model system, MnCH₂. The obvious disadvantage of this choice for direct comparison with Schrock's compound and other transition metal carbenes synthesized to date is the lack of additional ligands. However, from a certain perspective, the consideration of the unencumbered MnCH₂ species is of special value. For some time, we have felt¹⁶ that the development of a molecular understanding of surface chemistry and catalysis has been hindered by a lack of structural and (especially) energetic information concerning transition metal-carbon bonds. In comparison to organic chemistry, with its rather precisely characterized single, double, and triple bonds, the organometallic field is found to be particularly lacking in this regard. For this reason we feel that reliable theoretical studies of some of the key organometallic "building blocks" may play an important role in understanding the currently fuzzy relationships between organometallic chemistry,⁴ surface chemistry,¹⁷ and catalysis.¹⁸ The same basic idea is being pursued by Goddard and coworkers,¹⁹ who are studying the bonding of the nickel atom to various organic fragments.

After the present research was well under way, we were pleasantly surprised by the appearance of a paper²⁰ reporting the synthesis of the diazo compound Mn₂(CO)₁₀CH₂N₂. Upon electron impact ionization, the primary chain of events is

Thus the MnCH_2^+ ion, studied here along with the neutral species, appears to have at least a fair degree of stability.

Theoretical Approach

The simplest, although not necessarily most reliable, means of exploring the electronic structure of MnCH_2 is to begin with the two separated fragments. The Mn atom has a ^6S ground state, arising from electron configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5 \quad (3)$$

The first excited electronic state is of ^6D symmetry, lying $17,052 \text{ cm}^{-1} = 48.8 \text{ kcal higher}^{21}$ and arising from the

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^6 \quad (4)$$

configuration. Another low-lying state, the ^8P state at $18,402 \text{ cm}^{-1} = 52.6 \text{ kcal}$, has its origin in the orbital occupancy

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s 4p 3d^5 \quad (5)$$

Finally the Mn atom has an ionization potential of $7.43 \text{ eV} = 171.4 \text{ kcal}$, and the Mn^+ ground state also has a half-filled 3d orbital

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^5 \quad (6)$$

Similarly the CH_2 radical has a $^3\text{B}_1$ ground state

$$1a_1^2 2a_1^2 1b_2^2 3a_1 1b_1 \quad (7)$$

and $^1\text{A}_1$ first excited state lying at $19.5 \pm 0.7 \text{ kcal/mole}^{22}$

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 \quad (8)$$

We have in the present research restricted ourselves to C_{2v} geometries of the $MnCH_2$ complex. That is, the complex is assumed to be coplanar and the Mn nucleus to lie along the bisector of the HCH bond angle. To resolve the Mn atomic orbitals into appropriate molecular orbitals, we note²³ that

$$\begin{aligned} s &\rightarrow a_1 \\ p &\rightarrow a_1 + b_1 + b_2 \\ d &\rightarrow 2a_1 + a_2 + b_1 + b_2 \end{aligned} \quad (9)$$

This means that the Mn ground state configuration (3) becomes

$$1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2 4a_1^2 5a_1^2 2b_1^2 2b_2^2 6a_1^2 7a_1 8a_1 1a_2 3b_1 3b_2 \quad (10)$$

corresponding to a 6A_1 molecular state. Since the Mn 1s, 2s, 2p, 3s, and 3p atomic orbitals should have little to do with the bonding in $MnCH_2$, (10) may be simplified as

$$\dots\dots 6a_1^2 7a_1 8a_1 1a_2 3b_1 3b_2 \quad (11)$$

Similarly we will suppress the $1a_1$ orbital of CH_2 and refer to (7) as

$$\dots\dots 2a_1^2 1b_2^2 3a_1 1b_1 \quad (12)$$

We can now easily write down the electron configuration for the high spin state which dissociates to $Mn({}^6S) + CH_2({}^3B_1)$

$$\dots\dots 7a_1^2 3b_2^2 8a_1^2 9a_1 10a_1 11a_1 1a_2 3b_1 4b_1 4b_2 \quad (13)$$

With seven unpaired spins, the state of interest has 8B_1 symmetry.

We know²⁴ of course that orbital occupancy (13) will also give rise to 14 2B_1 states, 14 4B_1 states, and 6 6B_1 states. However Hund's rules are known to be valid in situations of this type and thus our single configuration self-consistent-field (SCF) theoretical studies will be restricted to the 8B_1 state, which should lie below the other 34 states arising from (13). Similarly, we will consider in detail only the 6A_1 state of Mn CH₂ arising from Mn(6S) + CH₂(1A_1)

$$\dots\dots 7a_1^2 3b_2^2 8a_1^2 9a_1^2 10a_1 11a_1 1a_2 3b_1 4b_2 \quad (14)$$

For the 4s 3d⁶ configuration (6D state) the situation is more complicated since any one of the five d orbitals may be doubly-occupied. When these five possibilities are combined with the 3B_1 state of CH₂, the resulting MnCH₂ electron configurations are (assigning the 8a₁ orbital to correspond to 4s Mn and the 4b₁ orbital to the 1b₁ orbital of CH₂)

$$^8B_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1 10a_1^2 11a_1 1a_2 3b_1 4b_1 4b_2 \quad (15)$$

$$^8B_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1 10a_1 11a_1^2 1a_2 3b_1 4b_1 4b_2 \quad (16)$$

$$^8B_2 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1 10a_1 11a_1 1a_2^2 3b_1 4b_1 4b_2 \quad (17)$$

$$^8A_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1 10a_1 11a_1 1a_2 3b_1^2 4b_1 4b_2 \quad (18)$$

$$^8A_2 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1 10a_1 11a_1 1a_2 3b_1 4b_1 4b_2^2 \quad (19)$$

Comparison of configurations (13), (15), and (16) demonstrates clearly that these three states cannot simultaneously be correctly treated within the single configuration Hartree-Fock approximation. That is, as far as the Hartree-Fock equations²⁵ are concerned, these three states are identical--they each have eight doubly-occupied and three singly-occupied a_1 orbitals. Although the present SCF calculations may provide a reasonable description of the lowest 8B_1 state, a configuration interaction (CI) treatment will be necessary to make reliable predictions for all three states.

