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Relative Strengths of Early Transition Metal M–H and M–C Bonds in Substituted Niobocenes and Tantalocenes. Thermodynamic Trends and Electronic Factors of Olefin Insertion into a Metal–Hydride Bond

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Abstract: Principles of M–C and M–H bonding interactions are examined experimentally by high-resolution valence photoelectron spectroscopy. Gas-phase He I and He II photoelectron spectra are reported for the following series of d^0 and d^2 bent metallocenes: Cp_2MH_3 (M = Nb, Ta), $Cp_2M(CO)L$ (M = Nb, Ta; L = H and M = Nb; L = CH_3), and $Cp_2M(C_2H_4)L$ (M = Nb, Ta; L = H and M = Ta; L = C_2H_5) (Cp = η^5-C_5H_5). The ligand replacements represented by this series of complexes allow stepwise comparison and assignment of each individual low-energy valence ionization band. The He I/He II spectral comparisons show that the lowest ionization energy band of the carbonyl complexes is higher in metal character than the corresponding ionization of the ethylene complexes. This trend indicates extensive electron delocalization in the metal–ethylene bonding that corresponds more accurately to a metallacyclopropane description with relatively strong metal–carbon bonds. The photoelectron data for the early transition metal hydride and alkyl species show that the metal–hydrogen bonds are slightly more stable than the metal–carbon bonds. Correlation of the ionization information for these substituted early metallocenes reveals that the stabilization of the metallacyclopropane–hydride structures, $M(C_2H_4)H$, relative to the olefin-inserted metal–alkyl structure, $M(C_2H_5)$, is partly due to stabilization of the metal electron density by back-bonding to the olefin as indicated by earlier theoretical studies. However, this factor alone is not sufficient to offset the energy required to convert a carbon–hydrogen bond in $M(C_2H_5)$ to a metal–hydrogen bond in $M(C_2H_4)H$. The additional important factor is the stabilization derived from conversion of the metal–alkyl σ bonding to the more favorable delocalized M–C_2 σ-bonding situation in the metallacyclopropane hydride.

The nature and relative energetics of metal–hydrogen and metal–carbon bonding is a subject of great importance that is currently receiving much attention.[2] Knowledge of the relationship between metal–carbon and metal–hydrogen bond strengths is fundamental to understanding details of the chemical or physical transformations involved in broad areas of organometallic chemistry and catalysis. Unfortunately, direct thermochemical measurement of the bond energies of interest is quite difficult.[2-8] Many workers have commented on the paucity of

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high-quality thermodynamic quantities that are necessary for the full understanding of a wide range of organometallic transformations.[2-10] Valence ultraviolet photoelectron spectroscopy (UPS) can provide an experimental measure of the electronic factors that contribute to the stability and reactivity of organometallic complexes.[11] The technique has been used extensively to provide an understanding of the strengths of bonding interactions and electron distributions in metal–ligand interactions.[11-13] As we have shown recently, the ionization energies are actually directly related to the thermodynamic bond strengths.[14] The ionization energies are simply part of a well-defined thermodynamic cycle that includes the bond energies in the neutral molecules and positive ions.[15,16]

The bent metallocenes of niobium and tantalum display some of the most intriguing combinations of coordinated ligands known in organometallic chemistry.[17-24] There have been numerous investigations of the factors contributing to the bonding, stability, and reactivity of these complexes.[17,25-27,32] The most widely accepted model of bent metallocene electronic structure is that of Lauher and Hoffmann.[28] This model has been successfully used to help explain several chemical and physical properties of these complexes. For example, Lauher and Hoffmann discuss the conformational barrier to rotation of $Cp_2Ta(CH_2)CH_3$ (Cp = η^5-C_5H_5), the resistance to intramolecular olefin insertion of $Cp_2Nb(C_2H_4)H$, the carbonyl insertion reaction of $Cp_2Zr(Cl)R$ (R = alkyl), and the oxidative coupling reaction of $Cp_2Ti(C_2H_4)$. The stability of $Cp_2Nb(C_2H_4)H$ relative to olefin insertion into the metal–hydride bond to form $Cp_2Nb(C_2H_5)$ is attributed by these calculations to stabilization of the metal d^2 orbital density through favorable back donation to the ethylene π^* orbital.[28] Clearly, experimental information on the relative energies of the orbitals involved in these interactions is important for understanding the underlying stability of the early transition metal bent metallocenes.

Photoelectron spectroscopy has contributed to characterization of the electronic structure of a wide variety of early transition metal bent metallocenes, including some substituted niobocenes and tantalocenes similar to those in the present study.[29-31] These studies have already revealed useful electronic structure principles for the bent metallocenes, especially for the metallocene dihalides.[30] The photoelectron spectroscopy studies have largely supported the model of Lauher and Hoffmann. However, many more specific details regarding the bonding interactions are still not fully understood. This paper reports the gas-phase He I and He II valence ionization data for niobium and tantalum bent metallocenes with hydride, methyl, ethyl, ethylene, and carbonyl ligands. The ionization energies related to key orbitals in both the ethylene–hydride and related bent metallocene–alkyl complexes have been determined, allowing ionization energy correlations for the olefin insertion reaction to be made.

Of special interest are the thermodynamic trends provided by the relative ionization energies obtained in the photoelectron spectroscopic measurements. Most interesting are the metal–hydrogen and metal–carbon bond strengths and the electronic factors contributing to the special stability of the metallacyclopropane species.[22,25] The predominance of the metallacyclopropane bonding model in these complexes is directly evidenced by experimental observables in the photoelectron spectra, and the relative ionization energies provide a thermodynamic basis for the stability of the metallacyclopropane structures. The data show that the electronic factors responsible for stabilizing the olefin–metal–hydride (η^2-C_2H_4)–M–H complex relative to the isomeric olefin-inserted metal–alkyl M–C_2H_5 involve fundamental aspects of metal–carbon, metal–hydrogen, and carbon–hydrogen bond strengths in addition to the back-bonding stabilization of metal electron density mentioned by Lauher and Hoffmann.

While in the process of submitting this work, a paper appeared in this journal that described the results of a beautiful kinetic and mechanistic study of the insertions of substituted olefins into niobium–hydride and tantalum–hydride bonds.[32] The information we have obtained from the photoelectron ionizations with regard to the relative stabilities of these complexes agrees with the conclusions from the mechanistic study. Furthermore, the description of the bonding and electron distribution that emerges from characterization of the ionizations provides a model for understanding the relative rates of olefin insertion into the metal–hydride bond. These points will be discussed after the information from the photoelectron ionizations is made clear.

