result may well be somewhat different for various metal centers. Use of the spectroscopic parameters for Cr^{III}, for example, in our discussion above, would have resulted in the opposite conclusion for the distortion route of the CuO_2N_4 systems since, for this metal, $e_\sigma(H_2O) > e_\sigma(NH_3)$ (Table I).

Discussion

The two very simple ideas outlined above are capable of rationalizing qualitatively most of the available data on octahedrally distorted Cu^{II} species without using *any* symmetry arguments of the Jahn–Teller sort that involve the d-orbital manifold—the traditional way to view such effects. (Our approach at present, however, is not able to rationalize the great variations in the size of the distortions observed.) Our previous discussion[13] showed why such distortions are larger for the d⁹ case compared to similar "Jahn–Teller" distortions of high-spin d⁴ Cr^{II} complexes for example. The MOSE associated with the axial linkages is less than that for the equatorial ones but importantly, in contrast to the d⁹ case, is not zero. We may also comment on the small distortions, if any, found for orbitally degenerate systems containing asymmetric occupation of the octahedral t_{2g} orbitals. For a $(t_{2g})^5(e_g)^2$ moiety (e.g., high-spin Co^{II}) the MOSE for square-planar, square-pyramidal, and octahedral geometries

is simply $ne_\sigma + 4e_\pi$, where n is the number of ligands. So while the π contribution is coordination number independent, just like the corresponding MOSE values for the d⁹ systems (which contain only σ contributions for this electronic configuration), analogous distortion arguments do no apply. The ligands are each bound (with a MOSE of e_σ per linkage) in all three structures. The details of the structure in this case will surely be dominated by the σ manifold.

To conclude, this paper provides a unified way to view distorted Cu^{II} complexes irrespective of which particular variant of the Jahn–Teller approach is conventionally[17] used. This one-electron approach is similar to the one we have used to understand angular geometries in transition-metal systems.[3,18,19]

(17) It is interesting to recall Kettle and Jotham's comment: "It is possible that it [a static first-order Jahn–Teller distortion] has never been observed" (Kettle, S. F. A.; Jotham, R. W. *Inorg. Chim. Acta* **1971**, *5*, 183).
(18) Burdett, J. K. *Inorg. Chem.* **1975**, *14*, 931.
(19) Burdett, J. K. *Chem. Soc. Rev.* **1978**, *7*, 507.

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Electronic Structure and Photoelectron Spectrum of Tris(π-allyl)chromium, Cr(η³-C₃H₅)₃

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The He I and He II photoelectron spectra of $Cr(\eta^3\text{-}C_3H_5)_3$ have been recorded for the gaseous material at ca. 17 °C. The details observed have been interpreted with reference to the intensity changes observed from He I to He II ionization and to the results of ab initio molecular orbital calculations, which included consideration of configuration interaction to allow for the effects of orbital relaxation upon ionization. The two lowest spectral features, at 7.13 (4) and 7.76 (3) eV, are attributed to ionization from the metal localized $(6a')^1$ and $(6e')^2$ levels. The latter ionization is considered to overlap with the ionization from the highest filled ligand level, $(4e'')^4$, which correlates with the $1a_2$ π molecular orbital of the allyl group; the other level which correlates with this ligand orbital, $(4a'')^2$, is considered to be responsible for the ionization at 8.69 (3) eV. There is a significant amount of metal character in the $4e''$ and $4a''$ orbitals, arising from the interaction of the $1a_2$ ligand orbitals with empty chromium 3d and 4p orbitals; these overlaps are considered to be primarily responsible for the metal–ligand bonding interactions. The remaining peaks in the photoelectron spectra are attributed to ionizations from orbitals which are essentially localized on the ligands: the features at 10.37 (4) and 11.47 (6) eV are attributed to ionizations from the $5e'$ and $5a'$ molecular orbitals which correlate with the $1b_1$ allyl π orbital; the peaks at 12.62 (6), 14.11 (2), 15.41 (5), 18.15 (15), and 21.90 (15) eV are attributed to ionizations from the molecular orbitals which correlate with the $3b_2$, $4a_1$, $3a_1$ and $2b_2$, $2a_1$, and $1b_2$ allyl σ orbitals, respectively.