The interaction of the $4s3d^6$ configuration with singlet methylene provides five more orbital occupancies

$${}^6A_1 \dots\dots 7a_1^2 \ 3b_2^2 \ 8a_1 \ 9a_1^2 \ 10a_1^2 \ 11a_1 \ 1a_2 \ 3b_1 \ 4b_2 \quad (20)$$

$${}^6A_1 \dots\dots 7a_1^2 \ 3b_2^2 \ 8a_1 \ 9a_1^2 \ 10a_1 \ 11a_1^2 \ 1a_2 \ 3b_1 \ 4b_2 \quad (21)$$

$${}^6A_2 \dots\dots 7a_1^2 \ 3b_2^2 \ 8a_1 \ 9a_1^2 \ 10a_1 \ 11a_1 \ 1a_2^2 \ 3b_1 \ 4b_2 \quad (22)$$

$${}^6B_1 \dots\dots 7a_1^2 \ 3b_2^2 \ 8a_1 \ 9a_1^2 \ 10a_1 \ 11a_1 \ 1a_2 \ 3b_1^2 \ 4b_2 \quad (23)$$

$${}^6B_2 \dots\dots 7a_1^2 \ 3b_2^2 \ 8a_1 \ 9a_1^2 \ 10a_1 \ 11a_1 \ 1a_2 \ 3b_1 \ 4b_2^2 \quad (24)$$

As in the previous paragraph, we note that only a single 6A_1 SCF computation provides a variational result.¹⁵ The minimum qualitatively acceptable treatment of the lowest three states would involve (14), (20), and (21) in a 3×3 CI.

Turning to the $4s4p3d^5$ configuration (8P state) we note that one of the p_x , p_y , and p_z components will be singly-occupied. Combining with triplet methylene (12) one obtains

$$^{10}B_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1 10a_1 11a_1 12a_1 1a_2 3b_1 4b_1 4b_2 \quad (25)$$

$$^{10}A_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1 10a_1 11a_1 1a_2 3b_1 4b_1 5b_1 4b_2 \quad (26)$$

$$^{10}A_2 \dots\dots 7a_1 3b_2^2 8a_1 9a_1 10a_1 11a_1 1a_2 3b_1 4b_1 4b_2 5b_2 \quad (27)$$

Similarly the interaction with singlet methylene yields (with the $5b_1$ orbital being Mn 4p)

$$^8A_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1^2 10a_1 11a_1 12a_1 1a_2 3b_1 4b_2 \quad (28)$$

$$^8B_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1^2 10a_1 11a_1 1a_2 3b_1 5b_1 4b_2 \quad (29)$$

$$^8B_2 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1^2 10a_1 11a_1 1a_2 3b_1 4b_2 5b_2 \quad (30)$$

Note here that at the asymptotic limit $Mn + CH_2$, (28) is the second electronic state of 8A_1 symmetry, (18) lying $(3.8 + 19.5) = 23.3$ kcal lower. Thus a single configuration SCF calculation on (28) will not be a variational result, i.e., the energy will not be a rigorous upper bound to the exact second 8A_1 eigenvalue. However, electron configurations (18) and (28) are distinct, and thus an SCF treatment of (28) should still be physically meaningful.²⁶ However (29) is essentially the same configuration as (13), (15), and (16), and therefore Hartree-Fock results for (29) cannot be considered reliable. Finally, although (30) is of the same 8B_2 symmetry as (17), the two electron configurations are distinct and SCF treatments of both should be meaningful.

For the Mn^+ ion, only the $4s 3d^5$ configuration (7S state) has been given serious consideration. Interacting with triplet and singlet methylene, one readily finds the following two $Mn CH_2^+$ configurations

$${}^9B_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1 10a_1 11a_1 1a_2 3b_1 4b_1 4b_2 \quad (31)$$

$${}^7A_1 \dots\dots 7a_1^2 3b_2^2 8a_1 9a_1^2 10a_1 11a_1 1a_2 3b_1 4b_2 \quad (32)$$

In addition another low-lying state

$${}^7B_1 \dots\dots 7a_1^2 3b_2^2 8a_1^2 9a_1 10a_1 1a_2 3b_1 4b_1 4b_2 \quad (33)$$

was studied in some detail.

Our general procedure than was to perform ab initio single configuration SCF calculations on the electron configurations (13)-(33), a total of 21 different electronic states. As noted above, while computations on (15), (16), (20), (21), and (29) are feasible (and in fact were completed in several cases) these results are of questionable validity. It should certainly be apparent that most available SCF methods are not currently applicable to such systems as (25)-(27) which each have nine unpaired electrons. For this purpose we used the OCBSE technique developed by Hunt, Hay, and Goddard²⁷ and implemented on the Cal Tech-Ohio State-Berkeley version of POLYATOM.²⁸

Basis Set Evaluation

The choice of basis set for transition metal atom systems is quite hazardous. Furthermore, a multitude of errors may be hidden from view in a single calculation on a transition metal complex at its experimental equilibrium geometry. However, in the present situation, with a variety of dissociation limits, the weaknesses of even a carefully chosen basis are quickly brought to light. Before continuing let us note that our choices of C(9s 5p/4s 2p) and H(4s/2s) contracted gaussian basis sets were the standard and time-tested Huzinaga-Dunning sets.²⁹

For the Mn atom the primitive (12s 6p 4d) set of Roos, Veillard, and Vinot³⁰ was adopted. In its uncontracted form this basis yields an energy -1149.5527 hartrees, compared to the near Hartree-Fock result of Clementi,³¹ -1149.8657. The contraction to double zeta (8s 4p 2d) was that of Dunning³² and is in our opinion the best available for this primitive set. Since Dunning's basis has not been published in the open literature, we include it as Table I here. For the 6S Mn atom ground state this contracted basis yields a total energy of -1149.5473 hartrees, only 0.0054 above the totally uncontracted result.

Our initial feeling was that the most serious limitation of the above basis was the lack of Mn 4p functions. Since the 4p atomic orbital is nearly degenerate with the 4s, it seems unbalanced to include the 4s and neglect the 4p. Therefore two new primitive p functions were added with exponents $\alpha = 0.2659$ and 0.0842 , following the "even-tempered" criterion of Raffanetti and Ruedenberg.³³ This basis, labeled Mn(12s 8p 4p/8s 6p 2d), was used in most of the computations reported here. The 6S Mn energy is now -1149.5624 hartrees, only 0.0150 hartrees lower than the

original³² double zeta set. For the 8P state ($4s4p3d^5$) however these additional functions lower the SCF energy from -1148.0862 to -1149.5113 hartrees. Thus the 6S - 8P separation is predicted to be 0.0511 hartrees or 32.1 kcal. This is somewhat less than the experimental separation (52.6 kcal), as expected, since the $4s^2$ pair has more electron correlation¹⁵ associated with it than the parallel spin $4s4p$ pair.

