Ia is favored over Ib. In Ia only an H atom passes another H atom in the course of the 60° rotation, whereas in Ib a Br atom passes a Br atom and a Cl atom passes an H atom. Consequently the formation of *cis*-BCE (path Ia) from *cis*-DBE should be kinetically more favorable than that of *trans*-BCE. From the same line of reasoning, in reaction of Cl atoms with *trans*-DBE, the formation of *trans*-BCE is favored over *cis*-BCE; path IIa is preferred over path IIb since the latter involves more unfavorable steric interactions.

ICl* is only 3.2 kcal/mol below its dissociation limit. Thus the $C_2H_2Br_2Cl$ radical formed from ICl* has at least 3.2 kcal/mol less energy than the same radical formed from Cl atoms. (This energy difference may be even greater if the resulting fragments recoil with excess translational energy.) In this regard ICl* is an exceptionally interesting chlorinating agent in that it may be viewed as a source of Cl atoms with negative energy. This may account for the high quantum yields since the intermediate radicals may not have sufficient energy to expel a Cl atom. Furthermore, the lower energy of the radical may accentuate the preference for the stereochemical pathway of lowest energy.

Acknowledgments. We are grateful to the Department of Energy for financial assistance through Grant EY-76-S-03-0326-PA2.

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$$\% \ {}^{37}\mathrm{Cl} = \frac{0.505R}{0.505R + 0.495}$$

where R = *m/e* 144/140. To obtain the "true enrichment" in the DCE product due to the reaction of ICl* with BCE, the following formula was used:

$$\% \ {}^{37}\mathrm{Cl} = \frac{5(35.1R - 4.9)}{R + 1}$$

where R = *m/e* 63/61. See S. Datta, Ph.D. Thesis, Columbia University, New York, N.Y., 1978.

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Conformational Preferences and Electronic Structures of $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$

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Abstract: Nonempirical molecular electronic structure theory has been applied to the organometallic systems bis(η^2-ethene)nickel(0) and tris(η^2-ethene)nickel(0). Three types of contracted Gaussian basis sets have been used in conjunction with restricted self-consistent-field theory. The middle basis set may be labeled Ni(14s 9p 6d/10s 6p 3d), C(10s 6p/6s 3p), H(5s/3s) and is perhaps the most complete basis set used to date for an experimentally known organotransition metal complex such as $Ni(C_2H_4)_3$. The chosen basis comes very close to reproducing the exact Hartree-Fock term splittings for the nickel atom. For $Ni(C_2H_4)_2$ the twisted (D_{2d}) and "planar" (D_{2h}) conformations are predicted to lie energetically within 0.1 kcal of each other. For the $Ni(C_2H_4)_3$ complex, however, the planar conformation lies ~24 kcal lower than the upright form. Both of these predictions are in qualitative accord with the earlier semiempirical work of Rösch and Hoffmann. The lowest D_{2h} triplet state of $Ni(C_2H_4)_2$ is of $^3B_{3u}$ symmetry, and a number of other electronic states were also investigated. The ionization potentials of both molecules were predicted and large deviations from Koopmans' theorem were found. Mulliken population analyses are also reported and used to qualitatively discuss the electronic structures.

Introduction

One of the most remarkable organometallic species synthesized in recent years is the tris(η^2-ethene)nickel(0) molecule.[2a] This was the first transition-metal complex prepared in solution with ethylenes alone as its ligands. In 1973 Fischer, Jonas, and Wilke prepared $Ni(C_2H_4)_3$ in a diethyl ether solution, which was found to be pale yellow in color. Upon crystallization from solution at 195 K they obtained colorless needle-shaped crystals. Fischer, Jonas, and Wilke assumed the molecule to have the "planar" D_{3h} structure seen in Figure 1 and reported nuclear magnetic resonance and infrared spectroscopic data consistent with this assumption. More recently the analogous $Pt(C_2H_4)_3$ molecule has been synthesized by Green, Howard, Spencer, and Stone.[2b]

Our attention was first drawn to tris(ethylene)nickel(0) by the excellent theoretical study of Rösch and Hoffmann.[2c] They elucidated the qualitative features of the electronic structures of $Ni(C_2H_4)_n$ for n = 2, 3, and 4, and supported their findings with extended Hückel calculations. Rösch and Hoffmann were able to predict the conformational preferences of both $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$. In the first case, they found little preference for the D_{2d} or twisted form (see Figure 2) over the D_{2h} or planar (that is, all four C atoms lie in a plane) geometry.

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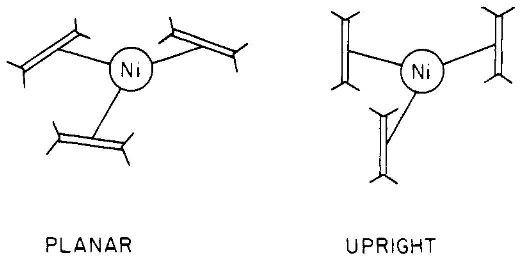


Figure 1. Geometries of the "planar" (left) and upright (right) geometries of tris(η^2-ethene)nickel(0).

However, for $Ni(C_2H_4)_3$ the planar structure was favored by 17 kcal over the upright geometry of Figure 1.

Two other experimental reports of tris(η^2-ethene)nickel(0) have appeared since the pioneering synthesis of Fischer, Jonas, and Wilke. In the first, Atkins, McKenzie, Timms, and Turney[3] made $Ni(C_2H_4)_3$ in an ethylene matrix in the course of preparing a number of palladium complexes. Even more recently Huber, Ozin, and Power[4] made $Ni(C_2H_4)_3$ at 15 K in C_2H_4 and C_2H_4/Ar matrices.

