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A "Double-Zeta" Type Wavefunction for an Organometallic: Bis-(π-allyl)Nickel

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A wavefunction which is of double-zeta quality at the level of the valence orbitals [based on a (11, 7, 5/8, 4/4) gaussian basis set contracted to (4, 3, 2/3, 2/2)] is reported for the *bis*-(π-allyl)nickel molecule. Independant SCF calculations for two ionized states substantiate the conclusion reached previously for a number of organometallics with a minimal basis set that Koopmans' theorem is not valid for these molecules, namely that the highest occupied orbital from the ground state calculation for the neutral molecule is mostly a ligand π orbital whereas the lowest ionization potential corresponds to the removal of an electron from a molecular orbital which is mostly a metal 3*d* orbital. The nature of the bonding in *bis*-(π-allyl)nickel is discussed on the basis of the possible interactions between the metal orbitals and the π orbitals of the allyl group. The interaction between the filled nonbonding π orbital of the allyl group and the empty $3d_{xz}$ orbital of the Ni atom appears responsible for most of the bonding, together with some backbonding through an interaction between the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals and the σ and π orbitals of the ligands. The computed value for the rotation barrier about the C—C allyl bond, 90 kcal/mole, rules out this rotation as one of the possible mechanisms which account for the equivalence of the terminal hydrogens in the proton magnetic resonance spectra of π-allyl complexes.

Key word: Bis-(π-allyl)nickel

1. Introduction

There is currently a strong interest in the photoelectron spectroscopy of organometallics involving a transition metal, especially in connection with theoretical studies of the electronic structure [1–8]. One incitement to photoelectron spectroscopy was the hope of deriving information regarding the electronic structure of the molecule in its ground state from the photoelectron spectrum and the sequence of ionization potentials. However recent theoretical work on a number of organometallics has shown that no conclusion can be drawn from the photoelectron spectrum regarding the sequence of MO's in the ground state of the neutral molecule, owing to the failure of Koopmans' theorem for these systems [6–10]. For the molecule of *bis*-(π-allyl)nickel, the lowest ionization potentials (I.P.'s) are associated with some orbitals ($3b_g$, $9a_g$, $10a_g$, and $11a_g$) of mixed metal-3*d* and ligand character, which have higher orbital energies than some orbitals which are mostly ligand-π orbitals in character ($7a_u$, $11b_u$) [10]. It has been pointed out that the distinction between metal *d*-type orbitals and ligand π-type or σ-type orbitals is less clear-cut in *bis*-(π-allyl)nickel than it has been assumed previously [10]. However, one limitation of the previous theoretical work [6–10] was the restriction to wavefunctions built from a minimal basis set (except for the use of split 3*d* functions). The corresponding lack of flexibility in the wavefunction could alter significantly some of the results. For instance, it was found that there is little electronic relaxation upon ionization from a ligand π orbital (e_{1u} or e_{1g} or a_{2u}) of ferrocene [9]. However, this might be a consequence of the fact that the π molecular orbitals of the cyclopentadienyl anion, in a minimal basis set, are determined by the symmetry properties (although some additional flexibility is introduced in the molecule of ferrocene by the mixing of the π ligand orbitals with the metal 3*d* functions, as evidenced for the e_{1g} orbital in Table 1 of Ref. [9]). To ascertain the validity of the previous results, we have reinvestigated some of the above conclusions for *bis*-(π-allyl)nickel by using a wavefunction of double zeta quality for the valence orbitals.

2. The Calculations

LCAO-MO-SCF calculations were carried out with a (11, 7, 5/8, 4/4) set of gaussian functions, contracted to [4, 3, 2/3, 2/2]. Exponents for the C and H atoms were taken from Ref. [11]. The basis set for the Ni atom is taken from Ref. [12] (basis set 12, 6, 4). The lowest two *s* exponents of Ref. [12] (corresponding to the 4*s* atomic orbital) were discarded and replaced with one *s* function of exponent 0.2. This basis set was incremented with one additional *p* function of exponent 0.25 and one additional *d* function of exponent 0.2. These additional exponents were chosen so that the corresponding gaussian functions have a maximum of radial density about at mid-point between the Ni and C atoms. Diffuse *s* functions optimized for the neutral atom in its ground state $3d^{n-2}4s^2$ would provide for a description of the electron density in the vicinity of the ligand atoms, not in the "bonding region" between the metal and the ligands [13]. The contracted basis set corresponds to a minimal set for the inner-shells and the 4*s* and 4*p* orbitals of the metal, to a "double-zeta" set for the metal 3*d* and the carbon and hydrogen valence orbitals (from the previous theoretical work [6–10] the metal 4*s* and 4*p* orbitals appear relatively unimportant for the description of the bonding in these organometallics and it is probably safe to represent these orbitals with one contracted function). The choice of axis and the numbering of the atoms is represented in Fig. 1. The interatomic distances were taken from the experimental data for *bis*-(π-methylallyl)nickel [14]