From Veillard's analysis³⁴ it would appear that our Mn basis may also be in need of an additional (more diffuse) primitive d function and a primitive s function located between the widely separated $3s$ - and $4s$ -describing basis functions. Therefore we tentatively added $\alpha_d = 0.1280$ and $\alpha_s = 0.2831$ by the Raffennetti-Ruedenberg even-tempered criterion. Note that the chosen s function is equidistant from $\alpha = 0.7911$ and 0.1013 , which respectively describe the outer part of the $3s$ and inner part of the $4s$ orbital.

In Table II we present a comparison of the various basis sets beyond the Roos-Dunning double zeta level. In addition to the various atomic species, representative results are present for the two most strongly bound states of $Mn-CH_2$.

The most important conclusion drawn from Table II is that the additional d function ($\alpha = 0.128$) has a large effect on the positioning of the $4s3d^6$ state relative to the $4s^23d^5$ ground state. Dunning's original basis predicts the 6D state to lie 117.5 kcal above the ground state, and the additional s function and two p functions have little effect, changing the 6S - 6D separation to 110.1 kcal. However the extra set of d functions reduces this separation to 72.5 kcal, compared to the experimental result, 48.8 kcal.

The above observations have important implications. First, however, it should be noted that the tendency of the Hartree-Fock approximation to favor the s^2d^n configuration relative to sd^{n+1} is well known for the atoms Mn, Co, Fe, and Ni. For example, for the Mn atom the near Hartree-Fock $\Delta E(^6S-^6D)$ of Clementi and Roetti³³ is 76.9 kcal. Thus we see that correlation effects will lower this separation by 28.1 kcal to the experimental result. However it must be stated that there is one significant difference between the Clementi-Roetti (CR) calculation and those reported here. Namely, the CR results are spatially restricted, i.e., all five d orbital components have the same radial form. For the $4s^23d^5^6S$ state this restriction is actually not a constraint at all. But for the $4s3d^6$ state, one of the d components is doubly-occupied, and our experience is that this orbital prefers to be somewhat more diffuse, i.e., to have a larger value of $\langle r \rangle$. Since our treatment of the $MnCH_2$ complex necessarily uses C_{2v} symmetry, the analogous treatment of the atom only requires the five d components to transform as $a_1(2)$, a_2 , b_1 , and b_2 . Accordingly we find the doubly-occupied d component to be more extended in space and to have a higher orbital energy. This means that if we ran a C_{2v} Mn atom calculation with the CR Slater basis, the result would be a $\Delta E(^6S-^6D)$ value a few kcal less than 76.9 kcal. Thus it appears that the present C_{2v} atomic separation of 72.5 kcal is close to the result which would be obtained in the limit of a complete basis.

One conclusion made on the basis of Table II is that an optimized basis for the s^2d^n state may be far from optimum for the analogous sd^{n+1} state. We suspect that this lack of basis set equality may be in part

responsible for the difficulties encountered by Walch and Goddard¹⁹ for the Ni-CO system. With this in mind, Swope³⁵ has reoptimized the Roos (12s 6p 4d) primitive Mn basis³⁰ for the $4s3d^6\ ^6D$ state. The total energy obtained is -1149.3939 hartrees, compared to -1149.3646 hartrees with the original basis. The energy of the 6S state using this $4s3d^6$ basis is -1149.5386 hartrees, yielding a 6S - 6D separation of 90.8 kcal/mole. Thus if one is limited to a (12s 6p 4d) basis for manganese, it would appear advisable to use the Swope basis (appropriately contracted). An alternative procedure used here was to employ the (5d) set obtained by adding the set of d functions with $\alpha = 0.128$ to those optimized by Roos³⁰ for the $4s^2 3d^5$ ground state.

The additional set of d functions is also seen in Table II to have a critical effect on the Mn-CH₂ dissociation energy. In particular, for the 8A_1 state [electron configuration (18)] the added d function is much more important for the dissociation limit Mn(6D) + CH₂(3B_1) than for MnCH₂ near its equilibrium separation. Thus the predicted 8A_1 binding energy decreases from 76 kcal to 38 kcal when a proper description of the $4s3d^6$ state is allowed. It is interesting to note that the 8B_1 dissociation energy is not qualitatively affected by the $\alpha = 0.128$ d function. This may be an indication that the $4s^2 3d^5$ description (to which the 8B_1 state goes asymptotically) carries over to the MnCH₂ complex.

Finally, we note here the actual basis used for the different potential curves and geometry optimizations. For the states arising from the $4s^2 3d^5$ and $4s4p3d^5$ Mn electron configurations the DZ + 2p basis was used. But for the states arising from $4s3d^6$ manganese, it was necessary to use the DZ + 2p + d basis described in the previous paragraph.

Results and Discussion

In our initial studies the geometry of the CH_2 ligand was frozen at either the triplet ($r(\text{CH}) = 1.08 \text{ \AA}$, $\theta(\text{HCH}) = 134^\circ$) or singlet ($r(\text{CH}) = 1.11 \text{ \AA}$, $\theta(\text{HCH}) = 102.4^\circ$) experimental geometries.^{13,14} The triplet geometry was used for electron configurations (13), (17)-(19), (25)-(27), and (31), namely those which dissociate to $\text{Mn} + {}^3\text{B}_1 \text{CH}_2$. Similarly the singlet methylene structure was assumed for electron configurations (14), (22) - (24), (28), (30), and (32).

SCF potential energy curves for the approach of Mn to rigid CH_2 are given in Figures 2 (triplet CH_2) and 3 (singlet CH_2). These diagrams are not, of course, intended to imply any presumption that the CH_2 bond angles will necessarily be either 102 or 134 in the MnCH_2 complex.

Turning first to the states arising from triplet methylene, we see in Figure 2 that the ${}^3\text{B}_1$ state, corresponding to electron configuration (13), is the predicted ground state. It is clear from the figure that there is a discontinuity in the MnCH_2 potential curve near $2.75 \text{ \AA}$. As we will discuss later this is due to an avoided crossing with an electronic state arising from a higher dissociation limit. A proper configuration interaction (CI) description of the ${}^8\text{B}_1$ state would allow the ground state to have a smooth potential curve.

