Organometallics 1985, *4*, 285–290

The Effect upon the Hydrogen Atoms of Bonding an Allyl Group to a Transition Metal. A Theoretical Investigation and an Experimental Determination Using Neutron Diffraction of the Structure of Bis(η^3-allyl)nickel

R. Goddard,[1a] C. Krüger,*[1a] F. Mark,[1b] R. Stansfield,[1c] and X. Zhang[1b,d]

Max-Planck-Institut für Kohlenforschung and Max-Planck-Institut für Strahlenchemie, 4330 Mülheim a.d. Ruhr, West Germany, Institut Laue-Langevin, 156 X Centre de Tri, 38042 Grenoble Cedex, France, and Dalian Institute for Chemical Physics, Dalian, Liaoning, People's Republic of China

Received February 21, 1984

Ab initio SCF calculations at the double-ζ level have shown that the total energy of *trans*-bis(η^3-allyl)nickel is lowered by 187 kJ/mol when the hydrogen atoms are allowed to move out of the planes of the allyl groups. It is found that in the most stable geometry the syn and meso hydrogen atoms are bent 6.7 and 13.4°, respectively, toward the metal and the anti hydrogen atoms are bent 31.4° away. This has been confirmed by a neutron diffraction study of the compound at 100 K, where the corresponding values are 8.9 (4), 15.8 (1), and 29.4 (7)°. The change in the total energy can be attributed to three effects, which are a reduction of steric repulsion between the nickel atom and the anti hydrogen atoms, a destabilization of the allyl ligands, and an enhancement of the interaction between the metal and the allyl group as a consequence of rehybridization of the carbon atoms. Although geometrical optimization of the structure leads to a slight rearrangement of the energy levels, the observed failure of Koopmans' theorem to describe the photoelectron spectrum of bis(η^3-allyl)nickel remains. The compound crystallizes in the monoclinic space group $P2_1/a$ with cell constants a = 7.888 (2) Å, b = 8.076 (2) Å, c = 5.092 (2) Å, and β = 110.24 (2)°.

Introduction

When unsaturated molecules bond to transition metals, their geometry alters.[2] Changes in bond distances in the π-framework are usually associated with a bending of substituents toward or away from the metal. In the specific case of (η^3-allyl)nickel systems, the distortions of various substituents have been experimentally determined.[3] These distortions are, however, unknown when the substituent is hydrogen itself. Indeed, all previous theoretical calculations on unsubstituted η^3-allyl transition-metal complexes by ab initio,[4–6] semiempirical,[7,8] and more recently Xα[9] methods have been based on the assumption that the allyl group is completely planar. In one example, the interpretation of the photoelectron spectrum of bis(η^3-allyl)nickel and the claimed failure of Koopmans' theorem were based on results obtained for such a model geometry.[5,6,9–12] Uttech and Dietrich have, however, pointed out that for bis(η^3-methallyl)nickel the anti hydrogen atoms interfere strongly with the nickel atom if they are assumed to lie in the plane of the allyl carbon skeleton[13] and furthermore suggested that a distortion is induced which indirectly results in the the meso methyl group bending 12° out of the carbon atom plane toward the nickel atom. Since a distortion of the hydrogen atoms in bis(η^3-allyl)nickel may appreciably affect the ordering of the energy levels, the positions of the hydrogen atoms have been optimized and the bonding has been investigated by means of ab initio theoretical calculations.

Although bis(η^3-allyl)nickel was first prepared some 20 years ago,[14] its structure has eluded structural chemists until now, mainly because of the compound's low melting point (1 °C) and high pyrophoricity. Once cooled and protected from oxygen bis(η^3-allyl)nickel is stable. By maintaining these conditions, it has been possible to collect an extensive set of neutron diffraction data and determine the structure of *trans*-bis(η^3-allyl)nickel[14b] at −173 °C. The determination of the crystal structure was undertaken to verify the theoretical predictions.

This contribution is the first part of an investigation into the electronic structure and conformational properties of *trans*-bis(η^3-allyl)nickel. We plan to use the positional and thermal parameters of the nuclei determined here for a subsequent determination of the electronic deformation density of the molecule.

Theoretical Calculations

Computational Details. Calculations were performed by the single-configuration LCAO-SCF method using Gaussian lobe functions.[15] The two basis sets used by Veillard and co-workers[6,16] were chosen. They were contracted to a minimal basis for the core orbitals and were either single-ζ (SZ) or double-ζ (DZ) quality for the valence orbitals.

(a) DZ Basis Set. The Ni atom basis was derived from a (12,6,4) atomic set[17] by discarding the two outermost s

---

(1) Max-Planck-Institut für Kohlenforschung. (b) Max-Planck-Institut für Strahlenchemie. (c) Institut Laue-Langevin. (d) Permanent address: Dalian Institute for Chemical Physics.

(2) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(3) Jolly, P. W.; Wilke G. "The Organic Chemistry of Nickel", Academic Press: New York, 1974; Vol. 1, p 331.

(4) Veillard, A. *Chem. Commun.* **1969**, 1022, 1427.

