

Generalized Valence Bond Studies of the Electronic States of NiCH₂ and NiCH₃

Anthony K. Rappé and William A. Goddard III*

Contribution No. 5424 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.

Received September 10, 1976

Abstract: Generalized valence bond and configuration interaction calculations were carried out for NiCH₂ and NiCH₃. In both cases the lower states have the character of Ni (4s¹3d⁹) with the Ni 4s orbital bonding to the singly occupied Cσ orbital. The geometries were optimized, leading to NiC = 1.78 Å for NiCH₂ and NiC = 1.87 Å for NiCH₃. The calculated bond energies are *D*(Ni-CH₃) = 60 kcal and *D*(Ni-CH₂) = 65 kcal, with a weak π bond in the latter case.

Although metal-carbon bonds play an important role in both homogeneous and heterogeneous catalysis of hydrocarbons,² little is known about the precise character of such bonds from either experimental or theoretical viewpoints.³ As a first step in studying such systems theoretically, we have examined the bonding of CH₃ and CH₂ to a single Ni atom.



Hartree-Fock (HF), generalized valence bond⁴ (GVB), and configuration interaction (CI) calculations were carried out using a basis set of double zeta quality⁵ (and including *d* functions on the carbon). All calculations are *ab initio* except that a modified effective potential^{6,7} is used to replace the argon core of the Ni (reducing Ni to a ten-electron atom).

For NiCH₂, Ni-C bond lengths from *R* = 1.60 Å to *R* = ∞ were considered and HCH bond angles were optimized near the optimum *R*. The CH bond lengths were optimized near the optimum *R* and HCH angles. For NiCH₃ the CH bond length was fixed at 1.098 Å (a typical CH bond length for a methyl group and the optimum value calculated for NiCH₂) and the Ni-C bond length and the NiCH bond angle were fully optimized. In the GVB calculations we correlated all Ni-C and C-H bonds, leading to GVB(4) for both NiCH₂ (¹A₁) and NiCH₃. Similar calculations were carried out for all relevant excited states.

In the CI calculations we included the optimum GVB orbitals for the Ni-C bonds plus two sets of Ni *d* orbitals (obtained from the various states). The CI included all the GVB correlations; in addition, for each state all single excitations into the virtual space were allowed. The result was 328 to 1030 spin eigenfunctions (380 to 3792 determinants) for NiCH₂ and 128 to 530 spin eigenfunctions (152 to 999 determinants) for NiCH₃.

Consider first the bonding of Ni to CH₃. In order to understand the character of these states recall that there are two low-lying states of Ni: ³F(4s²3d⁸) and ³D(4s¹3d⁹) separated by 1 kcal. We find that for Ni the 4s orbital is ~2.5 times the size of the 3d orbital, and hence the interaction of Ni 4s with Cσ (the nonbonding singly-occupied sp³-like orbital of CH₃ radical) dominates the bonding. The interaction of Cσ with (4s)¹(3d)⁹ is quite attractive (bonding of Cσ and 4s), while the interaction of Cσ with (4s)²(3d)⁸ is repulsive (Pauli repulsion of (4s)² and Cσ) at large *R* and only moderately attractive for small *R*. Given that Ni has the overall character of 4s¹3d⁹ leads to five configurations of NiCH₃ depending upon which of the five *d* orbitals is singly occupied (or equivalently which has the hole). These states will be denoted as

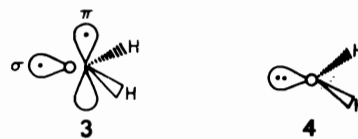
$$d\delta^+ = x^2 - y^2, \quad d\delta^- = xy, \quad d\pi^+ = yz, \quad d\pi^- = xz, \\ d\sigma = 2z^2 - x^2 - y^2,$$

where the σ , π , δ indicate the symmetry with respect to the Ni C axis and the + or - indicate the symmetry with respect to a particular NiCH molecular plane.

Just as in NiH⁷ and NiCO⁸ we find that the best state has the hole in a δ orbital ($d\delta^+$ or $d\delta^-$) with the $d\pi^+$ state 9.0 kcal higher and the $d\sigma$ state 9.8 kcal higher. The optimum geometry for the ground state is *R*_{NiC} = 1.87 Å and ∠NiCH = 109.4° and the calculated bond energy is 60 kcal. The bond energies of these various states are given in Figure 1. The total charge transfer from the Ni to CH₃ is 0.42 electrons (based on Mulliken populations). The two GVB orbitals of the NiCσ bond have an overlap of *S* = 0.751 and hybridizations of Ni 4s¹4p^{0.014}3d^{0.32} and C 2s¹2p^{2.93}3d^{0.024}.