Introduction

Transition-metal complexes involving the allyl ligand are amongst the simplest organometallic complexes known. For this reason, they have been the subject of many experimental and theoretical studies[1] to elucidate their electronic structure. In particular, the low-energy photoelectron (PE) spectra of $Ni(\eta^3\text{-}C_3H_5)_2$ and its methyl-substituted derivatives have been extensively studied, and the PE spectrum of $Pd(\eta^3\text{-}C_3H_5)_2$ has also been measured.[2,3] Calculations of the ionization energies

(IE) of $Ni(\eta^3\text{-}C_3H_5)_2$ by the ab initio SCF–MO method have revealed the inadequacy of Koopmans' theorem for describing metal orbital ionization of this complex,[1] a feature also found in many other transition-metal complexes. In spite of these studies, there is no unambiguous assignment of the PE spectrum of $Ni(\eta^3\text{-}C_3H_5)_2$ nor is there an ab initio calculation that agrees with the most likely assignment.[2] Although the nickel complex has the advantage of a small number of ligands, which should assist in the interpretation of its PE spectrum, the large number of d electrons and the large degree of electron reorganization accompanying d electron ionization complicate the assignment of the PE spectrum. We have encountered

(1) Rohmer, M.-M.; Demuynck, J.; Veillard, A. *Theor. Chim. Acta* **1974**, *36*, 93. Rohmer, M.-M.; Veillard, A. *J. Chem. Soc., Chem. Commun.* **1973**, 250. Brown, D. A.; Owens, A. *Inorg. Chim. Acta* **1971**, *5*, 675. King, R. B.; "Transition Metal Chemistry—An Introduction"; Academic Press: New York, 1969; p 31.
(2) Batich, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 7585.
(3) Lloyd, D. R.; Lynaugh, N. In "Electron Spectroscopy"; Shirley, D. E., Ed; North-Holland Publishing Co.: Amsterdam, 1972; p 445.
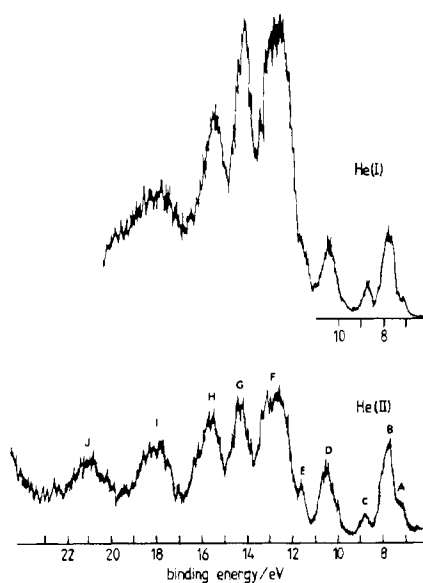
Figure 1. He I and He II PE spectra of Cr(C$_3$H$_5$)$_3$.

Table I. Ionization Energies (eV) of
Cr(η^3-C$_3$H$_5$)$_3$ and Ni(η^3-C$_3$H$_5$)$_2$

band[a]	Cr(η^3-C$_3$H$_5$)$_3$ IE	assignt[b]	orbital origin	Ni(η^3-C$_3$H$_5$)$_2$ IE[c]
A	7.13 (4)	6a'	Cr 3d$_{z^2}$	d
B	7.76 (3)	6e' / 4e''	Cr 3d$_{x^2-y^2}$, 3d$_{xy}$	d
C	8.69 (3)	4a''	allyl 1a$_2$(π)	d
D	10.37 (4)	5e'	allyl 1b$_1$(π)	10.44
E	11.47 (6) sh	5a'		11.56
F	12.62 (6)	3e'', 3a''	allyl 3b$_2$(σ)	12.75
G	14.11 (2)	4e', 4a'	allyl 4a$_1$(σ)	14.20
H	15.41 (5)	3e', 3a' / 2e'', 2a''	allyl 3a$_1$(σ) / allyl 2b$_2$(σ)	15.73
I	18.15 (15)	2e', 2a'	allyl 2a$_1$(σ)	17.67
J	21.90 (15)	1e'', 1a''	allyl 1b$_2$(σ)	