From Figure 2 the equilibrium separation is predicted to be $r_e(\text{Mn-C}) = 2.19 \text{ \AA}$, and the dissociation energy 24.1 kcal . However, due to constraining the CH_2 fragment to its triplet ground state geometry, these predictions cannot be taken too seriously. For this reason, a complete optimization of the C_{2v} geometry of MnCH_2 in the ${}^8\text{B}_1$ state was carried

out. The predicted structure is $r_e(\text{Mn}-\text{C}) = 2.16 \text{ \AA}$, $\theta_e(\text{HCH}) = 109^\circ$, and $r_e(\text{C}-\text{H}) = 1.09 \text{ \AA}$. The total energy at this equilibrium geometry is -1188.5275 hartrees, corresponding to an MnCH_2 dissociation energy of 32.6 kcal.

Perhaps the most interesting feature of our MnCH_2 electronic ground state structure is the methylene bond angle of 109° . This angle makes it obvious that the CH_2 group feels a very different environment in MnCH_2 than in the free methylene radical (134° angle). Furthermore and despite the absence of additional ligands in our model, the predicted bond angle is very close (perhaps fortuitously) to the $107^\circ \pm 9^\circ$ found by Guggenberger and Schrock¹¹ for $\text{Ta}(\text{C}_5\text{H}_5)_2 \text{CH}_3\text{CH}_2$.

Although the C-H distance is not particularly unexpected, the Mn-C equilibrium separation of $2.16 \text{ \AA}$ is of special interest, since it should correspond to an Mn=C double bond to satisfy the conventional valence requirements of carbon. Since very few manganese carbenes have been structurally characterized, comparison with experiment is necessarily limited. However the structure³⁶ of $\text{NMe}_4^+ [(\text{C}_5\text{H}_5)(\text{OC})_2 \text{Mn} \text{C}(\text{O})\text{Ph}]^-$ reveals an Mn=C distance of $1.96 \text{ \AA}$. In addition, work³⁷ in Fischer's laboratories has determined a Mn=C distance of $1.95 \text{ \AA}$ for the dimetal complex $\text{Mn}_2(\text{CO})_9 \text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$. Thus it is seen that the predicted ground state $\text{Mn}=\text{CH}_2$ separation is $\sim 0.2 \text{ \AA}$ longer than the two observed distances for Fischer carbenes. In light of the obvious differences between our model complex and the much larger molecules studied by X-ray techniques, this agreement seems adequate. In order to further probe the differences between Mn-C, Mn=C, and Mn $\equiv$ C bonds, we hope to carry out theoretical studies

of the Mn-CH_3 and $\text{Mn}\equiv\text{CH}$ species in the future. Before closing this paragraph it should be noted that the structures of a fairly large number of chromium carbenes have been determined. For example, in his 1972 review, Fischer notes seven such complexes, with $\text{Cr}=\text{C}$ distances all in the range 2.00 to 2.16 Å. Thus our ab initio prediction of 2.16 Å is not an entirely unreasonable one.

The electronic structure of $^8\text{B}_1$ MnCH_2 may be given a simple interpretation in terms of the Mulliken populations and orbital energies given in Table III. Probably the most interesting feature of Table III is the prediction of a +0.62 Mulliken positive charge on the Mn atom. By comparison with the separated $\text{Mn} + \text{CH}_2$ result, it is seen that the result of forming the MnCH_2 complex is a large increase in the electron density near the carbon atom. In Mulliken terms the carbon population increases from 6.36 to 6.94 "electrons". This result is consistent with Schrock's synthetic finding¹¹ that the methylene ligand in $\text{Ta}(\text{C}_5\text{H}_5)_2\text{CH}_2\text{CH}_3$ is nucleophilic. For example, Schrock finds the tantalum methylene complex to form an adduct with $\text{Al}(\text{CH}_3)_3$. In addition we rather suspect that other binary transition metal-methylene complexes may have this M^+CH_2^- character. This is of course not the case for the more common Fischer type carbenes, for which the carbene carbon atom is usually viewed as positively charged. For example, Kreiter and Formacek³⁸ have shown for pentacarbonyl [methoxy-(phenyl) carbene] chromium (0) that ^{13}C NMR measurements yield a result "well within the range of shifts exhibited by the carbo-cations of organic chemistry."⁷ However, this result is not necessarily inconsistent with our theoretical predictions, since the above Fischer type carbene has an electron with-

drawing oxygen atom connected to the carbene carbon. We hope to test this hypothesis in the future via theoretical studies of Fischer carbenes, for which a prototype would be $\text{Mn C} \begin{smallmatrix} \text{OH} \\ \text{H} \end{smallmatrix}$.

The Mulliken populations can also be used to explain why the CH_2 bond angle decreases from 134° at the dissociation limit to 109° for $^8\text{B}_1 \text{ MnCH}_2$. The reader should recall that the key feature of Walsh's diagram³⁹ for AH_2 molecules is the splitting of the $1\pi_u$ orbital into $3a_1$ and $1b_1$ components. The $1b_1$ orbital binding energy is essentially flat as a function of angle while the $3a_1$ orbital is greatly stabilized by smaller bond angles. Thus singlet methylene, with two electrons in the $3a_1$ orbital, is much more strongly bent than triplet CH_2 . Inspection of Table III shows that in the $^8\text{B}_1$ state of MnCH_2 , a methylene population of $\sim 3a_1^{1.69} 1b_1^{0.95}$ exists. That is, essentially all of the π -character in Mn^+CH_2^- goes toward the $3a_1$ orbital. Thus the bond angle of the $^8\text{B}_1$ state is closer to that of singlet CH_2 than that of the triplet state.

Further interrogation of Table III shows the $3d^5$ atomic shell to be virtually intact. The rearrangement in electron distribution upon formation of MnCH_2 is due to a) a departure of more than one electron from the Mn 4s orbital b) a buildup (from zero for the Mn atom) of essentially 1/2 Mulliken electron in the Mn 4p functions, and c) migration of electron distribution to the 2s and (especially) 2p functions of carbon. Thus the direct role of the d orbitals in the bonding is not apparent for the $^8\text{B}_1$ state.

Before going on to the MnCH_2 states arising from higher dissociation limits, it must be noted that Figures 2 and 3 are not precisely ab initio.

That is, the $\text{Mn}(4s3d^6)$ and $\text{Mn}(4s4p3d^5)$ dissociation limits have been adjusted to concur with their experimental values. This means, e.g., that the three potential curves dissociating to $\text{Mn}(4s4p3d^5) + {}^3B_1 \text{CH}_2$ have been uniformly displaced upward by 20.5 kcal. Similarly the three curves dissociating to $4s3d^6$ manganese have been uniformly lowered by 15.8 kcal. Clearly this procedure is neither aesthetically pleasing nor theoretically justifiable. However, it does seem to make more sense than presenting a set of potential curves dissociating to incorrect limits.