(5) Rohmer, M.-M.; Veillard, A. *J. Chem. Soc., Chem. Commun.* **1973**, 250.

(6) Rohmer, M.-M.; Demuynck, J.; Veillard, A. *Theor. Chim. Acta* **1974**, *36*, 93.

(7) Hillier, I. H.; Canadine, R. M. *Discuss. Faraday Soc.* **1969**, *47*, 27.

(8) Brown, D. A.; Owens, A. *Inorg. Chim. Acta* **1971**, *5*, 675.

(9) Hancock, G. C.; Kostić, N. M.; Fenske, R. F. *Organometallics* **1983**, *2*, 1089.

(10) Batich, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 7585.

(11) Böhm, M. C.; Gleiter, R.; Batich, C. D. *Helv. Chim. Acta* **1980**, *63*, 990.

(12) Böhm, M. C.; Gleiter, R. *Theor. Chim. Acta* **1980**, *57*, 315.

(13) Uttech, R.; Dietrich, H. *Z. Kristallograph.* **1965**, *122*, 60.

(14) (a) Wilke, G.; Bogdanović, B. *Angew. Chem.* **1961**, *73*, 756. (b) Bönnemann, H.; Bogdanović, B.; Wilke, G. *Angew. Chem.* **1967**, *79*, 817.

(15) Ahlrichs, R. *Theor. Chim. Acta* **1974**, *33*, 157. Driessler, F.; Ahlrichs, R. *Chem. Phys. Lett.* **1973**, *23*, 571.

(16) Veillard, A.; Demuynck, J. *Mod. Theor. Chem.* **1977**, *4*, 187.

(17) Roos, B.; Veillard, A.; Vinot, G. *Theor. Chim. Acta* **1971**, *20*, 1.

0276-7333/85/2304-0285$01.50/0

Table I. Optimization of H Atom Positions in *trans*-Bis(η^3-allyl)nickel

	iteration number					
	0		1		2	
	DZ[a]	SZ	DZ	SZ	DZ	SZ
energy, au	−1736.265 01	−1732.597 42	*c*	−1732.678 02	−1736.336 39[e]	−1732.679 88
energy diff, kJ/mol	0	0	*c*	−212	−187	−217
θ_2[b]	0	0	−13.6	−13.7		−13.4
θ_1'	0	0	34.7	28.6		31.4
θ_1	0	0	−6.7	−3.2		−6.7
α_1	0	0	*d*	−0.1		0.5
α_1'	0	0	*d*	3.0		3.1

[a] SZ = single-ζ; DZ = double-ζ; see text for details. [b] The distortion angles θ_1, θ_1', θ_2, α_1, and α_1' are defined in Figure 2. [c] Not calculated. [d] Not varied. [e] Using the distortion angles obtained from the SZ calculation.

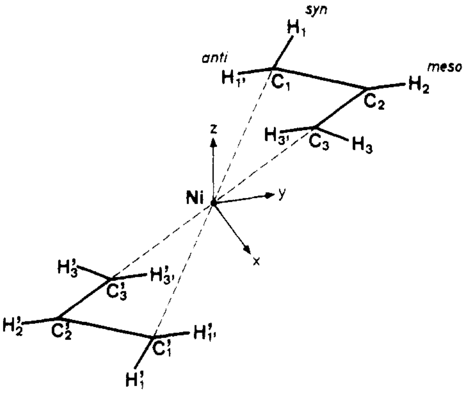

Figure 1. *trans*-Bis(η^3-allyl)nickel: choice of axes and numbering of atoms.

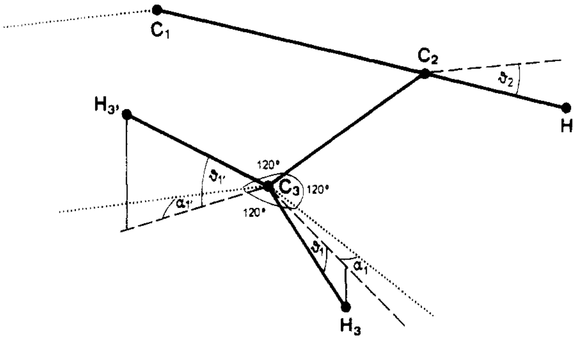

Figure 2. Definition of the angles θ_1, θ_1', θ_2, α_1, and α_1', which give a measure of the distortion of H atom positions from idealized trigonal geometry about the carbon atoms.

functions and by adding an s function (ζ_s = 0.2), a p function (ζ_p = 0.25), and a d function (ζ_d = 0.2). These functions allow for a description of the 4s, 4p, and 3d orbitals that are adapted for the molecular environment.[16] The expanded (11,7,5) set was contracted to (4,3,2). The (8, 4/3, 2) basis for carbon[18] and the (4/2) basis for hydrogen[19] were of DZ quality for the valence orbitals.

(b) SZ Basis Set. The Ni atom basis set was obtained from a (9,5,3) set for Ni^{2+}[17] that was augmented by an s, p, and d function as described in (a). This (10,6,4) basis was contracted to a minimal basis except for the d function, which was split. The (7,3) basis for carbon[20] and the (3) basis for hydrogen[19] were contracted to a minimal basis set.