Ozin and co-workers also prepared the simpler members $Ni(C_2H_4)$ and $Ni(C_2H_4)_2$ of the series and obtained infrared and visible-ultraviolet spectra for all three molecules. Primarily on the basis of Rösch and Hoffmann's theoretical work, Ozin assigned as $Ni(d) \rightarrow C_2H_4(\pi^*)$ the electronic transitions at 280 (mono), 250 (bis), and 236 nm (tris complex). In addition, these workers demonstrated the weakly bound nature of $Ni(C_2H_4)_3$ by observing that the fragmentation reaction

$$Ni(C_2H_4)_3 \rightarrow Ni + 3C_2H_4$$

occurs at about 273 K. These results were given further discussion in a 1977 review by Ozin.[5]

Several research groups have reported nonempirical pseudopotential calculations on the monoolefin complex $Ni(C_2H_4)$. Specifically noteworthy are those of Upton and Goddard,[6] Basch, Newton, and Moskowitz,[7] and Ozin, Power, Upton, and Goddard.[8] There seems to be agreement[6,7] that the electronic ground state is of $^3A_1$ symmetry and the dissociation energy is of the order of 10 kcal. More severe approximations have been made in the statistical exchange studies of Rösch and Rhodin[9] and of Messmer.[10] The only strictly ab initio study of $Ni(C_2H_4)$ with which we are familiar is that of Roos and co-workers.[11]

Over the past 5 years, ab initio studies of transition-metal complexes have in several cases nicely complemented experimental findings.[12] However, it cannot be realistically stated that work to date compares with the spectacular successes[13] achieved for molecules composed entirely of atoms smaller than neon. This gap between reliability of theoretical predictions for hydrocarbons (for example) and those for organometallic systems is due to a very practical problem—the basis set problem.[14] For first-row molecular systems it is usually possible to approach rather closely the Hartree-Fock limit by adopting successively larger basis sets.[15] In this way, all errors remaining at the self-consistent-field (SCF) level of theory may accurately be ascribed to the effects of electron correlation. Once chemically significant correlation effects are identified, these may be systematically treated through successively more elaborate configuration interaction (CI) procedures.[16]

For no real (i.e., experimentally characterized) organotransition metal complex has the Hartree-Fock limit been reasonably approached to date. Probably the closest approach to date has been that of Bagus[17] for the ferrocene molecule $Fe(C_5H_5)_2$. The only significant deficiency of their ferrocene basis set was a third set of d functions, needed to allow the expansion[18] of the 3d orbital relative to the isolated transition-metal atom. Here we report ab initio SCF studies of the conformers of $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$ using relatively large and flexibly contracted[19] basis sets. We should concede at the outset that there are still notable absolute differences between the present SCF energies and the (unknown) exact Hartree-Fock energies. However, major differences between the present relative energies (conformational differences, electronic excitation energies, ionization potentials) and experiment should be primarily due to correlation effects.

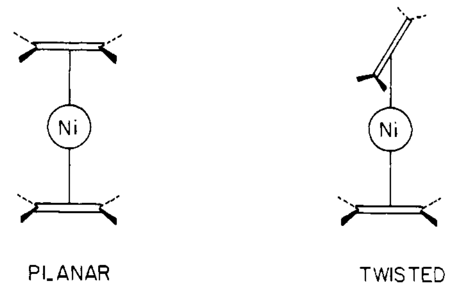


Figure 2. Structures of the "planar" D_{2h} (left) and twisted D_{2d} (right) conformers of bis(η^2-ethene)nickel(0).

Basis Sets

As mentioned above the choice of basis set places an immediate limit upon the reliability of any ab initio theoretical study. There are two widely cited papers concerning Gaussian basis sets for transition-metal atoms. In the first of these, by Roos, Veillard, and Vinot,[18] a (12s 6p 4d) set was introduced, based on optimization of the s^2d^n lowest electronic state. The second paper, that of Wachters,[20] reports a larger (14s 9p 5d) basis, with primitive Gaussian exponents optimized in the same manner.

Our "small" basis set began with the nickel atom (12s 6p 4d) set of Roos.[18] This was contracted quite flexibly to Ni(9s 5p 2d). The carbon basis functions were considered relatively uncontroversial, and the C(8s 4p) set of Huzinaga[21] was contracted to (5s 3p) in an obvious[19] manner (see Table I). Similarly, for the hydrogen atoms, Huzinaga's (4s) set[22] was contracted to (2s) and a scale factor of 1.2 applied.[19] Within this basis the total energy of the isolated ethylene molecule is −78.007 85 hartrees.

Beginning as described in the previous paragraph, a fair amount of basis set experimentation was carried out for the closed-shell singlet state of D_{2h} $Ni(C_2H_4)_2$. This exercise is summarized in Table II. The first addition to our starting "small" basis was the set of spatially extended[18] d functions recommended by Hay.[23] As discussed by Roos,[18] Hay,[23] and Swope,[24] these functions are necessary to allow the 3d orbital to become valence-like in nature. It is well known[25] that the 3d orbital of the isolated Ni atom has its maximum amplitude too close to the nucleus to participate in a significant way in chemical bonding with other atoms. As shown in Table II, this more diffuse set of d functions lowers the total energy of $Ni(C_2H_4)_2$ by a notable amount, 0.081 hartrees.

In the third entry of Table II, the two outermost s functions of the Roos basis have been deleted. However, to compensate, the $(x^2 + y^2 + z^2) = 3s$ functions arising from the three d sets have been added. This addition is a minor one since all the necessary Gaussian integrals have already been computed as required for the five genuine d functions. Interestingly, this set of $(7 + 3) = 10$ s functions actually yields a slightly lower energy than the original 9s set. The fourth entry differs from the third in that a set of diffuse p functions ($\alpha = 0.081$) has been added to each carbon atom. These are relatively ineffective, lowering the total energy by only 0.003 hartree. This indicates rather clearly that the ethylene ligands do not acquire any significant amount of anionic $C_2H_4^-$ character.

Table I. Contracted Gaussian Basis Sets for $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$[a]

