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Electronic Properties of and Reductive Elimination from Dimethylnickel. An ab Initio MO–SCF–CI Study

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Abstract: The structure and chemical properties of dimethylnickel and its bisaquo complex have been predicted by ab initio MO–SCF–CI calculations. Free dimethylnickel should have a linear, high-spin ground state. The nickel–carbon bonds are predicted to be strong, the overlap population being about 0.6. The bond should be strongly polarized with a negative charge on the methyl groups. Bending of the molecule leads to a considerable decrease in the bond strength but there is little change in the charge distribution. The energy difference between the ground state and the first singlet state (about 2 eV) is also unaffected by bending. However, addition of two water ligands to the bent form leads to a decrease in the energy difference to about 0.4 eV. Addition of more strongly coordinating ligands very probably results in a singlet ground state. Only the singlet state of the bent molecule has the correct symmetry for concerted reductive elimination, which may require thermal excitation to this state. However, the calculations indicate that reductive elimination may also take place directly from the triplet ground state by recoupling with excited states in the transition state.

I. Introduction

The properties of transition-metal alkyls have been extensively studied experimentally during the last decades, partly owing to their appearance as intermediates in various catalytic reactions.[2] Many aspects of the chemistry of transition-metal alkyls are therefore superficially fairly well understood, but extrapolations and rationalizations are often difficult owing to the lack of a deeper knowledge of the electronic structure of these compounds. For instance, a common reaction like reductive elimination appears to be either concerted (eq 1) or radical (eq 2) depending on the reaction conditions.

$$R_2ML_n \rightarrow R\text{-}R + ML_n \qquad (1)$$

$$R_2ML_n \rightarrow R\cdot + RML_n \rightarrow 2R\cdot + ML_n \qquad (2)$$

However, the manner in which the reaction conditions govern the reaction path is not very well understood.

Experimental examples are the two similar reactions (3) and (4), of which (3) is believed to be a concerted reaction[3a] while (4) probably takes a radical path.[3b]

$$L_2Pt(CH_3)_3I \rightarrow L_2Pt(CH_3)I + C_2H_6 \ldots \qquad (3)$$

$$C_5H_5Pt(CH_3)_3 \rightarrow C_5H_5Pt(CH_3)_2 + CH_3\cdot \rightarrow \text{products} \qquad (4)$$

For further discussion of this problem, see ref 2c and 2d.

In order to obtain a deeper insight into the electronic structure of metal alkyl compounds we have performed a series of ab initio MO-SCF and CI calculations, using dimethylnickel as a model for transition-metal dialkyls. Both linear and bent configurations were studied. In addition a few calculations were also made on the square-planar cis form of $Ni(CH_3)_2(H_2O)_2$ in order to investigate the effect of adding further ligands to the complex. Calculations have been performed on low-spin as well as high-spin states. Limited configuration interaction was added in order to account for the interaction between nearly degenerate states of the same symmetry. Some preliminary results of the calculations on dimethylnickel have been presented earlier.[4]

The nickel–carbon bond has recently been studied by Rappé and Goddard in a series of calculations on the fragments $NiCH_2$ and $NiCH_3$.[5] They find that the bonding is caused primarily by the 4s orbital in nickel combining with the lone-pair orbital in the radical. The dominating electron configuration on nickel is therefore d^9s with the 3d electrons localized on the metal. Similar results had earlier been obtained for the Ni–H and Ni–Ni bonds by Melius et al.[6,7] If these results can be taken over to dimethylnickel we would here expect a bond involving sp hybrids on nickel, and in this case eight localized 3d electrons. Support for such a picture is obtained from the calculations by Guse et al.[8] on NiH_2, where they find the dominating configuration to involve eight 3d electrons and sp hybrids in the Ni–H bonds.

The results of Rappé and Goddard give a Ni–C bond which has a large ionic character with a net charge on the methyl group of −0.42 electrons. The ionic character of the $Ni\text{-}CH_3$ bond has also earlier been demonstrated in a calculation on the olefin-alkyl complex $Ni(C_2H_4)(CH_3)_2$[9] and on $Ni(CH_3)_2$.[4]

II. Details of the Calculations

The calculations were of LCAO type, with the molecular orbitals expanded in atomic centered Cartesian contracted Gaussian type functions (CGTFs). The complete basis set was formed from six s-type, four p-type, and two d-type CGTFs on Ni, four s-type and two p-type CGTFs on carbon and oxygen, and two s-type CGTFs on hydrogen. For carbon, oxygen, and hydrogen the exponents and contraction coefficients were taken from Roos and Siegbahn's 7s-type, 3p-type[10] and Huzinaga's 4s-type[11] primitive atomic basis sets, respectively, with the hydrogen exponents scaled with a factor of 1.3. Parameters for the s- and p-type CGTFs on Ni were obtained from the atomic basis set (Ni/12,6,4)[12] with the 11th s-type function deleted and with two p-type functions with exponents 0.40 and 0.15 added to represent 4p orbitals. The d-type functions were formed from the (Ni/9,5,4) ion-optimized basis set,[12] adding one diffuse d function with exponent 0.30. Note that the s components $(x^2 + y^2 + z^2)$ of the 3d functions are included in the basis set, which render it essentially double ζ quality in the valence region.

