a maximum relative population of this state of 21% of the ground state. If this is the case then the band is actually "sharper" than it appears.

(21) J. H. D. Eland, "Photoelectron Spectroscopy", Wiley, New York, N.Y., 1974.

(22) R. B. Caton and A. E. Douglas, *Can. J. Phys.*, **48**, 432 (1970).

(23) R. K. Nesbet, *J. Chem. Phys.*, **43**, 4403 (1965).

(24) T. Berlin, *J. Chem. Phys.*, **19**, 208 (1951).

(25) R. F. W. Bader and A. D. Bandrauk, *J. Chem. Phys.*, **49**, 1653 (1968).

(26) W. M. Huo, *J. Chem. Phys.*, **43**, 624 (1965).

(27) N. Jonathan, A. Morris, M. Okuda, D. J. Smith, and K. J. Ross, *Chem. Phys. Lett.*, **13**, 334 (1972); C. H. King, H. W. Kroto, and R. J. Suffolk, *Chem. Phys. Lett.*, **13**, 457 (1972); N. Jonathan, A. Morris, M. okuda, K. J. Ross, and D. J. Smith, *Discuss. Faraday Soc.*, **54**, 48 (1972); D. C. Frost, S. T. Lee, and C. A. McDonald, *Chem. Phys. Lett.*, 17, 153 (1972); M. Okuda and N. Jonathan, *J. Electrom Spectrosc. Relat. Phenom.*, **3**, 19 (1974).

(28) W. G. Richards, *Trans. Faraday Soc.*, **63**, 257 (1967).

(29) L. Chun-Hau, R. S. Pashinkin, and A. V. Novoselova, *Russ. J. Inorg. Chem.*, 7, 496 (1962).

(30) The spectrum of $(Se)_n$, including Se_2 was produced by the vaporization of $GeSe_2$. Se_2 was also produced in the vaporization of SnSe(s): M. Wu, unpublished data. The spectrum of Se_2 has also been communicated to us by J. Berkowitz.

(31) D. C. Frost, S. T. Lee, and C. A. McDowell, *J. Chem. Phys.*, **59**, 5484 (1973).

(32) G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966.

(33) J. Berkowitz, J. L. Dehmer, and T. E. H. Walker, *J. Chem. Phys.*, **59**, 3645 (1973).

(34) S. Cradock and W. Duncan, *Mol. Phys.*, **27**, 837 (1974).

(35) A. W. Potts and W. C. Price, *Proc. R. Soc. London, Ser. A*, **326**, 165 (1972).

(36) S. Cradock and W. Duncan, *J. Chem. Soc., Faraday Trans. 2*, 71, 1262 (1975).

(37) R. Colin and J. Drowart, *Trans. Faraday Soc.*, **60**, 673 (1964).

(38) M Wu and T. P. Fehlner, unpublished work.

(39) R. F. Porter, *J. Chem. Phys.*, **34**, 583 (1961).

(40) J. M. Dyke, L. Golob, N. Jonathan, and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, 1026 (1975).

(41) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules", Van Nostrand, Princeton, N.J., 1950.

(42) A recent calculation [D. P. Chong, F. G. Herring, and D. P. McWilliams, *J. Electron Spectrosc. Relat. Phenom.*, 7, 429 (1975)] indicates a σ-π separation in BF of 8.7 eV. The fact that it is quite large is consistent with the trends illustrated in Figure 8.

(43) NOTE ADDED IN PROOF. The valence level photoelectron spectrum of Bi_2 has recently been reported (S. Süzer, S. T. Lee, and D. A. Shirley, *J. Chem. Phys.*, **65**, 412 (1976)). The σ-π separation is -1.07 eV for a Z_{UA} of 166. Thus, the behavior exhibited in Figure 8 for group 4-6 molecules is paralleled by group 5-5 molecules.

Photoelectron Spectroscopy of Bis(π-allyl)nickel and Its Methyl Substituted Derivatives: Support for the Near Validity of Koopmans' Theorem

Christopher D. Batich[1]

Physikalisch-chemisches Institut der Universität Basel, CH-4056 Basel,
Switzerland, and the Max-Planck Institut für Kohlenforschung,
433 Mülheim a.d. Ruhr, West Germany. *Received May 3, 1976*

Abstract: The He (I) photoelectron spectra of bis(π-methallyl)nickel, bis(π-crotyl)nickel, and bis(π-1,3-dimethylallyl)nickel are presented and related to bis(π-allyl)nickel (**1**). It is shown that a previous assignment for **1** should be modified by placing the $\pi(a_u)$ ionization energy within 0.4 eV of the first ionization energy. This new assignment substantially reduces the continuing disagreement between experiment and theoretical Koopmans type calculations. Methyl substituent effects are shown to be useful in assigning photoelectron spectra of organometallic systems. A detailed discussion of the assignment criteria is presented which includes a He (II) spectrum of bis(π-methallyl)nickel.

