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Electron Affinities in Bis(η^3-allyl)nickel, -palladium, and -platinum: Electron Transmission Spectra and MS–Xα Calculations

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The electron transmission spectra, in the 0–5-eV energy range, of the bis(η^3-allyl) complexes of nickel, palladium, and platinum are reported. Each spectrum displays three resonances associated with electron capture into the three empty π^* ligand orbitals. The measured electron attachment energies are well reproduced by MS–Xα calculations on the Ni and Pd compounds. Calculated charge distributions in the neutral states of these complexes predict a sizable negative charge density at the metal atom.

Introduction

Bis(η^3-allyl) transition metal complexes are the simplest "sandwich" compounds and show a variety of interesting chemical properties.[1,2] It is therefore not surprising that much experimental and theoretical work has been devoted to the study of the nature and energy sequence of the valence occupied MOs in (η^3-allyl)$_2$Ni. A variety of theoretical approaches have been employed, including SCCCMO,[3] EHT,[4] semiempirical ΔSCF INDO,[5] Xα–SW[6] and ab initio CI[7] calculations, and ab initio[8] and semiempirical[9] Green's function methods. Because of large relaxation contributions to ionization events from orbitals with mainly metal character in transition metal complexes, (η^3-allyl)$_2$Ni became a model system in the discussion of the failure of Koopmans' theorem in the interpretation of the photoelectron spectra for this class of compounds and, after the first publication of its photoelectron spectrum,[10] the assignment of the first bands has been a matter of debate. Even experimental indications based on the ionziation energy (IE) shifts caused by methyl substitution at the ligands[5,11] and by replacement of the Ni atom with heavier atoms of the same group[5] or based on the relative ionization cross sections on going from He I to He II incident radiation[5,9,11] led to different conclusions, in particular on the assignment of the first band to ionization from the pure ligand 7a$_u$ orbital or from two essentially metal d orbitals.

If, on one hand, the ionization energy sequence in (η^3-allyl)$_2$Ni has been the subject of such controversial discussion, on the other hand nothing is known about the complementary electron affinity data. In this paper, we continue our study of the anion states and chemical bonding in transition metal complexes[12–16] and measure the electron affinities in bis(η^3-allyl)nickel, -palladium, and -platinum by means of electron transmission spectroscopy (ETS).[17] This technique takes advantage of the sharp variations in the total electron-molecule scattering cross section caused by resonance processes, that is, formation of temporary anion states. The energies (AEs) at which electron attachment occurs are the negative of the electron affinities (EAs), and in a Koopmans' theorem sense, they can be associated with the energies of the empty MOs.

Over the last years, we have employed multiple scattering Xα (MS–Xα) calculations,[18] with a stabilization procedure,[19] for reproducing the resonance energies measured in several transition metal complexes. The stabilization procedure accounts for the fact that during the lifetime of a shape resonance the extra electron is confined to the molecule by a replusive short-range potential, giving rise to a "quasi-bound" state. The results have demonstrated that this approach is reliable and accurate in

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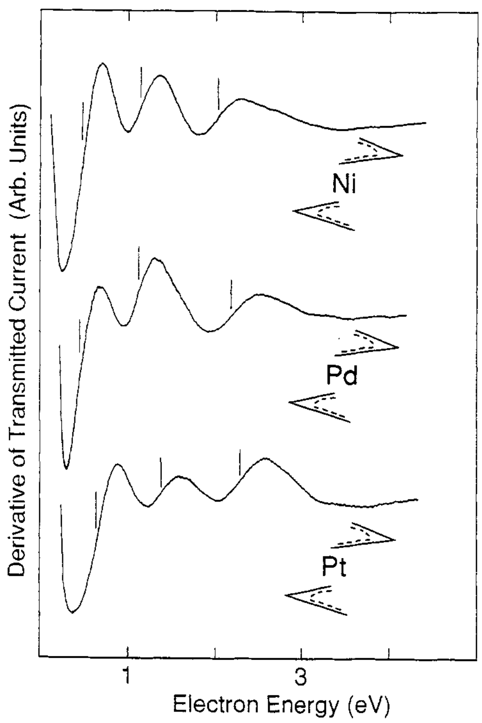

Figure 1. Derivative of the electron current transmitted through (η^3-allyl)$_2$Ni, (η^3-allyl)$_2$Pd, and (η^3-allyl)$_2$Pt vapors.