Experimental Section

Preparation of Compounds. Cp_2NbH_3,[33] $Cp_2Nb(CO)CH_3$,[34] $Cp_2Ta(C_2H_4)H$,[25] and $Cp_2Ta(C_2H_4)C_2H_5$[35] were prepared as described in the literature. Cp_2TaH_3 was synthesized from Cp_2TaCl_2 and lithium aluminum hydride by a method similar to Labinger's preparation of Cp_2NbH_3.[33]

Preparation of $Cp_2Nb(CO)H$. Cp_2NbH_3 (280 mg, 1.2 mmol) was dissolved in 25 mL of toluene in a 500-mL Pyrex flask, and 1 atm of carbon monoxide was introduced. The solution was irradiated at room temperature for 5 h with a pair of 15-Watt blacklights (General Electric Model F15T8 BLB, $\lambda_{max} \approx 355$ nm). The toluene was removed under vacuum and sublimation of the residue at 100 °C and 10^{-3} Torr gave purple crystals in nearly quantitative yield.

Preparation of $Cp_2Ta(CO)H$. Cp_2TaH_3 (1.0 g, 2.9 mmol) was dissolved in 40 mL of 1,2-dimethoxyethane in a quartz reaction vessel, and 1 atm of carbon monoxide was added. The solution was photolyzed at room temperature for 2 h with a 450-W Hanovia medium-pressure mercury lamp. The cloudy brown solution was cooled to −78 °C, the

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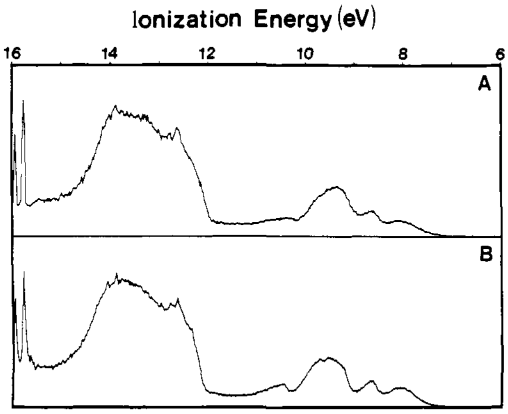

Figure 1. Full He I photoelectron spectra of (A) Cp_2NbH_3 and (B) Cp_2TaH_3.

gases (H_2 + CO) were pumped out of the vessel, and 1 atm of pure CO was introduced. This procedure of photolysis, removal of gas, and reintroduction of CO was repeated four times (for a total time of 8 h). The solvent was removed under vacuum, and sublimation of the residue at 70 °C and 10^{-3} Torr provided 0.25 g (23% yield) of purple crystalline product.

Preparation of $Cp_2Nb(C_2H_4)H$. Ethyl magnesium bromide (4.6 mL, 13.8 mmol) in diethyl ether was added dropwise to a slurry of 200 mg (6.8 mmol) of Cp_2NbCl_2 in 120 mL of diethyl ether. After stirring for 2 h at room temperature, the solvent was removed in vacuo, leaving a brown residue. The residue was extracted with 100 mL of petroleum ether, and this extract, after solvent removal, was sublimed at 80 °C and 10^{-3} Torr, affording 870 mg (51% yield) of bright yellow crystals.

Photoelectron Spectra. The He(I) and He(II) photoelectron spectra were recorded with special instrumentation and techniques described earlier.[36-38] For all samples, the cell was heated to 85-90 °C to achieve and maintain sufficient sample pressure. All experiments showed clean vaporization and ionization of the sample except the photoelectron spectrum of $Cp_2Ta(CO)H$, which shows weak impurity peaks at 8.2, 11.5, and 12.7 eV. The 12.7-eV peak is due to HCl. The presence of impurity peaks is easily recognized because they vary in intensity relative to the other ionizations in the spectrum during the data collection process and from one run to the next.

The photoelectron data are corrected for the experimentally known spectrometer analyzer transmission function. The He II data are also corrected for the He II β-excitation line (48.4 eV; 12% of the He II α intensity). The ionization energies, half-widths, and relative intensities for all bands of interest are in Table I. The analytical representations of the data in Table I were obtained with program GFIT,[39] which assumes asymmetric Gaussian functional forms for the peaks. If peaks are overlapping such that there is not a clear inflection between their maxima, the peaks are constrained to have the same shape. These situations can be identified in Table I when adjacent peaks have the same high half-widths and also the same low half-widths. The analytical representation for each overlapping region was obtained with the minimum number of asymmetric Gaussians that would account for the experimental peak area. No additional physical interpretation should be given to the individual Gaussian peak parameters that are obtained. The analytical data in Table I have estimated uncertainties (3σ level) of 0.02 eV in band positions and half-widths, 5% in He I relative intensities, and 10-20% in He II relative intensities. In the case of strongly overlapping bands, the estimated uncertainties are 0.05 eV in individual band positions and half-widths, 15% in He I relative intensities, and 30% in He II relative intensities. Although there are greater uncertainties in the features of individual peaks when they are overlapping, the overall combined contour and area of the overlapping ionizations is still represented well by the analytical data. The combined area of overlapping peaks is listed in the table in these cases.

Results and Valence Ionization Band Assignments

This section will summarize the general ionization features and assignments of the photoelectron spectra of these complexes. The

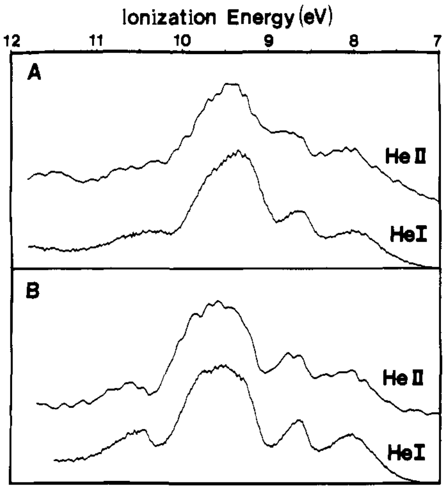

Figure 2. He I and He II spectrum comparisons for (A) Cp_2NbH_3 and (B) Cp_2TaH_3.