nickel		carbon		hydrogen
		Small Basis Set		
s 73 850.4 ⎫	p 493.637 ⎫	s 2779.47 ⎫	p 9.689 47 ⎫	s 19.2406 ⎫
s 10 939.2 ⎪	p 116.498 ⎭	s 417.661 ⎪	p 2.053 69 ⎭	s 2.8992 ⎪
s 2504.61 ⎪	p 36.5669	s 95.4879 ⎪	p 0.558 755	s 0.6534 ⎭
s 720.706 ⎭	p 12.8762	s 27.0796 ⎭	p 0.154 484	s 0.1776
s 240.114	p 3.545 85	s 8.749 24	p 0.081	
s 86.8503	p 1.121 60	s 3.043.59		
s 22.4686	p 0.32	s 0.527 582		
s 9.505 08		s 0.161 372		
s 2.579 10	d 27.9859 ⎫			
s 1.029 58	d 7.47243 ⎪			
s 0.125 776	d 2.256 54 ⎭			
s 0.046 377	d 0.608 474			
	d 0.1481			
		Largest Basis Set		
s 284 878.0 ⎫	p 1774.18 ⎫	s 9470.52 ⎫	p 25.6271 ⎫	s 33.6444 ⎫
s 41 997.9 ⎪	p 423.403 ⎪	s 1397.56 ⎪	p 5.846 07 ⎪	s 5.057 96 ⎪
s 9627.67 ⎪	p 138.311 ⎪	s 307.436 ⎪	p 1.799 35 ⎪	s 1.146 80 ⎭
s 2761.96 ⎪	p 53.1703 ⎭	s 84.6057 ⎪	p 0.654 333 ⎭	s 0.321 144
s 920.488 ⎭	p 22.3874	s 26.9218 ⎭	p 0.248 692	s 0.101 309
s 341.805	p 9.928 48	s 9.412 99	p 0.090 927	
s 138.023	p 4.116 25	s 3.479 82		
s 59.2587	p 1.710 31	s 1.071 23		
s 20.3712	p 0.672 528	s 0.400 791		
s 8.594 00	p 0.32	s 0.135 166		
s 2.394 17	p 0.146 588			
s 0.918 169	p 0.044 447			
s 0.35				
s 0.130 176	d 48.9403 ⎫			
s 0.046 392	d 13.7169 ⎪			
	d 4.639 51 ⎭			
	d 1.574 33			
	d 0.486 409			
	d 0.1316			

[a] Functions contracted together are connected by a right bracket.

Table II. Investigation of Basis Sets Dependence of Total Energies for D_{2h} $Ni(C_2H_4)_2$ in Its Closed-Shell Singlet State[a]

Ni basis	C basis	H basis	total energy, hartrees	remarks
(12s 6p 4d/9s 5p 2d)	(8s 4p/5s 3p)	(4s/2s)	−1662.210 33	starting small basis set
(12s 6p 5d/9s 5p 3d)	(8s 4p/5s 3p)	(4s/2s)	−1662.291 43	add spatially extended set of d functions
(10s 6p 5d/7s 5p 3d)	(8s 4p/5s 3p)	(4s/2s)	−1662.292 02	delete Ni 4s functions, but add s functions ($x^2 + y^2 + z^2$) from three sets of d functions
(10s 6p 5d/7s 5p 3d)	(8s 5p/5s 4p)	(4s/2s)	−1662.295 37	add spatially extended set of p functions on carbon atoms
(10s 7p 5d/7s 6p 3d)	(8s 4p/5s 3p)	(4s/2s)	−1662.313 59	add p function to describe nickel 4p orbital

[a] These studies all began with the "small" basis set described in the text.

The final entry shows the effect of adding a set of p functions designed to roughly approximate the nickel 4p orbital. The energy lowering is significant, 0.018 hartree, but not earthshaking. All of the basis functions tested in Table II are collected in the first part (labeled "small basis set") of Table I.

The present "large" basis set began with the nickel atom (14s 9p 5d) set of Wachters.[20] This was rather loosely contracted to (10s 6p 2d). Again the comparable set of carbon functions was considered relatively uncontroversial and Huzinaga's (10s 6p) set[21] was contracted to (6s 3p). Finally the hydrogen basis was the (5s) set of Huzinaga,[22] contracted to (3s), to which no scale factor was appended. For the ethylene ground state this basis yielded an SCF energy of −78.022 58 hartrees, while a scale factor of 1.1 for the hydrogen s functions yielded a slightly higher energy, −78.022 44 hartrees.

For most of the wave functions determined here, the "large" basis consisted of the above functions plus the set of spatially extended d functions ($\alpha = 0.1316$) recommended by Hay.[23] The only possibly serious problem with this large basis is that no functions explicitly describing the nickel 4p orbital are included. Fortunately, this is not as serious a problem as with the Roos (6p) set since the smallest p exponent there is 1.121 60, whereas with the Wachters (9p) set the smallest p exponent is 0.672 528.

For $Ni(C_2H_4)_2$ the above "large" basis set was made larger. No fewer than three additional sets of p functions ($\alpha = 0.32$, 0.146 588, 0.044 447) were appended, as was an additional s function ($\alpha = 0.35$) designed to span the sizable space between the atomic nickel 3s and 4s orbitals. This largest of basis sets is given in the second half of Table I. The D_{2h} energy of $Ni(C_2H_4)_2$ with this basis is −1662.709 53, as compared to −1662.706 67 with the large basis of the previous paragraph.

Table III. Nickel Atom Self-Consistent-Field Relative Energies (eV) Compared with Experiment

basis set	$E(sd^9\ ^3D)$	$E(s^2d^8\ ^3F)$	$E(d^{10}\ ^1S)$
(12s 7p 5d/9s 6p 3d)	0.00		4.13
(14s 9p 6d/10s 6p 3d)	0.00	−1.29[a]	4.22
(15s 12p 6d/11s 9p 4d)	0.00		4.20
numerical Hartree-Fock[b]	0.00	−1.28	4.19
expt[c]	0.00	0.03	1.74

[a] Obtained with uncontracted basis set. [b] Reference 23. [c] From ref 27. Here we have averaged over the spin-orbit components to provide nonrelativistic "experimental" results. The $^3F_4$ component actually lies 0.03 eV below the $^3D_3$ component.

This difference of less than 3 mhartrees would seem to justify the neglect of these additional s and p functions in the $Ni(C_2H_4)_3$ studies.

Atomic Nickel

It is reasonable to ascertain how the theoretical methods used here describe the lowest electronic states of the nickel atom. This question is answered in Table III for the three basis sets primarily used in this work. Since only relative energies are given in Table III, we should note that the absolute energies for the ^3D ground state are −1506.398 59, −1506.767 86, and −1506.769 44 hartrees. These may be compared with the Hartree-Fock limit[23,26] ^3D energy of −1506.824 41 hartrees.

All three of our basis sets yield good agreement with the numerical Hartree-Fock term splittings. This means that with respect to this particular property the basis sets are well balanced. Unfortunately, the Hartree-Fock model itself has severe and well-known[28] failings for these atomic term splittings. Namely, the $s^2d^8\ ^3F$ state is predicted to lie too low by 1.31 eV relative to the ^3D state. Even more severe is the fact that the closed-shell $d^{10}\ ^1S$ state lies 2.45 eV higher than it should above the ^3D state.