Transition metal complexes involving the allyl radical as a three-electron ligand represent the simplest "sandwich" compounds known. Because of this, and their extensive and interesting chemistry,[2-4] they are an obvious choice for the application of theoretical methods to organometallic systems. Although the mode of bonding has been discussed in general books on the subject,[5,6] only a description couched in broad terms could be used because of uncertainties about relative energies of the occupied molecular orbitals. Recently a number of theoretical methods have been used to calculate the electronic structure of bis(π-allyl)nickel (**1**); among them: SCCCMO (self-consistent charge and configuration MO method),[7] EHT (extended Hückel type),[9] and an ab initio method using contracted Gaussian functions.[8] Although there was a variation in orbital energies and their relative sequence, the methods were unanimous in predicting a ligand (allyl) orbital as the highest occupied MO (HOMO). Shortly thereafter, a He (I) photoelectron (PE) spectroscopic investigation of **1** arrived at the quite different ordering that the HOMO was mainly a metal 3d type with the π-ligand orbitals lying lower by about 1.3 eV.[10] This interpretation invoked Koopmans' theorem[11] which equates the vertical ionization energy (IE) with a negative SCF-orbital energy. Subsequently another ab initio calculation was published taking into account electron reorganization after ionization[12] which is neglected in the Koopmans approximation.[11,13] Ionization energies stemming from mainly d orbitals were found to be stabilized by reorganization vastly more than those corresponding to ligand ionization. This implied that the HOMO was mainly a ligand type although the first ionization energy referred to a metal d orbital—i.e., Koopmans' theorem fails for **1**. Although there had been earlier examples of this failure,[13-15] they applied to smaller differences in energy and were not nearly so dramatic as in this case. The PE spectral interpretation was now, however, in substantial agreement with the most extensive calculation done on such a molecule. Since that time, bis(π-allyl)nickel has become an oft quoted example for the large scale failure of Koopmans' theorem.[16] However, some skepticism has remained and Fenske for instance has suggested further examination of this system.[17]

During the course of an investigation of methyl substituent effects on **1** as studied by PES, we began to question this seemingly settled question. In this paper we present evidence which supports an ordering more consistent with the earlier MO results and hence a nearer validity of Koopmans' theorem. It is also of some interest to examine the effect of subtle changes in a ligand upon the overall electronic levels since ligand change is of profound influence on the catalytic activity of a given metal atom. Bis(π-allyl)nickel is a reasonable choice here also because of the catalytic activity of nickel complexes

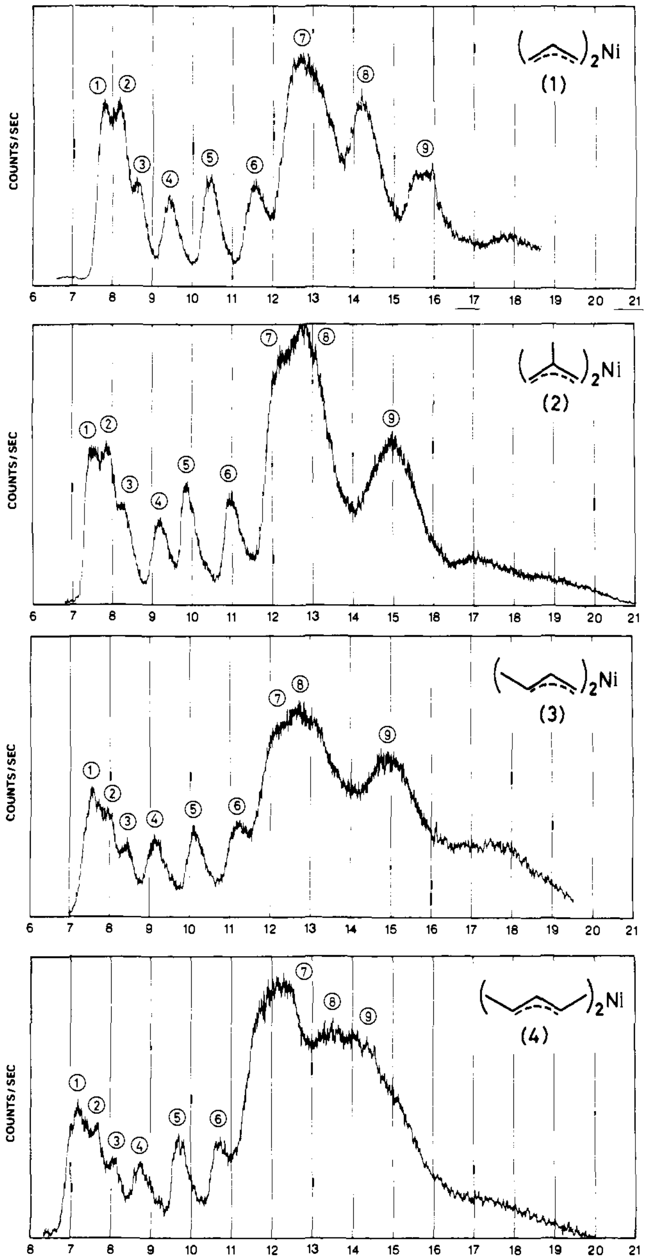


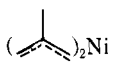
Figure 1. He (I) photoelectron spectra of the diallylnickel complexes 1 through 4.

and the occurrence of allyl–nickel species in many organic reactions.[3,18]

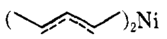
Experimental Section

In Figure 1 are shown the He (I) PE spectra of bis(π-allyl)nickel (1), bis(π-methallyl)nickel (2), bis(π-crotyl)nickel (3), and bis(π-1,3-dimethylallyl)nickel (4). They have been prepared according to


1


2


3


4

previously described methods.[2,19] The spectra were obtained on a modified Perkin-Elmer-16 spectrometer based on the design of Turner[20] and calibrated by simultaneous admission of xenon and argon. The data are also collected in Table I for the indicated bands and are in good agreement with a spectrum of 1 which has been published previously.[10] A He (II) spectrum was obtained on an instrument constructed in the Basel laboratory using a Perkin-Elmer heated inlet and lamp assembly which had been somewhat modified. The He (II) radiation of 304 Å was produced by the usual low pressure and high current density mode of operation.