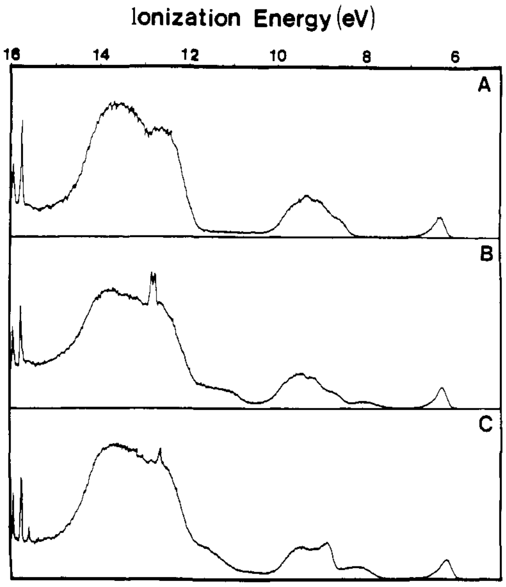

Figure 3. Full He I photoelectron spectra for (A) $Cp_2Nb(CO)H$, (B) $Cp_2Ta(CO)H$, and (C) $Cp_2Nb(CO)(CH_3)$. The $Cp_2Ta(CO)H$ spectrum contains impurity peaks at 8.2, 11.5, and 12.7 eV (HCl).

relationship of these features to the electronic structure, bonding, and chemistry of these complexes will be discussed in the following section.

Cp_2MH_3 (M = Nb, Ta). The full valence photoelectron spectra of the niobocene and tantalocene trihydrides are shown in Figure 1. The spectrum of Cp_2TaH_3 has been reported previously,[29] and our results are in agreement. The Nb and Ta species give almost identical spectra, as might be expected for the predominantly ligand-based ionizations of these formally d^0 complexes. The broad band of ionizations between 12 and 15 eV corresponds to ionizations associated with the cyclopentadienyl rings. These ionizations involve the C-C and C-H σ bonds and the symmetric π orbital (correlating with the a_1'' of planar Cp^-) of each cyclopentadienyl ring. This broad ionization appears in this region of the spectra of all complexes discussed in this study. The other cyclopentadienyl π ionizations (correlating with the e_1'' of planar Cp^-) appear as the most intense of the outer valence ionizations centered at 9.5 eV. The position of these ionizations is also essentially the same in the spectra of all complexes studied. The band profile in this region changes somewhat throughout the series due to overlap with other ligand-based ionizations. In the trihydride complexes, all three of the metal-hydrogen bond ionizations (at 8.0, 8.6, and 10.4 eV) can be distinguished from the Cp π ionizations. The comparative He I/He II spectra of Cp_2NbH_3 and Cp_2TaH_3 are shown in Figure 2, and the analytical

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Table I. Valence Band Positions, Half-Widths, and Relative He I/He II Intensities for Substituted Niobocenes and Tantalocenes

		position,	half-width		rel area	
complex	peak	eV	high	low	He I	He II
Cp_2NbH_3	A	8.00	0.83	0.71	1.00	1.00
	B	8.64	0.42	0.33	0.67	0.60
	C	9.27	0.55	0.51	3.40	2.43
	D	9.71	0.55	0.51		
	E	10.37	0.83	0.42	0.53	0.40
$Cp_2Nb(CO)H$	A	6.39	0.26	0.26	1.00	1.00
	A′	6.65	0.26	0.26		
	B	8.69	0.86	0.46	1.51	0.80
	C	9.11	0.86	0.48		
	D	9.35	0.86	0.48	4.57	1.93
	E	9.61	0.86	0.48		
$Cp_2Nb(CO)CH_3$	A	6.20	0.28	0.25	1.00	1.00
	A′	6.47	0.28	0.25		
	B	8.18	1.09	0.60	1.59	0.74
	C	8.88	0.94	0.26		
	D	9.32	0.94	0.26	5.11	2.15
	E	9.54	0.94	0.26		
$Cp_2Nb(C_2H_4)H$	A	6.53	0.64	0.42	1.00	1.00
	B	8.23	0.55	0.30	1.11	0.71
	C	8.86	0.84	0.40		
	D	9.33	0.84	0.40	5.08	2.80
	E	9.54	0.84	0.40		
Cp_2TaH_3	A	8.03	0.77	0.60	1.00	1.00
	B	8.66	0.42	0.26	0.58	0.66
	C	9.35	0.60	0.49	3.14	3.14
	D	9.81	0.60	0.49		
	E	10.48	0.77	0.26	0.59	0.38
$Cp_2Ta(C_2H_4)H$	A	6.59	0.62	0.42	1.00	1.00
	B	8.22	0.49	0.36	1.10	0.80
	C	8.91	0.67	0.48		
	D	9.34	0.67	0.48	5.09	3.85
	E	9.77	0.67	0.48		
$Cp_2Ta(C_2H_5)(C_2H_4)$	A	6.53	0.76	0.39	1.00	
	B	7.98	0.85	0.72	1.53	
	C	8.76	0.67	0.40		
	D	9.27	0.67	0.40	6.83	
	E	9.75	0.67	0.40		

representation of the data is summarized in Table I. There are no statitistically significant differences in the relative intensities of the Cp π and metal–hydrogen ionizations in the He I/He II comparison of either of these complexes, indicating the similar small metal character associated with all of these ionizations.