The latter fact is particularly significant since the Ni atom is traditionally throught[29] to possess a d^{10} configuration in typical organometallic complexes such as $Ni(CO)_4$. If our atomic findings were directly carried over to molecular systems, one might naively anticipate that the lowest triplet state of $Ni(CO)_4$ would lie (within the restricted Hartree-Fock approximation[30]) 3.76 eV too low relative to the closed-shell singlet. In any case we must take careful account of these atomic correlation errors in assessing the reliability of our molecular results.

Bis(η^2-ethene)nickel(0)

In these studies, the geometry of the ethylene ligand was fixed at the experimental[31] equilibrium structure of the isolated molecule: $R(CH) = 1.086$ Å, $R(CC) = 1.339$ Å, $\theta(HCH) = 117.6°$. Following Rösch and Hoffmann, the distance from the nickel atom to the center of the C═C bond was fixed at 2.0 Å.

Neglecting the argon core of nickel and the carbon 1s orbitals, the electron configuration of "planar" or D_{2h} $Ni(C_2H_4)_2$ is

$$\ldots 5a_g^2 4b_{1u}^2 2b_{2g}^2 4b_{3u}^2 1b_{3g}^2 3b_{2u}^2 6a_g^2 5b_{1u}^2 1b_{1g}^2 \\ 1a_u^2 7a_g^2 6b_{1u}^2 2b_{3g}^2 8a_g^2 2b_{1g}^2 3b_{2g}^2 9a_g^2 \quad (1)$$

while that for the "twisted" or D_{2d} geometry is

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

The total energies of these closed-shell singlet states are given in Table IV.

Table IV. Total Energies (hartrees) and Relative Energies (kcal) for Bis(η^2-ethene)nickel(0)[a]

basis set	planar (D_{2h})	twisted (D_{2d})
Ni(10s 7p 5d/7s 6p 3d) C(8s 4p/5s 3p) H(4s/2s)	−1662.313 59 0.00	−1662.313 39 0.13
Ni(14s 9p 6d/10s 6p 3d) C(10s 6p/6s 3p) H(5s/3s)	−1662.706 67 0.06	−1662.706 76 0.00
Ni(15s 12p 6d/11s 9p 4d) C(10s 6p/6s 3p) H(5s/3s)	−1662.709 53	

[a] The first basis set also includes the s-like functions $(x^2 + y^2 + z^2)$ from the three sets of d functions.

Table V. SCF Wave Functions, Energies, and Nickel Atom Mulliken Populations for Several Electronic States of $Ni(C_2H_4)_2$[a]

electronic state		rel energy, eV	nominal configuration	nickel Mulliken populations
$3b_{2g}9a_g10a_g^2$	$^3B_{2g}$	4.48	$4s^23d^8$	
$3b_{2g}9a_g^27b_{1u}$	$^3B_{3u}$	2.37	$3d^94p$	
$3b_{2g}9a_g10a_g4b_{2u}$	^5A_u	1.93	$4s3d^84p$	
$3b_{2g}^29a_g4b_{1u}$	$^3B_{1u}$	1.73	$3d^94p$	
$3b_{2g}9a_g5b_{3u}10a_g$	$^5B_{1u}$	0.77	$4s3d^84p$	
$3b_{2g}9a_g^210a_g$	$^3B_{2g}$	0.74	$4s3d^9$	
$3b_{2g}9a_g^24b_{2u}$	^3A_u	0.68	$3d^94p$	
$3b_{2g}^29a_g^2$	^1A_g	0.00	$3d^{10}$	$3d^{9.4}4s^{0.4}4p^{0.1}$
$3b_{2g}^29a_g10a_g$	^3A_g	−0.08	$4s3d^9$	$3d^{8.7}4s^{1.9}4p^{0.2}$
$3b_{2g}^29a_g4b_{2u}$	$^3B_{2u}$	−0.22	$3d^94p$	$3d^{8.8}4s^{0.4}4p^{1.3}$
$3b_{2g}9a_g^25b_{3u}$	$^3B_{1u}$	−1.25	$3d^94p$	$3d^{8.9}4s^{0.4}4p^{0.5}$
$3b_{2g}^29a_g5b_{3u}$	$^3B_{3u}$	−1.73	$3d^94p$	$3d^{8.8}4s^{0.4}4p^{0.5}$

[a] The basis set used in every case was Ni(15s 12p 6d/11s 9p 4d), C(10s 6p/6s 3p), H(5s/3s).

The striking conclusion of Table IV is that the "planar" and twisted forms of $Ni(C_2H_4)_2$ are very nearly equal in energy. With the small basis set, the planar form is predicted to lie lower by 0.13 kcal. The large basis set reverses this order, with the twisted geometry now lying lower by 0.06 kcal. As noted in the Introduction, Rösch and Hoffmann's extended Hückel calculations[2a,b] also predicted the two structures to be very similar energetically. Specifically, they predicted the twisted D_{2d} structure to lie 1.5 kcal below the planar D_{2h} form. The earlier ab initio study of Bachmann, Demuynck, and Veillard,[32] using a smaller basis set, favors the D_{2d} structure by 0.75 kcal.

Using our largest basis set, other electronic states were examined at the restricted SCF level of theory.[30] These results are summarized in Table V. Since these results are now approaching Hartree Fock quality, it is interesting to compare a typical predicted excitation energy to that obtained with the small basis set, the final entry of Table II. With the small basis set the lowest $^3B_{1u}$ state ($3b_{2g} \rightarrow 5b_{3u}$ excitation) is predicted to lie 0.67 eV below the d^{10} closed-shell singlet. Unfortunately, Table V shows that the much more complete basis set predicts an SCF energy separation of 1.25 eV for the same two states. This points to an obvious weakness in the small basis set, most likely the absence of an adequate description of the nickel 4p orbital.