reproducing not only the experimental trends of the negative EAs but also their absolute values. The advantage lies in the radial flexibility of the Xα wavefunctions which LCAO methods do not contemplate. In addition, the MS–Xα method is particularly appropriate also for estimating IEs, since electron relaxation effects (important in transition metal complexes) are taken into account by the calculations.[20] We compare here the AE and IE values calculated at the MS–Xα level in bis(η^3-allyl)nickel and -palladium to the corresponding experimental data. Moreover, we calculate the MS–Xα charge density distributions in the neutral ground states. In the previously studied transition metal complexes, in fact, both the ET spectra and the computed charge densities indicated a strong net transfer of negative charge from the ligands to the central metal atom.[14–16]

Results and Discussion

The ET spectra of the bis(η^3-allyl) complexes of Ni, Pd, and Pt are reported in Figure 1. These complexes are expected to possess three empty low-energy π^* orbitals. The allyl radical, in fact, possesses three π electrons and three π orbitals, with bonding (π_1), nonbonding (π_2), and antibonding (π_3) character. The LUMO in the bis(allyl) complexes is the out-of-phase combination of the nonbonding allyl orbital (π_2^{*-}, of b_g symmetry in the C_{2h} point group) destabilized by large mixing with the d_{xz} orbital,[5] while the corresponding filled in-phase combination π_2^+ (a_u) does not mix by symmetry with the metal d orbitals. The remaining two empty π^* MOs are the in-phase and out-of-phase combinations of the antibonding allyl orbital, $\pi_3^{*+}(a_g)$ and $\pi_3^{*-}(b_u)$. The three empty π^* MOs are sketched in Figure 2. Each spectrum displays three resonances below 2.5 eV, that is, one resonance for each

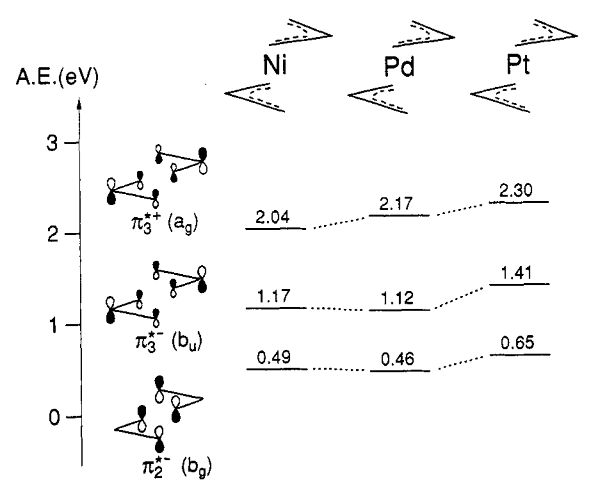

Figure 2. Correlation diagram among the AE values in (η^3-allyl)$_2$Ni, (η^3-allyl)$_2$Pd, and (η^3-allyl)$_2$Pt.

of the expected empty π^* orbitals, thus indicating that even the ground anion state is unstable in these complexes. Figure 2 reports the measured AE values and shows that they are only slightly affected by the central metal atom. Table I reports the AE and IE values predicted by the MS–Xα calculations for the Ni complex, together with the calculated localization properties of the corresponding orbitals. The calculated AEs are very close to experiment, all of them being shifted 0.2–0.4 eV to a higher energy. The first resonance is assigned, as expected, to electron capture into the b_g empty orbital, and the calculated localization properties confirm that this MO arises from strong mixing between the π_2^{*-} allyl orbital (no charge density at the central allyl carbon atoms) and metal d orbitals of the same symmetry (the Ni contribution predicted by the calculations is only slightly smaller than the ligand contribution). In agreement, the filled d counterparts $6b_g(d_{xz})$ and $5b_g(d_{xz})$ possess significant allyl terminal carbon character, especially the latter which points toward the ligands, thus allowing greater mixing. The energy separation (0.9 eV) between the two higher-lying π^* resonances observed in the ET spectrum is close to that (1.2 eV) measured between the IEs from the two innermost filled π orbitals, namely the in-phase ($10a_g$) and out-of-phase ($11b_u$) combinations of the allyl π_1 bonding orbital. The MS–Xα calculations accurately reproduce these energy separations, as well as the absolute AE and IE values. It is interesting to note that the calculations, in agreement with previous assignments,[5,11] predict the energy sequence $\pi_1^+(a_g)$ below $\pi_1^-(b_u)$ for the filled orbitals (the ordering expected in the case of dominant through-space interaction) but the opposite ordering for the empty orbitals, that is, $\pi_3^{*+}(a_g)$ above $\pi_3^{*-}(b_u)$. This inversion indicates that through-space interaction between the two allyl fragment orbitals is small, and implies the occurrence of significant (destabilizing) mixing of the in-phase $\pi_3^{*+}(a_g)$ combination with metal filled d orbitals of the same symmetry. The calculated localization properties confirm that $\pi_3^{*+}(a_g)$ possesses a sizable Ni character (about one-fifth with respect to the allyl contribution), while the $\pi_3^{*-}(b_u)$ combination has no contribution from the metal atom. Also when the filled $\pi_1^+(a_g)$ and $\pi_1^-(b_u)$ MOs are considered, the calculated localization properties (see Table I) suggest that their energy sequence can be accounted for by mixing with metal orbitals, without needing to invoke through-space inter-

