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Molecular Orbital Studies of Bonding, Photoelectron Spectra, and Photoionization Transition States of Bis(π-allyl)nickel

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We report a molecular orbital study of bis(π-allyl)nickel, (η^3-C_3H_5)$_2$Ni. Calculations were performed by using both the Xα–SW and the Fenske–Hall methods. The two methods yield very similar results in terms of their eigenvectors and their sequences as well as their orbital populations and atomic charges. The HOMO is composed predominantly of the allyl $a_2(\pi^{NON})$ orbital. The Ni–allyl bonding involves the 4p as well as 3d functions of nickel. Xα–SW calculations were also performed on 12 transition states of the complex, formed by removing half an electron from each of the 12 uppermost filled molecular orbitals. Calculated ionization potentials correlate well with the photoelectron spectrum. The first ionization seems to arise from the HOMO. Transition-state eigenvalues of the orbitals localized on the metal atom depend appreciably upon the molecular orbital from which the half of an electron is removed, whereas transition-state eigenvalues of the orbitals localized on the ligand do not. Electron reorganization is most important for ionizations from molecular orbitals with large contributions from metal atomic functions.

1. Introduction

Since they were first isolated,[1] the allyl derivatives of transition metals have undergone substantial investigation. The literature abounds with details of the structure and chemistry of these compounds; this knowledge has often been reviewed.[2] Theoretical studies of the bonding and electronic structure of metal–allyl complexes have also been reported.[3-7] In particular, bis(π-allyl)nickel (η^3-C_3H_5)$_2$Ni has been the subject of a number of molecular orbital calculations,[6-13] at various levels of sophistication. Veillard and co-workers have performed rigorous Hartree–Fock calculations on the complex,[8,10,11] while the remainder of the studies employed semiempirical methods such as CNDO[9] and INDO,[13] among others.[7,12]

Despite the number of investigations, considerable confusion remains over which of the findings of these studies, if any, constitutes an accurate description of the electronic nature of bis(π-allyl)nickel. The different calculational methods have given widely different results for the energies and orderings of the molecular orbitals and for the ionization potentials. Attempts by the authors of these studies to interpret the photoelectron spectrum of the complex in terms of their calculations have lead to some controversy over the assignment of the spectral bands. Efforts to correlate the calculated and experimental ionization potentials have been further complicated by disagreement among spectroscopists as to the assignments of the spectral bands based upon purely experimental evidence.[9,13]

The validity and reliability of the individual calculations performed on (η^3-C_3H_5)$_2$Ni may also be questioned. Though the Hartree–Fock method is a rigorous and powerful tool for predicting the electronic structure of molecules, its applicability to large systems such as bis(π-allyl)nickel is limited, mainly because it neglects electron correlation and the formalism makes no attempt to compensate for it.[14] In the study by Veillard and others,[11] it was claimed that better agreement between calculated and experimental ionization potentials was obtained when a minimal basis set, rather than a double-ζ basis set, was used, due to a cancellation of error with neglect of the correlation energy. This suggests that correlation is important for this molecule and varies for different states of the system. Because these same studies found that Koopmans' theorem is invalid for this molecule, ionization potentials were calculated as the difference of energies between the ground state and the (η^3-C_3H_5)$_2$Ni$^+$ ion. This procedure leads to a loss of accuracy in the calculated ionization potentials and is extremely time consuming, and only values for a few of the uppermost ionizations were reported. The assignment of the lowest energy ionizations to removal of an electron from orbitals that lie 6–8 eV lower in energy than the HOMO indicated by the Hartree–Fock calculations has also been criticized.[14] The semiempirical studies of bis(π-allyl)nickel, though they involve more expedient calculations and are, therefore, more applicable to large systems, suffer from the potential for ambiguity due to the choice of values for the parameters associated with the calculations and sometimes they run the risk of being overparameterized.[14-16] Certainly the need is clear for a new theoretical study of bis(π-allyl)nickel based upon calculational methods that are well suited to the problem and that hopefully will provide new understanding into the electronic structure and bonding of this complex.

We have conducted a study of bis(π-allyl)nickel using both the Xα–SW and Fenske–Hall methods. Though not

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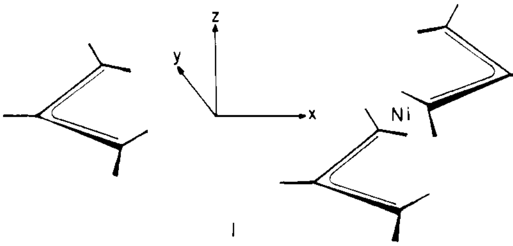
strictly ab initio, the Xα–SW method[17] is very rigorous and does not make use of empirical data. At the same time, it is less time consuming and more applicable to many-electron systems than is Hartree–Fock. The parameters the Xα–SW calculation does employ have been chosen by nonempirical means and in a manner consistent with many previous Xα studies. The Xα method makes possible the direct calculation of ionization potentials using Slater's transition-state theory,[18] making it very useful for interpretation of the photoelectron spectrum. The Fenske–Hall method[19] is an ab initio technique which involves approximations based on crystal field theory that make it quite useful in the studies of transition-metal complexes. Though neither of these methods treats electron correlation explicitly, it is hoped that the computational methods involved in each will compensate to some degree for the effect. We also hope that providing parallel studies on the same molecule with different calculational methods will provide some understanding of both the molecule being studied and the applicability of approximate (but nonempirical) molecular orbital techniques.

In our study of bis(π-allyl)nickel, we performed Xα–SW calculations on the free allyl radical and on the ground and many transition states of the complex. We projected the Xα–SW molecular orbitals for the ground state and for three transition states of $(\eta^3\text{-}C_3H_5)_2Ni$ onto a basis set of Slater-type orbitals and completed a Mulliken population analysis in order to investigate the electronic nature of these states and the nickel–allyl bonding in them. A Fenske–Hall calculation was carried out on the ground state of the complex.

2. Calculation Details

The Xα–SW method has been described elsewhere.[17] The coordinate systems used for these calculations are shown in 1. The geometry of bis(π-allyl)nickel was taken from crystallographic studies of bis(π-methallyl)nickel.[20] The allyl groups were planar. All C–H bond lengths were set equal to 1.09 Å and all H–C–H bond angles to 120°. The geometry of the allyl used in the unrestricted Xα–SW calculation of the free radical was the same as that of the allyl ligand in the complex. Initial molecular potentials were obtained by the method of Herman and Skillman.[21] Radii of the atomic spheres in the allyl radical were 88% of the corresponding atomic radii obtained in the calculation of the initial molecular potential for this molecule. In bis(π-allyl)nickel, the atomic sphere radii were 92% of the corresponding radii in the initial potential of the complex, in order to allow the atomic sphere of nickel to overlap with the atomic spheres of all six carbon atoms in the molecule. In both cases, all adjacent atomic spheres overlapped with one another, as Johnson and others recommend,[22] and the radii satisfied Norman's nonempirical rule for choosing them.[23] The outer sphere in every calculation was tangent to the outermost atomic spheres. The α_{HF} values for all atoms were those given by Schwarz,[24] except for H, which was 0.777 25, as suggested by Slater.[25] For the intersphere region, α was taken to be an average of the atomic values weighted by the number of valence electrons of each atom.