The two methyl groups in $Ni(CH_3)_2$ were chosen to be in an eclipsed arrangement, whereby the bent forms conveniently could be described in the C_{2v} point group, and the conformation having a linear arrangement of the Ni–C bonds in the D_{3h}

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Table I. Total SCF Energies for the Lowest Electronic States of $Ni(CH_3)_2$ (au)

state (C_{2v})	state[a] (D_{3h})	energy[b] $\alpha = 180°$	135°	90°	d-orbital occ[c] ($d_{x^2-y^2} + d_{z^2}$) a_1	d_{xz} b_2	d_{yz} a_2	d_{xy} b_1
1^3A_1			−0.4650	−0.3938	2	2	2	2
1^3B_1	$^3E'$	−0.4875	−0.4656	−0.3935	3	2	2	1
1^3B_2			−0.4749	−0.4243	3	1	2	2
1^3A_2	$^3E''$	−0.4852	−0.4552	−0.3923	3	2	1	2
1^1A_1			−0.3829	−0.3093	2	2	2	2
1^1B_1	$^1E'$	−0.4077	−0.3833	−0.3079	3	2	2	1
1^1B_2			−0.4002	−0.3638	3	1	2	2
1^1A_2	$^1E'$	−0.4103	−0.3835	−0.3075	3	2	1	2
2^1A_1	$^1A_1'$	−0.4044	−0.3722	−0.2808	2	2	2	2
3^1A_1	$^1A_1'$	−0.3591	−0.3754	−0.3675	4	0	2	2

[a] D_{3h} nomenclature is used for $\alpha = 180°$. [b] SCF energy + 1582 au. [c] Only the sum of the occupation numbers for d_{z^2} and $d_{x^2-y^2}$ are given, since these two orbitals can mix in the low C_{2v} symmetry used in all calculations. The symmetry notations are chosen to give b_1 orbitals π symmetry and b_2 orbitals σ^* symmetry.

point group. There is here a minor difference from the previous investigation[4] where a staggered conformation was chosen. Five conformations of $Ni(CH_3)_2$ with C–Ni–C angles, α in Figure 1 of 180, 172, 160, 135, and 90° were chosen, and a Ni–C bond distance of 2.0 Å was used. This value is very close to the optimum value found for the internuclear separation in the low-spin complex, 2.003 Å.[4]

The Ni–O bond distance was in the study of (planar) $Ni(CH_3)_2(H_2O)_2$ taken to be 2.10 Å. In this case the angle α as well as the O–Ni–O angle was taken to be 90° (cf. Figure 1).

The CH_3 moiety was assumed to have a tetrahedral structure, with a CH bond distance of 1.09 Å. The bond distance and angle in the water molecule were taken as the standard values, $r_{OH} = 0.96$ Å and $\theta_{HOH} = 104.5°$.

SCF calculations on $Ni(CH_3)_2$ were performed for the $(d_{x^2-y^2})^2(d_{xz})^2(d_{yz})^2(d_{xy})^2$ (CSI) and the $(d_{x^2-y^2})^2(d_{z^2})^2(d_{yz})^2(d_{xy})^2$ (CSII) closed-shell configurations (the former being the lowest CS state for the linear case), and on the singlet and triplet open-shell states formed from distributions of seven electrons in the $d_{x^2-y^2}$, d_{xz}, d_{yz}, and d_{xy} orbitals, keeping the d_{z^2} orbital singly occupied. For $Ni(CH_3)_2(H_2O)_2$ SCF calculations were done on the same closed-shell configurations as for $Ni(CH_3)_2$, and open-shell calculations were carried out on the triplet configurations $(d_{x^2-y^2})^2(d_{z^2})^1(d_{xz})^1(d_{yz})^2(d_{xy})^2$, $(d_{x^2-y^2})^2(d_{z^2})^1(d_{xz})^2(d_{yz})^1(d_{xy})^2$, and $(d_{x^2-y^2})^2(d_{z^2})^1(d_{xz})^2(d_{yz})^2(d_{xy})^1$ (i.e., one less configuration than for $Ni(CH_3)_2$).

Full internal configuration interaction calculations were carried out for $Ni(CH_3)_2$ in the space determined by the valence orbitals—Ni 3d and 4s—and all methyl orbitals except the innermost CH bonding orbital, which is predominantly carbon 2s. The configuration state functions occurring in the various CI expansions are thus those which arise when two holes are distributed among 12 valence orbitals ($4a_1$, $2b_1$, $4b_2$, and $2a_2$). The molecular orbitals used in the construction of the configuration state functions were obtained from the above-mentioned SCF calculations on open-shell singlet and triplet states for each geometry, the chosen configurations being those which yield the lowest total energy for the linear case. No CI was performed for $Ni(CH_3)_2(H_2O)_2$.

All calculations presented here employed the joint MOLECULE-ALCHEMY program system.[13]

III. Results

The first question to answer regarding the electron structure of dimethylnickel concerns the configuration and spin state of the lowest electronic state. The results from the SCF calculations are given in Table I and illustrated in Figure 2. They show the lowest electronic states to be d^8 triplet states with an energy difference to the lowest singlet state of around 2 eV for the linear geometry. There are a number of closely spaced triplet states corresponding to rearrangements within the d^8 electron configuration. These general results are in agreement with the electronic structure of NiH_2 given by Guse et al.[8]

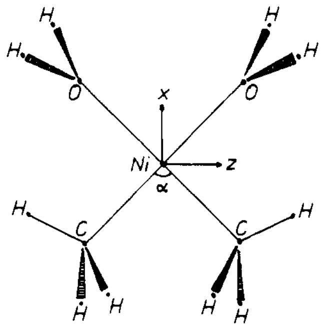


Figure 1. Geometry and coordinate system for $Ni(CH_3)_2$ and $Ni(CH_3)_2(H_2O)_2$.

From quite simple ligand field theoretical arguments it would follow that the lowest closed-shell configuration is the one where the d_{z^2} orbital, which points toward the negative methyl groups (for the linear case), is empty. This was also confirmed by the calculations. However, this state is not the ground state. It is not even the lowest state of $^1A_1$ symmetry (cf. Table I). The splitting of the well-localized 3d orbitals in the presence of the methyl groups is rather small, and the increase of energy which the system would experience by moving an electron into the empty d orbital is more than compensated by the decrease in energy resulting from the separation of two paired electrons. As a consequence the ground state of the linear system (as obtained from the SCF results) is $^3E'$, in D_{3h} nomenclature. This state is almost degenerate with the $^3E''$ state (Table I and Figure 2).

It should be mentioned that in some of the open-shell states the two d orbitals of a_1 symmetry mix with each other. Except for the closed-shell configurations no effort is subsequently made to distinguish between these orbitals.