Geometry Optimization. The crystal structure of bis(η^3-allyl)nickel was unknown before the theoretical investigation was undertaken. From NMR data a trans arrangement of ligands had been postulated,[14b] and this was the geometry adopted in the calculations. A C_{2h} geometry was assumed throughout the optimization. Some of the structural parameters were taken from previous experimental data, and the remainder were determined by minimizing the total energy of the complex. The Ni–C and C–C distances were taken from the structure of the bis(η^3-methallyl)nickel complex:[13] Ni–C_1 = Ni–C_3 = 2.01 Å; Ni–C_2 = 1.98 Å; C–C = 1.41 Å. The choice of axes and the numbering scheme for the atoms are given in Figure 1. [Subscripts are used in the atomic numbering scheme for the theoretical model so as to distinguish it from the experimental one (Figure 3).] The C–H distance was assumed to be 1.08 Å, and the C–C–C bond angle in the allyl group was fixed at 120°. The hydrogen atom positions were determined by varying the angles θ_1, θ_1', θ_2, α_1, and α_1' subject to the constraint that the C_{2h} symmetry was retained. These angles are shown in Figure 2. The distortion of a hydrogen atom from the idealized trigonal geometry of the carbon atom to which it is attached can be specified by the angles θ and α, where θ is defined as the angle between the vector along the bond C–H and its projection on the plane spanned by the three carbon atoms of the allyl group and α is the angle between the projection of the bond vector C–H on the allyl plane and the bond vector expected if the carbon atom had ideal trigonal geometry. Thus, θ gives a measure of the deviation of the hydrogen atom from the allyl plane, with a positive sign indicating a displacement away from the nickel atom, and α gives the deviation of the coordination about the carbon atom from the ideal 120°, a positive sign indicating a C–C–H bond angle of greater than 120°.

The optimization was carried out by expanding the total energy in a second-order polynomial in the parameters θ_1, θ_1', θ_2, α_1, and α_1'. The first- and second-order derivatives were approximated by difference quotients. With use of the SZ basis, all parameters were approximately optimized by minimizing the energy with respect to one or two of the parameters in turn.

No optimization of the Ni–C distances was attempted since quite accurate values had already been experimentally determined,[13] and the Ni–C distance had been optimized for a number of organometallic complexes using relatively large and flexible basis sets.[21,22] It is also worth noting that a more comprehensive basis set for iron than the one used here for nickel gave only a poor estimate for the metal–ring distance in ferrocene.[23] Relatively small

---

(18) Whitman, D. R.; Hornback, C. J. *J. Chem. Phys.* **1969**, *51*, 398.

(19) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(20) Roos, B.; Siegbahn, P. *Theor. Chim. Acta* **1970**, *17*, 209.

(21) Spangler, D.; Wendoloski, J. J.; Dupuis, M.; Chen, M. M. L.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1981**, *103*, 3985.

(22) Pitzer, R. M.; Goddard, J. D.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1981**, *103*, 5681.

(23) Lüthi, H. P.; Ammeter, J.; Almlöf, J.; Korsell, K. *Chem. Phys. Lett.* **1980**, *69*, 540. Lüthi, H. P.; Ammeter, J. H.; Almlöf, J.; Faegri, K., Jr. *J. Chem. Phys.* **1982**, *77*, 2002.

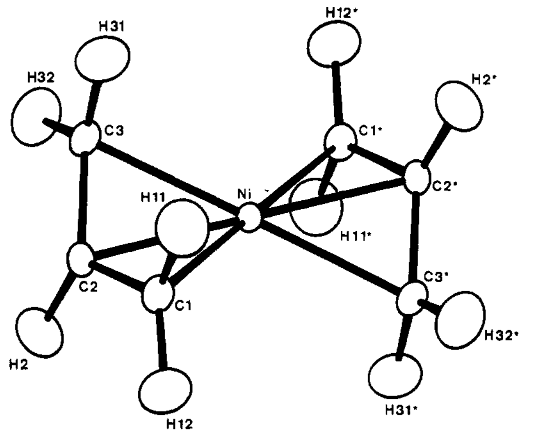

Figure 3. The molecular structure of bis(η^3-allyl)nickel showing the arbitrary atomic numbering scheme.

basis sets have, however, been found sufficient to describe the geometries observed in the structural investigations of ligands that are both free and complexed to transtion metals.[24-26]

The Optimized Hydrogen Atom Positions. The total energy of *trans*-bis(η^3-allyl)nickel is found to be lowered by 187 kJ/mol in the DZ calculation and by 217 kJ/mol in the SZ calculation when going from a planar to a distorted geometry. Table I gives a summary of the results of the calculations. The largest changes occur at the anti hydrogen atoms, which are pushed away from the metal. The metal–hydrogen distance increases in this case from 1.97 Å for the idealized geometry to 2.42 Å, a value which is characteristic for a transition metal to hydrogen atom minimal nonbonded distance.[27] Concomitantly, the meso hydrogen atoms and the syn hydrogen atoms, but these to a much lesser extent, are displaced toward the nickel atom. The resulting bond angles $C_2{-}C_1{-}H_1' = 117.8°$ and $H_1{-}C_1{-}H_1' = 116.0°$ indicate that the terminal carbon atoms of the allyl group are tending toward a tetrahedral type of geometry. The bond angle at C_2, $C_1{-}C_2{-}H_2 = 119.1°$, shows that the coordination around this atom changes little.