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The initial SCF calculations on the allyl radical and on the ground state of the complex could not converge, apparently because the desired molecular potentials of these systems were sufficiently different from the initial molecular potentials that they could not be attained by the SCF iterative procedure. When a Watson sphere[26] was applied to the molecules, the iterations converged rapidly and easily. The Watson sphere technique has long been used to stabilize the orbitals in Xα–SW calculations of anions.[27] Johnson and Smith have noted that the sequence of molecular orbitals and their energies are essentially unchanged by the presence of the Watson sphere.[28] In effect, the Watson sphere lowers the Xα–SW eigenvalues by a constant. In our calculations, the Watson sphere was concentric with the outer sphere with a radius slightly greater than that of the outer sphere. The charge on the outer sphere was 1.5+, which was the smallest charge that allowed convergence of the SCF calculations. To correct for the presence of the Watson sphere, the calculated eigenvalues were raised by a constant, q/R, where q is the charge on the Watson sphere and R is the radius. The constant is equal to the value of the electrostatic potential produced within the sphere by the uniformly distributed charge on the surface of the sphere. Only the corrected eigenvalues are presented in this paper.

The transition states[29] of the complex were formed by removing half of an electron from each of the 12 uppermost molecular orbitals. The resulting 0.5+ charge of these states had a sufficient effect upon the molecular potentials to allow convergence without the aid of a Watson sphere, and no Watson sphere was used in the calculations on the transition states.

The Xα–SW molecular orbitals were projected onto a basis set of Slater-type orbitals.[30] This basis set, optimized to the Xα atomic functions, was taken from the literature.[31] The basis set was better than minimal; it included double-ζ functions for the 3d, 4s, and 4p functions of nickel and for the 2s and 2p functions of carbon.

The Fenske–Hall method has also been described previously.[19] The method is devoid of adjustable parameters, so that results of the calculation are determined completely by molecular geometry and the basis functions. The ge-

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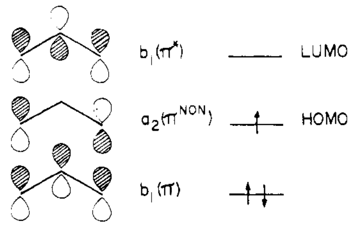
ometry of the complex was the same as that used in the Xα treatment. The STO basis functions for Ni were taken from the tables,[32] except that the exponent for the 4s function was 2.00. The basis functions for carbon were those of Clementi.[33] Only the 2p function, however, was kept in double-ζ form. The 1s and 2s functions were curve fit to single-ζ forms,[34] so that the number of exponents was minimized. The exponent for the 1s function of hydrogen was 1.16.

In our Fenske–Hall study of bis(π-allyl)nickel, we first carried out a separate calculation on $(C_3H_5)_2$, with the same geometry it has in $(\eta^3\text{-}C_3H_5)_2Ni$. The resulting molecular orbitals of the free ligand were used as a basis for the calculation on the complex, in order that the orbitals of the complex could be more easily interpreted in terms of their contributions from the allyl groups.

3. Xα Results: Bonding and Ionization Potentials

The allyl ligand has C_{2v} symmetry. Its three π molecular orbitals are $b_1(\pi)$, $a_2(\pi^{NON})$, and $b_1(\pi^*)$; they are shown in **2** and populated as in the allyl radical. The Xα–SW eigenvalues of its most important filled molecular orbitals are given in Table I. Note that the allyl radical is an open-shell system, and each of its molecular levels consists of two nondegenerate spin orbitals. The unpaired electron in $a_2(\pi^{NON})$ is assumed to have its spin up. The eigenvalues of the spin-up spin orbitals include the energy of an exchange interaction between these orbitals and the unpaired electron in $a_2(\pi^{NON})$. This interaction lowers the energies of the spin orbitals with their spins up relative to those with their spins down which are not subject to exchange with the unpaired electron. Because both the $b_1(\pi)$ and $a_2(\pi^{NON})$ orbitals are localized on the p_z functions of the carbon atoms, the exchange interaction is strongest for the spin-up spin orbital of the $b_1(\pi)$ level, and it is in this level that the difference between the energies of the spin-up and spin-down spin orbitals is largest. The energy of the exchange interaction is on the order of electronvolts. The exchange interaction with the unpaired electron in $a_2(\pi^{NON})$ is weaker for the $b_2(\sigma)$ and $a_1(\sigma)$ orbitals which are σ orbitals in the allyl plane with large contributions from the p_x and p_y functions of the carbon atoms.



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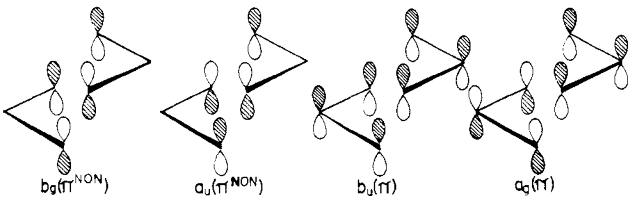
The Xα eigenvalues for the allyl radical are different from what one might expect them to be on the basis of experiment or the results of other calculations. The Xα eigenvalue of the HOMO $a_2(\pi^{NON})$ is predicted to be only −0.82 eV. A useful approximation to the Hartree–Fock eigenvalue of this orbital is obtained from an ab initio LCAO-SCF calculation on allyl cation, in which the eigenvalue of $a_2(\pi^{NON})$ (the LUMO of the cation) is −6.46 eV.[35] Applying Koopman's theorem, the Hartree–Fock eigenvalue is in reasonable agreement with the measured ionization potential of the radical at 8.13 eV.[36] Not only does the Hartree–Fock eigenvalue for the HOMO lie 5.64 eV below that obtained by Xα, but also it lies below the Xα eigenvalues for the filled $b_1(\pi)$ and $a_1(\pi)$ orbitals. This discrepancy between Xα and Hartree–Fock eigenvalues does not mean, however, that the Xα results are not meaningful. It must be remembered that Xα and Hartree–Fock eigenvalues have different theoretical bases and different physical meanings. In particular, Koopmans' theorem is invalid in Xα theory, and the Xα eigenvalues are not good approximations to the ionization potentials. The Xα orbital energies are raised relative to the corresponding Hartree–Fock energies by an unphysical coulomb repulsion between the orbital and itself.[37] The energy of this repulsion is the same as that of an exchange interaction between the orbital and itself, but with opposite sign. As indicated above, this energy may be on the order of electronvolts. More importantly, our results for allyl radical are consistent with Xα–SW results for other planar organic molecules, whose eigenvalues are also too high by several electronvolts, as indicated by comparison of the calculated ionization potentials and the experimental values.[38,39] Although the absolute magnitudes of the molecular orbital eigenvalues may be poor, these studies have shown that the sequences of the molecular orbitals and the energy separations between them are useful in the interpretation of molecular spectra. The discrepancy between the calculated and observed ionization potentials has been attributed to the muffin-tin approximation of the SW method,[22,40] which is particularly severe for planar molecules.[38] The use of overlapping atomic spheres in the molecular potential does improve upon the muffin-tin approximation in which the atomic spheres do not overlap, but it does not completely correct the difference between the calculated ionization potentials and the observed values. The Xα–SW method may not give good values for the orbital energies and for the total energy, but it does give the correct relative positions of the one-electron energies of many molecules.[22] In this work we will be concerned only with the sequence of the molecular orbitals and with the energy separations between them, and it is in light of the encouraging results of previous Xα studies that our findings are presented here.