Population analysis data for some of the SCF and CI wave functions are presented in Table II. The calculations show that the total d populations for the open-shell states are very close to eight for the linear configuration. It follows from the overlap populations that the binding characteristics of the different open-shell states are almost identical in the linear case. These results, together with the fact that the overlap populations between Ni and C in orbitals with mainly 3d character are almost zero, indicate that the bonding in linear $Ni(CH_3)_2$ is caused by interaction between the 4s and 4p orbitals on Ni with

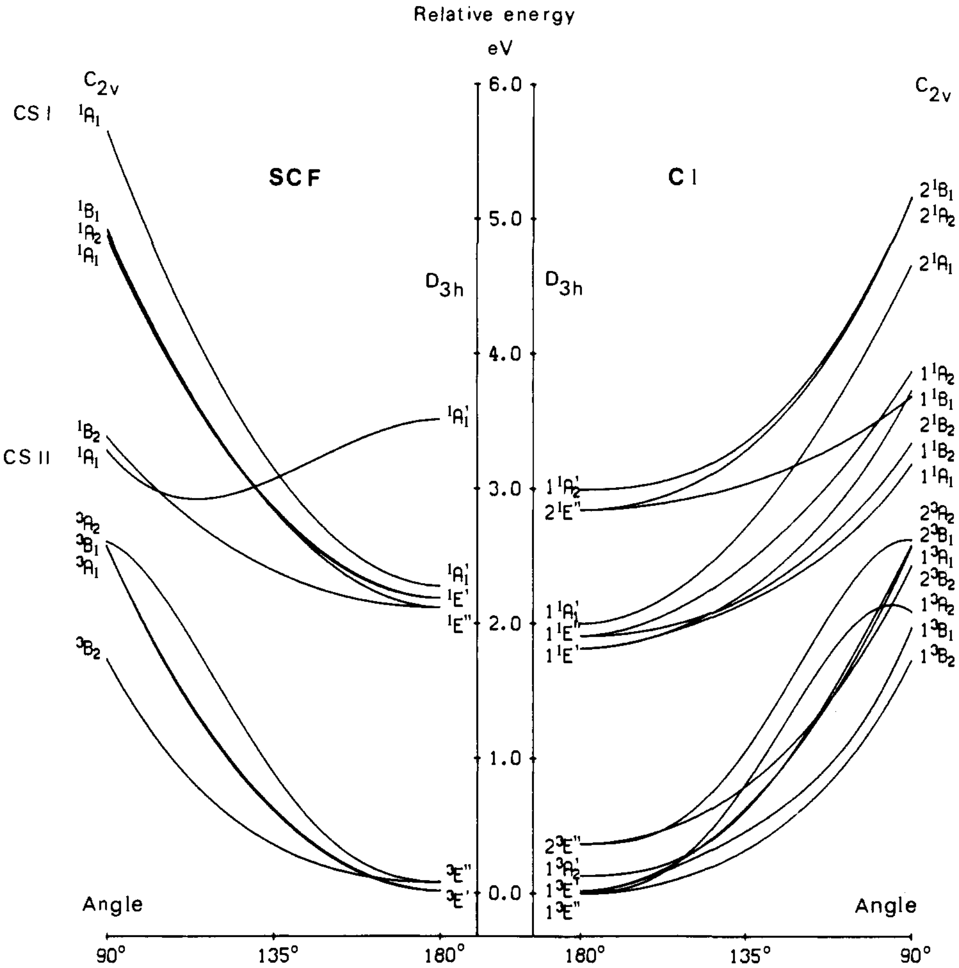


Figure 2. SCF and CI energies for $Ni(CH_3)_2$ as functions of the C-Ni-C angle (eV).

Table II. Mulliken Population Analysis for Some of the Lowest States of $Ni(CH_3)_2$ as a Function of Bond Angle. SCF and CI Results[a]

angle, deg	state	Ni(4s)	Ni(4p)	Ni(3d)	o(Ni-C)[b]	o(C-C)[b]	q(Ni)[c]
180	1^3B_2	0.69	0.34	7.99	0.60	−0.01	0.98
		0.67	0.34	8.00	0.60	−0.01	0.98
	1^1B_2	0.59	0.33	8.08	0.59	−0.01	1.00
		0.62	0.33	8.04	0.59	−0.01	1.01
	1^2A_1	0.59	0.34	8.07	0.59	−0.01	0.99
		0.64	0.34	8.02	0.60	−0.01	0.99
	(CSI)2^1A_1	0.34	0.30	8.30	0.54	−0.02	1.05
		0.53	0.34	8.13	0.59	−0.01	0.99
135	1^3B_2	0.62	0.38	8.03	0.61	−0.01	0.97
		0.61	0.39	8.04	0.61	−0.01	0.97
90	1^3B_2	0.52	0.38	8.14	0.58	−0.10	0.96
		0.52	0.37	8.14	0.58	−0.10	0.96
	1^1B_2	0.40	0.23	8.66	0.40	−0.01	0.72
		0.40	0.25	8.60	0.42	−0.02	0.74
	(CSII)1^1A_1	0.54	0.52	8.03	0.60	−0.11	0.92
		0.57	0.35	8.26	0.58	−0.09	0.82
	2^1A_1	0.53	0.53	8.00	0.60	−0.10	0.94
		0.55	0.51	7.99	0.60	−0.11	0.95

[a] The first row for each state gives SCF results, the second CI results. [b] Overlap populations Ni-C and C-C. [c] Total charge on nickel.

the methyl lone pair orbitals. The bonding orbitals are $11a_1$ and $7b_2$. The 4s and 4p populations, 0.67 and 0.34, respectively, for the linear 1^3B_2 state, originate almost entirely from these two orbitals. The eight 3d electrons remain localized on the metal, and the recoupling in this open shell to form different spin states does not have any noticeable effect on the nickel-carbon bond in the linear case. This model for the Ni-C bond is in agreement with the results of Melius et al.[6,7] for $Ni{-}CH_3$ and $Ni{=}CH_2$ where the corresponding electron configuration can be classified as d^9s.