At the Hartree-Fock level of theory, Table V makes it clear that the $^3B_{3u}$ state ($9a_g \rightarrow 5b_{3u}$ excitation) is the electronic ground state. An important question to ask is whether correlation effects[14] will reverse this finding and make the closed-shell singlet structure the ground state, as expected. Although the $^3B_{3u}$ state lies 1.73 eV below the ^1A_g state, the former corresponds to an sd^9 electron configuration, while the latter

Table VI. Mulliken Populations for the Planar D_{2h} and Twisted D_{2d} Geometries of $Ni(C_2H_4)_2$[a]

	nickel			carbon		hydrogen
	s	p	d	s	p	s
planar	6.376	12.007	9.444	3.263	3.108	0.836
twisted	6.353	12.006	9.459	3.270	3.098	0.839
free C_2H_4				3.221	3.075	0.852

Mulliken charges	Ni	C	H
planar	+0.173	−0.371	+0.164
twisted	+0.182	−0.368	+0.161
free C_2H_4		−0.296	+0.148

d orbital populations	$d_{3z^2-r^2}$	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
planar	1.912[b]	1.912[b]	2.008	1.607	2.006
twisted	1.856	1.993	2.008	1.801	1.801

[a] These results were obtained with the standard large basis set. [b] Average value of $3z^2 - r^2$ and $x^2 - y^2$. The individual values could not be obtained from populations of x^2, y^2, z^2 Cartesian basis functions.

is d^{10}. Table V confirms the approximate nature of these labels. The actual Mulliken populations of the two states are $3d^{8.8}4s^{0.4}4p^{0.5}$ and $3d^{9.4}4s^{0.4}4p^{0.1}$, respectively. Viewing the atomic results discussed in the previous section, we saw that restricted Hartree–Fock theory predicts the d^{10} ^1S state to lie 2.35 too high (relative to experiment) above the sd^9 ^3D state. If we carried this number directly over to the molecular $Ni(C_2H_4)_2$ results, a ^1A_g closed-shell ground state would be predicted. However, the simplicity of that model is apparent and this prediction must be considered a very weak one. We can predict with confidence that the $^3B_{3u}$ and ^1A_g states should lie energetically very close to each other.

To better understand the energetics set out in Table V it is necessary to characterize a few of the molecular orbitals of planar D_{2h} $Ni(C_2H_4)_2$. The highest occupied molecular orbital (HOMO), the $9a_g$ orbital, is 12% Ni 4s, 76% Ni 3d, and 12% carbon 2p from the closed-shell ground state wave function obtained with the largest basis set. The $3b_{2g}$ orbital, also quite high-lying, is 78% Ni 3d and 20% carbon 2p in the Mulliken picture. They are the two orbitals from which electrons are promoted to form many of the lowest lying excited states.

The lowest unoccupied (LU) molecular orbital of $Ni(C_2H_4)_2$ is the $5b_{3u}$ orbital. In the lowest triplet state (the $9a_g \rightarrow 5b_{3u}$ $^3B_{3u}$ state) this $5b_{3u}$ orbital is 32% Ni 4p and ~68% carbon π^*. Basch, Newton, and Moskowitz also noted strong Ni 4p–C_2H_4 π^* mixing in their pseudopotential studies.[7] The SLUMO (S = second) for planar $Ni(C_2H_4)_2$ is the $4b_{2u}$ orbital, which is almost entirely nickel 4p, consistent with qualitative expectations. Finally, the $10a_g$ orbital is also low lying and is primarily nickel 4s in its Mulliken character.

In this light it is seen that the two lowest excited electronic states of planar $Ni(C_2H_4)_2$ formally involve Ni 3d → Ni 4p excitations. In practice Table V shows that more like half an electron is transferred from 3d to 4p. For the next triplet state, the $^3B_{2u}$, the 4p population really does increase by 1.2 electrons relative to the closed-shell ground-state 4p population. However, about half of this increase in 4p character comes from the ethylene ligands. The next electronic state, the ^3A_g state, is formally of Ni 3d → Ni 4s character. This description notwithstanding, the ^3A_g state may not be realistically analyzed in such a one-electron picture. While the three other low-lying electronic states have a small *positive* Mulliken charge on the Ni atom, the ^3A_g and $^3B_{2u}$ states have *negative* Mulliken nickel charges of 0.80 and 0.55. Thus accompanying these nominally one-electron promotions there are notable changes in the nature of lower MOs.

Total populations for planar and twisted $Ni(C_2H_4)_2$ are summarized in Table VI. We see first that the Mulliken breakdown is consistent with the classical designation of these structures at zerovalent nickel. More precisely, the planar and twisted geometries have Mulliken charges of +0.17 and +0.18, respectively. The careful observer will note a small discrepancy between Table VI and the nickel atom populations of Table V. Table V was obtained from a wave function constructed from our largest basis, which includes three extra 4p-like functions and one extra 4s function relative to the standard large basis used in Table VI. Thus it is not surprising that Table V predicts a 4p population of 0.1 Mulliken electron, while Table VI suggests 4p populations less than 0.01. However, both Mulliken analyses agree that the 4s population is 0.4 and the 3d population 9.4.

Table VI suggests small movements of electronic charge as follows: (1) The d orbitals of the same symmetry class as the 4s orbitals ($3z^2 - r^2$ and $x^2 - y^2$ for planar, $3z^2 - r^2$ for twisted) lose somewhat less than 0.2 electron to the 4s orbitals. (2) The d orbitals of the correct symmetry for π^* back-bonding (xz for planar, xz and yz for twisted) lose a total of 0.4 electron, presumably to the C_2H_4 π^* orbitals. (3) The 4s populations close to 0.4 imply a flow of 0.2 electron from the C_2H_4 π orbitals. (4) These changes give net charges of 0.2 on the Ni atom and −0.1 on each ethylene ligand. A quantitative examination of the charge distribution of each of the valence MOs confirmed the details of this analysis, which in summary is

0.2 electron Ni3d → Ni4s (metal rearrangement)
0.2 electron $C_2H_4\pi \rightarrow$ Ni4s (ligand-to-metal donation)
0.4 electron Ni3d → $C_2H_4\pi^*$ (metal-to-ligand back-donation)

The stabilization due to this donation and back-donation is no doubt the source of the calculated binding energy (relative to d^{10} Ni) of 31 kcal/mol, and is consistent with the Dewar–Chatt–Duncanson model.[33]

Basch et al.,[7] also using population analysis, found smaller amounts of donation and back-donation in the d^9 NiC_2H_4 complex, but Ozin et al.[8] found no evidence for back-donation in their orbital contour plots for this system. They also point out that inclusion of $\pi \rightarrow \pi^*$ configuration interaction for the C_2H_4 molecules would tend to reduce the back-donation into the π^* orbitals from the metal d orbitals.