The kinds of bonding interactions that may be found in bis(π-allyl)metal complexes have been discussed in detail,[3,6] and a brief review of these qualitative findings will be given here before we present the results of the molecular orbital calculations. The bis(allyl) fragment has C_{2h} symmetry, and its molecular orbitals are in-phase and out-of-phase combinations of the molecular orbitals of the individual allyl groups. The orbitals formed in this manner from the $a_2(\pi^{NON})$ and from the $b_1(\pi)$ orbitals of two allyl radicals are shown in **3**. Since the distance between the



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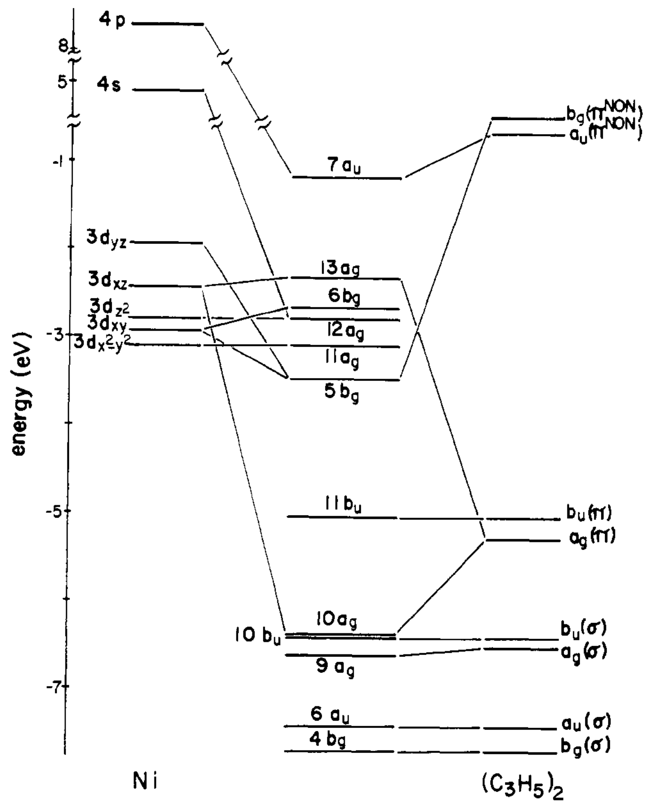

Figure 1. Molecular orbital diagram for (η^3-C$_3$H$_5$)$_2$Ni based on an Xα–SW calculation.

allyl ligands in the complex is great, we expect the orbital interactions between them to be weak. Thus, the molecular orbitals of (C$_3$H$_5$)$_2$ have nearly the same energies as the allyl molecular orbitals from which they are formed, and the energy separation between the in-phase and out-of-phase combinations is small. The two half-filled a$_2$(π^{NON}) orbitals of the individual allyl radicals give rise to the HOMO a$_u$(π^{NON}) and LUMO b$_g$(π^{NON}) in the bis(allyl) fragment. The filled b$_1$(π) orbitals give rise to the bis(allyl) orbitals a$_g$(π) and b$_u$(π). Of these four molecular orbitals only the a$_g$(π) and b$_g$(π^{NON}) combinations have proper symmetry to interact with the d orbitals of the central metal atom; by symmetry, b$_g$(π^{NON}) will mix with d$_{xy}$ and d$_{yz}$, and a$_g$(π) will mix with d$_{z^2}$, d$_{x^2-y^2}$ and d$_{xz}$. Of these interactions, those involving d$_{xz}$ and d$_{yz}$ will be the strongest because these d functions are the ones directed most toward the allyl ligands and have the greatest overlap with the ligand orbitals. The a$_g$(π) orbital of (C$_3$H$_5$)$_2$ may also interact with the metal s functions. The a$_u$(π^{NON}) and b$_u$(π) molecular orbitals, however, are allowed by symmetry to mix only with the metal p functions. Large differences in energy between the low-lying orbitals of the ligand and the valence functions of the metal atom prevent significant mixing of these orbitals, even when the overlaps between them may be large. Thus the low-lying molecular orbitals of the bis(allyl) fragments do not contribute appreciably to bonding in the complex. For (η^3-C$_3$H$_5$)$_2$Ni, we expect the most significant bonding interactions to occur between the b$_g$(π^{NON}), a$_u$(π^{NON}), a$_g$(π), and b$_u$(π) orbitals of (C$_3$H$_5$)$_2$ and the 3d$_{xz}$, 3d$_{yz}$, 4s, and 4p$_y$ functions of the nickel atom.

This qualitative description of the bonding in bis(π-allyl)nickel is in complete agreement with the results of the Xα calculation on the ground state of the complex. The Xα eigenvalues and eigenvectors are presented in Table II and in Figure 1. The placements of the energy levels of the nickel and free bis(allyl) orbitals in the MO diagram are inferred from the energies of the molecular

Table I. Energies of the Uppermost Filled Spin Orbitals of Allyl Radical

orbital	energies, eV spin up	energies, eV spin down
a$_2$(π^{NON}) (HOMO)	−0.82	
b$_1$(π)	−5.65	−4.44
a$_1$(σ)	−6.43	−6.17
b$_2$(σ)	−7.15	−7.06

Table II. Energies and Percent Compositions of the Uppermost Filled MOs of the Ground State of (η^3-C$_3$H$_5$)$_2$Ni, from an Xα Calculation