The closed-shell configuration 2^1A_1(CSI) behaves slightly differently. Here the d_{z^2} orbital is empty. This results in a significant d_{z^2} contribution in the symmetric Ni-C bonding orbital (which for this state is $10a_1$), causing the total d population to be 8.3 rather than 8.0. The 4s population is at the same time decreased from around 0.6 to 0.4, yielding an almost unchanged total charge on Ni. This kind of mixing is prevented in the open-shell cases by the presence of electrons in both the d orbitals of a_1 symmetry. Interaction with the methyl orbitals would cause the d orbital to increase in energy and this effect dominates over the stabilizing influence of hybridization in the a_1 Ni–C bonding orbital.

These properties of the nickel-carbon bond are only to a minor extent affected by configuration interaction (cf. Tables II and III). There is a decrease in some of the total energies, the largest occurring for the $^1E'$ state. A number of nearly degenerate states are shown to exist close to the ground state (cf. Figure 2) resulting in a somewhat band-like character for the energy level diagrams. The populations remain essentially unchanged, and the bonding picture obtained on the SCF level is unchanged by the configuration mixing. As will be seen later this is not the case for the bent structure of $Ni(CH_3)_2$.

The ground state obtained from the CI is different from the SCF ground state, but they are still very close in energy. It is therefore not possible from the present study to differentiate between the $^3E_1'$ and $^3E_1''$ as the ground states in the linear case.

Upon bending of the molecule the negatively charged methyl ligands move away from the d_{z^2} orbital toward the d_{xz} orbital. The effect of this is nicely illustrated by the SCF results for the two configurations CSI (d_{xz} populated) and CSII (d_{z^2} populated) where the former has the lowest total energy at $\alpha = 180°$ and the latter is lowest at $\alpha = 90°$. In fact CSII is the lowest $^1A_1$ state at $\alpha = 90°$ (cf. Figure 2).

This "ligand-field" picture of the system is naturally a bit oversimplified, as can be seen for the results for the B_2 states. For the bent system both the B_2 triplet and singlet states (particularly on SCF level) have a low energy in accordance with the electrostatic picture. However, the bonding characteristics are substantially changed when α is changed from 180 to 90°. For the $^3B_2$ state this change is manifested as an increased 3d participation in the Ni–C bond, the d_{xz} population in the bonding b_2 orbital being increased from zero at 180° to 0.30 at 90°. This effect is partially compensated by a decreased d population in the singly occupied b_2 orbital, i.e., the orbital which is of pure d type for $\alpha = 180°$. The remaining 3d orbitals largely keep their character, and these effects result in an increase of the total d population when α changes from 180 to 90°.

The change in electron structure is similar, but much larger, in the $^1B_2$ state. This state is more properly characterized as d^9 than as d^8 at $\alpha = 90°$, with an electron configuration $(d_{x^2-y^2})^2(d_{z^2})^1(d_{xz})^2(d_{yz})^2(d_{xy})^2(\mathrm{NiC}, b_2)^1$. The singly occupied b_2 orbital is the binding Ni–C orbital, while the doubly occupied d_{xz} orbital has some antibonding character with a total population on the methyl groups of around half an electron. The bonding orbital is an equal mixture of a methyl lone pair and a dp hybrid on nickel. The net result of this reversed occupation is a decrease in the total overlap population from 0.6 to 0.4. This state has thus only three bonding electrons, instead of four. We can expect the Ni–C bond to be considerably weaker in this state than in the ground state.

The configuration interaction calculations on the bent system, the results of which are summarized in Table III, proved important for the understanding of the behavior of some of the excited states of the complex. First the lowest singlet state after CI is $^1A_1$ rather than $^1B_2$. The CSII configuration and the open-shell configuration $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xz})^1(\mathrm{NiC},b_2)^1(d_{yz})^2(d_{xy})^2$ are equally important in this state, the coefficient in the CI vector being 0.6 for both. The remaining contributions to the CI vector come from d^8-type configurations. The open-shell configuration given above is of d^9 type and has the same form as that constituting the $^1B_2$ state, i.e., it has one electron less in the Ni–C bonds.

Table III. Total CI Energies for the Lowest Electronic States of $Ni(CH_3)_2$ (au)[a]

angle, deg	symmetry	*E* (root 1)	*E* (root 2)	*E* (root 3)	*E* (root 4)
180	$^3E'(^3A_1, ^3B_1)$	−0.4875			
	$^3E''(^3B_2, ^3A_2)$	−0.4882	−0.4747		
	$^3A_2'(^3B_1)$	−0.4834	−0.3788		
	$^1E'(^1A_1, ^1B_1)$	−0.4214	−0.3782		
	$^1E''(^1B_2, ^1A_2)$	−0.4181	−0.3837		
	$^1A_1'(^1A_1)$	−0.4147	−0.3848		
135	$^3A_1$	−0.4650			
	$^3B_1$	−0.4713	−0.4655		
	$^3B_2$	−0.4732	−0.4589		
	$^3A_2$	−0.4584	−0.4492		
	$^1A_1$	−0.4089	−0.3884	−0.3759	−0.3593
	$^1B_1$	−0.4060	−0.3651		
	$^1B_2$	−0.4076	−0.3765		
	$^1A_2$	−0.3985	−0.3674		
90	$^3A_1$	−0.3938			
	$^3B_1$	−0.4158	−0.3935		
	$^3B_2$	−0.4248	−0.3990		
	$^3A_2$	−0.4114	−0.3919		
	$^1A_1$	−0.3711	−0.3171	−0.3053	−0.2851
	$^1B_1$	−0.3512	−0.2988		
	$^1B_2$	−0.3655	−0.3528		
	$^1A_2$	−0.3460	−0.2985		

[a] Energies + 1582 au.

The first two $^1B_2$ states are nearly degenerate (cf. Figure 2). The lowest state is almost identical with the SCF wave function, i.e., a d^9 state, while the second $^1B_2$ state is mainly of d^{10} character. The d^8 configuration does not contribute substantially until the third state.