[a] See Figures 1 and 2. [b] See Table II for orbital character.
[c] Cf. ref 2. [d] Ionizations at 7.85, 8.17, 8.59, and 9.48 eV are also found, but no direct correlation with Cr(η^3-C$_3$H$_5$)$_3$ is presented.

Figure 2. He I and He II PE spectra of Cr(C$_3$H$_5$)$_3$; expansion of low-energy region.

(η^3-C$_3$H$_5$)$_3$. A sample, freshly prepared at −20 °C and sealed in an evacuated glass vial was placed in the gas cell of the spectrometer. After evacuation, the vial was broken and the vapor pressure obtained was adequate for measurement of the PE spectra at room temperature (ca. 17 °C). The spectra obtained by using He I and He II ionization are shown in Figures 1 and 2, and the measured IE's are listed in Table I. These spectra showed no evidence of propylene or Cr$_2$(C$_3$H$_5$)$_4$,[8] which are the principal products of the dimerization reaction.

Computational Details

The ab initio SCF–MO calculations were carried out for Cr(η^3-C$_3$H$_5$)$_3$ with a molecular structure similar to that reported[9] for Cr(η^3-C$_3$H$_5$)$_3$(c). The molecule was assumed to conform to C_{3h} symmetry with all the atoms of the allyl group coplanar and C–C and C–H bonds of length 1.40 and 1.08 Å, respectively, and all the interbond angles 120°. The chromium atom was placed 2.045 Å perpendicularly from the center of gravity of the allyl group. A basis of contracted Gaussian-type functions (GTF) was employed. For chromium, a 5s4p2d basis was constructed from the 12s6p4d primitive set of Roos et al.[10] The two most diffuse s primitives were replaced by functions having exponents of 0.32 and 0.08. Functions with these exponents were also added to the p basis, and a GTF of exponent 0.12 was added to the d basis. A near minimal basis was used to represent the ligand functions. For carbon, the 9s basis of Dunning[11] was contracted to 3s, as in Table 2a of ref 11, the carbon 2p function being a Hartree–Fock orbital expanded in four GTF's.[12] The hydrogen 1s orbital was a Slater-type orbital having exponent of 1.2, expanded in four GTF's. Although this basis is somewhat unbalanced, being double ζ for the metal valence orbitals and near minimal for those of the ligands, a basis of this quality

similar problems in the discussion of the PE spectra of the metal dihalides MCl$_2$ (M = Cr, Mn, Fe, Ni).[4]

In an attempt to shed further light on the electronic structure and PE spectra of π-allyl system, herein we report an experimental and theoretical study of Cr(η^3-C$_3$H$_5$)$_3$. Although this complex contains an additional ligand as compared to Ni(η^3-C$_3$H$_5$)$_2$, the smaller number of d electrons and the smaller relaxation energy accompanying d electron ionization[4] are expected to facilitate spectral interpretation.

Experimental Section

The PE spectra were recorded with the use of the PE spectrometer described previously,[5] which has been modified so that spectra may be measured for gaseous species at temperatures up to 400 °C with use of He I and He II ionizing radiation.