$Cp_2M(CO)H$ (M = Nb, Ta). The He I spectra of these carbonyl–hydride complexes of niobocene and tantalocene are also very similar to each other, as shown in Figure 3. As described in the experimental section, the spectrum of the $Cp_2Ta(CO)H$ complex contains some weak ionizations that are identified as ionizations due to impurities or decomposition products. The spectrum of this tantalum complex will not be discussed in detail. These complexes are formally described as metal d^2 species and thus should show a single low-energy band with characteristics of a predominantly metal-based ionization. This ionization occurs at 6.3 eV in the spectrum of $Cp_2Nb(CO)H$. Similar to the metal-based ionizations of other metal–carbonyl complexes, a shoulder due to carbonyl stretching vibrational fine structure is observed on the high binding energy side (vide infra, Figure 10).[40-42] The set of bands between 8.0 and 10.5 eV contain the metal–hydrogen σ-bond ionization in addition to the Cp π ionizations as discussed above for the trihydrides. The shoulder at 8.69 eV most likely has a predominant contribution from the M–H σ bond, since it ionizes within 0.5 eV of the analogous M–H ionization of local b_2 symmetry in the trihydride spectrum (vide infra). A previous UPS study of $Cp_2Ta(CO)H$ placed the M–H σ ionization at 9.4–9.6 eV.[31] The spectra of other complexes in this study will further support our assignment. Comparison of the He I and He II spectra of $Cp_2Nb(CO)H$ is shown in Figure 4, and the analytical data are summarized in Table I. The intensity of the metal ionization (bands A + A′, where A′ is the carbonyl vibrational fine structure shoulder) increases 20% relative to the ligand ionizations (bands B + C + D + E) with a change from He I to He II radiation. Relative intensity changes within the ligand ionization bands between 8.0 and 10.5 eV are not conclusive, although a slight intensity increase is shown by the 8.69-eV shoulder assigned as the M–H bond ionization (band B) relative to the Cp π ionizations (bands C–E).

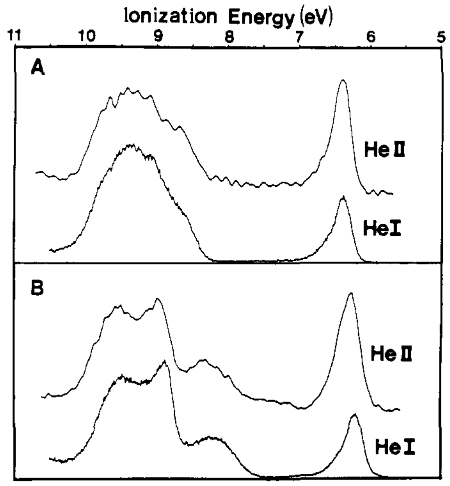

Figure 4. He I and He II spectrum comparisons for (A) $Cp_2Nb(CO)H$ and (B) $Cp_2Nb(CO)(CH_3)$.

$Cp_2Nb(CO)CH_3$. The full He I spectrum for this complex is shown in Figure 3, and the closeup He I and He II spectra for $Cp_2Nb(CO)CH_3$ are shown in Figure 4. The ionization profile is similar to that of the corresponding carbonyl–hydride complex. The metal d^2 band (A) appears at 6.2 eV, again with a shoulder due to carbonyl vibrational fine structure (band A′). The most significant change between this spectrum and that of the carbonyl–hydride discussed above is the ionization associated with the M–C(alkyl) bond in place of the ionization associated with the M–H bond. This M–C bond ionization is observed at 8.2 eV (band B) and is separated from the Cp π ionizations at 8.5–10.5 eV (bands C–E). This ionization energy is typical for M–C σ bonds.[13] Observation of this separate M–C σ-bond ionization in this methyl complex is further support for assignment of the 8.69-eV shoulder in the spectrum of the carbonyl–hydride complex to the M–H σ ionization. The C–H σ-bond ionization of the methyl group is seen as a low-energy shoulder (11.5 eV) on the characteristic broad band of Cp and CO ionizations. These assignments agree with those reported for related niobocene propyl carbonyl complexes.[31] The 20% intensity increase of the metal band (A + A′) relative to the ligand bands (B + C + D + E) is clearly observed. There may also be a slight increase of the area of the M–C(alkyl) ionization relative to the Cp π ionizations.

$Cp_2M(C_2H_4)H$ (M = Nb, Ta). The He I spectra of the ethylene–hydride complexes of niobocene and tantalocene are shown in Figure 5. The formally metal d^2 ionization is again at lowest ionization energy (6.5 eV), but no distinct vibrational shoulder is seen on this band. Rather, an overall band broadening and shift to slightly higher ionization energy is observed compared to the corresponding band in the carbonyl–hydride complexes.

A distinct ionization is observed near 8 eV, similar to that observed in the other metal–hydride complexes. This ionization precedes the Cp π ionization region, which starts at 8.5 eV. The Cp π ionization region is also broadened compared to this region in the spectra of the other complexes. This is due to the additional contribution of the ethylene π ionization to this region. The detailed nature of these ionizations will be discussed later. The C–H σ-bond ionizations of the coordinated ethylene occur at 11.2 eV. These ionizations are shifted substantially to lower binding

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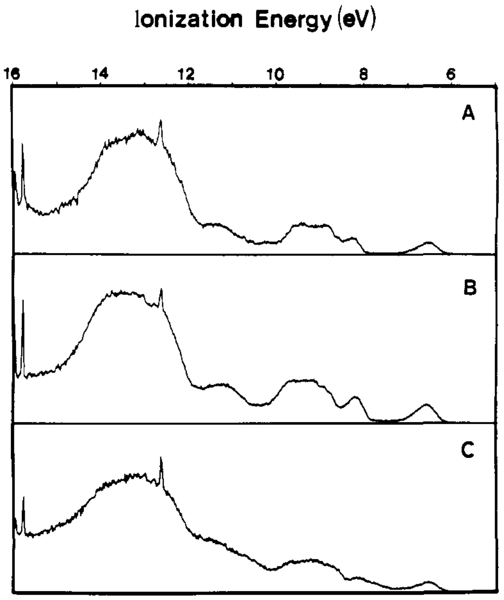

Figure 5. Full He I photoelectron spectra for (A) $Cp_2Nb(C_2H_4)H$, (B) $Cp_2Ta(C_2H_4)H$, and (C) $Cp_2Ta(C_2H_4)(C_2H_5)$.

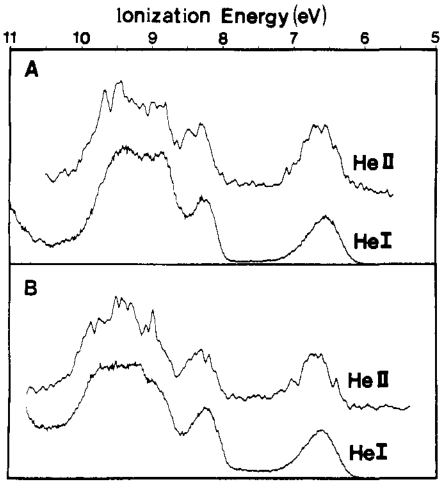

Figure 6. He I and He II spectrum comparisons for (A) $Cp_2Nb(C_2H_4)H$ and (B) $Cp_2Ta(C_2H_4)H$.

energy from the C–H σ-bond ionizations of uncoordinated ethylene, which occur at 14.5 eV.[43] The destabilization of these ionizations indicates a increase of negative charge in the region of the ethylene when it is coordinated to this metal center.