For the singlet states the bonding in bent $Ni(CH_3)_2$ is thus similar to the d^9-type Ni–C and Ni–H bonds found in previous calculations.[5–7]

In order to illustrate the bonding characteristics in dimethylnickel we have plotted the total difference density and the nickel–carbon bonding orbitals of a_1 and b_2 type for three angles, α = 180, 135, and 90° (Figure 3). The difference densities, i.e., the electron density difference between $Ni(CH_3)_2$ and the constituent atoms (d^8s^2 ^3F for Ni), are presented in Figure 3a for the ground state $^3B_2$, calculated from the CI wave function.

The charge flow from nickel to carbon, which forms the ionic nickel–methyl bonds, is nicely illustrated in these figures. The structure around Ni shows the expected redistribution of the 3d electrons from a spherical distribution in the nickel atom to a configuration where d_{z^2} and d_{xz} are singly occupied.

The bonding orbital $10a_1$ is shown in Figure 3b. Clearly this orbital is dominated by the 4s orbital on nickel combined with the methyl lone-pair orbitals, as discussed earlier. The pictures of the antisymmetric $7b_2$ orbital, shown in Figure 3c, show the increased importance of $3d_{xz}$ when the angle α decreases. For $\alpha = 180°$ the nickel contribution to this orbital is mainly 4p, while for $\alpha = 90°$ the region around the nickel atom shows the characteristic features of a dp-hybrid orbital.

Complexes containing dialkylnickel also contain other ligands and are of the general type $X_nNi(CH_3)_2$ (where *n* normally is 2 or 3). So far we have not considered the influence of the ligands. In order to accommodate some of the effects of these ligands we have also carried out SCF calculations on the model complex $Ni(CH_3)_2(H_2O)_2$ (cf. Figure 1). The states considered were the closed-shell configurations CSI and CSII and the open-shell states $^3B_2$, $^3B_1$, and $^3A_2$ with the same configurations as for $Ni(CH_3)_2$.

The most striking effect of the two water ligands is the lowering of CSII relative to all the remaining states (cf. Table IV and Figure 4), thus placing it below the $^3A_2$ and $^3B_1$ states and only 0.4 eV above the $^3B_2$ ground state.

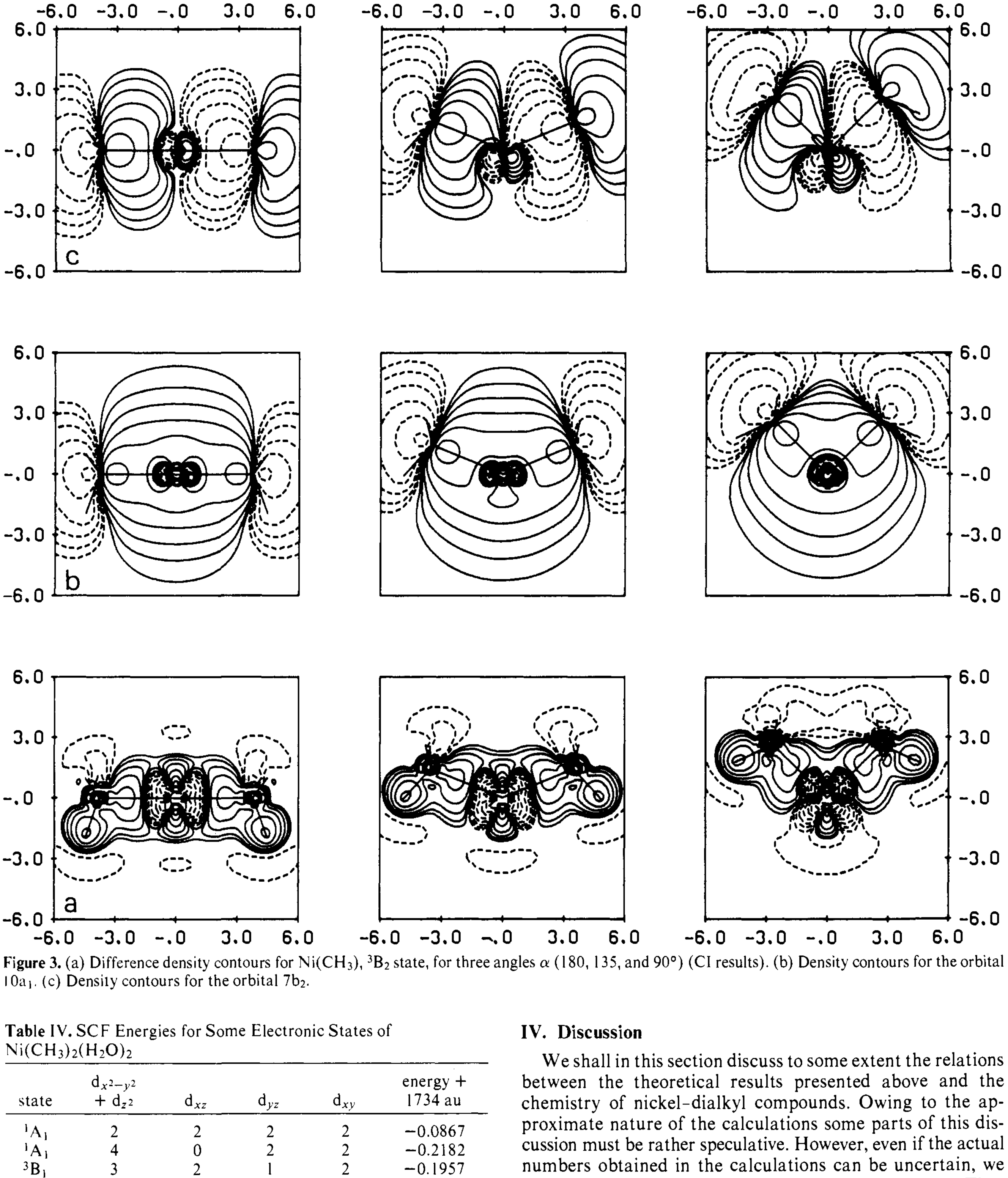


Figure 3. (a) Difference density contours for Ni(CH$_3$)$_2$ $^3B_2$ state, for three angles α (180, 135, and 90°) (CI results). (b) Density contours for the orbital $10a_1$. (c) Density contours for the orbital $7b_2$.