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Table I. Experimental and Calculated (MS–Xα) AEs and IEs (eV) in (η^3-allyl)$_2$Ni and Calculated Transition-State Localization Properties of the Corresponding Orbitals[a]

	energy		charge distribution, %					
sym (C_{2h})	exptl	Xα	Ni	C$_{cen}$	C$_{ter}$	INT	OUT	r_w
	AE							
a$_g$(π_3^{*+})	2.04	2.47	7	19	14	20	40	13.0
b$_u$(π_3^{*-})	1.17	1.58	0	17	15	31	37	12.0
b$_g$(π_2^{*-})	0.49	0.67	34	0	40	20	6	*b*
	IE							
7a$_u$(π_2^+)	7.8	7.0	6	0	56	36	2	
13a$_g$(d)	8.2	8.2	78	1	10	10	1	
12a$_g$(d)	8.6	8.8	92	2	1	5	0	
6b$_g$(d)		8.9	87	0	7	5	1	
11a$_g$(d)	9.4	9.4	90	2	1	7	0	
5b$_g$(d)		9.4	72	0	17	10	1	
11b$_u$(π_1^-)	10.4	10.2	6	34	29	30	1	
10a$_g$(π_1^+)	11.6	11.4	18	27	26	28	1	

[a] The Watson sphere radii (r_w) used for the anion states are also reported. The experimental IE values are taken from ref 5. [b] Energy and charge distribution do not change in the range $10.0 < r_w < 14.0$,due to the absence of low-energy continuum-like states for this symmetry.

Table II. Experimental and Calculated (MS–Xα) AEs and IEs (eV) in (η^3-allyl)$_2$Pd and Calculated Transition-State Localization Properties of the Corresponding Orbitals[a]

	energy		charge distribution, %					
sym (C_{2h})	exptl	Xα	Pd	C$_{cen}$	C$_{ter}$	INT	OUT	r_w
	AE							
a$_g$(π_3^{*+})	2.17	2.41	5	16	15	18	46	13.0
b$_u$(π_3^{*-})	1.12	1.54	0	20	17	36	27	11.5
b$_g$(π_2^{*-})	0.46	0.72	30	0	42	22	6	*b*
	IE							
7a$_u$(π_2^+)	7.6	6.9	4	0	58	36	2	
13a$_g$(d)	8.7	8.9	54	6	18	21	1	
12a$_g$(d)		10.8	85	2	3	8	2	
6b$_g$(d)	9.3	10.4	72	0	14	8	0	
11a$_g$(d)	9.5	11.4	83	4	2	11	0	
5b$_g$(d)	9.8	11.4	76	0	13	11	0	
11b$_u$(π_1^-)	10.5	10.3	4	34	30	31	1	
10a$_g$(π_1^+)	11.6	12.0	32	23	21	23	1	

[a] The Watson sphere radii (r_w) used for the anion states are also reported. The experimental IE values are taken from ref 5. [b] Energy and charge distribution do not change in the range $10.0 < r_w < 14.0$, due to the absence of low-energy continuum-like states for this symmetry.