Theoretical calculations on monomeric allyllithium[28,29] and allylsodium[29] show a similar geometry for the hydrogen atoms on the allyl groups.

Experimental Results

Neutron Diffraction Study. The results of the experimental determination of the structure of bis(η^3-allyl)nickel are summarized in Figure 3, which gives the arbitrary numbering scheme. Table II lists important bond distances and angles. The molecule possesses an exact center of symmetry passing through the nickel atom so that C1, C3, Ni, C1*, and C3* are coplanar and define a plane tilted at 110° to one through C1, C2, and C3. The distance of the nickel atom to the meso carbon atom of the allyl group, C2, at 1.980 (1) Å is nevertheless significantly shorter than that to its two neighbors, C1 and C3 (mean 2.029 Å). The C–C distances (mean 1.416 Å) are normal for a conjugated system π-bonded to a metal.

Table II. Interatomic Distances (Å) and Angles (deg) Obtained in the Neutron Diffraction Experiment, with Standard Deviations in Parentheses

(a) Bond Distances

Ni-C1	2.031 (1)	C1-H11	1.091 (2)
Ni-C2	1.980 (1)	C1-H12	1.093 (2)
Ni-C3	2.027 (1)	C2-H2	1.093 (2)
C1-C2	1.414 (1)	C3-H31	1.094 (2)
C2-C3	1.417 (1)	C3-H32	1.086 (2)

(b) Bond Angles

C1-Ni-C3	74.6 (1)	C1-C2-C3	120.5 (1)
C1-Ni-C2	41.2 (1)	Ni-C1-H11	99.1 (1)
C3-Ni-C2	41.4 (1)	Ni-C1-H12	122.9 (1)
C2-C1-H11	120.4 (1)	Ni-C2-H2	114.8 (1)
C2-C1-H12	119.6 (1)	Ni-C3-H31	100.1 (1)
C1-C2-H2	118.2 (1)	Ni-C3-H32	123.3 (1)
C3-C2-H2	118.9 (1)	H11-C1-H12	115.9 (2)
C2-C3-H31	120.3 (1)	H31-C3-H32	115.5 (2)
C2-C3-H32	119.5 (1)		

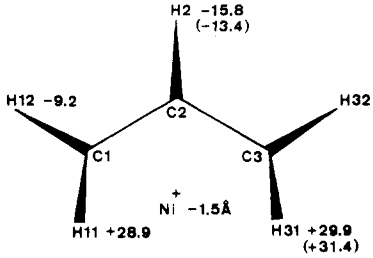

Figure 4. Deviations (°) of the hydrogen atoms out of the plane of the allyl group from the neutron experiment and from the theoretical calculations (in parentheses).

Of particular interest are the positions of the hydrogen atoms. The relationship of the hydrogen atoms to the carbon skeleton of the η^3-allyl group is shown in Figure 4. It shows the degree of bending of the C–H bonds out of the plane defined by C1, C2, and C3. A negative sign indicates a bend toward the nickel atom, which lies 1.5 Å below the plane. The anti hydrogen atoms H11 and H31 appear to lie as much as 30° out of the plane, away from nickel. The other three hydrogen atoms on the allyl group are bent toward the nickel atom (H12, H2, H2–15.8°, and H32, –8.6°), the meso hydrogen atom being bent the most. The average C–H distance is 1.091 (3) Å. In spite of the considerable distortion of the allyl group on complexation to the nickel atom, the C–C–C and C–C–H angles remain remarkably close to 120°. The distortion appears to manifest itself most markedly in the H–C–H angles of the methylene carbon atoms, which decrease to 115.7° (mean).

A distortion of the hydrogen atoms in an allyl group has also been observed in the structure of bis(η^3-allyl)(trimethylphosphine)nickel; though in this case the hydrogen atoms were not so well located because the structure was determined by using X-ray data.[30] The interpretation of the ^{1}H and ^{13}C NMR spectra of allyllithium is also in qualitative agreement with these observations.[31]

Of all the intramolecular nickel–hydrogen contact distances, it is found that those involving the anti hydrogen atoms are the shortest (mean 2.46 (1) Å) even though these two atoms are bent the most out of the plane of the allylic carbon atoms. For comparison, the Ni···H2 distance is

---

(24) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531. Schleyer, P. v. R.; Dill, J. D.; Pople, J. A.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497. Mayr, H.; Förner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032.

(25) Åkermark, B.; Almemark, M.; Almlöf, J.; Bäckvall, J.-E.; Roos, B.; Støgård, Å. *J. Am. Chem. Soc.* **1977**, *99*, 4617.

(26) Dedieu, A.; Rohmer, M.-M.; Veillard, A. *J. Am. Chem. Soc.* **1976**, *98*, 5789.