Table IV. SCF Energies for Some Electronic States of Ni(CH$_3$)$_2$(H$_2$O)$_2$

state	$d_{x^2-y^2}$ + d_{z^2}	d_{xz}	d_{yz}	d_{xy}	energy + 1734 au
$^1A_1$	2	2	2	2	−0.0867
$^1A_1$	4	0	2	2	−0.2182
$^3B_1$	3	2	1	2	−0.1957
$^3A_2$	3	2	2	1	−0.1946
$^3B_2$	3	1	2	2	−0.2331

The population analysis (cf. Table V) shows a decreased Ni (4s) and (4p) population especially in the $^1A_1$ state. This leads to an increased positive metal charge in the $^3B_2$ state. In the $^1A_1$ state the decreased sp population is instead counterbalanced by an increase in the d-orbital population. The strength of the nickel-carbon bond is lowered when the extra ligands are added. The bond also becomes more polar with an increased negative charge on the methyl groups.

IV. Discussion

We shall in this section discuss to some extent the relations between the theoretical results presented above and the chemistry of nickel-dialkyl compounds. Owing to the approximate nature of the calculations some parts of this discussion must be rather speculative. However, even if the actual numbers obtained in the calculations can be uncertain, we believe the qualitative features to be essentially correct. They are also, in cases where a comparison can be made, in agreement with other studies on similar compounds.[4-8]

Thermochemical and spectroscopic data for a number of transition-metal alkyls indicate that metal-carbon bonds are frequently strong.[2] The high calculated overlap populations obtained for the nickel-carbon bond (0.4-0.6) indicate that this is true also for carbon-nickel bonds. From the SCF energies given in Table I and the corresponding energies for Ni (^3F) and CH$_3$, obtained with the same basis set, we estimate the bond strength to be 60 kcal/mol (see also ref 4). Even if this energy falls into the expected range, it can be considered only as a crude estimate, owing to the different approximations

Table V. Mulliken Population Analysis for $Ni(CH_3)_2(H_2O)_2$ for the Two Lowest States. SCF Results

state	Ni(4s)	Ni(4p)	Ni(3d)	o(Ni-C)[a]	o(Ni-O)[a]	o(C-C)[a]	$q(CH_3)$[b]	$q(H_2O)$[b]	q(Ni)[b]
$^3B_2$	0.41	0.39	8.14	0.48	0.14	−0.13	−0.62	+0.10	+1.05
$^1A_1$	0.42	0.31	8.38	0.46	0.16	−0.08	−0.55	+0.10	+0.89

[a] Overlap population. [b] Gross atomic charges.

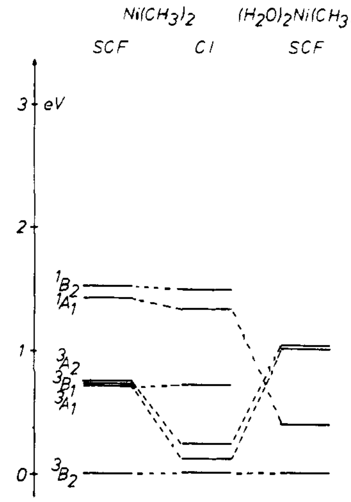


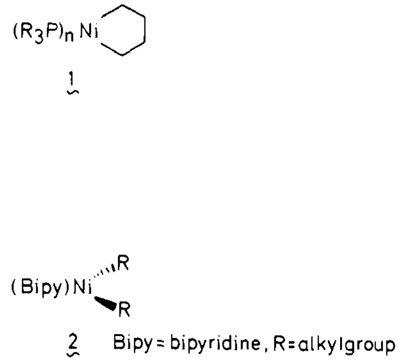
Figure 4. Relative energies for the lowest electronic states of $Ni(CH_3)_2$ and $Ni(CH_3)_2(H_2O)_2$ (eV).

involved in calculating it. Even so, the results predict that nonconcerted radical reactions are unlikely, a conclusion supported by a recent study of neophylnickel complexes.[14]

The population analyses (Tables II and V) show a decrease in the Ni-C bond strength on bending and as extra ligands are added. Actually, the calculated bond strength for the 90° configuration is ½ of its original value, a result which is not changed by configuration interaction (cf. Tables I and III). Comparing the energies of $Ni(CH_3)_2$ at 90° and $(H_2O)_2Ni(CH_3)_2$ we find the bond energies for the water molecules to be of the same size as those of the methyl groups. This result is in agreement with experimental thermochemical data, which suggest that transition metal-alkyl bond strengths often drop to half of their original values when extra ligands are added to the metal.[15] As can be seen from Tables II and V the addition of two water ligands also makes the Ni-C bond more polar.

These results on the Ni-CH_3 bond strength seem to be in contrast to the well-known fact that addition of extra ligands in general has a stabilizing effect on the complex.[2,16] $Ni(CH_3)_2$ itself is thus a very unstable complex, which exists only at low temperatures,[17] while addition of ligands like PR_3[17,18] and bipyridine[19-21] leads to a considerable stabilization. Different explanations have been provided for this stabilization, the most generally accepted being that the ligands increase the gap between the highest occupied and lowest unoccupied orbital. This result is, however, not obtained here. Actually the HOMO(b_2)-LUMO(a_1) energy difference is the same in $Ni(CH_3)_2$ (90°) and $(H_2O)_2Ni(CH_3)_2$ for the CSII state, the only difference being a uniform positive shift of around 2 eV in these orbital energies. The destabilization of the nickel-carbon bond seems to be mainly due to the bending of the complex, which leads to an increase of the orbital energies in both the Ni-C bonding orbitals ($10a_1$ and $7b_2$). Steric interactions between the negatively charged methyl groups also favor the linear arrangement. It is therefore not surprising that the Ni-C bond strength is smaller in the water complex, at least when the two methyl groups are in a cis position.