actions. The π_1^+(a$_g$) MO, which possesses large Ni character, is stabilized by interaction with metal d orbitals of the same symmetry whereas the π_1^-(b$_u$) MO, which cannot mix with d orbitals for symmetry reasons, is destabilized by interaction with lower-lying p orbitals. The IE values supplied by the MS–Xα calculations for (η^3-allyl)$_2$Ni, reported in Table I, deserve some comments. First of all, they support the assignment, by Böhm et al.,[5,8] of the first photoelectron band to ionization from the π_2^+(a$_u$) MO, largely localized at the ligands. The calculations also closely reproduce (within 0.2 eV) the energies of the two inner π (b$_u$ and a$_g$) orbitals, which give rise to the fifth and sixth bands in the photoelectron spectrum. The calculations predict the five ionization events from orbitals with dominant d character to give rise to three bands at 8.2 (a$_g$), 8.8 (a$_g$, b$_g$), and 9.4 (a$_g$, b$_g$) eV, in almost perfect agreement with the experimental energies (8.2, 8.6, and 9.4 eV) of the second, third, and fourth peaks observed in the photoelectron spectrum. Although a different distribution of the five d ionization events in these three bands (that is, four d orbitals would contribute to the 8.2- and 8.6-eV bands, and a single orbital to the 9.4-eV band) has been deduced on the basis of the relative intensities,[5] the present MS–Xα IEs are by far more accurate than those obtained with other theoretical approaches previously reported in the literature, except for the LCGTO-LSDF calculations by Anzdelm et al.[21]

When the ET spectra of the Pd and Pt derivatives are also considered (see Figures 1 and 2), it is apparent that the AEs associated with the three empty π^* orbitals do not undergo large variations with respect to those of bis(allyl)nickel. In agreement, the π IEs have also been found to be rather insensitive to metal exchange along this series.[5] The MS–Xα calculations on bis(allyl)palladium (see Table II) closely reproduce the experimental AEs and confirm that both the π AE and IE values are not much different from those of the Ni analogue. The calculations, however, fail to reproduce the IEs of the four localized d orbitals, which are predicted to be about 1 eV higher with respect to experiment. We ascribe this failure to the fact that the relative Pd–ligand position assumed by the calculations (see Experimental Section below) could be significantly different from reality, owing to the absence of structural data for the complex. A consequently wrong charge transfer between metal and ligands would mainly affect the energies calculated for MOs essentially localized at a single atom.

Charge Distributions. The charge distributions calculated on the neutral states at the MS–Xα level are

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Table III. Calculated Atomic Charge Densities in the Neutral Ground States of the Bis(allyl) Complexes of Ni and Pd[a]

	metal	C_{cen}	C_{ter}	H_{cen}	H_{ter}^{syn}	H_{ter}^{anti}
$(\eta^3\text{-}C_3H_5)_2Ni$	−0.60 $(d^{9.24}s^{0.54}p^{0.72}f^{0.08}g^{0.02})$	+0.09	−0.125	+0.06	+0.10	+0.10
$(\eta^3\text{-}C_3H_5)_2Pd$	−0.32 $(d^{9.28}s^{0.42}p^{0.52}f^{0.09}g^{0.01})$	+0.06	−0.17	+0.06	+0.09	+0.10

[a] The numbers in parentheses give the Ni and Pd orbital populations above [Ar] and [Kr], respectively.

Table IV. Atomic Sphere Radii (au)

	metal	C_{cen}	C_{ter}	H_{cen}	H_{ter}^{syn}	H_{ter}^{anti}	OUT
$(\eta^3\text{-}C_3H_5)_2Ni$	2.21231	1.72843	1.77601	1.27892	1.26134	1.28309	6.66709
$(\eta^3\text{-}C_3H_5)_2Pd$	2.28437	1.73391	1.78018	1.28097	1.26535	1.28491	6.81923

presented in Table III. They are characterized by a sizable negative charge at the metal atom (0.60 e for Ni), a small negative charge at the allyl terminal carbon atoms, and a small positive charge at the central carbon atoms and at the hydrogen atoms. Substantially different results have been previously found using INDO[5] and ab initio[22] calculations, which predict a much higher negative charge at the allyl terminal carbon atoms and a large positive charge (0.78 e[5]) at the Ni atom. The present MS–Xα results, as well as their pronounced discrepancy with LCAO calculations, are in line with those we previously obtained for other complexes with aromatic, carbonyl, and nitrosyl ligands.[14–16] We have already suggested two possible sources of the systematic discrepancies in the calculated charge densities between the two theoretical approaches.[15] Although in the present case comparison with the AE values in the free bis(allyl) ligand is not possible, in complexes previously studied the positive charge at the ligands predicted by the MS–Xα calculations has been found consistent with the ET spectra, that is, with the sizable stabilization of ligand anion states upon complexation. ^{195}Pt NMR data[23] support the negative charge at the metal atom predicted by the present calculations. The chemical shift observed in bis(η^3-allyl)platinum, in fact, is even larger than that observed in Pt(0) complexes. While the LCAO calculations only emphasize the strong charge transfer from d metal to π^* ligand orbitals, the present population analysis also accounts for this interaction, but predicts in addition an even larger transfer of negative charge from the allyl ligands to the Ni 4s and 4p orbitals (see Table III), thus supplying a wider picture on the nature of the chemical bond in these complexes and pointing out the important role played by the metal empty orbitals. Significant transfer of negative charge from the allyl fragments back to the 4s and 4p Ni orbitals was previously indicated by Xα–SW calculations, although the net charge on the Ni atom was found to be positive.[6]