Table I. Vertical Ionization Potentials (peak maxima) from the Photoelectron Spectra of Compounds 1 through 4[a]

Band	1	2	3	4
1	7.7_6	7.5_3	7.5_3	7.2_2
2	8.1_9	7.9_1	8.0_0	7.6_8
3	8.5_8	8.3_2	8.4_0	8.1_0
4	9.4_0	9.2_2	9.1_3	8.7_8
5	10.3_8	9.8_6	10.1_0	9.7_3
6	11.5_5	10.9_3	11.1_5	10.7_0
7	12.7	12.2	12.3	12.2
8	14.2	12.7	12.8	13.4
9	15.6	15.0	15.0	14.0

[a] Averages of at least three spectra for each compound; see text for designations.

Results and Discussion

1. General Considerations. First we will present a very qualitative picture of the molecular orbital interactions in **1**. The more sophisticated methods mentioned earlier in general reproduce the results of such an approach for simple systems. In fact, cautiously used simple Hückel type methods are frequently better than more rigorous calculations at predicting molecular properties.[21,22] An x-ray structure determination of **2** has indicated a "staggered-sandwich" conformation of C_{2h} symmetry[23] and this geometry will be assumed for the other allyl complexes also. Symmetry designations for orbitals of **1**, **2**, and **4** will be kept in **3** although the molecular point group is now changed. Furthermore, we will assume the validity of Koopmans' approximation for the convenience it allows in using orbital language. Once a consistent picture is formed we will again step outside of this simplified viewpoint and discuss our interpretation from a more restrictive "state" point of view.

Considering first the separate fragments, there is general agreement that the first IE of the allyl radical corresponds to removing an unpaired electron from the a_2 π-orbital (in C_{2v} symmetry). An early mass spectroscopically derived value for this energy is 8.16 eV.[24] The next orbital would most likely be also π of b_1 symmetry and lower by 1.414 β in a simple Hückel picture. Two σ orbitals of similar energy would then follow in a more complete calculation with all others well separated. (See Figure 2a.)

Placement of the nickel atomic orbitals is more complex. Although the first IE of Ni is 7.6 eV,[25] attachment of ligands might stabilize this from 1 to 3 eV (although the amount is by no means clear) with the 4s level remaining slightly less stable and 4p levels several electron volts less stable.[26] Although, in a related case, the first IE of chromium was used as the d-orbital energy,[27] this quantity is extremely difficult to rigorously define in a large system.[28] The 3p metal orbital of course lies very much lower (near −68 eV).[29] This is qualitatively represented in Figure 2d. Hence the five filled d levels on Ni^0 will be of about the same energy (before interaction) as the a_u π ligand. Since Hückel MO energies can be nicely fit to IE's of hydrocarbons by using $\beta \cong 2.7$ eV,[21,30] and the interactions between the two allyl groups will not be very large at their separation, one can make an estimate of the lower π-orbital energies. The predicted split of 1.4 β for allyl radical itself implies $(1.4)(2.7) = 3.8$ eV separation between allyl a_2 and b_1 and hence $(8.2 + 3.8 - 7.6) = 4.4$ eV below the first IE of Ni. These π-orbital energies (b_u and a_g in the allyl pair) should then lie well below the first nickel ones.

An examination of the spectra reveals a lack of sharp bands and consequent approximate values for IE's indicated in the table. This almost certainly results from a lack of rigidity in these molecules and the probable presence of several isomers which has been demonstrated in solution by NMR.[2,31] Calculations on PdA_2 (A = allyl) show that orbital energies of the C_{2h} and C_{2v} conformers are approximately the same[32] and hence should only broaden PES peaks. As has been pointed out earlier,[10] intensities in the PES of **1** suggest that bands 1 and 2 are each doubly degenerate and are followed by four nondegenerate peaks. It is probable that the two peaks 7 and 8 which are at higher IE's are also each doubly degenerate although considerably broader. According to our interaction diagram in Figure 2, bands 1 through 4 fall within the range of orbital energies expected for the metal d orbitals and the ligand π (a_u) orbital. Bands 5 and 6 are compatible with the π (b_u) and π (a_g) IE's, respectively, while 7 and 8 fit nicely with the two σ levels each doubly degenerate, i.e., $a_g + b_u$ and $b_g + a_u$. We will not be concerned further with these σ levels.

To decide where the highest ligand IE lies among bands 1 through 4 we will make use of (a) the simple Hückel description, (b) relative band intensities, (c) the effect of methyl substitution, and (d) changes in the spectrum when a He (II) light source is used.