		Ni									C						H		
											terminal			central			terminal		central
orbital	energy, eV	3d$_{z^2}$	3d$_{x^2-y^2}$	3d$_{xy}$	3d$_{xz}$	3d$_{yz}$	4s	4p$_x$	4p$_y$	4p$_z$	2p$_x$	2p$_y$	2p$_z$	2p$_x$	2p$_y$	2p$_z$	1s	1s	1s
7a$_u$	−0.14								17				83						
13a$_g$	−1.31				83		4						6						
6b$_g$	−1.64			59		33							3						
12a$_g$	−1.76	87	3				9												
11a$_g$	−2.06		91				3												
5b$_g$	−2.44			37		36							23						
11b$_u$	−4.04												58			40			
10a$_g$	−5.38				9		5						52			33			
10b$_u$	−5.41										12			20			10	16	36
9a$_g$	−5.60				3		4				11			20			10	14	34
6a$_u$	−6.42										16	30					38	16	
4b$_g$	−6.70					5					13	32					39	11	

Table III. Orbital Populations (in Electrons) and Atomic Charges in the Ground State of $(\eta^3\text{-}C_3H_5)_2Ni$, from an Xα Calculation

atomic orbital	Ni	atomic orbital	C terminal	C central	atomic orbital	H terminal	H terminal	H central
$3d_{z^2}$	1.81	2s	1.07	0.88	1s	1.06	1.06	1.11
$3d_{x^2-y^2}$	1.90	$2p_x$	0.96	0.95				
$3d_{xy}$	1.94	$2p_y$	1.03	1.06				
$3d_{xz}$	1.93	$2p_z$	1.02	0.75				
$3d_{yz}$	1.53							
4s	0.35							
$4p_x$	−0.02							
$4p_y$	0.32							
$4p_z$	−0.04							
atomic charges	0.28		0.08−	0.36		0.06−	0.06−	0.11−

orbitals to which they contribute and are only approximate. The Xα molecular orbital energies for the complex are much higher than the corresponding ab initio eigenvalues[11] and ionization potentials,[9] but they are very similar to the Xα–SW results for free allyl radical. The consistency of the Xα eigenvalues obtained in separate calculations on allyl radical and on the complex indicates that the high energies of the molecular orbitals of bis(π-allyl)nickel result from the Xα–SW treatment of the allyl ligands and not from its treatment of the complex as a whole. In view of our arguments presented above for the relevance of the Xα–SW results for allyl radical and in view of the success of Xα calculations on similar transition-metal complexes,[41–43] we believe that the results for bis(π-allyl)nickel are quite meaningful.

As the PXα results in Table II show, mixing of metal and ligand orbitals is small. The only significant interactions (greater than 10% contributions from both metal and ligand orbitals in the resulting molecular orbitals) occur between the $b_g(\pi^{NON})$ orbital of bis(allyl) fragment and the $3d_{yz}$ and $3d_{xy}$ orbitals of nickel to form the $5b_g$ orbital in the complex and between the $a_u(\pi^{NON})$ orbital of the ligand and $4p_y$ function of nickel to form $7a_u$. The $a_g(\pi)$ orbitals of $(C_3H_5)_2$ and the nickel $3d_{xz}$ function also mix somewhat with each other to form the molecular orbitals $10a_g$ and $13a_g$. The nickel $3d_{z^2}$ and $3d_{x^2-y^2}$ functions remain essentially unperturbed in the molecule, as does the $b_u(\pi)$ orbital of the ligands; they correspond to the molecular orbitals $12a_g$, $11a_g$, and $11b_u$ of the complex, respectively. The other low-lying orbitals in $(\eta^3\text{-}C_3H_5)_2Ni$ are either essentially pure ligand ($10b_u$ and $6a_u$) or are ligand orbitals only slightly perturbed by the metal orbitals ($9a_g$ and $4b_g$).

The Mulliken populations[44] of atomic orbitals in the ground state of bis(π-allyl)nickel, shown in Table III, reveal a complex donor–acceptor relationship between the allyl ligands and the nickel atom. The calculated occupation number of Ni $3d_{yz}$ is only 1.53 e, while for the other d functions it is almost 2.00 e. As mentioned above, $3d_{yz}$ is directed toward the ligands and overlaps with the ligand orbitals. In particular, $3d_{xz}$ is directed toward the terminal carbons of the allyl groups and overlaps the empty $b_g(\pi^{NON})$ orbital. Because $3d_{yz}$ and $b_g(\pi^{NON})$ overlap and because they are strongly mixed in the $5b_g$ molecular orbital of the complex ($5b_g$ is 36% d_{yz}, 37% d_{xy}, and 24% $b_g(\pi^{NON})$), charge is transferred from the nickel atom to the $2p_z$ functions of the terminal carbon atoms. At the same time, mixing and overlap of the $a_u(\pi^{NON})$ orbital of the bis(allyl) fragment with nickel $4p_y$ leads to a donation of charge from these same carbon p_z orbitals back to the metal. In a similar way, charge is transferred from the ligands to nickel 4s by its interaction with the bis(allyl) $a_g(\pi)$ orbital. The net effect of these and other less important interactions is a small positive charge on the metal atom, and a charge on the terminal carbon atoms that is considerably more negative than that of the central carbon atoms. The negative populations of the nickel $4p_x$ and $4p_z$ functions are due to the out-of-phase mixing of these orbitals with low-lying ligand orbitals.[45] Most theorists agree that Mulliken atomic charges are often not true in the absolute sense but that their qualitative pattern is realistic.[46] This population analysis of bis(π-allyl)nickel shows that the nickel $3d_{yz}$, 4s, and $4p_y$ functions make the most significant contributions to bonding in the complex. This is an especially interesting result since previously reported molecular orbital studies on this molecule either failed to include the Ni 4p functions in their calculations or neglected to report what influence, if any, these functions had on their results.

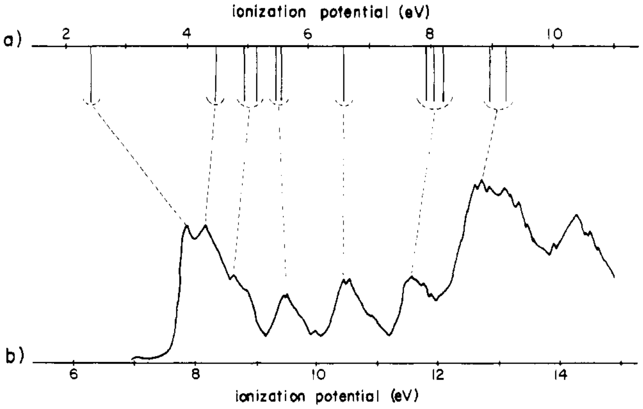

Figure 2. Calculated ionization potentials (a) and actual photoelectron spectrum (b) of $(\eta^3\text{-}C_3H_5)_2Ni$.

We performed Xα–SW calculations on 12 transition states formed by removing half of an electron from each of the 12 uppermost filled molecular orbitals of the complex. The calculated eigenvalues for the molecular orbitals in these states appear in Table IV. The absolute values

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(41) (a) Rösch, N.; Rhodin, T. N. *Phys. Rev. Lett.* **1974**, *32*, 1189–92. (b) Rösch, N.; Messmer, R. P.; Johnson, K. H. *J. Am. Chem. Soc.* **1974**, *96*, 3855–60. (c) Rösch, N.; Johnson, K. H. *Chem. Phys. Lett.* **1974**, *24*, 179–84. (d) Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064–9.