$$\mathrm{Ni{-}C_1} = 1.98\,\text{Å} \qquad \mathrm{Ni{-}C_2} = 2.01\,\text{Å}$$

$$\mathrm{C_1{-}C_2} = 1.41\,\text{Å} \qquad \mathrm{C{-}H} = 1.08\,\text{Å}\ \text{(assumed)}$$

with idealized bond angles of 120° in the allyl group (which is assumed to be planar). The molecular point group is C_{2h}.

3. Discussion

We have reported in Table 1 the orbital energies and the results of the population analysis for the valence molecular orbitals. The corresponding results for the minimal basis set calculation are given in the Table of Ref. [10]. The relationship between the energy levels of the allyl anion $C_3H_5^-$ and the ones of *bis*-(π-allyl)nickel is shown in Fig. 2. This calculation supports our previous conclusion that the

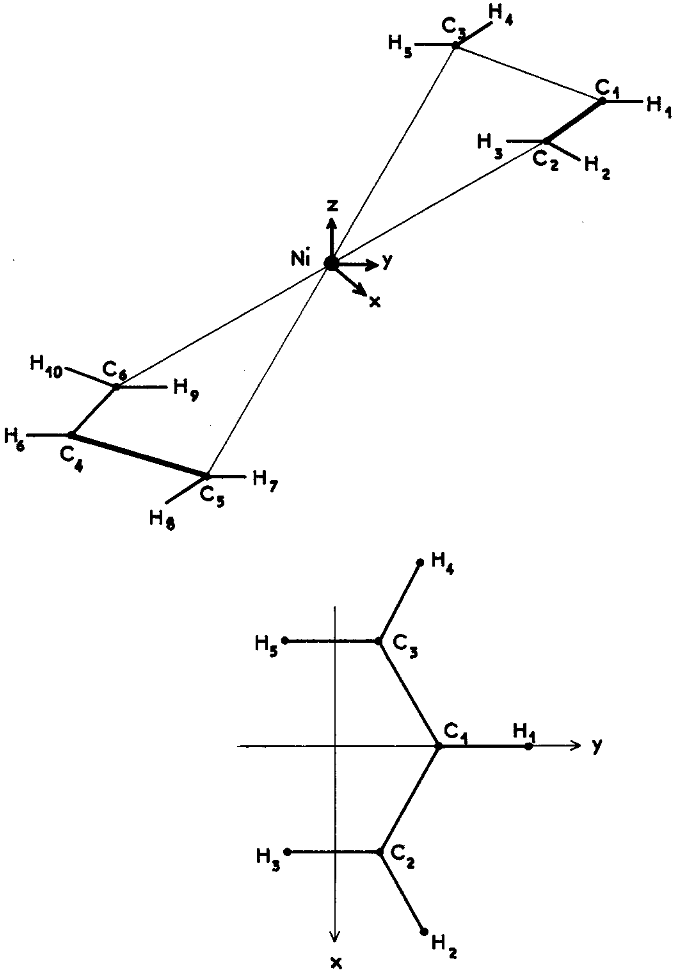


Fig. 1. Choice of axis and numbering of the atoms for *bis*-(π-allyl)nickel

highest occupied orbitals are the orbitals $7a_u$, $6b_g$, $13a_g$, and $11b_u$ which are predominantly π orbitals of the allyl groups. However there is a slight interversion of the next levels with respect to the previous calculation [10]. From the results of Ref. [10] the four levels ($12a_g$, $5b_g$, $6a_u$, $10b_u$) below the π ligand orbitals were predominantly σ ligand orbitals in nature, at slightly higher energies than some levels like the $11a_g$ and $10a_g$ which were predominantly metal $3d$ orbitals. From Table 1, one finds now below the π levels two levels ($12a_g$ and $5b_g$) with a strong metal $3d$ character and at lower energies four levels (from $11a_g$ to $4b_g$) which are mostly ligand σ orbitals. This interversion is a relatively minor one since the corresponding orbital energies are very close (the six orbitals from $12a_g$ to $4b_g$ have their orbital energies in the range -0.512 to -0.554 a.u.). Even if the Koopman’s theorem was valid for this molecule, one of the main difficulties