The sizable reduction of negative charge on the metal atom predicted by the calculations on going from the Ni to the Pd complex could stem from the assumption of a wrong geometry for the latter (as mentioned above). It can be noted that a larger negative charge on Pd would lead to a reduction of the calculated IE values from d orbitals and therefore to better agreement with the experiment.

Experimental Details and Computations

Our electron transmission apparatus is in the format devised by Sanche and Schulz[24] and has been previously described.[25] The present spectra have been obtained by using the apparatus in such a mode as to detect the nearly total scattering cross section.[26] To enhance the visibility of the sharp structures that appear in the scattering cross section because of the formation of temporary anion states, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the transmitted current is measured directly by a synchronous lock-in amplifier. The energy scales were calibrated with reference to the $(1s^1\ 2s^2)$ anion state of He. The estimated accuracy is ±0.05 eV. The sample temperature required to obtain a sufficient vapor pressure ranged from −5 (Ni) to 20 °C (Pt).

The complexes investigated were prepared by reactions between the appropriate metal halide and allylmagnesium halide.[27,28] Syntheses and manipulations were carried out under dry argon.

Multiple scattering Xα (MS–Xα) calculations[18] were carried out on Ni and Pd bis(allyl) complexes. The structural parameters for the Ni complex were taken from the experimental geometry of bis(η^3-methallyl)nickel.[29] The C–H bond lengths were set equal to 1.08 Å. The allyl moieties were assumed to be planar, although the hydrogen atoms have recently been found to be bent away from the metal in the solid phase structure.[30] In fact, it was suggested that this finding could arise from crystal packing effects, since the agreement between theoretical and experimental gas phase ionization energies worsens slightly on going from the planar to the bent structure.[21] Our preliminary calculations confirmed this and also demonstrated that the EAs are almost insensitive to hydrogen bending. A model structure was used for the Pd complex, because the experimental geometry is not available. The structural parameters for the allyl ligands were taken from the Ni complex. The allyl ligands were then removed away from the Pd atom along the Pd–C_{cen} direction, keeping the allyl planes parallel to each other. The Pd–C_{cen} distances were set equal to 2.1 Å, that is, the mean Pd–C distance in similar complexes.[31,32] In the calculations, the local exchange parameters,[33] α, were taken from the tabulation of Schwarz[34] and a valence weighed average was employed for the inter (INT) and outer (OUT) sphere regions. The radii ratios for the atomic spheres were determined using the nonempirical procedure of Norman.[35] The atomic radii

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(reported in Table IV) satisfy the virial ratio in the neutral molecules. It is worth pointing out that reliable absolute IE and AE values were obtained using this criterion. MS–Xα calculations on the Ni complex eploying atomic radii proportionally much larger than those used in the presence calculations provided IEs 4–5 eV lower than the experiment.[6] The electronic charge within the atomic spheres was normalized using the double-counting correction.[36] Core electrons were not frozen during the SCF procedure, and eigenvalues converged to better that 0.001 eV. Wavefunctions were expanded in partial waves up to $l = 0$ for hydrogen, $l = 1$ for carbon, and $l = 4$ for the metal and outer spheres. IEs and AEs were computed with the transition state method.[37] A positively charged sphere (Watson sphere) was employed to stabilize the unbound states. AEs were then determined from the stability of transition state eigenvalues (corrected for the stabilization energy generated by the Watson sphere) in stabilization graphs constructed as a function of the Watson sphere radius by keeping the stabilization potential fixed to 8.0 Rydbergs.[38] The charge distributions in the neutral molecules were computed by partitioning the inter and outer sphere charges among atoms according to the procedure suggested by Case and Karplus.[39]

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