This discussion of the electronic structure of $Ni(C_2H_4)_2$ is concluded with an analysis of the ionization potentials of the planar and twisted geometries. The ionization potentials were predicted first from Koopmans' theorem, in which the positive ion orbitals are assumed identical with those of the neutral molecule. Secondly, direct SCF calculations[14] on the positive ion states were carried out, allowing for "relaxation" of the ion

Table VII. Theoretical Ionization Potentials (eV) for Bis(η^2-ethene)nickel(0) in Its Planar D_{2h} and Twisted D_{2d} Conformations

	Koopmans' theorem	direct SCF treatment
planar $Ni(C_2H_4)_2$	$\epsilon(9a_g) = 7.76$	$E(^2A_g) - E(^1A_g) = 2.03$
	$\epsilon(2b_{1g}) = 9.46$	$E(^2B_{1g}) - E(^1A_g) = 2.09$
	$\epsilon(8a_g) = 9.61$	$E(^2A_g) - E(^1A_g) = 2.17$
	$\epsilon(2b_{3g}) = 9.74$	$E(^2B_{3g}) - E(^1A_g) = 2.18$
	$\epsilon(3b_{2g}) = 7.26$	$E(^2B_{2g}) - E(^1A_g) = 2.65$
	$\epsilon(6b_{1u}) = 10.75$	$E(^2B_{1u}) - E(^1A_g) = 9.99$
	$\epsilon(7a_g) = 12.10$	$E(^2A_g) - E(^1A_g) = 11.22$
twisted $Ni(C_2H_4)_2$	$\epsilon(8a_1) = 8.07$	$E(^2A_1) - E(^1A_1) = 2.01$
	$\epsilon(2b_1) = 9.32$	$E(^2B_1) - E(^1A_1) = 2.04$
	$\epsilon(7b_2) = 9.19$	$E(^2B_2) - E(^1A_1) = 2.08$
	$\epsilon(6e) = 8.25$	$E(^2E) - E(^1A_1) = 2.41$
	$\epsilon(6b_2) = 10.79$	$E(^2B_2) - E(^1A_1) = 10.02$
	$\epsilon(7a_1) = 12.08$	$E(^2A_1) - E(^1A_1) = 11.20$

Table VIII. Total Energies (hartrees) and Relative Energies (kcal) for Tris(η^2-ethene)nickel(0)[a]

basis sets	planar	upright
Ni(10s 7p 5d/7s 6p 3d)	−1740.320 69	−1740.280 72
C(8s 4p/5s 3p)	0.0	25.1
H(4s/2s)		
Ni(14s 9p 6d/10s 6p 3d)	−1740.725 66	−1740.687 89
C(10s 6p/6s 3p)	0.0	23.7
H(5s/3s)		

[a] The first basis set also includes the s-like functions $(x^2 + y^2 + z^2)$ from the three sets of d functions.

molecular orbitals.[34] For the nickel d orbitals and ethylene π orbitals, corresponding to the 14 electrons in highest lying orbitals, the theoretical IPs are given in Table VII.

The most obvious conclusion drawn from Table VII is that the ordering of IPs is quite different based on Koopmans' theorem than from the ΔSCF treatment. The latter ordering, of course, is the more reliable from a theoretical perspective, although the direct SCF IPs are probably all too low. This is because there is more correlation energy associated with the neutral ground state than with typical molecular positive ion states. This ordering reversal is most clearly demonstrated by the $3b_{2g}$ orbital, which based on Koopmans' theorem should correspond to the lowest IP. However, the ΔSCF treatment predicts the $^2B_{2g}$ state to be the fourth excited electronic state of the positive ion at this geometry.

Fortunately, this result can be understood once the very large relaxation energies of the first five positive ion states are acknowledged. Such relaxation energies are typical[35] for the d electrons of transition-metal systems. Here the larger relaxation energies range from 4.61 ($3b_{2g}$) to 7.56 eV ($2b_{3g}$), a considerable span. The $3b_{2g}$ orbital has a relatively small relaxation energy, since it has one of the smallest amounts of 3d character, only about 78%. The $9a_g$ orbital, with only 76% Ni 3d character (Mulliken analysis), also has a relatively small (for Ni d orbitals) relaxation energy, 5.73 eV. The three orbitals with large relaxation energies, $2b_{3g}$ (7.56 eV), $8a_g$ (7.44 eV), and $2b_{1g}$ (7.37 eV), all have very large percentages of Ni 3d character, namely, 97, 95, and 98%.

From the perspective of wanting to understand the chemical bonding in organometallic systems, the above relaxation energies are particularly significant. In the classical picture,[29] which is reflected in the nickel(0) label in the official name, the nickel atom in $Ni(C_2H_4)_2$ is considered zerovalent. If in addition there were no mixing between the metal and ligand orbitals, the five highest occupied orbitals would be purely nickel 3d in character and have nearly identical relaxation energies. Our Mulliken populations suggest a charge of +0.17 for Ni in planar $Ni(C_2H_4)_2$, and the more theoretically meaningful relaxation energies support the idea that there is some positive charge associated with the Ni atom. Although not discussed here, an examination of the bottom half of Table VII shows again the large relaxation energies associated with the metal d orbitals for the twisted or D_{2d} geometry.

Tris(η^2-ethene)nickel(0)

The electron configuration for the closed-shell ground state of "planar" (see Figure 1) $Ni(C_2H_4)_3$ is

$$\ldots 5a_1'^2 5e'^4 6e'^4 2a_2'^2 3a_2''^2 1e''^4 6a_1'^2 7e'^4 2e''^4 1a_1''^2 7a_1'^2 8e'^4 9e'^4 3e''^4 8a_1'^2 \quad (3)$$

where the argon core of nickel and the carbon 1s orbitals have been omitted. For the corresponding upright structure (also seen in Figure 1) the closed-shell electron configuration is

$$\ldots 5a_1'^2 4e'^4 4a_2''^2 2e''^4 5e'^4 1a_2'^2 6a_1'^2 6e'^4 3e''^4 1a_1''^2 7a_1'^2 7e'^4 4e''^4 8a_1'^2 8e'^4 \quad (4)$$

The total SCF energies of these two $^1A_1'$ conformers are given in Table VIII.