2. Hückel Model. As stated just before, a simple Hückel model of the allyl group predicts a splitting of about 3.8 eV between the two π levels using $\beta = 2.7$ as derived from photoelectron data.[21] In **1** two π orbitals have odd parity (u) and hence cannot interact with the metal d orbitals (or the 4s for that matter) since these are all even (g). The lowest π-orbital is a_g and could theoretically interact but is the furthest removed and hence limited by a second-order effect due to the large energy difference. Hence, the mean of the two lower π IE's should be separated from the mean of the upper two (a_u and b_g) by approximately the mentioned difference: 3.8 eV. If the splitting between these two upper levels is approximately the same as between the lower two (1.17 eV), then one can estimate a mean splitting (see Figure 2b) for each of the four bands with respect to the mean of the lower π bands. Using this relationship:

$$\mathrm{IE}_n - \left(\frac{1.17}{2}\right) - \left(\frac{10.38 + 11.55}{2}\right) = \text{mean split}$$

or

$$\mathrm{IE}_n - 11.54 = \text{mean split}$$

where IE_n equals the measured band maximum, one obtains:

Band	IE_n	Calcd mean split
1	7.76	3.78
2	8.19	3.35
3	8.58	2.96
4	9.40	2.14

Error limits for this original estimate of β were 0.33 eV[21] which imply errors in this case of $(1.4)(0.33) \simeq 0.46$, or calculated mean splits from 3.34 to 4.26 eV. Due to the various unstated assumptions implicit in extrapolating such an approach to **1**, these limits should be somewhat larger. Neglecting the obviously fortuitous exact agreement of band 1 with the calculated value, bands 1 and 2 are consistent with the assignment of a π IE. Bands 3 and 4 are, however, unlikely contenders with 4, the band previously assigned as π (a_u),[10] almost certainly excluded.

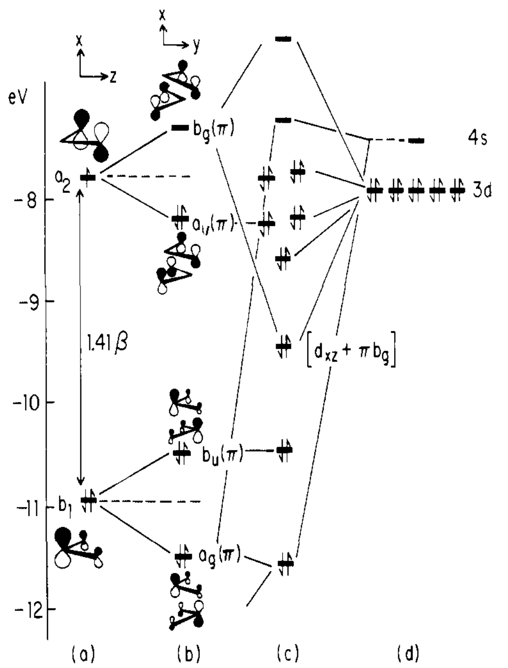


Figure 2. Ligand–metal interaction scheme for bis(π-allyl)nickel: (a) allyl radical Hückel-MO's in C_{2v} symmetry, (b) paired allyl radicals in C_{2h} symmetry, (c) MO ordering implied by PES data, (d) very approximate metal orbital placement.

3. Intensities. The a priori calculation of accurate PES intensities, or, more exactly, photoionization cross sections, remains an unsolved problem, especially for large molecules. Nevertheless, several qualitative or semiquantitative methods of estimation have been used which are especially useful in determining *relative* cross sections.[33-36] Since the spectra under consideration contain many overlapping bands which seem to be of about the same band width, we will make use of band height to measure intensity (as is frequently done in ion cyclotron resonance and ESCA[37] experiments) although the area under the band would be more accurate. A factor to correct for the direct influence of the energy of a photoejected electron upon the intensity is used to adjust these measured heights, i.e., $I_{\mathrm{corr}} = (I_{\mathrm{meas}})(21\ \mathrm{eV} - \mathrm{IE}_n)^{-1}$.

Theoretical[33] as well as experimental[38,39] conclusions indicate that 3d orbitals have a cross section for He (I) ionization which is less than that for 2p-carbon orbitals by a factor of 0.5–0.7. Hence ionizations from metal 3d orbitals are expected to give significantly smaller PES peaks than from ligand 2p orbitals. Recently published PES of metal carbonyls[38] present an analysis of $Cr(CO)_6$ where the first two peaks are very well separated and assigned to metal 3d and ligand 2p orbitals, respectively. The ratio of these corrected intensities is 0.5, i.e., consistent with expectation. Corrected intensities for the indicated PES bands of **1** are shown below.

	Band						
	1	2	3	4	5	6	7
Height relative to band 5	1.4	1.5	0.8	0.7	(1.0)	1.1	2.6

Band 5, corresponding to electron ejection from a π (b_u) orbital, was chosen as a basis since (1) its assignment is less in question, (2) it is well separated from neighboring bands, and (3) the parity (odd) precludes interaction with metal orbitals–metal 4p orbitals lying too high for significant interaction here.

Aside from giving support to the degeneracy pattern which we have accepted based on the original interpretation, a significant difference is seen between bands 5 and 6 and those at lower ionization energies (1 to 4). A weighted average of these first bands: $(1.4 + 1.4 + 0.8 + 0.7)/6 = 0.7_3$ shows that the expected reduction in intensity does occur for metal 3d orbitals. However, examination of the individual intensities can only eliminate band 4 as being π and perhaps create some prejudice against 1. It should be noted that this "highest π" orbital is also of odd parity and hence should be comparable to band 5 in intensity—which 4 clearly is not, even looking at the uncor-

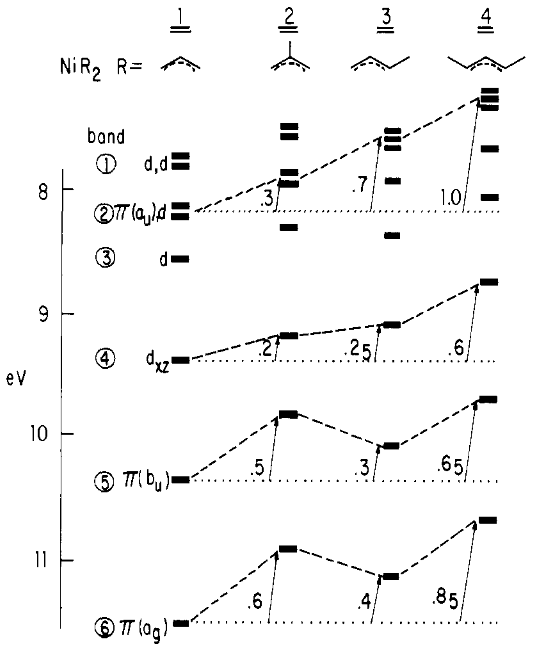


Figure 3. Correlation diagram for the ionization energies of the allyl-nickel complexes 1 through 4. The bands and assignments refer to 1.

rected spectrum. This means that band 4 is at least partly of metal-3d character, which eliminates π (a_u).