Table 1. Orbital energies and population analysis for the ground state

Orbital	Orbital energy (in a.u.)	Ni $3d$	Composition of the MO (in percentage)	
			Ligand π	Ligand σ
$7a_u$	-0.288	—	94	—
$6b_g$	-0.327	39	52	9
$13a_g$	-0.435	34	51	15
$11b_u$	-0.449	—	96	3
$12a_g$	-0.512	85	2	13
$5b_g$	-0.516	76	—	23
$11a_g$	-0.524	17	31	51
$6a_u$	-0.541	—	—	100
$10b_u$	-0.545	—	2	97
$4b_g$	-0.554	9	—	91
$10a_g$	-0.561	81	5	13
$9a_g$	-0.598	50	7	42
$5a_u$	-0.613	—	—	99
$3b_g$	-0.636	23	—	77

in the interpretation of the photoelectron spectrum of this type of molecules would be certainly the close proximity of many energy levels (in the present case, there are seven levels, from $12a_g$ to $10a_g$, within 1.3 eV).

In order to check our previous conclusion regarding the lack of validity of Koopmans' theorem (since the sequence of ionization potentials cannot be predicted from the sequence of orbital energies, with the lowest I.P.'s of *bis*-(π-allyl)nickel corresponding to some orbitals, predominantly metal $3d$, with lower energies than the ligand π orbitals) we have carried SCF open-shell calculations for the corresponding positive ion in two electronic configurations, corresponding respectively to the removal of one electron from the $7a_u$ orbital and the $9a_g$ orbital of Table 1. These two MO's correspond respectively to the highest orbital energy ($7a_u$) and to the lowest I.P. ($9a_g$) according to the previous calculation [10]. The results of the open-shell calculations are given in Table 2. They substantiate our previous conclusion that the orbital $9a_g$ (which is mostly metal $3d$) has a lower I.P. than the highest occupied orbital $7a_u$ (π-ligand orbital) of the ground state. The dramatic effect of electronic relaxation upon ionization of the $9a_g$ orbital (namely the difference of more than 10 eV between the I.P. computed according to Koopmans' theorem and the I.P. given as the difference of the total energies for the molecule and the ion) is about the same as in the previous calculation with a smaller basis set (10.6 eV from Table 2 *versus* 10.3 eV in Ref. [10]). We substantiate further our previous conclusion that Koopmans' theorem is approximately valid for MO's which are nearly pure ligand orbitals [9, 10], as evidenced in Table 2 for the $7a_u$ orbital with the computed I.P. equal to 7.3 eV *versus* an orbital energy of 7.8 eV. This indicates that our previous conclusion regarding the unimportance of electronic reorganization for the ligand orbitals (both σ and π) was not a consequence of the lack of flexibility in the basis set used. The relative importance of electronic relaxation for the different types of orbitals

Table 2. Computed ionization energies

Molecule	State	Energy (in a.u.)	Computed I.P. (in eV)
$Ni(C_3H_5)_2$	^1A_g	−1736.2476	—
$Ni(C_3H_5)_2^+$	^2A_g	−1736.0377	5.71[a](16.27)[b]
	^2A_u	−1735.9793	7.30(7.84)

[a] I.P. computed as the difference of the energy value for the molecule and the ion.

[b] I.P. computed according to Koopmans' theorem.