(27) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(28) Clark, T.; Jemmis, E. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Organomet. Chem.* **1978**, *150*, 1.

(29) Clark, T.; Rhode, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344.

(30) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 449.

(31) Schlosser, M.; Stähle, M. *Angew. Chem. Suppl.* **1982**, 198. Ahlbrecht, H.; Zimmermann, K.; Boche, G.; Decher, G. *J. Organomet. Chem.* **1984**, *262*, 1.

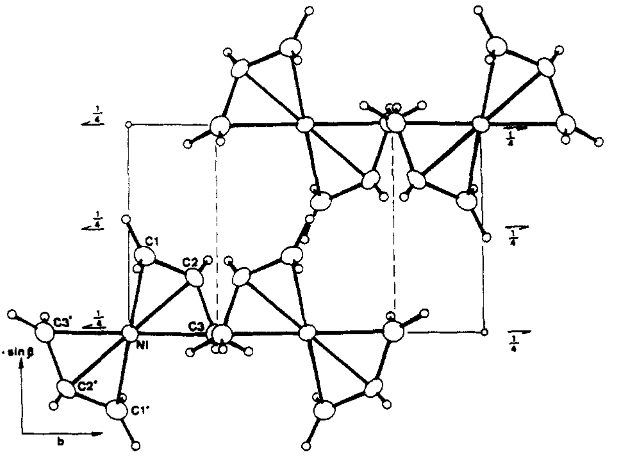

Figure 5. The contents of the unit cell of bis(η^3-allyl)nickel, viewed down *a* looking toward the origin.

2.632 (2) Å and the average distance from the nickel atom to the syn hydrogen atoms is 2.778 (4) Å. These distances are appreciably larger than a nickel–hydrogen bond distance (1.46 (10) Å for a terminal hydrogen atom and 1.67 (2) Å for a bridging hydrogen atom[32]) while at the same time are slightly smaller than the sum of the van der Waals radii[33] of a hydrogen atom (1.20 Å) and a nickel atom (1.81 Å) so some weak interaction between the nickel atom and the hydrogen atoms cannot be ruled out.

The C3-H32 distance is more than three standard deviations shorter than the other C–H distances, and this might be caused by either a weakness in the measured data or crystal packing effects. It seems, however, unlikely that the positions of the hydrogen atoms are strongly influenced by intermolecular forces since the shortest intermolecular distance between hydrogen atoms (H11···H2(0.5 + *x*, 0.5 − *y*, *z*) = 2.497 (3) Å) is at least as great as the corresponding shortest nonbonding intramolecular distances (H11···H2 = 2.473 Å), is more than twice the van der Waals radius of hydrogen (2.4 Å), and, above all, does not involve H32. Figure 5 gives the contents of one unit cell viewed down *a* toward the origin.

Discussion

The change in the total energy of bis(η^3-allyl)nickel when the hydrogen atoms are allowed to move out of the planes of the allyl groups can be attributed to three effects. The first is a reduction in the repulsion between the nickel atom and the anti hydrogen atoms. The second is a destabilization of the allyl ligands, and the third is an increased interaction between the ligand and the metal. The *first effect* appears to be the primary driving force for the distortion. If the coupling between the out-of-plane deformations by different hydrogen atoms is neglected by deleting all the nondiagonal elements of the Hessian matrix, then a strong out-of-plane bending, $\tilde{\theta}_1' = 28.9°$, a small bending, $\tilde{\theta}_1 = -3.9°$, and almost no bending in $\tilde{\theta}_2$, −0.5°, are predicted. These values can be compared with the DZ values of column 4 in Table I, which were obtained by including the nondiagonal elements of the Hessian. Whereas $\tilde{\theta}_1'$ is not far from the optimized value θ_1', inclusion of the coupling between the out-of-plane bending angles is essential to bring $\tilde{\theta}$ and $\tilde{\theta}_2$ close to θ_1 and θ_2 θ_2', respectively. Thus, the distortion of the syn and meso hydrogen atoms appears to be mainly a consequence of the distortion of the anti hydrogen atoms.

Table III. Orbital Energies in *trans*-Bis(η^3-allyl)nickel for Planar and Optimized (opt) Allyl H Atom Geometry

planar		optimized		
orbital	orbital energy, eV	orbital	orbital energy, eV	diff (opt − planar),[a] eV
7A_u	−7.73	7A_u	−8.44	−0.71
6B_g	−8.96	6B_g	−9.58	−0.62
13A_g	−11.85	11B_u	−11.51	+0.55
11B_u	−12.06	13A_g	−12.43	−0.58
12A_g	−14.16	12A_g	−13.21	+0.95
5B_g	−14.30	11A_g	−14.10	+0.28
11A_g	−14.38	5B_g	−14.13	+0.17
6A_u	−14.75	10B_u	−14.44	+0.33
10B_u	−14.77	6A_u	−14.47	+0.28
4B_g	−15.12	4B_g	−14.73	+0.38
10A_g	−15.66	10A_g	−15.23	+0.43
9A_g	−16.57	9A_g	−15.96	+0.62

[a] Differences are taken between corresponding orbitals of the same symmetry.