4. Effects of Methyl Substitution. Attaching a methyl group to a hydrocarbon π system has a well-documented destabilizing effect upon that π orbital energy.[22] In almost every case the magnitude of this shift can be related directly to the squared coefficient of the atomic p orbital at the point of attachment using a LCAO model (for a rare exception see ref 14). As seen in Figure 2, the two allyl π orbitals have quite different HMO coefficients and should shift to a different extent with methyl substitution.

The correlation diagram of Figure 3 presents our PES data for **1**, **2**, **3**, and **4** with relative shifts of important bands indicated as well as the only assignment we consider consistent with these shifts. Despite the extensive overlapping of bands 1 and 2, which restricts a quantitative analysis, certain conclusions can be drawn. From the averaged behavior of bands 1 to 4 compared with 5 and 6 it is seen that two effects are operative. First there is a general destabilization of all levels by about 0.2 eV per methyl group regardless of its location. Secondly, the expected "specific shift" is seen for bands 5 and 6 which have different HMO squared coefficients at the terminal and central carbon atoms: 0.25 and 0.50, respectively.[40] This effect is especially evident comparing **2** with **3** and will be even larger in the highest π orbital since the central carbon atom is at a node. Because of this, the behavior of band 4 is clearly unlike that expected and one is left with trying to sort out the overlapping initial peaks. Band 1 can be excluded since the first IE of **2** and **3** are essentially the same. Although band 3 at first sight might seem a reasonable choice, a sharp stabilization of one d orbital in going from **2** to **3** is then required which is unlikely. Thus band 2 is the only one consistent with assignment to π (a_u) ionization.

Examination of the spectra themselves supports this interpretation. For **1** and **2** this first region is unchanged except for an overall shift, and bands 1 and 2 remain of about the same intensity with 2 a bit higher. The spectra of **3** and **4** show, however, a significant change within this region. A distinct shift has now occurred so that the most intense band is now the first although overlapping makes any quantitative estimation of intensities impossible. Hence we conclude that band 2 in **1** contains the ligand π (a_u) ionization.

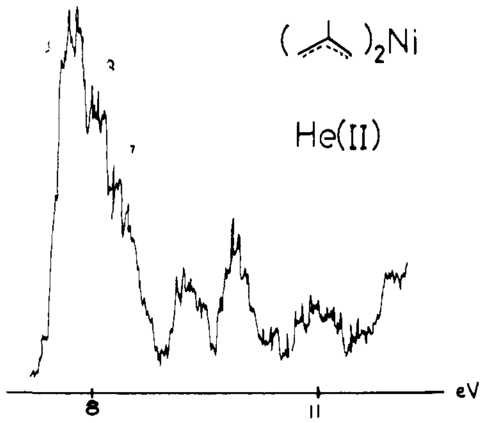


Figure 4. He (II) photoelectron spectrum of bis(π-2-methylallyl)nickel (**2**).

5. He (II) Spectrum. As a final piece of evidence, we present the He (II) spectrum of **2** and a consideration of *changes* in peak intensities. Only this molecule was studied since it is the most stable and its spectrum is most similar to **1**. In Figure 4 is pictured the first part of the He (II) spectrum of **2**. Since ionizing radiation is now 40.8 instead of 21.2 eV, changes in intensity may be expected to occur[33] and are indeed observed as has been noted with other systems before. For instance, with $Cr(CO)_6$ the relative intensity of 3d to 2p intensities changes by a factor of about 1.6.[38] Again taking the "pure-2p" band 5 as a calibration point, one obtains the following changes in corrected relative intensities on going from He (I) to He (II) induced ionization:

	1	2	3	4	5	6
σ_{II}/σ_I	1.8	1.3	1.7	1.1_5	(1.00)	0.6_5

Although bands 1, 2, and 3 show changes expected for our assignment of 3d, 3d + 2p, and 3d, respectively, bands 4 and 6 are significantly lower than our simplified analysis at first predicts. By improving the originally described model slightly, this result is seen to be well accounted for.

So far only filled orbitals have been explicitly considered in our interpretation, but since bonding does in fact occur between nickel and the allyl groups, antibonding orbitals must also be involved. The most likely virtual orbitals in this picture are the ligand π (b_g) and nickel 4s (a_g) which will interact with the metal $3d_{xz}$ (b_g) and ligand π (a_g) orbitals, respectively. Aside from accounting for the uniquely large shift observed for this d_{xz} orbital, support is found in the published computations for bis(π-allyl)palladium.[32] In this calculation every d orbital has a computed self-consistent charge of about 1.9 electrons except the d_{xz} orbital for which the value is 1.3, indicating strong donation to a ligand virtual orbital. Similar behavior is also seen in the improved calculation for **1**.[41] This explains the smaller increase in intensity of this peak on changing radiation. the corresponding orbital has significant ligand character.