Table 3. Molecular orbitals for the molecule and the ion

	Orbital	LCAO coefficients[a]
$7a_u$	$Ni(C_3H_5)_2$	$0.23z^1(C_2)+0.32z^2(C_2)$
	$Ni(C_3H_5)_2^+$	$0.24z^1(C_2)+0.30z^2(C_2)$
$9a_g$	$Ni(C_3H_5)_2$	$0.60d_{yz}^1-0.23d_{x^2-y^2}^1+0.12s^2(C_1)+0.12s^1(H_1)-0.11s^1(H_2)$
	$Ni(C_3H_5)_2^+$	$0.94d_{yz}^1-0.17d_{x^2-y^2}^1-0.18d_{z^2}^1$

[a] Only the greater coefficients appear in this table.

is also evidenced in Table 3 through a comparison of the $7a_u$ and $9a_g$ orbitals from the wavefunctions for the neutral molecule and the ion.

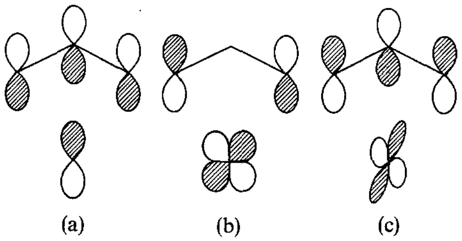
The agreement with the experimental values of the I.P.'s is certainly less good than in our previous work [10]. The experimental value for the first I.P. is about 7.9 eV whereas the computed I.P. for the $9a_g$ orbital is now 5.7 eV instead of 7.9 eV in Ref. [10]. It turns out that the previous calculation benefited from an almost exact cancellation of errors through the use of too small a basis set together with the neglect of correlation energy. SCF calculations of ionization potentials for transition metal complexes and organometallics, as they approach the Hartree-Fock limit, tend to produce computed values which are too low by about 3–4 eV. Van der Velde and Nieuwport, using a very large basis set, obtained for the first ionization potential of $Ni(CO)_4$ (corresponding to the $9t_2$ orbital) a value of 4.90 eV compared to an experimental value of 8.98 eV [15].

The nature of the bonding in π-allyl complexes has been discussed previously by several authors either in a qualitative way [16] or based on semiempirical calculations [17, 18]. It is generally considered that a π-allylic system may be formally regarded as a bidentate ligand and a similar type of bonding has been postulated for π-allyl and π-cyclopentadienyl-metal complexes [19]. Based on symmetry considerations, essentially three interactions are considered to be possible between the metal orbitals and the π orbitals of the allyl group [16]:

(a) between the bonding π orbital of the allyl group and the orbitals $3d_{z^2}$, $4s$, and $4p_z$ of the metal. This interaction must correspond to a ligand to metal electronic transfer. If the $3d_{z^2}$ orbital of the metal is doubly occupied, this interaction will be effective only through the participation of the $4s$ and $4p_z$ orbitals;

(b) between the nonbonding π orbital of the allyl group (which is singly occupied in the allyl radical and doubly occupied in the anion) and the $3d_{xz}$ orbital of the metal. The corresponding electronic transfer may be either from the ligand to the metal or from the metal to the ligand, depending on the respective occupancy of these two orbitals;

(c) between the antibonding π orbital of the allyl group and the $3d_{yz}$ orbital of the metal. This interaction must be of the backbonding type, provided that the $3d_{yz}$ orbital of the metal is occupied.



In this qualitative description the metal $3d_{xy}$ and the $3d_{x^2-y^2}$ orbitals are considered to be non-bonding. However, one knows that in ferrocene these two orbitals interact with the ligands σ and π orbitals in the sense of a backbonding transfer from the metal to the ligands [9].

It is immaterial whether we consider the allyl group in *bis*-(π-allyl)nickel as a radical or an anion, since the number of electrons supplied by the allyl group to the molecule can be formally compensated by a change in the valency of the metal atom [19]. *For the sake of convenience* we consider that the molecular orbitals of *bis*-(π-allyl)nickel may be described in terms of an interaction between two allyl anions and a Ni(II) $3d^8$ metal atom. The allyl anion has its bonding and nonbonding orbitals, as represented in (a) and (b), doubly occupied. From the computed wavefunction of Table 1 and Fig. 2, the Ni(II) atom has, to a first