The He II spectra in Figure 6 as well as the analytical data in Table I do not show as large an intensity increase for the lowest ionization energy band (A) relative to the ligand bands (B–E) as was observed for the metal d^2 bands in the carbonyl–hydride and carbonyl–metal complexes. For the niobium complex, the lowest energy ionization band increases 12% relative to the ligand bands in the He II experiment, as opposed to the 20% relative intensity increase seen in the carbonyl complexes. For the tantalum complex, band A increases only 5% relative to the ligand bands (B–E) upon changing to He II excitation. These differences in relative band intensity, position, and width of the first ionization band are important to the discussion of the electronic structure of these complexes.

$Cp_2Ta(C_2H_5)(C_2H_4)$. The He I spectra for this complex are shown in Figures 5 and 7 and are most conveniently discussed in comparison with the corresponding ethylene–hydride species. The lowest energy ionization does not shift significantly between the two complexes. On the other hand, the metal–alkyl M–C σ-bond ionization appears at 8.0 eV, 0.5 eV lower than the M–H σ-bond ionization in the ethylene–hydride complex. This M–C σ ionization is cleanly separated from the overlapping Cp π and ethylene π ionization bands between 8.5 and 10 eV in this case. The coordinated ethylene and ethyl C–H σ-bond ionizations occur between 10.5 and 12.0 eV. In free ethylene and ethane, the C–H σ-bond ionizations occur at 14.5 and 11.5–14.5 eV, respectively. The destabilization of the C–H σ-bond ionizations of the coordinated ligands compared to the free molecules again indicates the negative charge being transferred to these groups from the metal.

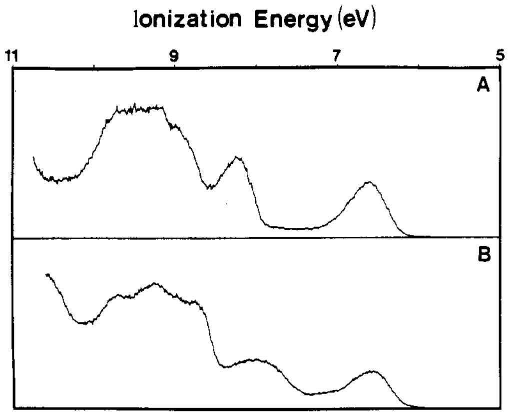

Figure 7. Closeup He I comparison for (A) $Cp_2Ta(C_2H_4)H$ and (B) $Cp_2Ta(C_2H_4)(C_2H_5)$.

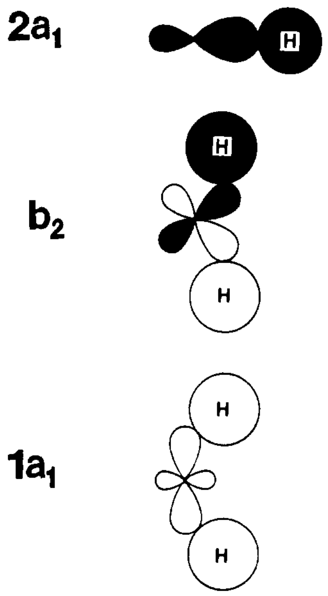

Figure 8. Frontier orbitals of the bent Cp_2M fragment. The symmetry combinations formed from the three hydrogen orbitals are included to show the locations of the atoms.

Discussion

Metal–Hydrogen and Metal–Carbon Bond Ionizations. The experimental information obtained on the valence electronic structures of the molecules in this study will be discussed primarily in terms of ligand interactions with the frontier metal-based orbitals of the bent Cp_2M unit (C_{2v} symmetry) labeled by Lauher and Hoffmann.[28] The most significant of these metal-based orbitals are the $1a_1$, b_2, and $2a_1$, which are illustrated in Figure 8 for the convenience of discussion. These orbitals are shown in the molecular mirror plane that contains the metal–ligand bonds, and the positions of the hydride atoms in the trihydride complexes show the orientation with respect to the ligands. In the Cp_2M fragment with no coordinated ligands and hence no bonding interactions, these fragment orbitals have the energy ordering $2a_1$ (least stable) $< b_2 < 1a_1$ (most stable). The three hydride orbitals

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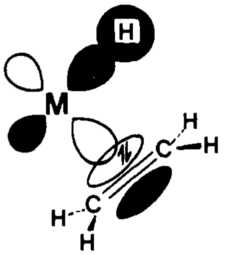
(44) Calabro, D. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6846–52.

also form the familiar $1a_1$, b_2, and $2a_1$ symmetry combinations with zero, one, and two nodes, respectively. However, it is not useful to retain this picture of the trihydride combinations in the Cp_2MH_3 molecule because of the strong mixing in the a_1 levels. In the complex, one of the resulting MH_3 bonding a_1 orbitals has its primary contribution from the two outside hydrogens. The other mixed orbital has its primary contribution from the center hydrogen. The b_2 combination in the trihydrides remains relatively pure hydride character because the wide angle between the outer hydrogens[45] reduces the overlap with the metal b_2 orbital.

There is little doubt as to the identity and location of the three metal–hydrogen bond ionizations in the spectra of the metallocene trihydrides, Cp_2MH_3 (M = Nb, Ta). Our results and assignments agree with those previously published.[29] The two a_1 ionizations at 8.0 and 10.4 eV are broad relative to the b_2 ionization at 8.6 eV, indicating that substantial M–H_3 bonding is taking place in the a_1 orbitals. It should be noted in general that there is substantial mixing between metal–ligand σ bonds, particularly when they are close in energy.