Despite the similar behavior of bands 2 and 4 upon changing from He (I) to He (II) ionization, there is at least one gross inconsistency if their assignments are reversed. Such a reversal would require that the very strongly interacting d_{xz} orbital is not shifted to a lower ionization energy than all the other d's. According to the bis(π-allyl)palladium calculation again, this shift is expected to bring d_{xz} (with its mixture of π (b_g)) about 2. eV lower than all of the other d's which are clustered within a 1 eV range. In the SCCCMO calculation on NiA_2, once more an orbital of b_g symmetry occurs midway between what are almost certainly the other metal 3d's and the ligand π (b_u) orbital.

Although the assignment of band 6 is not questioned, a similar explanation accounts for the decrease in intensity observed. We are not aware of results for photoionization cross sections of 4s-type orbitals, but the similarity of 2p and 3p behavior and also the sharp decrease anticipated for a 3s-type orbital[33] leads us to expect that the 4s would also drop sharply. In fact, a very large difference is anticipated for this orbital because only a small contribution to band 6 can occur due to the large energy difference of basis functions.

With a more refined empirical or theoretical background, it should be possible to derive relative contributions of basis orbitals to resulting MO's from such intensity measurements. Presently, however, even such an approximate approach as used here should not be relied upon without supporting evidence. For instance, there was no clear evidence for $2p\pi$ contributions to band 4 in the earlier discussion of He (I) intensities, and no consideration has been given to the influence of symmetry on these cross sections.

Conclusion and Comments

We have carefully examined a series of related compounds to obtain a consistent assignment for the observed ionization energies. A very detailed discussion of the assignment was given because of the frequent comparison of experimental IE values to calculated schemes for bis(π-allyl)nickel. This assignment is different from a previous study and our results show that earlier Koopmans type calculations do not fail as badly as had been thought. Hence we feel that continued use of Koopmans' approximation for organometallic systems is not excluded as a first-order test of calculations. In this spirit we have indicated our results in Figure 2c as an MO diagram. In a more rigorous sense, these are observed ionization energies and consequently differences in energy between states. Molecular orbital energies, not being physically observable quantities, are significant only in that they are the most useful way of visualizing such data at the present time. It is becoming increasingly likely that metal 3d orbitals have an unusually large reorganization energy;[42] however the magnitude may not be overriding. Although it is difficult to unequivocally assert that Koopmans' theorem fails when comparing calculations not near some stable point such as the Hartree-Fock limit, it is probably a reasonable evaluation in these cases—since in fact, it also fails for the transition metal atoms in a manner of speaking.[28,44] In any case, the SCEI-MO calculation of PdA_2 for which the most extensive analysis is available,[32] reproduces or ordering for NiA_2 almost exactly. A calculation done for both metals indicates that the order of MO's does not change on going from nickel to palldium.[7]

Some of the methods used here to assign the IE's do not give unambiguous answers. However, overall agreement about the main features is very strong evidence for this assignment. Additionally there are other aspects of the calculations which are supported by this interpretation, for instance the bond overlap populations of terminal vs. central carbon atoms and charge difference between these positions.[32] The main bonding interaction is seen to be $3d_{xz}$ "donating" to ligand π (b_g) and a smaller contribution from ligand π (a_g) "back-donating" to metal 4s. Hence one would expect a positive charge on the metal atom. This bonding picture is also consistent with a ^{13}C NMR study on palladium allyl complexes which found that the terminal carbon atoms were sp^2 hybridized and contributed mainly to the bonding with the metal atom.[43]

An independent means of testing the assignment and substituent shifts indicated by this work might be provided by generating certain radical cations and measuring their ESR spectra. Attachment of alkyl groups larger than methyl to the terminal carbons in **1** should raise the ligand π (a_u) orbital until it corresponds with the first ionization energy. In other words, an ESR spectrum of such a radical cation should be clearly π-ligand like. Although this is essentially a nonbonding orbital, the instability of bis(pentenyl)nickel (**4**) suggests that simple alkyl attachment may not work. However, the unusual stability[2] of bis(π-cyclooctenyl)nickel makes it a likely candidate unless some new factor intervenes.

Acknowledgment. This work is part 99 of project 2.159.74 of the Schweizerischer National fonds zur Förderung der wissenschaftlichen Forschung. For part 98 see ref 45. Support by Ciba-Geigy S.A., F. Hoffmann-La Roche & Cie, S.A., and Sandoz S.A. (Basel) is gratefully acknowledged. The compounds used in this work were generously prepared by Dr. B. Henc of the Max-Planck Institut für Kohlenforschung and the He (II) spectra run by Dr. John P. Maier of Basel. Professor E. Heilbronner and Professor G. Wilke's interest in this work is much appreciated.