Cr(η^3-C$_3$H$_5$)$_3$ was prepared according to published procedures[6,7] and characterized by mass and ^{1}H NMR spectroscopy. In view of the decomposition of Cr(η^3-C$_3$H$_5$)$_3$ to Cr$_2$(C$_3$H$_5$)$_4$ upon heating, the following method was adopted to record the PE spectrum of Cr-

(4) Lee, E. P. F.; Potts, A. W.; Doran, M.; Hillier, I. H.; Delaney, J. J.; Hawksworth, R. W.; Guest, M. F. *J. Chem. Soc., Faraday Trans. 2* **1980,** *76,* 506.
(5) Considine, M.; Connor, J. A.; Hillier, I. H. *Inorg. Chem.* **1977,** *16,* 1392.
(6) Aoki, T.; Furusaki, A.; Tomiie, Y.; Ono, K.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1959,** *42,* 545.
(7) O'Brien, S.; Fishwick, M.; McDermott, B.; Wallbridge, M. G. A.; Wright, G. A. *Inorg. Synth.* **1972,** *13,* 77.

(8) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowell, A. A., unpublished results.
(9) Dietrich, H. *Acta Crystallogr., Sect. A* **1969,** *25A,* 160.
(10) Roos, B.; Veillard, A.; Vinot, G. *Theor. Chim. Acta* **1971,** *20,* 1.
(11) Dunning, T. H. *J. Chem. Phys.* **1970,** *53,* 2823.
(12) Stewart, R. F. *J. Chem. Phys.* **1969,** *50,* 2485.

Table II. Calculated Ground State of Cr(η^3-C$_3$H$_5$)$_3$

orbital[a]		% atomic character					
sym-metry	E,[b] eV	Cr s	Cr p	Cr d	C s	C p	H s
6e'	−15.3 (8.0)		2	94		4	
6a'	−16.1 (8.2)			97		3	
4e''	−8.6 (6.7)			42		57	
4a''	−8.7 (7.4)	18				81	
3e''	−13.7					75	23
3a''	−13.8					75	23
5e'	−13.8		4	2		92	
5a'	−15.0	6				92	2
4e'	−16.2					56	43
4a'	−16.7	2				55	42
3e'	−18.2				16	52	31
2a''	−18.3				4	60	35
3a'	−18.4				14	56	30
2e''	−18.6				5	59	36
2a'	−21.7				27	39	34
2e'	−22.4				24	45	36
1e''	−26.8				56	28	18
1a''	−27.0				58	28	20

[a] The orbital numbering neglects core orbitals. [b] The orbital canonicalization used yields Koopmans' theorem orbital energies—the values in parentheses are ionization energies calculated by the configuration interaction method (see text).

Table III. Symmetry Correlations for Orbitals of Cr(η^3-C$_3$H$_5$)$_3$

ligand	complex	metal
C_{2v}	C_{3h}	
a$_1(\sigma)$, b$_1(\pi)$ ⟨ a'	3d$_{z^2}$, 4s	
	e'	3d$_{x^2-y^2}$, 3d$_{xy}$, 4p$_x$, 4p$_y$
b$_2(\sigma)$, a$_2(\pi)$ ⟨ a''	4p$_z$	
	e''	3d$_{xz}$, 3d$_{yz}$

Table IV. Relative Band Intensities in the Photoelectron Spectrum of Cr(η^3-C$_3$H$_5$)$_3$

band[a]	He I	He II
A,B	4.5[b]	7.4
C	1.0	1.0
D	4.0	5.5

[a] See Figures 1 and 2. [b] A, ~0.5; B, ~4.0.

has previously been found suitable for interpretation of the PE spectra of a number of transition-metal complexes.[13] The calculations, involving 96 contracted GTF's, were carried out with use of the ATMOL system of programs on the CDC 7600 computer of Manchester University. In view of the lack of experimental evidence concerning which chromium 3d orbitals are occupied in the molecular ground state, a number of symmetry equivalenced restricted Hartree–Fock calculations were carried out on quartet[14] states having different 3d orbitals occupied. These calculations predicted the ground state to be ^{4}A', corresponding to the occupancy 6a'(3d$_{z^2}$)^1 6e'-(3d$_{xy}$,3d$_{x^2-y^2}$)^2. A summary of the characteristics of the orbitals obtained from this calculation is presented in Table II.