(42) Barends, E. J.; Ros, P. *Chem. Phys. Lett.* **1973**, *23*, 391–3.

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(44) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–40.

(45) (a) Whangbo, M.-H.; Hoffman, R. *J. Chem. Phys.* **1978**, *68*, 5498–500. (b) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686–92.

(46) Schaefer, H. F. "The Electronic Structure of Atoms and Molecules"; Addison-Wesley: Reading, MA, 1972; p 384.

Table IV. Eigenvalues (in eV) of the Uppermost Filled MOs in the Transition States of $(\eta^3\text{-}C_3H_5)_2Ni$[a]

	ionized MO											
orbital	$7a_u$	$13a_g$	$6b_g$	$12a_g$	$11a_g$	$5b_g$	$11b_u$	$10a_g$	$10b_u$	$9a_g$	$6a_u$	$4b_g$
$7a_u$	$\underline{-2.48}$	−2.55	−2.56	−2.56	−2.56	−2.56	−2.55	−2.56	−2.49	−2.50	−2.48	−2.49
$13a_g$	−3.69	$\underline{-4.50}$	−4.59	−4.64	−4.65	−4.52	−3.78	−3.89	−3.71	−3.74	−3.67	−3.71
$6b_g$	−4.04	−4.91	$\underline{-5.01}$	−5.06	−5.07	−4.93	−4.13	−4.25	−4.05	−4.08	−4.02	−4.06
$12a_g$	−4.16	−5.04	−5.14	$\underline{-5.21}$	−5.22	−5.06	−4.24	−4.37	−4.17	−4.20	−4.12	−4.16
$11a_g$	−4.46	−5.36	−5.46	−5.52	$\underline{-5.53}$	−5.37	−4.55	−4.67	−4.47	−4.50	−4.42	−4.46
$5b_g$	−4.84	−5.59	−5.68	−5.74	−5.75	$\underline{-5.61}$	−4.93	−5.03	−4.85	−4.87	−4.83	−4.86
$11b_u$	−6.42	−6.52	−6.52	−6.53	−6.53	−6.53	$\underline{-6.57}$	−6.58	−6.52	−6.53	−6.46	−6.46
$10a_g$	−7.77	−7.94	−7.95	−7.95	−7.96	−7.95	−7.92	$\underline{-7.94}$	−7.85	−7.87	−7.80	−7.81
$10b_u$	−7.68	−7.74	−7.74	−7.74	−7.74	−7.75	−7.83	−7.82	$\underline{-8.04}$	−8.02	−7.76	−7.76
$9a_g$	−7.88	−8.02	−8.04	−8.05	−8.06	−8.03	−8.03	−8.03	−8.22	$\underline{-8.20}$	−7.96	−7.96
$6a_u$	−8.69	−8.74	−8.75	−8.73	−8.73	−8.75	−8.80	−8.79	−8.80	−8.80	$\underline{-8.96}$	−8.95
$4b_g$	−8.98	−9.07	−9.09	−9.09	−9.09	−9.09	−9.09	−9.09	−9.08	−9.09	−9.23	$\underline{-9.23}$

[a] Absolute values of the underlined numbers represent the calculated ionization energies.

of the underlined terms in this table are the calculated ionization potentials for each state, in the framework of Slater's transition state theory.[18]

A photoelectron "spectrum" of bis(π-allyl)nickel, constructed from the calculated ionization potentials, is shown schematically in Figure 2. The experimental spectrum,[9] drawn to the same scale, is shown below it for comparison. By comparing the spectra of bis(π-allyl)nickel to that of its Pd and Pt analogues, Böhm, Gleiter, and Batich[13] have given convincing evidence that the fifth peak in the experimental spectrum can be assigned to ionization from the ligand $b_u(\pi)$ orbital ($11b_u$ in the Ni compound). Thus we have arbitrarily aligned the experimental and calculated values for this ionization in our comparison. Except for the first band, there is good correlation between the two spectra. The actual photoelectron bands are quite broad, especially at high ionization energy, and the first three bands are barely resolved. If one considers these aspects of the observed spectrum, the calculated ionizations from $11a_g$ and $5b_g$ lie too close in energy to be resolved. We combined them into a single band. We did the same for the ionizations from $10a_g$, $11b_u$, and $9a_g$, from $6b_g$ and $5b_g$, and from $4b_g$ and $6a_u$. We give our final assignments of the photoelectron spectrum in Table V, along with the experimental ionization potentials and the qualitative assignments made by Böhm, Gleiter, and Batich from their empirical studies of the spectrum.[13] A comparison of these two assignments will be discussed later.

4. The Transition States

Although the transition states do not represent physically real systems, we believe that a comparative study of the eigenvalues, eigenvectors, and charge distributions of these "half-ionized" states relative to those of the ground state will show the same trends and qualitative behavior that would be observed if calculations were performed on the various "fully ionized" states.

Comparison of Tables III and IV shows that all molecular orbitals of bis(π-allyl)nickel are stabilized in each transition state. Some eigenvalues are as much as 3.5 eV lower in the transition states than in the ground state. The sequence of the levels is the same in these states as in the ground state, except for the inversion in some of the transition states of the orbitals $10a_g$ and $10b_u$, which lie very close in energy. The extent of stabilization for the orbitals that are largely ligand ($7a_u$, $11b_u$, $10a_g$, $10b_u$, $9a_g$, $6a_u$, $4b_g$) is fairly independent of the transition state. The energy of each of these orbitals varies by only 0.36 eV or less among the 12 transition states. For the five molecular orbitals that are largely centered on nickel ($13a_g$, $6b_g$, $12a_g$, $11a_g$, $5b_g$), the extent of stabilization depends upon the orbital from which the half electron is removed and is greatest when the "half-ionized" orbital is one of these same five. The energy of any one of these predominantly metal-localized orbitals varies by as much as 1.1 eV among the different transition states. A similar situation has been found in the Xα analyses of ferrocene[42] and of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$.[43] The behavior of the energies of various molecular orbitals in different transition states indicates that stabilization of orbitals upon formation of the "half-ionized" states is due primarily to the partial positive charge of these states. Mulliken population analyses of the transition states (to be presented later in this section) show that when electron charge is removed from the highly delocalized ligand orbitals, the resulting positive charge acts as if it were spread out over the whole molecule. However, electron charge removed from the metal-localized orbitals creates a positive charge in the vicinity of the nickel atom. Molecular orbitals with large metal character are affected most by the partial positive charge when it is localized near the metal atom, and so stabilization of these orbitals is greater upon ionization of the predominantly metal orbitals than upon ionization of the predominantly ligand orbitals. Molecular orbitals that are largely ligand in character are delocalized. The metal atom is situated at the center of symmetry of these orbitals. The influence of the partial positive charge upon the predominantly ligand orbitals is practically the same whether the charge is localized on the central metal atom or is spread symmetrically over the whole molecule, so the extent of stabilization is very similar for ionizations both from metal-localized orbitals and from ligand-localized orbitals. This conclusion is further supported by the observation that the energies of the predominantly metal molecular orbitals are consistently higher in the transition states formed by ionization of the $13a_g$ and $5b_g$ orbitals than in those formed by ionization of the other molecular orbitals, indicating that the extent of stabilization of the metal orbitals is smallest for these two transition states. This is just as one would expect since the partial positive charge resulting from ionization of $5b_g$ or $13a_g$ (which are predominantly metal in character but contain significant contributions from ligand orbitals) is less localized on the nickel atom than the positive charge resulting from ionization of an orbital with more metal character. Decrease in the interelectron repulsion upon partial ionization also contributes to stabilization of the molecular orbitals.