References and Notes

(1) Current address: Central Research and Development Department, E. I. duPont deNemours and Co., DuPont Experimental Station, Wilmington, Delaware 19898.
(2) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew, Chem.*, **78**, 157 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966).
(3) R. Baker, *Chem. Rev.*, **73**, 487 (1973).
(4) H. Clarke, *J. Organomet. Chem.*, **80**, 369 (1974).
(5) R. B. King, "Transition Metal Chemistry-An Introduction", Academic Press, New York, N.Y., 1969, p 31.
(6) M. L. H. Green, "Organometallic Compounds vol. 2, The Transition Elements", 3d ed, Methuen and Co., London, 1968, p **45**.
(7) D. A. Brown and A. Owens, *Inorg. Chim. Acta*, **5**, 675 (1971).
(8) R. Seeger, Tesis 1974, Basel, Switzerland.
(9) A. Veillard, *Chem. Commun.*, 1022, 1427 (1969).
(10) D. R. Lloyd and N. Lynaugh in "Electron Spectroscopy", D. E. Shirley, Ed., North-Holland, Amsterdam, 1972, p 445.
(11) T. Koopmans, *Physica (Utrecht)*, 1, 104 (1934).
(12) M. Rohmer and A. Viellard, *J. Chem. Soc., Chem. Commun.*, 250 (1973).
(13) W. G. Richards, *J. Mass Spectom. Ion Phys.*, **2**, 419 (1969).
(14) F. Brogli, P. Clark, E. Heilbronner, and M. Neuenschwander, *Angew. Chem.*, **85**, 414 (1973); *Angew, Chem., Int. Ed. Engl.*, **12**, 422 (1973).
(15) M. Coutiere, J. Demuynck, and A. Veillard, *Theor. Chim. Acta*, **27**, 281 (1972).
(16) B. Higginson, D. Lloyd, S. Evans, and A. Orchard, *J. Chem. Soc., Faraday Trans. 2*, 1913 (1975).
(17) R. Fenske, *Prog. Inorg. Chem.*, **21**, 189 (1976).
(18) C. Moberg, *J. Organomet. Chem.*, **108**, 125 (1976).
(19) G. Wilke and B. Bogdanovic, *Angew. Chem.*, **73**, 756 (1961).
(20) D. W. Turner, *Proc. r. Soc. London, Ser. A*, **307**, 15 (1968).
(21) F. Brogli and E. Heilbronner, *Theor. Chim. Acta*, **26**, 289 (1972).
(22) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973).
(23) H. Dietrich and R. Uttech, *Naturwissenschaften*, **50**, 613 (1963); *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **122**, 60 (1965).
(24) F. P. Lossing, K. U. Ingold, and I. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).
(25) C. E. Moore, *Natl. Bur. Stand. (U.S.) Circ.*, **2**, 467 (1952).
(26) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972, Chapters 19 and 20; C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory", W. A. Benjamin, New York, N.Y., 1964, Chapter 18.
(27) D. A. Brown in "Transition Metal Chemistry", Vol. 3, R. Carlin, Ed., Marcel Dekker, New York, N.Y., 1966, p 48.
(28) T. M. Dunn in "Physical Chemistry an Advanced Treatise" vol V "Valency", H. Eyring, Ed., Academic Press, New York, N.Y., 1970, pp 210–220.
(29) W. Bremser, *Top. Curr. Chem.*, **36**, 16 (1973).
(30) B. Hudson, J. Ridyard, and J. Diamond, *J. Am. Chem. Soc.*, **98**, 1126 (1976).
(31) J. Becconsall, B. Job, and S. O'Brian, *J. Chem. Soc. A*, 423 (1967).
(32) I. H. Hillier and R. M. Canadine, *Discuss. Faraday Soc.*, **47**, 27 (1969).
(33) P. Dechant, A. Schweig, and W. Thiel, *Angew. Chem.*, **85**, 358 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 308 (1973).
(34) W. Thiel and A. Schweig, *Chem. Phys. Lett.*, **16**, 409 (1972); **12**, 49 (1971).
(35) A. Orchard and P. A. Cox, *Chem. Phys. Lett.*, 7, 273 (1970).
(36) R. L. DeKock, B. Higginson, and D. R. Lloyd, *Discuss. Faraday Soc.*, **54**, 84 (1972).
(37) C. K. Jorgensen and H. Berthou, *Faraday Discuss.*, **54**, 269 (1972).
(38) B. Higginson, D. R. Lloyd, P. Burroughs, D. Gibson, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, 1659 (1973).
(39) S. Evans, M. L. H. Green, B. Jewitt, G. H. King, and A. F. Orchard. *J. Chem. Soc., Faraday Trans. 2*, 356 (1974).
(40) One can further quantify these parameters using

$$\Delta IE_{(obsd)} - m\sum c^2 + n(\delta A)$$

whereΣc^2 = sum of squared Hückel allyl coefficients for positions with methyl attachment, n = number of methyl groups, δA = general destabilization per methyl group, and m = adjustable parameter (sensitivity to specific Me attachment). For the $n = 1$ cases, a least-squares fit gives $\delta A = 0.210$ eV, $m = 0.720$ eV with $\sigma = 0.108$ eV and $\sigma_{max} = 0.130$ eV. With these values one can calculate ΔIE's for the substituted molecules and compare with measured values: (cf. figure 3)

	a_u			b_u			a_g		
	2	**3**	**4**	**2**	**3**	**4**	**2**	**3**	**4**
Exptl	0.3	0.7	1.0	0.5	0.3	0.6_5	0.6	0.4	0.8_5
Calcd	0.21	0.57	1.0	0.57	0.39	0.75	0.57	0.39	0.75

(41) M. Rohmer, J. Demuynek, and A. Veilland, *Theor. Chim. Acta*, **36**, 93–102 (1974).
(42) I. Hillier, M. Guest, R. Higginson, and D. Lloyd, *Mol. Phys.*, **27**, 215 (1974).
(43) B. Mann, R. Pietropaolo, and B. Shaw, *J. Chem. Soc., Dalton Trans.*, 2390 (1973).
(44) Koopmans, of course, did not intend to apply this relationship to open shell cases, but with modifications they can be considered; cf. P. A. Cox et al., *Struct. Bonding (Berlin)*, **24**, 59 (1975).
(45) E. Heilbronner, Organic Photoelectron Spectroscopy, Sixth Conference on Molecular Spectroscopy, Durham, in press.