The NiC bond length (1.87 Å) is slightly shorter than the 1.90 Å calculated⁸ for NiCO, but slightly longer than the 1.82 Å found experimentally⁹ for Ni(CO)₄. The calculated bond energy is at the upper limit of the 40-60 kcal often estimated for alkane-transition metal bonds;¹⁰ however, no firm experimental values are known.¹¹

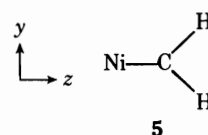
As a basis for describing the bonding in NiCH₂ we will now examine the CH₂ fragment. The ground state of CH₂, ³B₁ (σπ) has singly occupied a single electron in each of two nonbonding orbitals, denoted as Cσ and Cπ as in 3 leading to an HCH bond



angle of 135°,¹² while the first excited state ¹A₁ (σ²) (at 0.88 eV)¹³ can be viewed as having two electrons in the Cσ orbital as in 4 leading to an HCH angle of 102.4°.¹⁴

We find that the lower states of NiCH₂ are analogous to those of NiCH₃ with the Ni having the character ³D(4s¹3d⁹) and the CH₂ fragment of NiCH₂ having the character 3 of the σπ state. The interactions between the Cπ orbital and the Ni *d* orbitals is weak and hence we end up with ten low-lying states, a singlet and triplet for each of the five locations of the *d* hole on the Ni (the Cπ orbital being singlet or triplet paired with the singly occupied *d* orbital).

Taking the coordinate system as



we find the states of NiCH₂ to be very similar to those of NiCH₃ *except* for the $d\pi^-$ (d_{xz}) states. Thus the $d\delta^-$ state

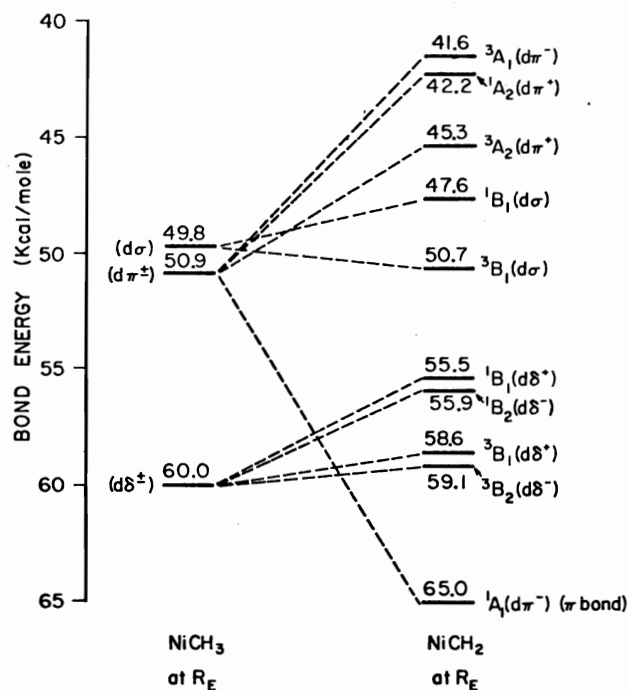


Figure 1. The bond energies $D_e(\text{Ni-CH}_n)$, in kcal/mol, for the lower states of NiCH_3 and NiCH_2 . In each case the geometry for the ground state is used (e.g., the D_e for $\text{NiCH}_2[{}^3\text{B}_2(d\delta^-)]$ is 62 kcal rather than the 59 kcal in the figure).

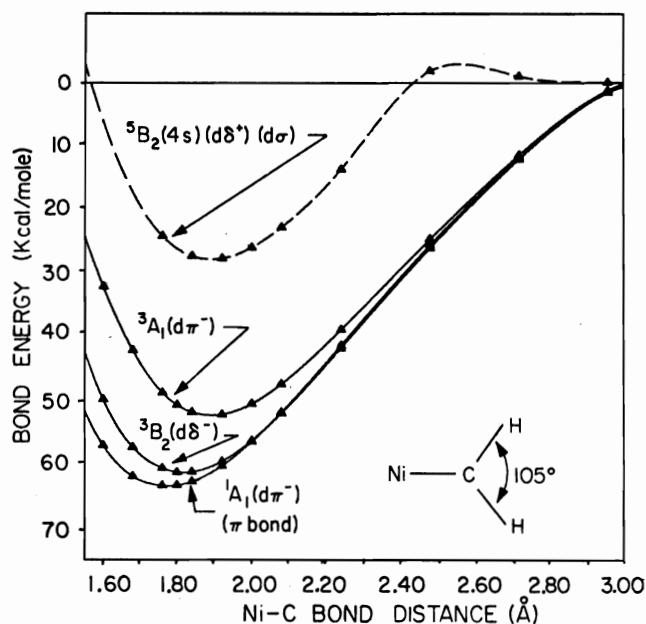


Figure 2. The potential energy curves for several states of NiCH_2 . Here the HCH bond angle is taken as 105° .