One of the states arising from $\text{Mn}(4s3d^6)$, the 8A_1 state, is seen to be rather strongly bound. This result is especially important since for Cr and Cu the lowest sd^{n+1} state is the electronic ground state and for Ni the lowest sd^{n+1} state is essentially degenerate with s^2d^8 . From Figure 3 (which, recall, corresponds to a fixed methylene angle of 134°) the dissociation energy and Mn-C separation are 37.8 kcal and 2.18 Å. A simultaneous optimization of the two most important geometrical parameters yields $r_e(\text{Mn-C}) = 2.18 \text{ Å}$, $\theta_e(\text{HCH}) = 142^\circ$ and a dissociation energy of 38.7 kcal. The metal-carbon bond distance is only slightly greater than that predicted for the 8B_1 state, but the bond angle is very different, in fact even larger than that of triplet methylene. Since the 8A_1 dissociation energy is only slightly greater than that predicted for ${}^8B_1 \text{MnCH}_2$, we predict the 8A_1 state to lie at ~ 43 kcal, not much less than the atomic ${}^6S-{}^6D$ separation. It should be emphasized here that these dissociation energy predictions could be strongly affected by the correlation energy. In general the correlation energy is greater for molecular species than for the separated fragments,¹⁵ and this differential effect might increase our

predicted dissociation energies by 10 or possibly even 20 kcal. Geometry predictions, of course, are relatively insensitive to correlation effects.

To interpret the above 8A_1 results, Table IV displays Mulliken populations and orbital energies, along with a comparison with separated $Mn + CH_2$. Perhaps most important, in keeping with our previous analysis, Table IV can be used to construct a methylene population with 8A_1 $MnCH_2$ of $3a_1^{0.79} 1b_1^{1.78}$. This illustrates a dramatic difference between the 8A_1 and 8B_1 states. In the latter case the negative charge arriving at the methylene was taken up by the $3a_1$ orbital. Here the $1b_1$ orbital is the big gainer. However the $1b_1$ population is not critical, since this orbital is flat on Walsh's diagram and should not affect the bond angle. Since the $3a_1$ orbital now has less than its one electron in free methylene, the bond angle should be greater than 134° . This analysis is in striking harmony with the ab initio prediction of 142° .

Note also in Table IV that the Mn d function population changes from 6.00 to 5.07 electrons in forming the 8A_1 state. This 0.93 population is of course primarily transferred to the $CH_2 1b_1$ orbital, but there is again a Mn 4p population of 0.5. In fact, a manganese atom hybridization of sp^2 (that is, $4s4p^2$) seems to appear consistently in the present research. This confirms our previously expounded hypothesis¹⁶ that the role of 4s and 4p orbitals in organometallic systems should not be ignored.

The other two electronic states dissociating to $4s3d^6 Mn + {}^3B_1 CH_2$ are seen in Figure 2 to be repulsive, the two potential curves being nearly indistinguishable. Similarly all three states dissociating to $4s4p3d^5 Mn + {}^3B_1 CH_2$ are essentially repulsive. Thus for transition metal-carbene systems for which the carbene triplet state lies much lower than the singlet, only two electronic states will be of primary importance. If the s^2d^n state of

the metal lies well below sd^{n+1} (as is the case for manganese), the state of the complex analogous to 8B_1 MnCH₂ will lie lowest. However, as the s^2d^n - sd^{n+1} separation decreases, the state(s) comparable to 8A_1 should lie lower. Clearly the above reasoning is oversimplified since it does not take account of the sometimes subtle differences between CH₂ and the larger carbenes more accessible to experimental study. In addition, of course, we have not attempted to assess the role of additional ligands. Nevertheless, these simple guidelines may be helpful in understanding transition metal-carbene properties.

Before moving on to a discussion of the states arising from singlet methylene, it must be noted that the predicted singlet-triplet separation using the present techniques is 32.5 kcal, compared to experiment,²² 19.5 ± 0.7 . As discussed elsewhere,⁴⁰ the primary reason for this discrepancy is the lack of carbon atom d functions in the basis. Thus, it might be appropriate to lower all the potential curves in Figure 2 by 13 kcal to compensate. Since we take as our zero point in Figure 2 the dissociation limit 6S Mn + 1A_1 CH₂, such an adjustment relative to the 6S Mn + 3B_1 CH₂ may be made trivially.

Among the singlet CH₂ states, the $4s^23d^5$ interaction is only very weakly bound. Actually this is not surprising if we recall that the $4s^23d^5$ interaction with 3B_1 CH₂ only becomes attractive after an avoided crossing with a potential curve arising from a higher dissociation limit of MnCH₂. The likely source of this 8B_1 avoided crossing is seen in Figure 2. This is the 8B_1 state (29) arising from ${}^8P(4s4p3d^5)$ Mn + 1A_1 CH₂. When SCF calculations on the latter 8B_1 state were performed, the result was an extremely attractive potential curve, which eventually

crosses the repulsive $4s^2 3d^5 + {}^3B_1$ curve. We cannot completely eliminate the possibility of substantial $4s3d^6 + {}^3B_1$ character [via configurations (15) and (16)] in the lowest 8B_1 state. However this seems less likely since the Mulliken populations (Table III) at the equilibrium geometry show essentially pure $3d^5$ character.

The 6B_1 state is seen in Figure 3 to be rather strongly bound, by 37.2 kcal at the minimum $r_e(\text{Mn-C}) = 1.90 \text{ \AA}$. This state is of particular interest since many carbenes have singlet ground states. One such example is the vinylidene radical: $\text{C}=\text{CH}_2$ for which the triplet excited state lies ~ 20 kcal higher.⁴¹ Thus for the CuCCH_2 complex (recall that for copper the sd^{n+1} state is the ground state), an electronic state comparable to the present 6B_1 state should be the ground state. Once again we see the potential richness provided by transition metal-carbene complexes. Actually, complexes of the vinylidene type MCCH_2 may be quite important, as Davidson⁴² has suggested that this isomer may in some cases be more stable than the conventional π -bonded acetylene complex. And Swope's recent work³⁵ on the $\text{Mn-C}_2\text{H}_2$ system does indeed suggest that the π -bonded complex is only weakly bound.

Holding the C-H distance fixed at $1.11 \text{ \AA}$ (the singlet CH_2 experimental value)¹³ a geometry optimization yielded $r_e(\text{Mn-C}) = 1.90 \text{ \AA}$ and $\theta_e(\text{HCH}) = 108^\circ$. This result is particularly fascinating due to the Mn-C distance, which is much shorter than that for the 8B_1 and 8A_1 states, and even a bit ($\sim 0.05 \text{ \AA}$) shorter than for the known manganese carbenes.^{36,37} The predicted dissociation energy is 37.7 kcal, quite comparable to that of the other two states. Again we caution that correlation effects might increase this predicted dissociation energy by 10-20 kcal.