Besides the changes in the eigenvalues, ionization brings about alterations in the compositions of the molecular orbitals. The orbitals of the $11a_g$, $5b_g$, and $11b_u$ transition states were projected onto the basis set of STOs, and the results are shown in Table VI. These transition states were chosen in order to investigate the effects of ionization from orbitals that are essentially pure metal in character ($11a_g$), orbitals that are essentially pure ligand ($11b_u$), and orbitals with significant contributions from both metal and ligand orbitals ($5b_g$) upon the electronic nature of bis(π-allyl)nickel. In the $5b_g$ and $11a_g$ transition states, all the high-lying molecular orbitals show significant changes in their atomic orbital compositions. Some molecular orbitals become more polarized in the same sense in which they were polarized in the ground state: $7a_u$ gains terminal carbon p_z character while $11a_g$, $12a_g$, and $5b_g$ all gain nickel d character. Other molecular orbitals become less polarized: $13a_g$ and $6b_g$ lose nickel d character, while $10a_g$, $9a_g$, and $4b_g$ lose ligand orbital character. The low-lying molecular orbitals that are essentially pure ligand in character are unchanged in these transition states. In the $11b_u$ transition state, however, only the molecular orbital $7a_u$ shows any appreciable change in its composition.

These findings support the claim[10] that significant electronic rearrangement occurs upon ionization from molecular orbitals that are largely localized on the metal atom but does not occur upon ionization from orbitals that are localized on the allyl ligands. Additional evidence that electronic reorganization is most important for ionizations from orbitals predominantly metal in character is obtained by comparison of the Mulliken populations of the transition states in Table VII with those of the ground state in Table III. In all but two atomic orbitals (d_{yz} of nickel and p_z of the central carbon atoms), the change in the atomic populations of the $11a_g$ and $5b_g$ transition states relative to the ground-state populations are greater than or equal to the changes found for the $11b_u$ transition state. This analysis also shows that the 0.5+ charge of the transition states is 46% localized on the metal atom for the $11a_g$ transition state and 36% localized on the metal atom for the $5b_g$ transition state and is spread over the ligands in the $11b_u$ transition state.

5. Fenske-Hall Results

The Fenske-Hall eigenfunctions and eigenvalues for the ground state of bis(π-allyl)nickel are presented in Table VIII and Figure 3. The use of a transformed basis for the ligand orbitals makes clear the role the bis(allyl) molecular orbitals have in bonding in the complex. The contributions from various ligand orbitals to each of the molecular orbitals of the complex are now apparent.

The Fenske-Hall calculation gives more reasonable orbital energies than does the Xα calculation. The eigenvalues are in the same range of energies as those obtained by ab initio Hartree-Fock calculations.[11] Nonetheless, the Fenske-Hall and Xα methods yield very similar sequences of the six uppermost filled molecular orbitals, of their energy differences, and of their compositions. The only difference between the results of the two calculations is in the relative positions of the lower lying levels. This discrepancy can be attributed, at least in part, to the alleged failure of methods that invoke the Mulliken approximation (the Fenske-Hall method is such) to correctly estimate the energy differences between σ and π orbitals in simple organic molecules.[47] In the Fenske-Hall results, the $b_u(\pi)$ and $a_g(\pi)$ levels of the bis(allyl) fragment lie among several σ levels. In the Xα results, however, the σ and π levels are well separated, as indicated by our calculation on allyl radical and by the 1.4-eV separation between $11b_u$ and $10b_u$ in the Xα results for the complex. Despite minor differences, the results of the two methods are consistent with each other. The orbital populations and the atomic charges in Tables III and IX are qualitatively the same. Transformation of the ligand basis set clearly shows electron transfer from $3d_{yz}$ into $b_g(\pi\text{-}^{NON})$, from $a_u(\pi^{NON})$ into $4p_y$, and from $a_g(\sigma)$ into 4s.

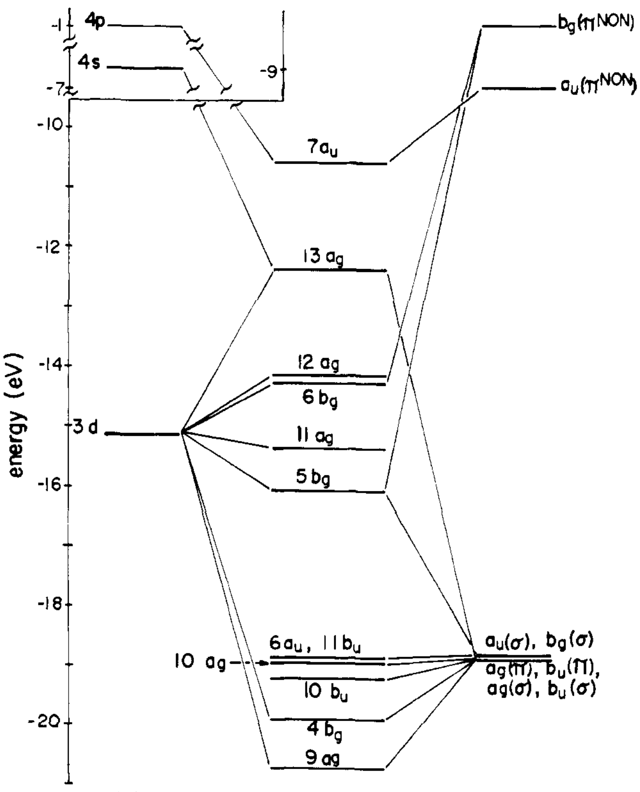

Figure 3. Molecular orbital diagram for $(\eta^3\text{-}C_3H_5)_2Ni$ based on a Fenske-Hall calculation.