leads to a bond length of 1.84 \AA (the optimum HCH bond angle is 120°) and a bond energy of 62 kcal, while excitation energies to the $d\delta^-$, $d\pi^+$, and $d\sigma$ states are similar to those of NiCH_3 as shown in Figure 1. As was expected, the $d\pi^-$ (d_{xz}) state is different since the $d\pi^-$ orbital overlaps the singly occupied π orbital of CH_2 . As a result, the singlet state gets extra bonding and one might represent this state as

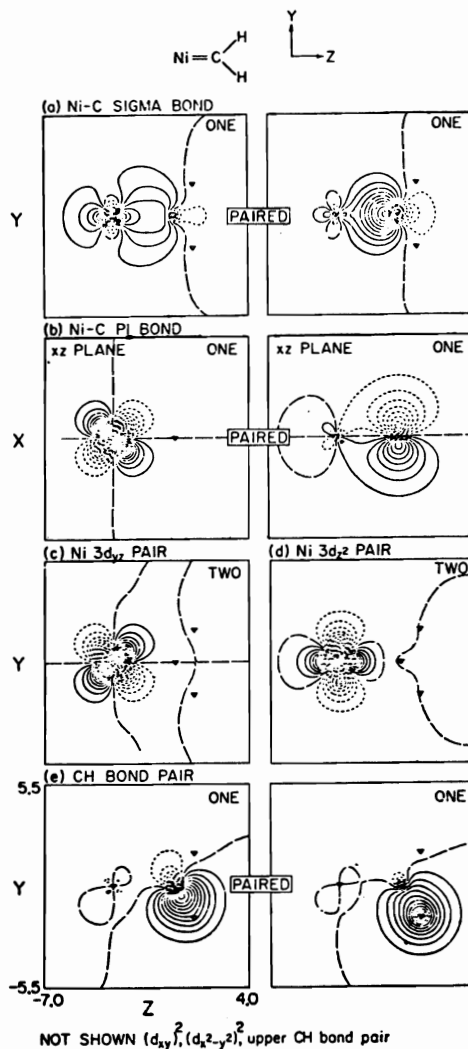
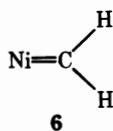
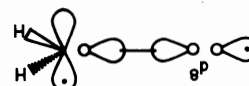


Figure 3. The GVB orbitals for the ${}^1\text{A}_1(\pi^-)$ ground state of NiCH_2 ($R_{\text{CH}} = 1.071 \text{ \AA}$, $R_{\text{NiC}} = 1.76 \text{ \AA}$, angle HCH = 110°). The long dashes indicate zero amplitude. All contours are separated by 0.05 au. The nuclei are indicated by triangles.

(Concomitantly, the triplet state gets extra antibonding.) However, because the Ni d orbitals are so much smaller than the bond orbital, the Ni $d\pi^-$, C π overlap is quite small ($S = 0.076$ for the atomic orbitals) and the extra π bonding is quite small. As a result, the singlet $d\pi^-$ state (${}^1\text{A}_1$) leads to a bond energy of 65 kcal, a NiC bond length of 1.78 \AA , and an HCH bond angle of 113.7° . Thus the state 6 with a π bond is only 3 kcal lower than the δ state without it. The corresponding $d\pi^-$ triplet state (${}^3\text{A}_1$) is 23 kcal higher (at R_e); thus we can consider the singlet $d\pi^-$ state to have ~ 12 kcal of π bonding (and the triplet state ~ 12 kcal of π antibonding). The reason why the π -bonded state is only 3 kcal below the δ state is that a state with a $d\pi$ hole is intrinsically 9 kcal higher than a state with a $d\delta$ hole (as found for NiCH_3).

The potential curves for the ${}^3, {}^1\text{A}_1(d\pi^-)$ and ${}^3\text{A}_2(d\delta^-)$ state are shown in Figure 2 along with one of the states that arises from bonding CH_2 to a $4s^23d^8$ configuration of Ni. At small R the bonding in this higher state can be visualized as



with two $4s4p$ hybrids each with one electron, one bonding to the CH_2 and one pointing the opposite direction.