These results may be discussed further in terms of the data given in Table V. A CH_2 fragment population of $3a_1^{1.76} 1b_1^{0.63}$ is found for the 6B_1 state, and again this analysis and the Walsh diagram allow a rationalization of the predicted bond angle. Namely, since the $3a_1$ orbital is somewhat depopulated relative to singlet methylene, the bond angle opens up a bit, from 102.4° to 108° . Another noteworthy point is that the 6B_1 state is the only one of the three strongly bound states to exhibit a distinctly non integer d function population, here 5.32. The source of this anomaly can be traced to the doubly occupied $3b_1$ orbital. This is a genuine bonding orbital with a large fraction of 3d character (65%), but in addition 4p(4%) and carbon 2p (32%) contributions. In fact one could describe the $3b_1$ orbital as a striking example of the Dewar-Chatt-Duncanson model.⁴³ That is, we have back donation from the doubly-occupied (the only doubly-occupied component for Mn) metal 3d orbital to the unoccupied $1b_1$ orbital of singlet methylene.

Finally, the predicted dipole moments of the 8B_1 , 8A_1 , and 6B_1 states are +1.48, +2.36, and -1.20 debye. A positive sign implies Mn^+C^- polarity. These results are readily understood in terms of the predicted dipole moments of triplet (-0.66) and singlet (-2.40) methylene. The 6B_1 state bears the strongest resemblance to singlet CH_2 and in addition has the smallest positive charge (0.33) on manganese. Thus the 6B_1 state is the only one for which the ${}^-\text{CH}_2^+$ polarity survives in the complex. Since the 8B_1 state has a slightly greater (0.62 vs. 0.53) Mulliken charge than the 8A_1 state, one might expect the 8B_1 dipole moment to be greater. However the key feature here is rather the HCH bond angle. For the 8A_1 state the large 142° bond angle essentially decimates the methylene dipole moment,

leaving little resistance to the Mn^+C^- tendency. For the $^8\text{B}_1$ case the 109° CH_2 angle greatly enhances the triplet dipole moment and provides a counterbalancing force to the Mn^+C^- electrostatics.

For completeness, Figure 4 gives potential energy curves for three states of MnCH_2^+ . Consistent with the larger dipole moment of singlet CH_2 , the $^7\text{A}_1$ state is the most strongly bound. Note that while the $^7\text{B}_1$ state does in fact dissociate to $^7\text{S Mn} + ^3\text{B}_1 \text{CH}_2$, this is not possible within the singlet configuration approximation.

Concluding Remarks

Perhaps the most intriguing prediction of the present theoretical study⁴⁴ concerns the richness of possible transition metal-carbene systems. Four distinct possibilities should be mentioned. The s^2d^n metal-triplet carbene combination is modeled by the 8B_1 state, and the s^2d^n -singlet carbene interaction is essentially repulsive. The 8A_1 state is representative of the sd^{n+1} -triplet carbene interaction and the 6B_1 state arises from sd^{n+1} -singlet carbene combination. When electron correlation is properly taken into account, all three of these uniquely different states may be bound by as much as 50 kcal. Thus, for example, we see that methylene appears to be more strongly bound to transition metals than is the carbon monoxide ligand.

References

1. W. Kirmse, Carbene Chemistry, second edition (Academic Press, New York, 1971).
2. F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.* 16, 487 (1972).
3. D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.* 72, 545 (1972).
4. R. F. Heck, Organotransition Metal Chemistry (Academic Press, New York, 1974).
5. R. R. Schrock and G. W. Parshall, *Chem. Rev.* 76, 243 (1976).
6. E. O. Fischer and A. Maasböl, *Angew. Chem. Int. Ed. Engl.* 3, 580 (1964).
7. A very recent example is the paper by E. O. Fischer, G. Huttner, T. L. Lindner, A. Frank, and F. R. Kreissl, *Angew. Chem. Int. Ed. Engl.* 15, 231 (1976). For a recent review see E. O. Fischer, *Adv. Organometallic Chem.* 14, 1 (1976).
8. U. Klabunda and E. O. Fischer, *J. Am. Chem. Soc.* 89, 7141 (1967).
9. D. J. Cardin, M. J. Doyle, and M. F. Lappert, *Chem. Comm.* p. 927 (1972); R. H. Grubbs, D. D. Carr, C. Hoppin, and P. L. Burk, *J. Am. Chem. Soc.* 98, 3478 (1976).
10. N. Calderon, *Accounts Chem. Res.* 5, 127 (1972).
11. R. R. Schrock, *J. Am. Chem. Soc.* 97, 6577 (1975); L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.* 97, 6578 (1975).
12. By comparison with the observed Ta-C single bond distance of 2.25 Å and Ta≡C triple bond distance of 1.76 Å. See L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.* 97, 2935 (1975).

13. G. Herzberg and J. W. C. Johns, Proc. Roy. Soc. 295A, 107 (1966).
14. R. A. Bernheim, T. Adl, H. W. Bernard, A. Songco, P. S. Wang, R. Wang, L. S. Wood, and P. S. Skell, J. Chem. Phys. 64, 2747 (1976).
15. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results (Addison-Wesley, Reading, Massachusetts, 1972).
16. W. C. Swope and H. F. Schaefer, J. Am. Chem. Soc. 98, 0000 (1976).
17. G. A. Somorjai, Principles of Surface Chemistry (Prentice-Hall, Englewood Cliffs, N.J., 1972).
18. J. R. Anderson, Structure of Metallic Catalysts (Academic Press, London, 1975).
19. S. P. Walch and W. A. Goddard, "The Generalized Valence Bond Description of the Low-Lying States of NiCO", to be published.
20. W. A. Herrmann, M. L. Ziegler, K. Weidenhammer, H. Biersack, K. A. Mayer, and R. D. Minard, Angew. Chem. Int. Ed. Engl. 15, 164 (1976).
21. C. E. Moore, "Atomic Energy Levels", Nat. Bur. Std. (U.S.) Circ. No. 467 (1949).
22. P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, J. Am. Chem. Soc. 98, 3731 (1976).
23. G. Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand, Princeton, 1967).
24. R. Pauncz, Alternate Molecular Orbital Theory (W. B. Saunders, Philadelphia, 1967).
25. F. B. Bobrowicz and W. A. Goddard, in Modern Theoretical Chemistry, editor H. F. Schaefer (Plenum, New York, 1976).
26. P. S. Bagus, Phys. Rev. 139, A619 (1965).