In $Cp_2Nb(CO)H$, the M–H σ-bond ionization is in the same region as the Cp π ionizations. The mixing of the M–H and M–CO σ-bond ionizations is less significant in this case because the major portion of the M–CO σ ionization is well separated at energies greater than 12 eV.[11] The shoulder on the low binding energy side of the primarily Cp π-ionization band in $Cp_2M(CO)H$ is in the same region as the b_2 ionization for Cp_2MH_3 (within 0.05 eV). This shoulder correlates with the M–H σ ionization, rather than a Cp π ionization as assigned previously.[31]

The M–H σ-bond ionization in the spectra of the $Cp_2M(C_2H_4)H$ (M = Nb, Ta) complexes cannot be discussed separately from the M–C_2H_4 bond ionizations. The ethylene–hydride spectra show a distinct ionization in the vicinity of 8 eV that is shifted a few tenths of an electronvolt to lower binding energy from the b_2 ionization of the trihydride complexes. It is temping to simply assign this 8-eV band to the M–H ionization. However, on the basis of our previous studies of the ionizations of ethylene coordinated to other metal centers,[44] there is reason to suspect that the metal–ethylene bond contributes to this ionization. The ethylene π ionization of the free molecule occurs at 10.5 eV. The ionization obtained from coordination to the metal is shifted by the change in bonding and electron distribution with the metal. The ionization is expected to be stabilized about 1 eV by the bonding with the metal. However, this bonding stabilization is countered by the rehybridization at the carbon centers and the increase in negative charge potential at the ethylene.[44] As an indication of the increase of negative charge at the ethylene, the ethylene C–H σ-bond ionizations are destabilized about 3 eV in comparison to those of free ethylene. Similar effects will cause the ethylene π ionization to be in the vicinity of the 8-eV band, along with the M–H σ ionization. Both the ethylene and the hydride are σ donors to the same b_2 orbital, and because they are energetically similar, there will be substantial mixing in these interactions, as shown in I. In fact, this 8-eV band was previously assigned as an ethylene π ionization in related propene and butene complexes, partly on the basis of the shift of this ionization with alkylation of the alkene.[31] This assignment is also misleading as to the true nature of this ionization. The shift of the ionization to lower energy with alkyl substitution for the H from $Cp_2Ta(C_2H_4)H$ to $Cp_2Ta(C_2H_4)C_2H_5$ shows that it also involves considerable M–H character. As will be discussed later, it is more correct to view these ionizations as the mixing of two M–C and one M–H interaction, similar to the mixing of the three M–H interactions in the case of the trihydrides.



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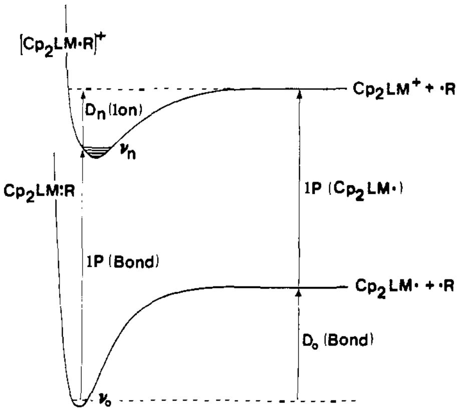

Figure 9. Relationship of the ionization energies of a Cp_2MLR complex and the $Cp_2LM^{\bullet}$ fragment to the Cp_2MLR potential wells in the neutral molecule and the ion.

The shift to lower ionization energy with alkyl substitution for the hydride has been observed for other analogous compounds.[46,47] The shift between ionizations associated with M–H and M–C(alkyl) bonds is more clearly observed in the spectra of $Cp_2Nb(CO)H$ and $Cp_2Nb(CO)CH_3$. The band at 8.69 eV in the spectrum of the hydride complex is replaced by a band at 8.18 eV in the spectrum of the alkyl complex. The shift of this band for the carbonyl complexes is twice the shift of the band in the vicinity of 8 eV for the ethylene complexes, showing the greater mixing of the metal–ligand bonds in the ethylene complexes.

Relative Thermodynamic Bond Strengths. The photoelectron data presented in this study reveal some interesting aspects regarding the relative metal–ligand bond strengths between related species as well as the relative overall thermodynamic stability of the complexes toward certain geometric and chemical transformations. Ionization energies of organometallic complexes have seldom been discussed directly in terms of thermodynamic properties. However, it should be remembered that the ionization energy is itself a fundamental thermodynamic quantity often used in thermodynamic cycles. Common examples are the use of ionization energies in Born–Haber cycles of ionic compounds[48] and the use of ionization energies with appearance potentials for determining proton affinities.[49] A detailed understanding of the chemically important valence ionizations of a species is closely related to its thermodynamic stability or chemical reactivity, since any physical or chemical transformation will alter the valence electronic structure and ionizations as bonds are compressed, elongated, broken, or formed. The amount of bonding that is lost in a valence ionization event is one factor that determines the ionization energy. Walsh pointed out over 4 decades ago that a molecular ionization energy characterizes both the orbital that is ionized as well as the contribution that that orbital makes to the bond strength.[50]

The relationship between the bond dissociation energy for a particular bond in a molecule and an ionization energy of that molecule can be appreciated by considering the pair of molecular potential energy diagrams shown in Figure 9. D_0(bond) is the homolytic dissociation energy of the bond for the neutral molecule, IP(bond) is a measured ionization potential of the molecule that

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corresponds to a final ion state with a change in that bond strength, $IP(Cp_2LM^\bullet)$ is the ionization potential of the metal fragment resulting from bond dissociation, and $D_n(\text{ion})$ is the bond dissociation energy from the appropriate vibrational state in the molecular ion. Figure 9 uses the vibrational state corresponding to the vertical ionization energy. For a given bond and ionization to a particular positive ion state

$$IP(\text{bond}) = D_0(\text{bond}) + IP(Cp_2LM^\bullet) - D_n(\text{ion}) \qquad (1)$$

Knowledge of three of the quantities in eq 1 provides the fourth.

If one is interested in comparing the bonds of two different species with a common fragment, such as comparing the hydride and methyl bonds with the same $Cp_2LM^\bullet$ fragment, two equations of type (1) can be written, one for the M–H bond and one for the M–C bond. The difference between these equations is

$$IP(M\text{–}H) - IP(M\text{–}C) = \{D_0(M\text{–}H) - D_n(M\text{–}H)^+\} - \{D_0(M\text{–}C) - D_n(M\text{–}C)^+\} \qquad (2)$$

where (M–L) represents the particular fragment–ligand bond for L = H or L = C(alkyl). The term $IP(Cp_2LM^\bullet)$ cancels when this difference is taken because both dissociations produce the same metal fragment in the potential energy diagram.