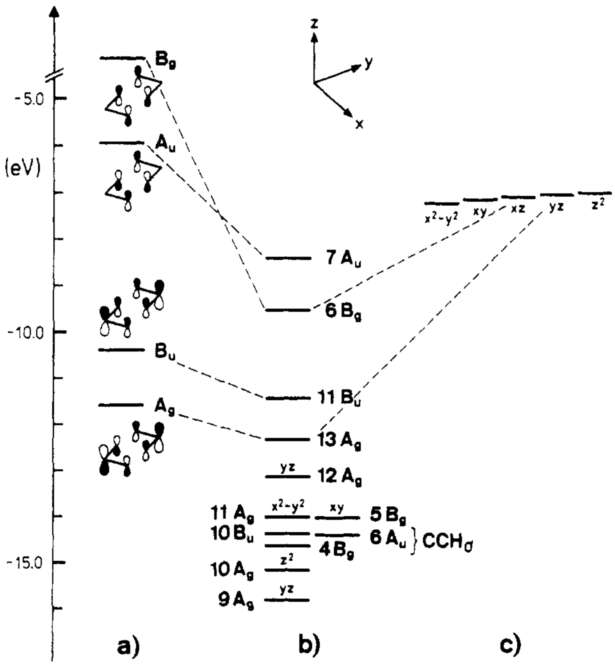

Figure 6. Ligand–metal interaction diagram for bis(η^3-allyl)nickel with optimized H atom positions: (a) bis(η^3-allyl) fragment; (b) bis(η^3-allyl)nickel molecule; (c) Ni atom in C_{2h} complex geometry.

The *second effect*, namely, the destabilization of the ligands, and the *third effect*, the increased interaction between the metal and the ligands, are reflected in the changes of the orbital energies and the overlap population upon distortion. Table III lists the energies of the high-lying orbitals for the two geometries. The highest and second highest orbital are shifted to lower energies. The 13A_g orbital is stabilized and the 11B_u is destablized to such an extent that an inversion of these energy levels occurs. Two further inversions are due to small energetic changes of close-lying levels. Except for the first, second, and fourth orbital, all other orbitals are destabilized. These changes can be rationalized by using the interaction diagram shown in Figure 6, where the orbitals of the optimised complex are derived from those of a Ni fragment and a fragment of two spin paired allyl radicals. [The orbital energies of these fragments have been obtained for the C_{2h} geometry using the full basis set of the complex for each of the fragments. In a calculation where only the basis set of the fragments themselves was used, the orbital energies of the bis(η^3-allyl) fragment remained almost unchanged,

---

(32) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(33) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, New York, 1973.

Table IV. Overlap Population between Bonded Atom Pairs in *trans*-Bis(η^3-allyl)nickel in the Optimized (opt) and Planar Allyl H Atom Geometries

atom pair	overlap pop. (opt)	diff (opt − planar)
Ni-C_1	0.153	+0.010
Ni-C_2	−0.046	+0.003
C_1-C_2	0.553	−0.044
C_1-H_1	0.814	−0.011
C_1-H_1'	0.789	+0.028
C_2-H_2	0.838	−0.011

while those of the metal d orbitals were shifted substantially from five quasi-degenerate levels between −7.26 and −7.06 eV to one at −14.2 eV. If the validity of Koopmans' theorem is assumed, the values obtained using the full basis set are close to the experimental ionization potential of Ni, which is 7.63 eV.[34] The large shift would seem to indicate that the basis set for the nickel atom used here, particularly for the d-type functions, is far from being complete.] The orbital A_g of the bis(η^3-allyl) fragment is the in-phase and B_u is the out-of-phase combination of the allylic bonding π-orbital (see Figure 6). The distortion at the methylene carbon atoms leads to better overlap between the allyl fragments. The increased interaction stabilizes the positive combination ($13A_g$) and destabilizes the negative combination ($11B_u$). An analogous reasoning applies to the pairs of orbitals A_u and B_g formed from the nonbonding π-orbital. The almost pure ligand orbital $7A_u$ is indeed strongly stabilized. However, the destabilization of B_g owing to an increased allyl–allyl interaction is more than compensated by the increased bonding interaction between the nickel atom and the allyl groups. Since the mixing coefficient of d_{xz} in the $6B_g$ orbital is larger than that of B_g, an overall energy decrease of $6B_g$ results.

The distortion causes changes in the overlap population between pairs of bonded atoms (see Table IV). The Ni–C_1 bond is strengthened, the Ni–C_2 bond becomes less antibonding, and hence the metal–ligand bonding increases. The bonds C_1–C_2, C_1–H_1, and C_2–H_2 are weakened, and the allyl groups are destabilized. The unfavorable bonding situation indicated by the low C_1–H_1' overlap population is also relieved.