Concluding Remarks

The molecular orbital description of bis(π-allyl)nickel obtained by our Xα-SW calculation is not very unlike those obtained by previous calculations on this molecule, but there are some, often major, differences. In agreement with the majority of the previous investigations,[7,8,10,11,13] our study shows the HOMO to be composed predominantly of the allyl $a_2(\pi^{NON})$ orbital. The compositions of the remaining molecular orbitals are similar to those obtained by the INDO[13] calculation but are very different from those obtained by the Hartree-Fock method.[10,11] In comparison to those of Xα, the Hartree-Fock eigenfunctions show a much greater degree of mixing between the ligand and Ni 3d orbitals, with eight of the 12 highest energy molecular orbitals showing greater than 10% contributions from both metal and ligand orbitals, as compared to two such molecular orbitals in the Xα results. The Hartree-Fock results also show considerable mixing between metal 3d orbitals and the σ orbitals of allyl, in contrast to the Xα results and to the qualitative predictions discussed in section 3.

The ordering and spacings of the molecular orbital energies predicted by Xα are quite different from those of earlier studies, especially in the position of the molecular orbital $11b_u$ relative to the other levels. Previous calculations[10,11,13] have placed $11b_u$ (essentially pure ligand in character) higher in energy than several orbitals that are predominantly Ni 3d in character ($12a_g$, $11a_g$, and $5b_g$),

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[47] Nicholson, B. J. *Adv. Chem. Phys.* **1970**, *18*, 249-312.

Table V. Experimental Ionization Potentials and Their Assignments for $(\eta^3\text{-}C_3H_5)_2Ni$

ionization potential, eV	assignments	
	this study	ref 13
7.85	$7a_u$	$7a_u$
8.17	$13a_g$	$13a_g$, $12a_g$, $11a_g$
8.59	$6b_g$, $12a_g$	$5b_g$
9.48	$5b_g$, $11a_g$	$6b_g$
10.44	$11b_u$	$11b_u$
11.56	$10b_u$, $9a_g$, $10a_g$	$9a_g$
12.75	$4b_g$, $6a_u$	$6a_u$, $10b_u$, $10a_g$, $4b_g$

Table VI. Percent Compositions of the Uppermost Filled MOs in Three Transition States of $(\eta^3\text{-}C_3H_5)_2Ni$

											C						H		
		Ni									terminal			central			terminal		central
		$3d_{z^2}$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	4s	$4p_x$	$4p_y$	$4p_z$	$2p_x$	$2p_y$	$2p_z$	$2p_x$	$2p_y$	$2p_z$	1s	1s	1s
$7a_u$	$11a_g$								14				86						
	$5b_g$								14				86						
	$11b_u$								14				86						
$13a_g$	$11a_g$				76		5				3		8						
	$5b_g$				78		5				3		8						
	$11b_u$				82		4				...		6						
$6b_g$	$11a_g$			42		46							4				3		
	$5b_g$			45		44							4				3		
	$11b_u$			59		33							3				...		
$12a_g$	$11a_g$	92	...				5												
	$5b_g$	91	...				5												
	$11b_u$	88	3				7												
$11a_g$	$11a_g$	...	96																
	$5b_g$	...	96																
	$11b_u$	3	94																
$5b_g$	$11a_g$			55		30							11						
	$5b_g$			52		32							12						
	$11b_u$			38		40							19						
$11b_u$	$11a_g$												58				40		
	$5b_g$												58				40		
	$11b_u$												58				40		
$10a_g$	$11a_g$				18		...				4		31	4		19	3	6	11
	$5b_g$				16		...				3		29	6		18	4	8	13
	$11b_u$				9		5				...		51	...		33	...	...	...
$10b_u$	$11a_g$										12			20			10	16	37
	$5b_g$										12			20			10	16	37
	$11b_u$										12			20			10	16	36
$9a_g$	$11a_g$				...		10				7		17	15		12	6	7	23
	$5b_g$				...		10				6		20	14		14	6	6	21
	$11b_u$				3		4				11		...	20		...	10	14	34
$6a_u$	$11a_g$										15	30					37	16	
	$5b_g$										15	30					38	16	
	$11b_u$										16	30					37	16	
$4b_g$	$11a_g$					8					12	32					38	9	
	$5b_g$					8					12	32					37	10	
	$11b_u$					5					13	31					37	12	

Table VII. Orbital Populations (in Electrons) and Atomic Charges in Three Transition States of $(\eta^3\text{-}C_3H_5)_2Ni$

atomic orbitals	ionized MO $11a_g$	$5b_g$	$11b_u$
	Orbital Populations		
	Ni		
$3d_{z^2}$	1.91	1.90	1.86
$3d_{x^2-y^2}$	1.48	1.96	1.95
$3d_{xy}$	1.96	1.70	1.95
$3d_{xz}$	1.94	1.94	1.92
$3d_{yz}$	1.72	1.56	1.62
4s	0.28	0.28	0.30
$4p_x$	−0.02	−0.02	−0.02
$4p_y$	0.26	0.26	0.26
$4p_z$	−0.04	−0.04	−0.04
	Terminal C		
2s	1.03	1.03	1.03
$2p_x$	0.95	0.96	0.96
$2p_y$	1.02	1.02	1.02
$2p_z$	1.10	1.09	1.06
	Central C		
2s	0.91	0.91	0.92
$2p_x$	0.95	0.95	0.96
$2p_y$	0.95	0.95	0.96
$2p_z$	0.74	0.74	0.65
	Terminal H		
1s	1.02	1.01	1.01
1s	1.05	1.05	1.05
	Central H		
1s	1.11	1.11	1.10
	Atomic Charges		
Ni	0.51	0.46	0.20
terminal C	0.10−	0.10−	0.07−
central C	0.45	0.45	0.07−
terminal H	0.02−	0.01−	0.01−
H	0.05−	0.05−	0.05−
central H	0.11−	0.11−	0.11−

while the Xα results indicate that $11b_u$ lies well below these orbitals in energy. Only the Wolfsberg–Helmholtz-like calculation of Brown and Owens[7] has produced the same ordering and qualitatively the same spacing of orbitals as the Xα–SW calculation.

The charge distribution within $(C_3H_5)_2Ni$ obtained by our calculation is also quite different from those of earlier studies,[10,11,13] especially in the degree of charge donation between the metal and its ligand. The authors of both the INDO and Hartree–Fock calculations have reported a transfer of charge from the Ni 3d orbitals to the $b_g(\pi^{NON})$ orbital of bis(allyl) of roughly the same magnitude as that predicted by Xα but have failed to report any degree of charge donation (if indeed, any was indicated by their calculations) from the $a_u(\pi^{NON})$ orbital of the ligand to the 4p functions of the metal atom. As a result, both the INDO and Hartree–Fock descriptions of the complex show a greater positive charge (by approximately half an electron) on the metal atom than is found in our Xα calculations. The stabilizing effect of the positively charged metal atom on the molecular orbitals with predominant metal character, and the corresponding destabilizing effect of the negatively charged ligands on the molecular orbitals with predominant allyl character, may explain in part the differences in the ordering of the molecular orbitals of bis(π-allyl)nickel obtained by the INDO and Hartree–Fock calculations and that found in our Xα calculations. Again, the Xα results agree most with those of the Wolfsberg–Helmholz-like calculation which indicates the same kinds of donations of charge among orbitals as the Xα calculation and only a small positive charge on the nickel atom.