Unlike the bis(η^2-ethene)nickel(0) results, Table VIII shows a clear energetic difference between the planar and upright geometries of $Ni(C_2H_4)_3$. With the smaller basis set the planar structure is predicted to lie 25.1 kcal lower. The same energetic ordering is found for the larger basis, with the planar structure lying lower by 23.7 kcal. These planar–upright energy differences are sufficiently large that one can state unequivocally that the planar structure corresponds to the true ground-state equilibrium geometry. Perhaps fortuitously, the planar structure is the geometry assumed by Fischer, Jonas, and Wilke.[1] In addition, Rösch and Hoffmann's extended Hückel prediction[2] of 17 kcal for the planar–upright energy separation is in good qualitative agreement with the near Hartree–Fock result of 23.7 kcal predicted here.

Mulliken population analyses for tris(η^2-ethene)nickel(0) are reported in Table IX. There we see that, while both planar and upright geometries are properly described as zerovalent nickel, the Mulliken charge on the former, 0.34, is significantly larger than the +0.26 found for the latter. It is noteworthy that the planar Mulliken Ni charge is just about twice that found for both conformations of $Ni(C_2H_4)_2$. The detailed nickel Mulliken "hybridizations" are $s^{0.3}d^{9.4}$ (planar) and $s^{0.2}d^{9.5}$ (upright), indicating relative little nickel 4p involvement. As for the bis complex, however, we expect the nickel 4p orbital to be occupied in several of the lowest lying excited electronic states of $Ni(C_2H_4)_3$.

The Mulliken populations in Table IX show charge redistributions of the same character as those in $Ni(C_2H_4)_2$. The amount of loss from Ni3d($3z^2 - r^2$) to Ni4s is small (less than 0.1 for planar, negligible for upright), perhaps owing to the additional effect of the third ligand in raising the energy of the 4s orbital. The $C_2H_4\pi \rightarrow$ Ni4s donation is close to 0.2 for both conformations. In going from upright to planar there is an increase from 0.45 to 0.6 in the amount of charge back-donated from the Ni3d ($x^2 - y^2$ and xy for planar, xz and yz for upright) orbitals to the C_2H_4 π^* orbitals. There is no doubt the reason for the significant energy difference between the two conformations. Note that the amount of back-donated charge, per C_2H_4, is 0.20 for $Ni(C_2H_4)_3$ planar and for both conformations of $Ni(C_2H_4)_2$, while it is 0.15 for $Ni(C_2H_4)_3$ upright. The overall stabilization energy (relative to d^{10} Ni) was computed to be 28 kcal/mol for $Ni(C_2H_4)_3$ planar.

Table IX. Mulliken Populations for the Planar and Upright (See Figure 1) Geometries of $Ni(C_2H_4)_3$[a]

	nickel			carbon		hydrogen
	s	p	d	s	p	s
planar	6.265	12.024	9.371	3.261	3.095	0.850
upright	6.239	12.014	9.490	3.253	3.090	0.850
free C_2H_4				3.221	3.075	0.852
Mulliken charges	Ni	C	H			
planar	+0.340	−0.356	+0.150			
upright	+0.258	−0.344	+0.150			
free C_2H_4		−0.296	+0.148			
d orbital populations	$d_{3z^2-r^2}$	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	
planar	1.930	1.705	1.705	2.016	2.016	
upright	1.985	1.977	1.977	1.775	1.775	

[a] These results were obtained with the standard large basis set.

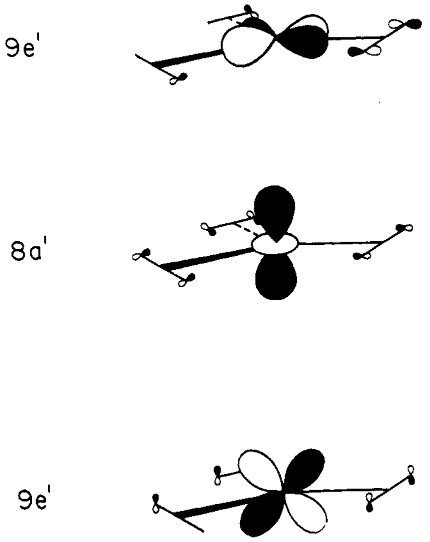


Figure 3. Qualitative sketches of the three highest occupied molecular orbitals of "planar" $Ni(C_2H_4)_3$.

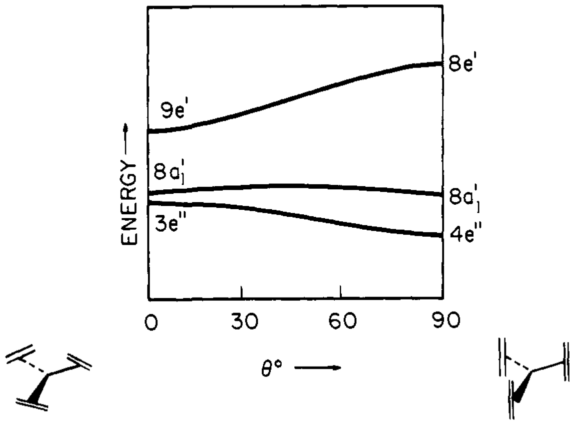


Figure 4. Extended Hückel one-electron energies[2c] for the three highest occupied molecular orbitals of $Ni(C_2H_4)_3$ as a function of rotation between the planar and upright conformers.

Ionization potentials for planar and upright $Ni(C_2H_4)_3$ are given in Table X. As with $Ni(C_2H_4)_2$ it is seen for the tris complex that there is a different energetic ordering of orbitals produced from Koopmans' theorem (i.e., the orbital energies ϵ) than by direct calculations on the appropriate positive ion states. For example, the 9e′ orbital is predicted to be the HOMO from its orbital energy, but in fact the more reliable ΔSCF treatment suggests that the $8a_1'$ orbital is the true HOMO. Extended Hückel theory[2] gives the Koopmans' theorem order for planar, but the ΔSCF order for upright.