The low stability of uncoordinated relative to coordinated complexes therefore has another explanation than the pure electronic effect of the ligands. It seems clear that blocking decomposition pathways like α- and β-elimination are important.[2] In the nickel series this is demonstrated by the reactions of the metallocycle **1**, which undergoes β-elimination when $n = 1$ and reductive elimination when $n = 2$.[22] Similar results are obtained in the decomposition of neophylnickel species.[14]



Bipy= bipyridine, R=alkylgroup

Figure 5.

The precipitation of metal in a highly active form may also be important. Also this type of reaction will be favored in the absence of coordinating ligands.

The nickel-carbon bond is, as expected, highly polar (i.e., the bonding orbitals have predominant carbon character) and this polarization is increased with the addition of two water ligands (cf. Tables II and V). As a consequence the methyl groups should have substantial carbanion character. This is shown chemically by the fact that weak acids like alcohols cleave the nickel-carbon bond by protonation at carbon[17b,23] and also by the nucleophilic character of alkyl and allyl groups attached to nickel.[18,24]

The arguments for the low stability of transition-metal bonds have also been used to explain the mechanism for reductive elimination (for a discussion, see ref 2).

V. Reductive Elimination

In the simple model for the nickel-carbon bonds in $Ni(CH_3)_2$ adopted here, a concerted dissociation to Ni(d^8s^2, ^3F) plus ethane would be a forbidden process by orbital symmetry arguments. A concerted decomposition to two methyl radicals is possible, but for energetic reasons such a process is unlikely, since the energy for two methyl radicals is about 3 eV higher than that of ethane.[4]

There are several states above the $^3B_2$ ground state which have the correct orbital symmetry for concerted reductive elimination. In the bent dimethylnickel, the first of these is the CSII state which has the configuration $d^8d_{xz}{}^0(a_1)^2(b_2)^2$. A correlation diagram, Figure 6, shows the symmetry-allowed formation of ethane and nickel(0) from this state. In this particular case a d^{10} configuration is assumed for nickel(0) but mixing the d orbitals of a_1 symmetry with 4s to yield d^9s^1 and d^8s^2 configurations will not affect the symmetry argument. The correlation diagram also shows that correlation between occupied nickel orbitals and the unoccupied σ* orbital of the product ethane can be avoided only if the d_{xz} orbital of dimethylnickel is unoccupied.

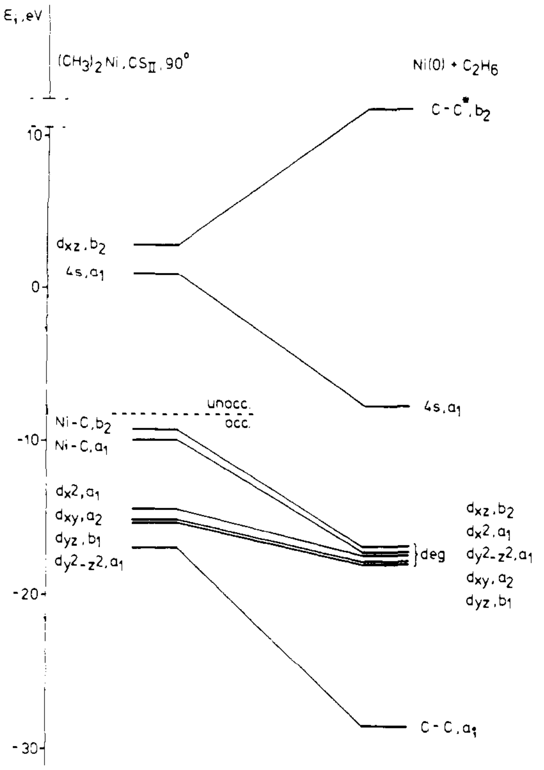


Figure 6. Orbital correlation diagram for the formation of ethane from dimethylnickel in the CSII configuration.

In the case of trimethylgold(III), in which the metal is isoelectronic with nickel(II), the state with the electronic configuration $d^{10}(a_1)^2$ seems to play an important role.[25] A related state, that is, $d^9(a_1)^2$, may be the reason for the extreme ease with which nickel(III) aryls and aryl alkyls undergo reductive elimination.[26] In this particular case the higher oxidation state of nickel may increase the importance of states related to $d^{10}(a_1)^2$ by transfer of charge from the nickel–carbon bond to nickel. For nickel(II) the first d^{10} state is an excited state (the third singlet state, cf. above and Figure 2). The excitation energy is, however, fairly low and it is possible that this state contributes to the reductive elimination reaction in some cases.

The results obtained in the present calculations indicate that the ground state of $L_2Ni(CH_3)_2$ is a low-spin $^1A_1$ state, at least with strongly coordinating ligands like phosphines. In such a state the antisymmetric d orbital in the C–Ni–C plane is unoccupied and a concerted reductive elimination process is then allowed according to orbital symmetry arguments. Strongly coordinating ligands should thus induce reductive elimination provided more than three coordination is achieved. This is quite contrary to the behavior of alkylgold(III) complexes but has some experimental support both in the nickel(II)[22,24a] and platinum(II) series.[27]

However, other factors than coordination number are most probably also important and the fact that the reaction is symmetry allowed does not necessarily mean that there is no energy barrier. Actually it is most likely that a barrier does still exist, since a large electron rearrangement is needed in any case. In the complex (assuming $^1A_1$ (CSII) to be the ground state), the electron configuration is