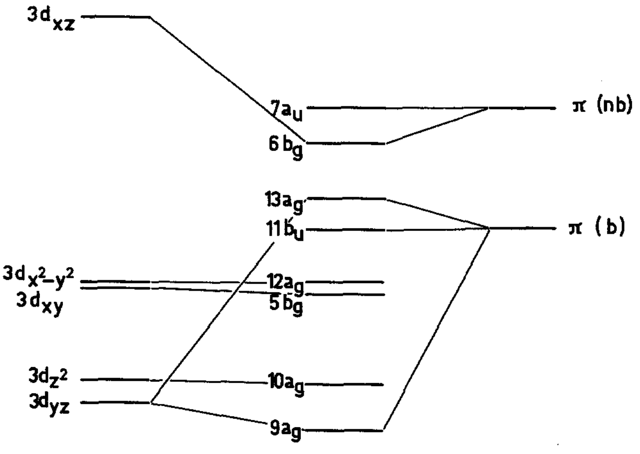


Fig. 2. A molecular orbital diagram showing the relationship between the MO's of *bis*-(π-allyl)nickel and the orbitals of the allyl group

Table 4. Metal-Carbon overlap populations for some valence molecular orbitals

Molecular orbital	Overlap population	
	Ni–$C_{(1)}$	Ni–$C_{(2)}$
$7a_u$	-0.004	0.031
$6b_g$	-0.052	0.059
$13a_g$	-0.038	-0.025
$11b_u$	0.027	0.016
$12a_g$	-0.002	-0.015
$5b_g$	-0.012	-0.009
$10a_g$	-0.036	-0.015
$9a_g$	-0.003	0.015

Table 5. Gross atomic and orbital populations

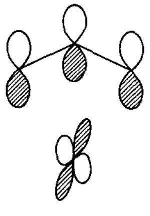
	Ni	$C_{(1)}$	$C_{(2)}$
$2s$ or $4s$	0.11	1.48	1.30
$2p_x$ or $4p_x$	0.11	0.93	0.86
$2p_y$ or $4p_y$	0.05	1.05	0.97
$2p_z$ or $4p_z$	0.12	0.88	1.25
$3d_{x^2-y^2}$	1.93		
$3d_{xy}$	1.86		
$3d_{xz}$	1.15		
$3d_{yz}$	1.99		
$3d_{z^2}$	2.03		
Formal charge	$+0.65$	-0.33	-0.38

approximation, four doubly occupied orbitals $3d_{yz}$, $3d_{z^2}$, $3d_{xy}$ and $3d_{x^2-y^2}$ (in the order of increasing energy) and one empty orbital, $3d_{xz}$ (besides the $4s$ and $4p$ orbitals). On this basis it is expected:

that interaction (a) between two filled orbitals will be unimportant;

that interaction (b) between the filled non bonding orbital of the allyl group and the empty $3d_{xz}$ orbital of the Ni atom will probably be responsible for most of the bonding.

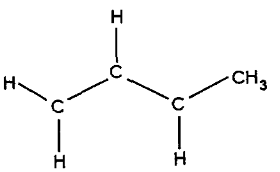
This is indeed substantiated by the metal-carbon overlap populations for some valence molecular orbitals in Table 4, the orbital population analysis of Table 5 and the molecular orbital diagram of Fig. 2. The largest bonding contribution comes from the molecular orbital $6b_g$ (which is mostly a ligand π orbital) and corresponds to the above type (b). An additional type of interaction (d) which



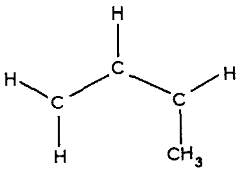
(d)

was not considered in Ref. [16] is found in the molecular orbital $13a_g$ (mostly an allyl π bonding orbital) and corresponds to an antibonding interaction between the Ni atom and the carbon atoms. The corresponding bonding interaction, somewhat weaker, is found in the $9a_g$ orbital, mostly a metal $3d_{yz}$ orbital. Backbonding from the metal to the ligand is not operative through a (c) type interaction as postulated in Ref. [16] (this may be seen from the population of 1.99 of the $3d_{yz}$ orbital), but rather results from some interaction between the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals and the σ and π orbitals of the ligands at the level of the $12a_g$ and $5b_g$ molecular orbitals. The importance of this backbonding appears comparable to the one in ferrocene (the orbital populations of the $3d_{xy}$ and $3d_{x^2-y^2}$ are respectively 1.86 and 1.93 in *bis*-(π-allyl)nickel *versus* a value of 1.86 for these degenerate orbitals in ferrocene)[1].