Again it is helpful to have some idea of the nature of the orbitals from which electrons are ejected in analyzing these results. Qualitative sketches of the three highest molecular orbitals are given in Figure 3. For the lower energy planar conformation, the $8a_1'$ HOMO is, in the Mulliken picture, 84% Ni 3d and 12% carbon 2p, and has a relaxation energy of 6.68 eV. The 3e″ orbital is the second highest occupied MO and is 96% Ni 3d, with a positive ion relaxation energy of 7.57 eV. The 9e′ orbital is markedly mixed in character (59% Ni 3d, 38% carbon 2p) and has associated with it a relaxation energy of 5.15 eV. Similarly the 8e′ orbital is 22% Ni 3d and 77% carbon 2p. Finally the $7a_1'$ is also primarily ethylene-like, being 13% Ni 3d and 81% carbon 2p.

All three of the highest occupied MOs are primarily metal 3d in character and have large relaxation energies. As found for the bis complex, the largest relaxation energy occurs for the molecular orbital (3e″) with the largest fraction of Ni 3d character. Further, the smallest relaxation energy (5.15 eV) accompanies the removal of an electron from the orbital (9e′) with the greatest admixture of ethylene character. Finally we must emphasize that the three lowest predicted ΔSCF IPs are almost certainly lower than the true (but unknown) ionization potentials. As noted earlier, the correlation energy of the closed-shell ground state should be greater than that of the lowest $^2A_1'$, $^2E''$, and $^2E'$ molecular ion states.

Also given in Table X are the upright conformer IPs. Since this structure is predicted to lie 24 kcal higher, these IPs are generally of less interest. However, the lowest upright IP is remarkably small, only 1.55 eV. This means that, for the Ni-C bond distance chosen, the upright $^2E'$ state is the lowest electronic state of the $Ni(C_2H_4)_3^+$ molecular ion. The absolute energies of these states in the large basis set are −1740.627 28 (planar $^2A_1'$) and −1740.631 03 hartrees (upright $^2E'$). Thus the upright molecular ion lies 0.10 eV = 2.4 kcal below the planar molecular ion. The upright form will of course be further lowered in energy by a (presumably small) Jahn-Teller distortion. Such a qualitative change in molecular structure in going from neutral molecule to positive ion is certainly quite noteworthy.

Concluding Remarks

Reasonably large basis sets have been adopted here in ab initio self-consistent-field studies of $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$. Remaining qualitative differences between the present theoretical predictions and future experiments on these fascinating molecules can be traced to the effects of electron correlation. Some of these differences, for example energy separations between molecular states corresponding to nickel

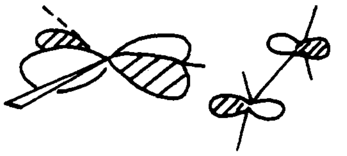
Table X. Predicted Ionization Potentials (eV) for Tris(η^2-ethene)-nickel(0) in Its Planar and Upright Conformations

	Koopmans' theorem	direct SCF treatment
planar	$\epsilon(8a_1') = 9.36$	$E(^2A_1') - E(^1A_1') = 2.68$
	$\epsilon(3e'') = 10.65$	$E(^2E'') - E(^1A_1') = 2.80$
	$\epsilon(9e') = 8.30$	$E(^2E') - E(^1A_1') = 3.15$
	$\epsilon(8e') = 10.87$	$E(^2E') - E(^1A_1') = 10.05$
	$\epsilon(7a_1') = 12.35$	$E(^2A_1') - E(^1A_1') = 12.11$
upright $Ni(C_2H_4)_3$	$\epsilon(8e') = 7.99$	$E(^2E') - E(^1A_1') = 1.55$
	$\epsilon(8a_1') = 9.56$	$E(^2A_1') - E(^1A_1') = 1.99$
	$\epsilon(4e'') = 7.84$	$E(^2E'') - E(^1A_1') = 2.29$
	$\epsilon(7e') = 11.46$	$E(^2E') - E(^1A_1') = 10.45$
	$\epsilon(7a_1') = 12.12$	$E(^2A_1') - E(^1A_1') = 11.46$

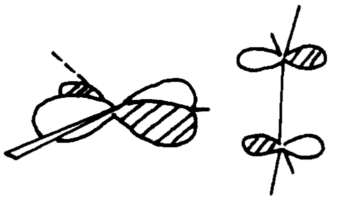
sd^9 and d^{10}, can be anticipated in advance and we have already suggested qualitative correlation corrections in some cases. For $Ni(C_2H_4)_2$ the planar and upright (see Figure 2) geometries are indistinguishable energetically. For the tris complex, however, the planar structure (Figure 1) is predicted to lie 24 kcal below the upright conformer. Quite surprisingly, the reverse order is found for the molecular ion $Ni(C_2H_4)_3^+$, with the upright ion predicted to lie 2 kcal below the planar form.

The reversal in $Ni(C_2H_4)_3$ conformational energetics with ionization may be discussed in terms of qualitative molecular orbital concepts. Rösch and Hoffmann[2c] have attributed the stability of planar $Ni(C_2H_4)_3$ over the upright geometry as being primarily due to the rising of the 2e′ orbital as the ethylenes rotate. This is explicitly illustrated in Figure 4. By simple extension it is seen that the removal of an electron from this highest occupied molecular orbital should at least lessen the preference for the planar geometry and may even disfavor it in $Ni(C_2H_4)_3^+$.

The same qualitative picture can be used to explain the diminished donation from Ni e′($d_{x^2-y^2}$, d_{xy}) into the π^* orbital of ethylene in the upright $Ni(C_2H_4)_3$ when compared with the planar. When the ethylenes are planar (5) the π^* orbitals of C_2H_4 have good overlap with $d_{x^2-y^2}$ and d_{xy} of Ni, so that the energy of 2e′ is low and the d→π^* donation is high. As the ethylenes rotate into the upright positions (6) this overlap is lost and the 2e′ orbital rises, while d→π^* donation is diminished. In brief, the stabilizing d→π^* donation is what favors planar $Ni(C_2H_4)_3$.


(5)

good overlap


(6)

no overlap

Both planar and upright $Ni(C_2H_4)_3$ can be qualitatively described as zerovalent nickel complexes, but the Mulliken charge on Ni of +0.34 in the former is significantly larger than +0.26 in the latter. Conversely, between the $Ni(C_2H_4)_2$ D_{2h} and D_{2d} conformations, where there was little energetic change when the ethylenes were rotated, the Ni charge remained constant.

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