It should be emphasized at this point that the theoretical calculations are only at the Hartree–Fock level. More accurate calculations where the effects of electron correlation have been considered will give quantitatively more accurate energy changes, but essentially the qualitive predictions for the geometry are expected to remain the same. The effect of the introduction of configuration interaction has been discussed for several nickel-containing complexes.[23,35–37]

The calculated ionization potentials of bis(η^3-allyl)nickel obtained from Koopmans' theorem are compared in Figure 7 with experimental values derived from the photoelectron spectrum.[12] Upon geometry optimization, the high-lying orbitals become more evenly spaced. However, the main feature of the level ordering remains the same and the d orbitals are found well below the ligand orbitals. This is not in accordance with the assignment of the experimental photoelectron spectrum given by Böhm and Gleiter.[12] Thus, the expected failure of Koopmans' theorem based on Hartree–Fock calculations[38] that has been demonstrated by Veillard and co-workers[5,6] for a planar allyl geometry persists for the optimized geometry.

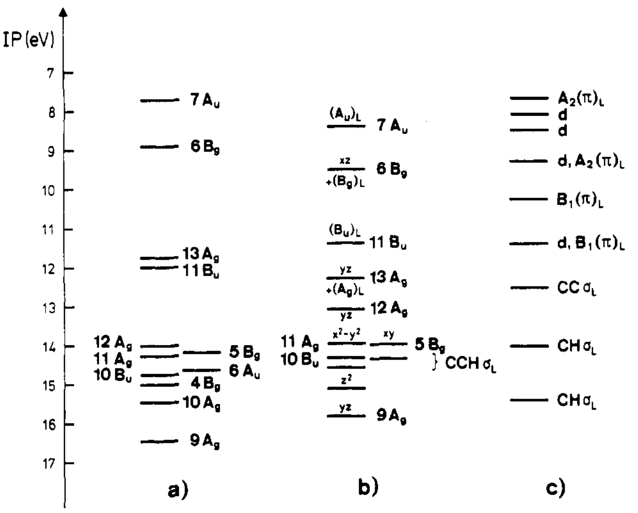

Figure 7. Ionization potentials for bis(η^3-allyl)nickel calculated according to Koopmans' theorem: (a) H atoms in the allyl plane; (b) optimized H atom positions; (c) experimental photoelectron spectrum with assignment by Böhm and Gleiter[10] (L = ligand).

Table V. Crystallographic Data for Bis(η^3-allyl)nickel

formula: $C_6H_{10}Ni$
mol wt: 140.9
a = 7.888 (2) Å
b = 8.076 (2) Å
c = 5.092 (2) Å
β = 110.24 (2)°
cryst system: monoclinic
space group: $P2_1/a$
V = 304.4 Å^3
F_{000} = 148 e
Z = 2
D_{calcd} = 1.54 g cm^{-3}

Conclusions

The molecular orbital calculations described here reveal that the hydrogen atoms in an allyl group bonded to a nickel atom are appreciably bent out of the plane of the three carbon atoms, and this is confirmed by the experimental results. The observation has been attributed to steric repulsion between the anti hydrogen atoms and the nickel atom and results in a better overlap between the end carbon atoms of the allyl group and the nickel atom. The change in the geometry does not yield the correct ionizations in the framework of Koopmans' theorem.

Experimental Section

Measurement of Neutron Diffraction Data. Intensity data were collected from a 1.54-mm^3 large crystal mounted on the D8 four-circle diffractometer situated at the high-flux beam reactor of the Institut-Laue-Langevin in Grenoble. The crystal was maintained in an inert atmosphere and cooled to 100 K by using an Air Products Displex cryostat.[39] The neutrons were monochromated by using the (220) face of a single copper crystal and had a wavelength of 1.2837 Å. Pertinent crystal data are given in Table V; the given cell parameters were obtained by a least-squares fit to the θ values of 69 automatically centered X-ray reflections of a smaller crystal of the same sample at the same temperature mounted on a Nonius CAD-4 diffractometer. These are considered to be better determined than those obtained from the θ values of nine reflections using neutrons (a = 7.848 (5) Å, b = 8.061 (3) Å, c = 5.071 (3) Å, β = 110.26 (4)°) and were used in the subsequent calculation of the bond distances and angles given in this paper.

Intensities were measured with a ω–2θ scan technique in a step–scan mode with 33 steps, the time taken to measure each

---

(34) Moore, C. E. *Natl. Bur. Stand.* (*U.S.*), *Circ.* **1952**, *2*, 467.

(35) Ozin, G. A.; Power, W. J.; Upton, T. H.; Goddard III, W. A. *J. Am. Chem. Soc.* **1978**, *100*, 4750.

(36) Upton, T. H.; Goddard III, W. A. *J. Am. Chem. Soc.* **1978**, *100*, 321.

(37) Basch, H.; Newton, M. D.; Moskowitz, J. W. *J. Chem. Phys.* **1978**, *69*, 584.

(38) Pitzer, R. M.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 7176.

(39) Allibon, J. R.; Filhol, A.; Lehmann, M. S.; Mason, S. A.; Simms, P. *J. Appl. Crystallogr.* **1981**, *14*, 326.

step being determined by the time to reach a fixed neutron count on a monitor placed between the source and the sample. The scanning interval was 2.0, 1.5, 2.1, 2.9, and 4.0° for $\theta = 0, 15, 30, 40$, and 56°, respectively, and interpolated for the θ values in between. The intensities and their standard deviations were evaluatd by a peak profile analysis using the Lehmann and Larsen algorithm.[40] Intensities were corrected for the effects of absorption by assuming the crystal to be spherical ($\mu R = 0.195$). A total of 1503 reflections $[+h,+k,+l]$ were measured in the range $6.68 < \theta < 57.05°$ and were averaged to give 727 independent reflections ($R_{av} = 0.014$),[41] and these were used in the subsequent refinement of the structure.