The Mechanism of Ligand Dissociation in Group 8 ML_5 Complexes

A. D. English,* P. Meakin,* and J. P. Jesson*

Contribution No. 2250 from the Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. *Received February 25, 1976*

Abstract: Free energies of activation ($\Delta G^{\ddagger}$) for dissociation in the equilibrium $M[P(OC_2H_5)_3]_5{}^{n+} \rightleftharpoons M[P(OC_2H_5)_4]_4{}^{n+} + P(OC_2H_5)_3$ have been determined for M = Co(I), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), together with $\Delta G^{\ddagger}$ values for dissociation in the equilibrium $RhL_5{}^+ \rightleftharpoons RhL_4{}^+ + L$ with L = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}n\text{-}C_3H_7)_3$, $P(O\text{-}n\text{-}C_4H_9)_3$, and $P(OCH_2)_3CCH_3$. The relationship between these parameters and the corresponding $\Delta G^{\ddagger}$ values for intramolecular exchange in the ML_5 compounds is discussed and evidence is presented to suggest a similarity between the reaction coordinates for intramolecular rearrangement and ligand dissociation. In particular, the planar association–trigonal bipyramidal reaction coordinate appears to involve tetragonal pyramidal intermediates or transition states, implying that the axial ligands in the trigonal bipyramid do not remain collinear with the metal throughout the reaction, as has been assumed in the current picture for planar substitution. For M = Rh and L = *n*-alkyl phosphite, it is suggested that two competing steric effects—crowding in the tetragonal pyramid and the steric assist to bond breaking—offset one another to give a free energy of activation for dissociation nearly independent of the steric size of L. The data were obtained from a line shape analysis of $^{31}P\{^1H\}$ NMR spectra as a function of temperature. The calculations employed are described in detail, using two-, three-, four- and five-site one-spin models, to show the origin of *unexpected line width increases* in the $RhL_5{}^+$ $^{31}P\{^1H\}$ doublet, at temperatures above the slow exchange limit as the [Rh]/[L] ratio is either *increased* or *decreased* from the value 1/5, assuming a first-order dissociation process. In some instances, equilibrium constants have been measured for the ligand dissociation reaction using spectrophotometric techniques.

Recent low temperature NMR studies[1-5] have shown that a wide range of group 8 ML_5 complexes have trigonal bipyramidal (D_{3h}) geometries in solution. At higher temperatures, both intramolecular and intermolecular exchange processes take place at rates which make NMR line shape investigations possible. In most cases, the free energies of activation are considerably higher for intermolecular exchange so that the two processes can be treated separately. Detailed line shape analyses[3,5] show that the intramolecular rearrangement mechanism involves simultaneous exchange of the two axial ligands with two equatorial ligands. A systematic investigation of the variation of the barriers to intramolecular rearrangement with the nature of the phosphorus ligand and the nature of the central metal has been reported[5] and preliminary $^{31}P\{^1H\}$ NMR studies of *intermolecular* exchange behavior[3,4] in $Rh[P(OCH_3)_3]_5{}^+$ have established a first-order dissociative mechanism.

In the present paper, we describe the details of a systematic $^{31}P\{^1H\}$ study of the *intermolecular* exchange behavior in these complexes, varying the ligand and the central metal. The data are all consistent with a simple dissociative process (eq 1); the free energies of activation for dissociation correlate closely with previously established free energies of activation for intramolecular rearrangement[5] suggesting similar square pyramidal transition states for two processes.

$$ML_5{}^{n+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_4{}^{n+} + L \tag{1}$$

Our recent predictions[4] for the dependence of the line widths in the $RhL_5{}^+$ doublet on [L]/[Rh] in the $RhL_5{}^+/RhL_4{}^+/L$ system near the slow exchange limit have been confirmed both experimentally and theoretically using the five-site model. Line shape calculations are described which clearly indicate why dramatic line width increases in the $^{31}P\{^1H\}$ doublet of $RhL_5{}^+$ occur at certain temperatures, when the metal to ligand ratio is either increased or decreased from 1/5, assuming a simple dissociative process. Similar line shape effects are calculated for $ML_5{}^{n+}/ML_4{}^{n+}/L$ systems in which the central metal M has no nuclear spin.

Previous two-, three-, and four-site models used to calculate the $^{31}P\{^1H\}$ NMR line shapes for "$ML_5{}^+$" ($[ML_5{}^+] \to 0$, $[L] \to 0$), "$ML_5{}^+/L$" ($[ML_4{}^+] \to 0$), and "$ML_5{}^+/ML_4{}^+$" ($[L] \to 0$), for the case where M = Rh, are justified both numerically and analytically.

Experimental Section

Methods of preparation of the complexes have been described earlier[2] as have the general nuclear resonance techniques employed.[1-3] In cases where small variations in rate from one system to another were important (e.g., effect of change of solvent on reaction rate), relative orderings were established by sequential measurements at a single temperature, instead of (or in addition to) complete temperature variation studies on each system separately. Spectrophotometric studies were carried out using a Cary 41 spectrophotometer.

Intermolecular Exchange Calculations. Data were presented earlier[4] for intermolecular exchange behavior in $Rh[P(OCH_3)_3]_5{}^+/$