The following discussion is devoted to the internal rotation of the methylene group around the C–C bond in *bis*-(π-allyl)nickel and related compounds. The detection of two isomers corresponding to the syn and anti forms in $C_4H_7Co(CO)_3$ indicates that rotation about the allylic C–C bond may be hindered in these complexes [19]. The proton magnetic resonance spectra of π-allyl complexes either are of the A_2M_2X type indicating restricted rotation about the allylic bond or are typical of an A_4X system, suggesting that the allyl group has equivalent terminal hydrogens [20]. *Bis*-(π-allyl)nickel shows an A_2M_2X spectrum at low temperatures and an A_4X spectrum at higher temperatures [20]. Different mechanisms have been postulated to account for the equivalence of the terminal hydrogens [20, 21]:



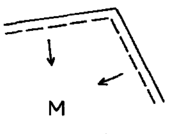
syn



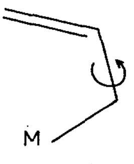
anti

1. rotation of the CH_2 group about the C–C allylic bond;

2. conversion from a π-allyl complex to a σ-allyl complex followed by a rotation of the ethylene group about the C–C "single" bond as proposed for the interconversion of the *syn* and *anti*-hydrogens in a methyl allyl rhodium complex [20]:



π-complex



σ-complex

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[1] No significance should be attached to the fact that the population of the $3d_{z^2}$ orbital is slightly greater than two since this is the population of *basis functions*, not atomic or molecular orbitals and we use two basis functions for each valence orbital.

The corresponding activation energies have been found in the range of 10–15 kcal/mole [21] [2]. The rotation about the C–C allyl bond has been ruled out for asymmetric π-(meth)allylpalladium complexes on the basis that it cannot account for the simultaneous exchange of nonequivalent methyl groups in the other ligands [21].

We have studied the rotation about the C–C allyl bond by performing an independant calculation with the $C_{(2)}H_{(2)}H_{(3)}$ group (see Fig. 1) rotated by 90° around the $C_{(1)}C_{(2)}$ axis. The computed barrier for rotation around the allyl bond has been found equal to 90 kcal/mole. In order to assess the accuracy of this calculation we have also computed the rotation barrier for the $C_3H_5^-$ anion, with the same geometry which was used in the complex and keeping the geometrical parameters fixed during the rotation process except for the rotation angle. This produced a rotation barrier of 37 kcal/mole while the experimental value is believed to be of the order of 20 kcal/mole [23]. Geometry optimization would be certainly more important for the transition state ("perpendicular allyl anion") and will decrease the computed barrier. We may then consider that the computed value of 90 kcal/mole for the barrier to rotation in *bis*-(π-allyl)nickel is overestimated. However it is dubious that further refinements in the theoretical approach will make rotation about the allyl bond an energetically favorable process. One of the reasons for this high value of the rotation barrier is rather obvious: upon rotation one of the hydrogen atoms $H_{(2)}$ or $H_{(3)}$ gets relatively close to the Ni atom (in the present calculation the corresponding distance was 1.81 Å) and this results probably in a strongly repulsive effect. Geometry optimization will certainly tend to reduce the repulsion, hence to decrease the computed barrier. This would be achieved probably through a distortion of the allyl group such that the distance from the Ni atom to the CH_2 group under rotation is increased, a situation somewhat reminiscent of the one in asymmetric π-methallyl compounds with unequal bond lengths between the Ni atom and the two carbon atoms C_2 and C_3 [21, 24]. Such a structure is considered as an intermediate between a π- and a σ-allyl complex, with two carbon atoms ($C_{(1)}$ and $C_{(2)}$) only weakly bonded to the metal atom. A possible mechanism for the conversion from a π- to a σ-allyl complex would begin with a rotation of one CH_2 group accompanied with a geometric distortion of the allyl group, then proceeds through an asymmetric π-complex to a σ-complex.

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[2] A third movement which has been postulated for the allyl group in π-allyl complexes corresponds to the "π-rotation" mechanism, namely an in-plane rotation of the allyl group about the metal-allyl axis [16–21]. For *bis*-(π-allyl)nickel this would interchange the D_{2h} and D_{2d} structures. It has been postulated that the two isomeric forms observed for Ni and Pd *bis*-(π-allyl) complexes and their 2-methyl derivatives correspond to these two structures [21]. Rosch and Hoffmann have pointed out that this rotation should be a high-energy process [22].

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