Results and Discussion

Lower Energy PE Spectral Region. Magnetic susceptibility measurements[14] have indicated that Cr(η^3-C$_3$H$_5$)$_3$ possesses a ground state with $S = {}^3/_2$, and the ab initio calculations described here suggest that the three unpaired electrons are contained in a' and e' MO's of predominantly chromium 3d character. Therefore, the PE spectra are interpreted in terms of ionizations from such a ^{4}A' ground state. On the basis of the formal electronic configurations of Cr^{3+}(d^3) and (allyl)$^-$ (...(1b$_1$)^2(1a$_2$)^2), the lowest energy ionizations of Cr(η^3-C$_3$H$_5$)$_3$ are expected to occur from (i) the metal (a')^1 and (e')^2 levels, (ii) the (a'')^2 and (e'')^4 levels which correlate (Table III) with the highest filled 1a$_2(\pi)$ MO's of the ligand, and (iii) the (a')^2 and (e')^4 levels which correlate with the 1b$_1(\pi)$ MO's of the

ligand. The assignment of the lowest energy region of the spectrum is assisted by the consideration of the relative band intensities presented in Table IV. Previous studies[15] have shown that for He I spectroscopy the observed intensity of an ionization from a chromium 3d orbital is less (by a factor of 0.4–0.7) than that from a carbon 2p orbital and that the former intensity increases relative to the latter from He I to He II ionization.[15] The shoulder A and the band B manifest the greatest increase in intensity, relative to the other peaks in the spectrum, from He I to He II ionization, and, therefore, ionizations from the chromium 3d orbitals are considered to be contained in this spectral region. The relative intensity of band B is so great that it must contain some ligand ionizations in addition to those of the metal. This conclusion is also consistent with the shoulder A increasing in intensity relative to B from He I to He II ionization. The lowest IE's from the ligand orbitals are expected to arise from the e'' and a'' (1a$_2$ (π)) MO's with significant chromium 3d character (see Table II). Therefore, a value of near 0.7:1 would seem appropriate for the ratio of the chromium 3d:allyl (1a$_2(\pi)$) cross sections in He I ionization. In the light of this value, the most internally consistent interpretation of the experimental intensity data (Table IV) between 7 and 9 eV is that the shoulder A and the peaks B and C arise, respectively, from ionization of the metal (a')^1, the metal (e')^2 and the ligand (e'')^4(1a$_2$), and the ligand (a'')^2(1a$_2$) levels. On the basis of the slight change in profile of peak B from He I to He II ionization, it is suggested that the metal (e')^2 ionization comprises the lower energy portion and the ligand (e'')^4 ionization comprises the higher energy portion of this peak.

Bands D and E are assigned to ionizations from the ligand (e')^4 and (a')^2 levels, arising from the 1b$_1$ (π) MO's, the relative intensity of these bands following from degeneracy considerations.

A straightforward description of the bonding in Cr(η^3-C$_3$H$_5$)$_3$ emerges from the ab initio calculation described here, the results of which are generally consistent with the above interpretation of the PE spectral data. The three unpaired electrons are considered to be contained in MO's (6e',6a') of essentially total metal character (Table II). The 4e'' and 4a'' MO's of the complex, which correlate with the 1a$_2(\pi)$ MO's of the ligands, have substantial metal character (particularly the 4e'') and provide the major contribution to the metal-ligand bonding which arises from the interaction of the 1a$_2$ ligand orbitals with the formally vacant chromium 3d and 4p orbitals of the appropriate symmetry (see Table III).

The Koopmans' theorem IE's calculated for the metal localized 6e' and 6a' MO's ($\sim$15 eV) are much greater than both of the experimental values ($\sim$8 eV) and the values calculated for the highest filled ligand levels ($\sim$9 eV). As found for other transition-metal complexes,[13] a much larger degree of electron reorganization is expected to accompany ionization from metal-localized MO's than from ligand-localized MO's. Although the effects of orbital relaxation accompanying ionization are traditionally allowed for through

(13) Coutière, M.-M.; Demuynck, J.; Veillard, A *Theor. Chim. Acta* **1972**, *27*, 281. Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R. *Mol Phys.* **1974**, *28*, 1193. Connor, J. A.; Derrick, L. M. R.; Hillier, I. H.; Guest, M. F.; Lloyd, D. R. *Ibid.* **1976**, *31*, 23.