27. W. J. Hunt, P. J. Hay, and W. A. Goddard, J. Chem. Phys. 57, 738 (1972); and references therein.
28. D. B. Neumann, H. Basch, R. L. Kornegay, L. C. Snyder, J. W. Moskowitz, C. Hornback, and S. P. Liebmann, POLYATOM 2, program no. 199, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.
29. S. Huzinaga, J. Chem. Phys. 42, 1293 (1965); T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).
30. B. Roos, A. Veillard, and G. Vinot, Theoret. Chim. Acta 20, 1 (1971).
31. E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables 14, 177 (1974).
32. T. H. Dunning, unpublished. This basis has also been used (and shown to compare favorably with a much larger set) in a study of the permanganate ion by H. L. Hsu, C. Peterson, and R. M. Pitzer, J. Chem. Phys. 64, 791 (1976).
33. R. C. Raffanetti, R. D. Bardo, and K. Ruedenberg, pgs. 164-169 in Energy, Structure, and Reactivity, editors D. W. Smith and W. B. McRae (Wiley, New York, 1973).
34. A. Veillard and J. Demuynck, in Modern Theoretical Chemistry, editor H. F. Schaefer (Plenum, New York, 1976).
35. W. C. Swope, unpublished.
36. E. Hädicke and W. Hoppe, Acta Crystallogr., Sec. B, 27, 760 (1971).
37. E. O. Fischer, Pure and Applied Chem. 30, 353 (1972).
38. C. G. Kreiter and V. Formacek, Angew. Chem. Int. Ed. Engl. 11, 141 (1972).
39. A. D. Walsh, J. Chem. Soc. 2260 (1953); and the following five papers in the same journal.

40. J. H. Meadows and H. F. Schaefer, J. Am. Chem. Soc. 98, 0000 (1976).
41. N. Bodor, M. J. S. Dewar, and J. S. Wasson, J. Am. Chem. Soc. 94, 9095 (1972).
42. A. Davidson, personal communication.
43. M. J. S. Dewar, Bull. Soc. Chim. Fr. 18C, 79 (1951); J. Chatt and L. A. Duncanson, J. Chem. Soc. (London) 2939 (1953).
44. For an interesting recent semi-rigorous theoretical study of the $(\text{CO})_5 \text{Cr}(\text{OCH}_3) \text{CH}_3$ molecule, see T. F. Block, R. F. Fenske, and C. P. Casey, J. Am. Chem. Soc. 98, 442 (1976).

Table I. Dunning double zeta basis set³² for the Mn atom.

Different contracted functions are separated by wavy lines.

Type	Exponent α	Contraction Coefficient
s	60370.0	0.003329
s	8911.0	0.026290
s	2009.0	0.129072
s	579.3	0.432556
s	192.4	0.522192
s	192.4	0.338204
s	69.07	0.701819
s	17.71	1.0
s	7.399	1.0
s	1.944	1.0
s	0.7911	1.0
s	0.1013	1.0
s	0.03912	1.0
p	383.7	0.021292
p	90.50	0.136698
p	28.22	0.898072
p	28.22	-1.422607
p	9.827	1.148404
p	2.649	1.0
p	0.8392	1.0
p	0.2659	1.0
p	0.0842	1.0
d	21.09	0.086051
d	5.519	0.384623
d	1.662	0.707470
d	0.4613	1.0

Table II. Comparison of different basis sets for Mn, Mn⁺, and MnCH₂. For the ion and neutral atom, total energies are given in hartrees. For the ⁸B₁ state, the energy at R(Mn-C) = 4.0 bohrs is given in kcal/mole relative to separated Mn(4s²3d⁵6s) + CH₂(³B₁). The results for ⁸A₁ MnCH₂ are also in kcal, but relative to Mn(4s3d⁶6d) + CH₂(³B₁).

Basis Set	Mn				MnCH ₂	
	Mn ⁺ 4s3d ⁵	4s ² 3d ⁵	4s3d ⁶	4s4p3d ⁵	⁸ B ₁	⁸ A ₁
Double Zeta (DZ)	-1149.3337	-1149.5473	-1149.3600	-1148.0862	- 3.2	-58.4
DZ + s	-1149.3345	-1149.5479	-1149.3611	-1148.0869	- 3.8	-58.9
DZ + 2p	-1149.3474	-1149.5624	-1149.3864	-1149.5113	-23.6	-76.4
DZ + d	-1149.3448	-1149.5608	-1149.4371	-1149.2191	-10.3	-24.4
DZ + s + 2p	-1149.3482	-1149.5630	-1149.3875	-1149.5119	-23.7	-76.4
DZ + 2p + d	-1149.3580	-1149.5753	-1149.4594	-1149.5297	-22.7	-37.7
DZ + s + 2p + d	-1149.3589	-1149.5758	-1149.4603	-1149.5303	-22.9	-37.8

Table III. A comparison of Mulliken populations and orbital energies for 8B_1 MnCH₂ and (in parentheses) Mn(⁶S) + CH₂(³B₁). The core electrons are omitted from this picture. The ordering of orbitals follows that of separated Mn + CH₂. Note that each of the two equivalent hydrogen atoms has associated with it the Mulliken populations given here.

		Mn				C			H		
Orbital	$\epsilon(\text{MnCH}_2)$	s	p	d	total	s	p	total	s	$\epsilon(\text{Mn}+\text{CH}_2)$	
7a ₁ ²	-0.8284	0.02 (-)	0.01 (-)	0.01 (-)	0.03 (-)	1.36 (1.25)	0.05 (0.10)	1.41 (1.36)	0.28 (0.32)	-0.8535	
3b ₂ ²	-0.5116	- (-)	- (-)	- (-)	- (-)	- (-)	1.07 (1.04)	1.07 (1.04)	0.46 (0.48)	-0.6028	
8a ₁ ²	-0.4041	0.21 (2.00)	0.08 (-)	0.05 (-)	0.34 (2.00)	0.17 (-)	1.29 (-)	1.46 (-)	0.10 (-)	-0.2439	
1a ₂	-0.6326	- (-)	- (-)	1.00 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.6214	
9a ₁	-0.6326	- (-)	- (-)	1.00 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.6214	
3b ₁	-0.6282	- (-)	- (-)	0.99 (1.00)	0.99 (1.00)	- (-)	0.01 (-)	0.01 (-)	- (-)	-0.6214	
4b ₂	-0.6213	- (-)	- (-)	0.99 (1.00)	0.99 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.6214	
10a ₁	-0.5959	0.04 (-)	0.02 (-)	0.95 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.6214	
11a ₁	-0.2653	0.65 (-)	0.32 (-)	- (-)	0.97 (-)	0.01 (0.18)	0.02 (0.79)	0.03 (0.97)	- (0.02)	-0.4666	
4b ₁	-0.3227	- (-)	0.04 (-)	0.01 (-)	0.06 (-)	- (-)	0.94 (1.00)	0.94 (1.00)	- (-)	-0.4049	
Totals		6.91 (8.00)	12.47 (12.00)	5.00 (5.00)	24.38 (25.00)	3.54 (3.43)	3.39 (2.93)	6.94 (6.36)	0.84 (0.82)		