The optimum GVB orbitals of the NiCH_2 ground state (singlet $d\pi^-$ or ${}^1\text{A}_1$) are shown in Figure 3. The two orbitals

of the σ bond are given in Figure 3a (these orbitals have an overlap of 0.79, typical of a σ bond). As the bond is dissociated, the left orbital becomes Ni 4s while the right orbital becomes $\sigma(\text{CH}_2)$. At R_c the hybridization of these orbitals is Ni $4s^1 4p^{0.034} 3d^{0.25}$ and C $2s^1 2p^{1.52} 3d^{0.014}$, respectively. The orbitals of the π bond are shown in Figure 3b (they have an overlap of 0.25). Here the hybridizations are Ni $3d^1 4p^{0.0002}$ and C $2p^1 3d^{0.0005}$, respectively. The self-consistent Ni $d\sigma$ and $d\pi^+$ orbitals are shown in Figure 3cd; they interact only weakly with the CH_2 group. The $d\delta^+$ and $d\delta^-$ orbitals are quite atomic-like and are not shown. THE CH bond pairs (only one is shown) are quite similar to the CH bond pairs of CH_2 (the carbon hybridization is $2s^1 2p^{1.88} 3d^{0.0069}$).

The total charge transfer from Ni to CH_2 is 0.56 electrons for 1A_1 ($d\pi^-$) and 0.51 electrons for 3A_2 ($d\delta^+$) (both based on Mulliken populations).

Because of the small overlap of the two orbitals in the π bond, HF calculations do extremely badly for the 1A_1 ($d\pi^-$) state. Consequently HF leads to a 3A_2 ($d\delta^+$) ground state and puts the correct ground state, 1A_1 , 3.8 eV higher. Clearly, HF is not adequate for studying transition metal-carbene systems.

In summary we find that $\text{Ni}=\text{CH}_2$ and $\text{Ni}-\text{CH}_3$ lead to bond energies of 65 and 60 kcal, bond lengths of 1.78 and 1.87 Å, and NiCH bond angles of 123.5° and 109.4° , respectively. In both cases the bonding is basically that of an Ni 4s orbital and a carbon lobe orbital with only a small contribution due to π bonding in NiCH_2 . Although the numbers are consistent with general ideas about metal-carbon bonds, there is little information with which to compare experimentally.¹⁵

References and Notes

- (1) (a) Partially supported by a grant (DMR7-04965) from the National Science Foundation and by a grant (PRF-7683-AC6) from the donors of the Petroleum Research Fund, administered by the American Chemical Society.
- (2) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974.
- (3) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. I, Academic Press, New York, N.Y., 1974, pp 151-157.
- (4) W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).
- (5) A. Wachters, *J. Chem. Phys.*, **52**, 1033 (1970); T. H. Dunning, Jr., *ibid.*, **53**, 2823 (1970).
- (6) C. F. Melius, B. D. Olafson, and W. A. Goddard III, *Chem. Phys. Lett.*, **28**, 457 (1974); C. F. Melius and W. A. Goddard III, *Phys. Rev. A*, **10**, 1528 (1974).
- (7) M. Sollenberger, M.S. Thesis, California Institute of Technology, 1975; C. F. Melius, W. A. Goddard III, and M. Sollenberger, unpublished results. The ab initio effective potential of ref 6 is modified so that the atomic wave functions lead to the experimental values for the $^3D(s^1d^9)$ to $^3F(s^2d^8)$ energy separation and the $^3D(s^1d^9)$ to $^2D(s^0d^9)$ ionization potential. See also ref 8.
- (8) S. P. Walch and W. A. Goddard III, *J. Am. Chem. Soc.*, in press.
- (9) (a) L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, **3**, 828 (1935); (b) J. Ladell, B. Post, and J. Frankuchen, *Acta Crystallogr.*, **5**, 795 (1952).
- (10) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, p 756.
- (11) Estimates of metal-carbon bond strengths have been made by J. A. Connor, *J. Organomet. Chem.*, **94**, 195 (1975). The approach here is to start with the ΔH_f for metal carbonyls and assume all bonding energies to be transferable. This allows empirical mean bond energies to be obtained for metal carbonyls. Assuming these average M-CO bond energies to be transferable to systems with other ligands, Connor derives bond energies to these other ligands. Although these are the best known estimates, this procedure may lead to errors of over 20 kcal/mol in the energy to break one of the metal-carbon bonds.
- (12) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972); D. R. McLaughlan, C. F. Bender, and H. F. Schaefer III, *Theor. Chim. Acta*, **25**, 352 (1972); E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Am. Chem. Soc.*, **92**, 7491 (1970); G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).
- (13) P. F. Zitter, G. B. Ellison, S. V. O'Neill, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3731 (1976).
- (14) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, D. Van Nostrand, Princeton, N.J., 1966.
- (15) Recently Hartree-Fock calculations have been carried out on MnCH_2 (B. R. Brooks and H. F. Schaefer III, unpublished). They find a MnC bond length of 2.16 Å and a bond strength of 33 kcal; these values are long and small, respectively, possibly because of the lack of electron correlation effects.