(14) Kurras, E.; Klimsch, P. *Monatsber. Dtsch. Akad. Wiss. Berlin* **1964**, *6*, 736; *Chem. Abstr.* **1965**, *63*, 5666c.

(15) Higginson, B. R.; Lloyd, D. R.; Burroughs, P.; Gibson, D. M.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1659. Higginson, B. R.; Lloyd, D. R.; Evans, S.; Orchard, A. F. *Ibid.* **1975**, *71*, 113. Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. *Mol Phys.* **1975**, *29*, 113.

the use of SCF calculations on the individual ionic states (ΔSCF method), we have shown that an alternative computational approach, a configuration interaction (CI) calculation involving single excitations from a root set of Koopmans' theorem configurations, may also be employed.[16] By this method, a single calculation with a small number of configurations yields those IE's corresponding to the root set of Koopmans' theorem configurations and is thus equivalent to a number of ΔSCF calculations. The CI calculation, performed in this study, consisted of single excitations from the six root configurations generated by ionization of the 4a″, 4e″, 6a′, and 6e′ MO's. The orbital space consisted of these MO's and the 5e″ ($3d_{xz}$, $3d_{yz}$) and 7e′, 7a′ (ligand 2b$_1$) virtual MO's. The CI calculation was carried out for the triplet states only; for although ionization from the 4e″ and 4a″ MO's will result in both triplet and quintet states, the splitting between them is expected to be <1 eV. The IE's resulting from this small CI calculation, involving approximately 200 configurations, are also presented in Table II. A large degree of orbital relaxation accompanying ionization from the 6e′ and 6a′ MO's is given by this CI calculation, and the corresponding calculated IE's (8.0, 8.2 eV) are now close to the measured values (7.8, 7.1 eV), although the calculated order of the ionic states (^{3}E′ < ^{3}A′) is the reverse of that deduced experimentally. However, the separation of the 6e′ and 6a′ ionizations given by the CI calculation (0.2 eV) is an improvement over that given by the use of Koopmans' theorem. The calculated 4e″ 4a″ IE's (6.7, 7.4 eV) are seen to be smaller than those arising from 6e′, 6a′ (metal) ionization in disagreement with the observed PE spectrum. However, this is considered to arise from the neglect of correlation effects in the CI calculation. The inclusion of such effects is not expected to alter significantly the IE's of the half-filled 6e′ and 6a′ MO's but is expected to increase those of the fully occupied 4e″ and 4a″ MO's. Therefore, the results of the calculations are not considered to be in conflict with the assignment of peaks B and C proposed above, the calculated separation of these peaks (0.7 eV) being close to the experimental value (0.9 eV). These latter separations are larger than that (0.1 eV) given by Koopmans' theorem for these orbitals, which may be associated with the larger relaxation energy (1.9 eV) associated with the ionization from the 4e″ MO than that (1.3 eV) associated with the ionization from the 4a″ MO, consistent with the former MO having substantially greater metal character than the latter.

The remaining valence MO's of Cr(η^3-C$_3$H$_5$)$_3$, 3e″–2e′, have little metal character and may be directly correlated with the appropriate ligand orbital. However, an anomalous result of the ab initio calculation (Table II) is that the first of these ligand ionizations is predicted to arise from the 3e″ and 3a″ MO's, which correlate with the 4b$_2$ (σ) ligand MO, rather than from the 5e′ and 5a′ MO's, arising from the 1b$_1(\pi)$ ligand MO. This may be due to the involvement of diffuse, chromium-centered s and p basis functions in the 5e′ and 5a′ MO's,

attempting to correct deficiencies in the minimal ligand p basis. Thus, this result may reflect the unbalanced basis set used. Therefore, despite the theoretical result, peaks D and E are assigned, respectively, to ionization from the 5e′ and 5a′ MO's the calculated splitting (1.2 eV) being close to the measured value (1.1 eV).