Structure Refinement. Atomic positional parameters taken from an earlier X-ray experiment were used as a starting point for the refinement with the neutron diffraction data. Refinement was by full-matrix least squares where the quantity minimized was $\sum w(|F_0| - |F_c|)^2$. Refinement converged at $R = 0.027$ and $R_w = 0.022$[42] ($w = 1/\sigma(F_0)^2$) with 79 parameters. Scattering lengths were taken from ref 43. In the final refinement cycle the mean shift to error ratio was less than 10^{-5}. Table VI gives the final atomic fractional coordinates and the thermal parameters. A list of observed and calculated structure factors has been deposited as supplementary material.

Acknowledgment. R.G. and C.K. are most grateful to Dr. M. Rubach for supplying the crystals. F.M. and X.Z. wish to thank Dr. P. J. Jolly and Dr. R. Benn for communicating and discussing recent experimental results. Part of this work was supported by the Deutsche Forschungsgemeinschaft.

Registry No. *trans*-Bis(η^3-allyl)nickel, 75110-62-2.

Supplementary Material Available: Crystal data, a table (Table VI) of positional and thermal parameters, and a list of observed and calculated structure factors for the neutron diffraction experiment (5 pages). Ordering information is given on any current masthead page.

---

(40) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* 1974, *A30*, 580.

(41) R_{av} defined as $\sum|<I> - I|/\sum|I|$, where $<I>$ is the local average for equivalent reflections.

(42) $R = \sum(|F_0| - |F_c|)/\sum|F_0|)$. $R_w = (\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2)^{1/2}$.

(43) The following scattering amplitudes were used: H, −0.374, C, 0.66, and Ni, 1.03×10^{-12} cm. Bacon, G. E. "Neutron Diffraction"; Oxford University Press: Oxford, 1962.

σ/π Interactions in Alkynyltin(IV) Compounds Studied by UV Photoelectron Spectroscopy and Pseudopotential "ab Initio" Calculations

Carla Cauletti* and Claudio Furlani

Dipartimento di Chimica, Università "La Sapienza" di Roma, 00185 Roma, Italy

Gaetano Granozzi

Istituto di Chimica Generale ed Inorganica, Università di Padova, Padova, Italy

Angelika Sebald and Bernd Wrackmeyer

Institut für Anorganische Chemie, Universität München, München, Federal Republic of Germany

Received April 11, 1984

Joint analysis of gas-phase UV photoelectron spectra (UPS) and pseudopotential "ab initio" calculations was used to gain insight into the nature and the mechanism of the interactions between the $\pi_{C\equiv C}$ and σ_{Sn-C} orbitals in a series of alkyltin acetylides. The results clearly indicate that the σ/π conjugation is quite extensive along the whole series and that the mechanism is critically controlled by the substituents at both the tin and the alkynyl moiety. Good agreement between the experimental ionization energies and the eigenvalues calculated by the pseudopotential "ab initio" model indicates that this method is suitable for a nonempirical description of the electronic structure of a molecule containing heavy atoms.

Introduction

σ/π interactions (where σ and π are referred to local bond symmetry) have been the subject of several investigations by means of gas-phase UV photoelectron spectroscopy (UPS), mainly in some alkyl-substituted acetylenic compounds.[1-6] In this class of molecules the mechanism of the σ/π conjugation is of a relatively simple nature, since the orbital energy of the σ orbitals is always lower than that of the $\pi_{C\equiv C}$ orbitals, and the effect of the interaction is therefore always destabilizing for the π levels. The same occurs in the case of silyl-substituted acetylenes, also studied by UPS.[2] The extention of these results to alkyltin derivatives of alkynes is not straightforward and extrapolation would not be warranted: in fact in these molecules the orbitals involved in the σ/π conjugation, that

---

(1) Brogli, F.; Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. *Helv. Chim. Acta* 1973, *56*, 2171.

(2) Ensslin, W.; Bock, H.; Becker, G. *J. Am. Chem. Soc.* 1974, *96*, 2757.

(3) Brogli, F.; Heilbronner, E.; Wirz, J.; Kloster-Jensen, E.; Bergmann, R. G.; Vollhardt, K. P. C.; Ashe III, A. J. *Helv. Chim. Acta* 1975, *58*, 2620.

(4) Carlier, P.; Dubois, J. E.; Masclet, P.; Mouvier, G. *J. Electron Spectrosc. Relat. Phenom.* 1975, *7*, 55.

(5) Bieri, G.; Heilbronner, E.; Kloster-Jensen, E.; Maier, J. P. *Phys. Scr.* 1977, *16*, 202.

(6) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* 1977, *60*, 2213.

0276-7333/85/2304-0290$01.50/0