Table VIII. Energies and Percent Compositions of the Uppermost Filled MOs in $(\eta^3\text{-}C_3H_5)_2Ni$ from a Fenske–Hall Calculation

orbital	energy, eV	$3d_{z^2}$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	4s	$4p_x$	$4p_y$	$4p_z$	$b_g(\pi^{NON})$	$a_u(\pi^{NON})$	$b_u(\pi)$	$a_g(\pi)$	$b_u(\sigma)$	$a_g(\sigma)$	$a_u(\sigma)$	$b_g(\sigma)$
$7a_u$	−10.48								16			83						
$13a_g$	−12.29	9			57		13							7		10		
$12a_g$	−14.07	78			13		2							2				
$6b_g$	−14.22			60		24					5							4
$11a_g$	−15.34		95															
$5b_g$	−15.98			31		19					25							23
$6a_u$	−18.79																99	
$11b_u$	−18.82												83		17			
$10a_g$	−18.91						2							78		18		
$10b_u$	−19.16									5			17		78			
$4b_g$	−19.84			3		18					5							70
$9a_g$	−20.67				19		2							13		60		

Table IX. Orbital Populations (in Electrons) and Atomic Charges for $(\eta^3\text{-}C_3H_5)_2Ni$ from a Fenske-Hall Calculation

Ni orbitals	pop.	$(C_3H_5)_2$ orbitals	pop.
$3d_{z^2}$	1.91	$b_g(\pi^{NON})$	0.70
$3d_{x^2-y^2}$	1.94	$a_u(\pi^{NON})$	1.67
$3d_{xy}$	1.94	$b_u(\pi)$	2.01
$3d_{xz}$	1.89	$a_g(\pi)$	2.01
$3d_{yz}$	1.41	$b_u(\sigma)$	1.89
4s	0.28	$a_g(\sigma)$	1.78
$4p_x$	0.01	$a_u(\sigma)$	1.98
$4p_y$	0.28	$b_g(\sigma)$	1.97
$4p_z$	0.09		

		C		H		
	Ni	terminal	central	terminal		central H
atomic charges	0.26	0.19−	0.21	0.02	0.02	0.04−

More importantly, the results of our calculations of ionization potentials by the Xα–SW method agree well with the qualitative assignments made by Böhm, Gleiter, and Batich in their careful comparative study of the photoelectron spectra of bis(π-allyl)nickel and its palladium and platinum analogues.[13] The assignments in Table V are very similar, minor discrepancies arising only when a given transition is assigned to one of two adjacent bands. Note that in some cases the authors of ref 13 had a choice in assigning a given ionization to one of two equally probably adjacent bands. The authors also used the integrated intensities of the spectral bands in determining how many assignments were to be made to each band, while ignoring possible variations in the photoionization cross sections. There are qualitative and semiquantitative methods of estimating the photoionization cross sections that indicate that the variation among these quantities for different ionizations may be substantial.[12] The poor resolution of the spectrum also makes such a method difficult. In view of these considerations, the minor discrepancies found between our assignments and those of ref 13 are not at all surprising or worrisome.

Both our results and those of ref 13 agree exactly upon the assignment of the first and fifth bands of the spectrum to ionizations from orbitals largely localized on the ligands. This is especially heartening to us because of Böhm, Gleiter, and Batich's convincing evidence for this assignment. Although earlier empirical studies[9,12] of the photoelectron spectra of $(C_3H_5)_2Ni$ have assigned the first band to ionization from orbitals with predominant Ni 3d character, Böhm, Gleiter, and Batich, by employing all of the experimental methods used in the previous studies, have shown that their assignments are consistent with all the experimental evidence. The assignments made in any study of photoelectron spectra depend a great deal on how the experimental observations are interpreted, and certainly none of the assignments for bis(π-allyl)nickel are completely free from some degree of ambiguity. However, we believe that the assignments of ref 13 support the results of our Xα–SW calculations and shown them to be reasonable and in good agreement with experimental evidence.

In regard to previous theoretical calculations of the ionization energies of bis(π-allyl)nickel, we should note that our Xα calculations are the first nonempirical calculations that show ionization from the HOMO $7a_u$ to be the source of the first band in the photoelectron spectrum. Hartree–Fock calculations[10,11] have indicated that the energy of ionization from this orbital is greater than that from several predominantly Ni 3d orbitals, due to the effects of substituted rearrangement of the molecular charge distribution upon removal of an electron from the metal 3d orbitals. Electronic rearrangement is also cited in both the Hartree–Fock and INDO studies[10,11,13] as the cause for other differences between the relative order of the molecular orbital energies and their corresponding ionization energies. The differences in order between the orbital energies and ionization energies are quite substantial; the energy of ionization for the orbital $11b_u$, for example, is several electronvolts higher than that of the orbitals $11a_g$, $12a_g$, and $5b_g$ in both the Hartree–Fock and INDO calculations, even though the energy of $11b_u$ is several electronvolts higher than those of these same orbitals in the ground state of the complex.

The Xα results also show an electronic rearrangement that is most pronounced for ionizations from metal orbitals (see section 4), but the effects produced by such a rearrangement on the calculated ionization potentials do not seem to be as dramatic as in the previous studies. The order of the ionization energies produced by Xα is the same as that of the eigenvalues in the ground state, which in turn is identical with the order of the eigenvalues in each of the transition states $11a_g$, $5b_g$, and $11b_u$. Thus, unlike those of the Hartree–Fock and INDO methods, the Xα eigenvalues provide a qualitative first approximation to the interpretation of the photoelectron spectrum of bis(π-allyl)nickel. Such is also the case for Xα–SW calculations on ferrocene[42] and $(\eta^4\text{-}C_4H_4)Fe(CO)_3$,[43] though many more calculations on a wider range of compounds will have to be performed before the generality and applicability of this observation is known.

The results of our Xα–SW calculations on bis(π-allyl)nickel, therefore, while reproducing many of the same features found in previous theoretical investigations on this compound, also have revealed some important differences, especially in the calculation of the ionization energies. At the same time, the Xα results seem to be in good agreement with experimental observations. The Fenske–Hall method, though less rigorous than Xα, produces the same qualitative and semiquantitative results as the Xα method. This agreement confirms the previous conclusion that, in general, both the Fenske–Hall and Xα methods give physically reasonable results for metal complexes and that these results are often better than those obtained by single-configuration Hartree–Fock calculations.[48] The success of these less strict and computationally easier methods has been incisively attributed to the approximations embodied in them,[49] and we believe that both methods will continue to be useful in the study of relatively large molecules.

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