Higher Energy PE Spectral Region. A comparison of the He I PE spectrum obtained for Ni(η^3-C$_3$H$_5$)$_2$[2,3] with that (Figure 1) for Cr(η^3-C$_3$H$_5$)$_3$ reveals that above 10 eV they have a very similar profile and the corresponding features occur at approximately the same IE, as detailed in Table I. These similarities suggest an assignment of the peaks D–J in the PE spectrum of Cr(η^3-C$_3$H$_5$)$_3$ to ionizations from ligand-localized MO's, a conclusion consistent with the results of the ab initio MO calculation (Table II). Furthermore, the assignment of this region of the Cr(η^3-C$_3$H$_5$)$_3$ PE spectrum should be applicable to that of Ni(η^3-C$_3$H$_5$)$_2$, Pd(η^3-C$_3$H$_5$)$_2$, and other simple allyl complexes. Comparisons between the PE spectra of Cr(η^3-C$_3$H$_5$)$_3$ and those of Ni(η^3-C$_3$H$_5$)$_2$ are simplified when it is recognized that the molecular conformation observed[9] for Cr(η^3-C$_3$H$_5$)$_3$(c) closely approximates to C_{3h} symmetry. Thus in the C_{2h} (or C_{2v}) symmetry of Ni(η^3-C$_3$H$_5$)$_2$ or the C_{3h} symmetry of Cr(η^3-C$_3$H$_5$)$_3$ each allyl orbital correlates with an (a + b) or (a + e) pair, respectively.

The features D and E of Figures 1 and 2 have been assigned above to ionization from the 5e′ and 5a′ MO's, respectively, which correlate with the ligand 1b$_1(\pi)$ orbital. Given this and the Koopmans' theorem IE's of Table II, the bands F–J are assigned to ionizations from the following MO's (all of which correlate with ligand σ MO's): F, 3e″, 3a″ (ligand 3b$_2$); G, 4e′, 4a′ (ligand 4a$_1$); H, 3e′, 3a′, 2a″, 2e″ (ligand 3a$_1$, 2b$_2$); I, 2a′, 2e′ (ligand 2a$_1$); J, 1e″, 1a″ (ligand 1b$_2$).

Conclusions

An interpretation of the PE spectrum of Cr(η^3-C$_3$H$_5$)$_3$ has been presented which takes account of the intensity changes from He I to He II ionization and is reasonably consistent with an ab initio MO calculation carried out for this molecule. The two lowest spectral features at 7.13 and 7.76 eV are assigned to ionization from the metal localized, half-filled, 6a′ and 6e′ orbitals. The latter IE is considered to occur together with that from the highest filled ligand orbital, 4e″, which correlates with the 1a$_2(\pi)$ molecular orbital of the allyl group. The IE for the other level which correlates with the 1a$_2$ ligand orbital, 4a″, is ca. 0.9 eV higher. The 4e″ and 4a″ orbitals have a significant amount of metal admixture, which arises from the overlap of the 1a$_2$ ligand orbitals with the formally vacant chromium orbitals of the appropriate symmetry. These orbitals are held to be responsibile for the majority of the metal–ligand bonding interactions. The remaining peaks in the PE spectra are attributed to IE's of orbitals which are essentially localized on the ligands in the sequence 1b$_1(\pi)$ < 3b$_2$ < 4a$_1$ < 3a$_1$ $\simeq$ 2b$_2$ < 2a$_1$ < 1b$_2$ (all σ). This sequence of allyl orbital IE's should also apply to other simple π-allyl complexes.

(16) Doran, M.; Hawksworth, R. W.; Hillier, I. H. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 164.