$$d^8(3d,\ b_2)^0(\mathrm{NiC},\ a_1)^2(\mathrm{NiC},\ b_2)^2 \tag{5}$$

while the configuration for the product is

$$d^8(3d,\ a_1)^0(4s,\ a_1)^2(\mathrm{CC},\ a_1)^2 \tag{6}$$

The b_2 orbital, which in the complex is predominantly a CH_3 lone-pair orbital, thus has to become a $3d_{xz}$ orbital. We can expect this charge transfer to be more difficult for a more polar bond. In such a model we would therefore expect the alkylnickel complex to be stabilized in the presence of donating ligands, while reductive elimination processes would be favored in the presence of acceptor-type ligands. This conforms nicely with available experimental information. Complexes like **2** are fairly stable. Addition of an extra ligand, with a low-lying acceptor orbital, e.g., acrylonitrile, O_2, Br_2, or chlorobenzene, to **2**, however, leads to rapid reductive elimination.[21,26,28] In the model suggested above, these ligands attract charge from the metal atom, which has the secondary effect of making the nickel–carbon bond less polar and lowering the barrier for reductive elimination. There is also some indirect evidence for such a charge-transfer mechanism. Thus reductive elimination from platinum(IV), isoelectronic with nickel(IV), is very rapid compared to that from platinum(II).[29] The higher stability of fluorinated alkyls,[2,16] e.g., $(CF_3)_2NiL_2$, may also be explained in the same way, that is, less electron transfer to the d orbitals on nickel owing to the higher stability of the carbon-centered orbitals of CF_3^- as compared to CH_3^-.

The model for reductive elimination discussed above assumes the low-spin state to be the ground state of $L_n(Ni(CH_3)_2$. A high-spin ground state leads, however, to a similar situation. The electronic structure in this case is

$$(3d^6,\ ^1A_1)(3d_{z^2},\ a_1)^1(3d_{xz},\ b_2)^1(\mathrm{NiC},\ a_1)^2(\mathrm{NiC},\ b_2)^2 \tag{7}$$

while the product has the configuration

$$(3d^6,\ ^1A_1)(3d_{z^2},\ a_1)^1(3d_{xz},\ b_2)^1(4s,\ a_1)^2(\mathrm{CC},\ a_1)^2 \tag{8}$$

and the reaction is symmetry forbidden. We would in this case expect a substantial barrier to a concerted elimination reaction. It is, however, possible that a third state may interact with (7) and (8) in the transition-state region where the orbitals (NiC, b_2) and (CC a_1) are nearly degenerate. This configuration is given as

$$(3d^6,\ ^1A_1)(3d_{z^2},\ a_1)^2(3d_{xz},\ b_2)^0(\mathrm{NiC},\ a_1)^2 (\mathrm{NiC},\ b_2)^1(\mathrm{CC},\ a_1)^1 \tag{9}$$

where the two last electrons are coupled to form a $^3B_2$ state. This state is most certainly more stable at the transition-state geometry than either (7) or (8), provided that the recoupling in the 3d shell from $^3B_2$ to $^1A_1$ does not cost any energy. The calculations tell us that these two states are nearly degenerate and a recoupling leading to a interaction between (7), (8), and (9) therefore seems quite feasible. Such a mechanism could lead to a considerable lowering of the barrier. A similar model has been suggested by Melius et al.[6] for dissociative chemisorption of hydrogen on a nickel surface. Also in this case a charge transfer of electrons from H to Ni is needed and the consequences of this with respect to the effect of other ligands, as discussed above, are still valid.

To complete the discussion on reductive elimination it should be mentioned that a high-spin d^8 complex should have a tetrahedral instead of a square-planar ground-state structure. This will make the low-spin configuration less favorable than estimated from the results presented in Table IV but it will not affect the previous discussion on reductive elimination.

VI. Conclusions

In the present work we have studied the lower electronic states of dimethylnickel. Free $Ni(CH_3)_2$ has been found to have a linear structure with a high-spin ground state. However, when two water ligands are added to the complex, a closed-shell state comes very close to the high-spin state and it cannot be ruled out as the ground state. Actually this is probably the ground state for a system with more strongly coordinated ligands.

It is suggested that the reductive elimination of ethane from $L_nNi(CH_3)_2$ is controlled by the possibility of a charge flow from the methyl groups to the metal atom. Such a charge flow is hindered by the presence of donating ligands L, which thus stabilize the complex. On the other hand, elimination is expected to proceed more easily when electron-attracting ligands are added to the system, which is in agreement with experiment.

We have suggested that the barrier to a concerted formation of ethane could be lowered considerably in the $^3B_2$ case, by a recoupling of the 3d electrons on the metal along the reaction path, the argument for such a mechanism being the closeness of the two states $^3B_2$ and $^1A_1$. Since such recoupling mechanisms may be of importance in other catalytic processes we intend to analyze the reaction in more detail in the future.

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Molecular Orbital Constrained Electron Diffraction Studies. Conformational Behavior of 1,2-Dimethylhydrazine

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Abstract: The results of a conformational analysis of 1,2-dimethylhydrazine are described which were obtained by applying MOCED (molecular orbital constrained electron diffraction). In this procedure primary structural parameters (differences between bond distances and bond angles), which can be reliably predicted by complete ab initio force relaxations, are used as constraints needed to interprete the gas electron diffraction data of a molecule. The diffraction data can be used to describe the conformational behavior of a molecule as a means to interpret the calculated ab initio conformational energy differences, which are usually less well established than ab initio structures because of basis set effects, correlation effects, and vibrational effects. Results for complete ab initio (4-31G) force relaxations of three gauche forms of 1,2-dimethylhydrazine are given. The investigation confirms the existence of the inner-outer conformer (CNNC torsional angle about 90°) as a major conformation. Details of analysis suggest the presence of at least one other conformer which cannot be definitely determined from the diffraction data. Both inner-inner (calculated CNNC angle 50°) and outer-outer forms (calculated CNNC angle 140°) must be considered. The study demonstrates the power of hybrid theoretical and experimental procedures in conformational analyses. It also demonstrates that ab initio conformational analyses using standard geometries can be misleading, since each conformation may deviate from the standard in an unpredictable manner.

Introduction

The ability of standard single determinant molecular orbital theory to reliably predict molecular equilibrium structures has been documented in countless studies. Primary structural parameters, such as bond distances, bond angles, and, in particular, relative differences between related parameters of this kind, can now be estimated very accurately on the basis of ab initio calculations. In some cases, such as in the recent investigations of glycine[2a] and beryllocene,[2b] the ab initio results have even affected interpretation of experimental data in a striking manner.

The power of ab initio techniques to generate molecular

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