The terms in brackets on the right of eq 3 are the differences in M–L bond dissociation energies between the neutral molecules and the positive ions. The dissociation energy of this bond in the molecular ion may be expressed as a proportion (λ_L) of the dissociation energy of this bond in the neutral molecule:

$$D_n(M\text{–}L)^+ = \lambda_L D_0(M\text{–}L) \qquad (3)$$

The proportionality factor λ_L depends on the degree of bond covalency. It is generally found that $0.5 \geq \lambda_L \geq 0$. In simple terms, if an electron is removed from a completely covalent bond, half of the bond order is removed and the remaining bond is approximately half as strong as the original. Thus $\lambda_L \approx 0.5$. For example, in the case of the hydrogen molecule the ionization energies and the bond energy show that λ has the value 0.49 (2).[14] In the case of organometallic complexes, ionization often essentially destroys the bond between the metal and the ligand, so in general for organometallic complexes $0.2 \geq \lambda_L \geq 0$. The ionization represents oxidation of the metal, and oxidation is a common chemical approach to effect disproportionation of organic ligands from metal complexes. The significance of this λ_L factor is discussed elsewhere.[14] If the degree of covalency in the two metal fragment–ligand bonds is assumed to be equal (similar λ_L values), then

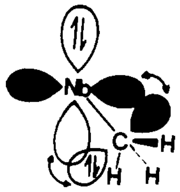
$$IP(M\text{–}H) - IP(M\text{–}C) = (1 - \lambda_L)\{D_0(M\text{–}H) - D_0(M\text{–}C)\} \qquad (4)$$

Thus the difference in ionization energies of two metal fragment–ligand bonds is approximately between 0.8 and 1.0 times the difference in bond dissociation energies.

From comparison of the spectra of $Cp_2Nb(CO)H$ and $Cp_2Nb(CO)CH_3$ as well as $Cp_2Ta(C_2H_4)H$ and $Cp_2Ta(C_2H_4)(C_2H_5)$, the relative ionization energies of early transition metal M–H and M–C(alkyl) bonds is observed to be M–H > M–C, and it can in turn be concluded from this trend that the M–H bond energy is greater than the M–C bond energy. In the case of the Nb(CO)H and $Nb(CO)CH_3$ complexes the energy of the Nb–H ionization is about 0.5 eV greater than that of the corresponding $Nb\text{–}CH_3$ ionization. This indicates that the Nb–H bond is about 12–14 kcal mol^{-1} more stable (using $\lambda_L = 0.0\text{–}0.2$) than a Nb–C(methyl) bond in these molecules. This result is in good agreement with thermochemical results of Marks and coworkers involving group IV and actinide bent metallocenes, where M–H > M–C by 11–15 kcal mol^{-1}.[5,51] The difference in M–H and M–C(ethyl) ionizations of the tantalum–ethylene complexes is smaller at 0.24 eV. This may be partly due to a slightly weaker metal–carbon bond in this case but probably reflects for the most part the mixing of these bonds with the ethylene π bond as described earlier. The mixing means that a larger proportion of the M–L bond strength will be retained in this particular positive ion state (larger λ_L). Aside from the particular quantitative comparisons, the important point for the following discussion is that the ionization energies give a measure of the relative strengths of comparable bonds and the stability of these complexes.

Electron Distribution in Early Metal Bent Metallocenes. In comparison to He I excitation, He II excitation enhances the intensity of metal-based ionizations relative to ligand-based ionizations. This trend has been demonstrated extensively in studying relative metal character in ionizations of organometallic molecules.[11,13] The formal metal d electron count of a complex is indicated by the number of ionizations that display this relative cross section increase from the He I and He II photoelectron spectra. For example, the trihydride complexes are formally considered to be d^0 electron systems and 5+ oxidation states. There is little relative intensity increase of any band below 11.15 eV, as seen in the comparative He I/He II spectra in Figure 2 and the data in Table I. These data indicate little metal character in any of these bands and suggest that all of the bond ionizations are primarily ligand based.

In the case of the formally d^2, M(III) $Cp_2Nb(CO)H$ and $Cp_2Nb(CO)(CH_3)$ complexes, the He I/He II spectra in Figure 4 and the data in Table I show a large increase in the intensity of the first ionization band relative to the Cp π and other ligand bands, indicating that the first ionization represents a pair of electrons that are largely localized on the metal center. It should be noted that determination of the formal d electron count (and hence oxidation state) by these experimental observables does not imply any conclusions with regard to the net electron charge potential at the metal center. Complexes with the same metal and formal oxidation state can have widely different electron charges at the metal center.[11,42] In this work, the methyl and hydride complexes have the same formal oxidation states, but the shifts of the metal-based ionizations reveal different electron charges at the metal centers. The methyl complex has the added possibility of a π-type interaction between the coordinated methyl group $e_{C\text{–}H}$ bonds and the metal $1a_1$. This destabilizing filled-filled interaction[9] is shown in diagram II. The interactions of methyl C–H bonds with metal orbitals have been examined in theoretical calculations.[9,52] There is still not agreement on the expected magnitude of these interactions. The d^2 metal ionization in $Cp_2Nb(CO)(CH_3)$ is slightly destabilized relative to the same orbital in $Cp_2Nb(CO)H$, and this interaction may contribute. The metal bands in both of these complexes have almost equivalent half-widths and He I/He II intensities relative to the ligand bands.



II

Additional evidence for the metal character in the first ionization of these complexes and the formal d^2 electron count for these systems comes from the carbonyl stretching vibrational fine structure, as can be seen from Table I and Figure 10. Observation of the ligand vibrational fine structure on a metal ionization band is an indication of metal → carbonyl π^* back-bonding.[40-42] The filled metal orbital that is the correct symmetry for π-back-bonding to a π^* orbital of the carbonyl is also the correct symmetry for π interaction with the methyl group. The destabilization of the metal density in the methyl complex results in greater π-back-bonding to the carbonyl, as reflected in the IR spectra of these species ($\nu_{CO} = 1902$ cm^{-1} for $Cp_2Nb(CO)H^{53}$ and $\nu_{CO} = 1890$ cm^{-1} for $Cp_2Nb(CO)CH_3{}^{54}$).