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Table IV. A comparison of Mulliken populations and orbital energies for 8A_1 MnCH₂ and (in parentheses) Mn(6D) + CH₂(3B_1). The core electrons are omitted from the picture. The ordering of orbitals follows that of separated Mn + CH₂.

Orbital	$\epsilon(\text{MnCH}_2)$	Mn				C			H	
		s	p	d	total	s	p	total	s	$\epsilon(\text{Mn}+\text{CH}_2)$
7a ₁ ²	-0.8270	0.01 (-)	0.01 (-)	0.01 (-)	0.03 (-)	1.38 (1.25)	0.01 (0.10)	1.39 (1.36)	0.29 (0.32)	-0.8535
3b ₂ ²	-0.5749	- (-)	0.01 (-)	0.01 (-)	0.01 (-)	- (-)	1.13 (1.04)	1.13 (1.04)	0.43 (0.48)	-0.6028
3b ₁ ²	-0.2709	- (-)	0.15 (-)	0.09 (2.00)	0.24 (2.00)	- (-)	1.76 (-)	1.76 (-)	- (-)	-0.2217
8a ₁	-0.6850	- (-)	- (-)	0.96 (-)	0.96 (-)	- (0.18)	0.04 (0.79)	0.04 (0.97)	- (0.02)	-0.4666
9a ₁	-0.6805	- (-)	- (-)	1.00 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.4411
1a ₂	-0.6809	- (-)	- (-)	1.00 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.4350
4b ₂	-0.6773	- (-)	- (-)	1.00 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.4350
10a ₁	-0.4343	0.30 (-)	0.03 (-)	0.04 (1.00)	0.36 (1.00)	0.03 (-)	0.55 (-)	0.58 (-)	0.03 (-)	-0.4076
4b ₁	-0.6577	- (-)	0.01 (-)	0.97 (-)	0.98 (-)	- (-)	0.02 (1.00)	0.02 (1.00)	- (-)	-0.4049
11a ₁	-0.2815	0.55 (1.00)	0.33 (-)	- (-)	0.88 (-)	0.01 (-)	0.10 (-)	0.11 (-)	- (-)	-0.2275
Totals		6.86 (7.00)	12.53 (12.00)	5.07 (6.00)	24.47 (25.00)	3.42 (3.43)	3.61 (2.93)	7.03 (6.36)	0.75 (0.82)	

Table V. Orbital energies ϵ and Mulliken populations for 6B_1 MnCH₂ and (in parentheses) Mn(6D) + CH₂(1A_1). The core electrons are omitted from this picture. The ordering of orbitals follows that of separated Mn + CH₂.

Orbital	$\epsilon(\text{MnCH}_2)$	Mn			total	C			total	H		$\epsilon(\text{Mn}+\text{CH}_2)$
		s	p	d		s	p			s		
7a ₁ ²	-0.8768	0.01 (-)	0.02 (-)	0.02 (-)	0.06 (-)	1.35 (1.29)	0.04 (0.13)	1.42 (1.42)	0.26 (0.29)	-0.9054		
3b ₂ ²	-0.5538	- (-)	- (-)	- (-)	- (-)	- (-)	1.09 (0.97)	1.09 (0.97)	0.45 (0.51)	-0.5674		
8a ₁ ²	-0.4624	0.13 (-)	0.07 (-)	0.09 (-)	0.28 (-)	0.16 (0.44)	1.34 (1.41)	1.50 (1.86)	0.11 (0.07)	-0.3849		
3b ₁ ²	-0.3158	- (-)	0.07 (-)	1.29 (2.00)	1.37 (2.00)	- (-)	0.63 (-)	0.63 (-)	- (-)	-0.2217		
9a ₁	-0.5993	- (-)	- (-)	1.00 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.4441		
1a ₂	-0.5986	- (-)	- (-)	1.00 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.4350		
4b ₂	-0.5896	- (-)	- (-)	1.00 (1.00)	1.00 (1.00)	- (-)	- (-)	- (-)	- (-)	-0.4350		
10a ₁	-0.5517	0.04 (-)	0.01 (-)	0.92 (1.00)	0.97 (1.00)	0.01 (-)	0.02 (-)	0.03 (-)	- (-)	-0.4076		
11a ₁	-0.2377	0.66 (1.00)	0.32 (-)	- (-)	0.98 (1.00)	0.01 (-)	0.01 (-)	0.01 (-)	- (-)	-0.2275		
Totals		6.85 (7.00)	12.50 (12.00)	5.32 (6.00)	24.67 (25.00)	3.54 (3.73)	3.13 (2.51)	6.67 (6.25)	0.83 (0.87)			

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Figure Captions

- Figure 1. The molecular structure of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)(\text{CH}_2)$, as reported by Guggenberger and Schrock.¹¹
- Figure 2. MnCH_2 potential energy curves arising from manganese atom plus triplet methylene. $^3\text{B}_1 \text{CH}_2$ is fixed at its equilibrium geometry here, namely $r(\text{CH}) = 1.08 \text{ \AA}$, $\theta(\text{HCH}) = 134^\circ$.
- Figure 3. MnCH_2 potential energy curves arising from manganese atom plus singlet methylene. $^1\text{A}_1 \text{CH}_2$ is fixed at its equilibrium geometry, namely $r(\text{CH}) = 1.11 \text{ \AA}$, $\theta(\text{HCH}) = 102.4^\circ$.
- Figure 4. MnCH_2^+ potential energy curves. The $^7\text{B}_1$ and $^9\text{B}_1$ curves were obtained using the triplet methylene equilibrium geometry. The $^7\text{A}_1$ curve assumed the equilibrium geometry of singlet methylene.

Fig. 1

XBL767-9108

Fig. 2

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Fig. 3

XBL 767-9107

Fig. 4

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