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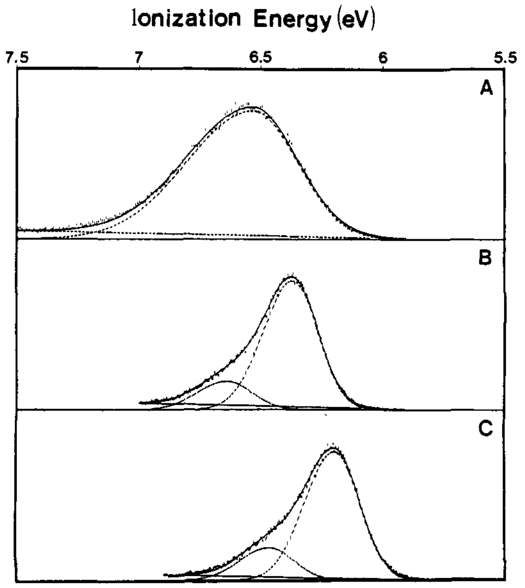
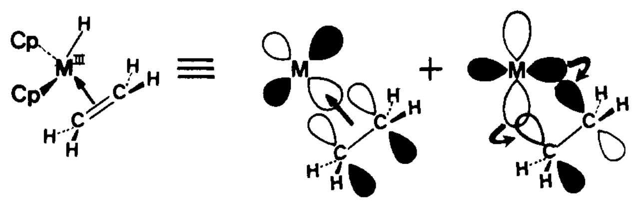


Figure 10. Low ionization energy region of the photoelectron spectra of (A) $Cp_2Nb(C_2H_4)H$, (B) $Cp_2Nb(CO)H$, and (C) $Cp_2Nb(CO)(CH_3)$.

The ethylene complexes ($Cp_2Nb(C_2H_4)H$, $Cp_2Ta(C_2H_4)H$, and $Cp_2Ta(C_2H_4)(C_2H_5)$) might be counted similar to the carbonyl complexes as d^2 and formally 3+ oxidation states. However, there is a substantial difference between the carbonyl and ethylene complexes with respect to electron distribution and localization as revealed by the comparative He I/He II spectral intensities. For the niobium–ethylene–hydrides, the data in Table I show only a 12% increase in the He II spectrum of the relative intensity of lowest energy band relative to the remaining ligand-based bands. This is in contrast to the larger increase observed in the carbonyl spectra discussed above. For the tantalum–ethylene–hydride, the relative intensity increase is even smaller at a negligible 5%. This trend indicates that the low-energy band has less metal character than the analogous bands in the carbonyl–hydride and carbonyl–methyl complexes. In the ethylene–hydrides, charge redistribution from the metal center into the ethylene π^* orbital is extensive. This charge redistribution is more pronounced in the tantalocene ethylene–hydride due to larger radial extent and bonding participation of the Ta orbitals as compared to the Nb orbitals[59] and the greater preference for the higher oxidation state. The metal centers of the ethylene–hydride complexes are electron poor relative to the metal centers of the corresponding carbonyl–hydride and methyl–carbonyl complexes due to this extensive delocalization throughout the coordinated metal–ethylene framework.

This result contrasts with previous studies comparing the carbonyl and ethylene bonding to a low oxidation state metal center. The previous studies utilized the $CpMn(CO)_2$ fragment, and in this case the π-back-bonding effectiveness of CO and C_2H_4 π^* orbitals was found to be essentially the same.[44] The He I/He II data described above indicate that the ethylene π^* orbital is accepting more electron density from the metal center than is the corresponding carbonyl π^* orbital, causing the electron density to be less localized on the metal center and more delocalized through the coordinated ligand ethylene framework. Thus, with these niobium and tantalum bent metallocene units and especially for tantalum, ethylene is much more effective at metal-to-ligand π-back-bonding than carbonyl.[55]

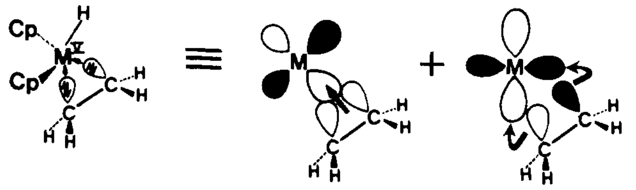
Metallacyclopropane Nature of $Cp_2M(C_2H_4)H$ Complexes. The description of metal–ethylene interactions in the previous section, based on π^* acceptance by the ligand, is in the terms of the Dewar–Chatt–Duncanson model.[56–58] The basic features of this model are represented by the primary valence bond (left side) and molecular orbital (right side) descriptions of a coordinated ethylene as shown below.



1a **2a**

The ethylene π bond donates electron density to the metal center (**1a**). The d^2 metal center, in turn, donates electron density to the unfilled π^* orbital of the ethylene (**2a**). With this synergic bonding, the formal oxidation state of the metal center reflects coordination of a neutral ethylene molecule.

However, the photoelectron information is not entirely consistent with this model of metal–ethylene interaction. The He I/He II intensity comparisons show that the lowest energy ionization has less metal character than would be expected if $Cp_2M(C_2H_4)H$ were considered a d^2 M(III) complex. The predominantly ligand character of this low-energy ionization is more consistent with a d^0 electron count corresponding to a 5+ oxidation state for Nb or Ta. This electron distribution and bonding is more accurately described as a metallacyclopropane hydride.[22,25,59,60] The primary valence bond (left side) and molecular orbital (right side) contributions for the metallacyclopropane model are shown below.



1b **2b**

As can be seen, the orbital descriptions are very similar in the Dewar–Chatt–Duncanson and metallacyclopropane models, with the primary differences occurring in the limits of the electron distributions. The metallacyclopropane model of metal–ethylene bonding is characterized by the description of a chelating $C_2H_4^{2-}$ ligand acting as a four-electron donor to the d^0, M(V) metal center, rather than a neutral ethylene coordinated to a d^2, M(III) metal center.[61] The symmetric combination of the two carbon lone pairs of $C_2H_4^{2-}$ correspond to donation of π electron density to the metal center (**1b**) as in the Dewar–Chatt–Duncanson model. However, there is no synergic back-bonding from the metal center. Instead, the metal is viewed as also accepting electrons from the antibonding combination of the carbon lone pairs of the dianion (**2b**), which correlate with the ethylene π^* orbital.

The He I/He II ionization intensity comparison is not the only experimental indication of the high formal oxidation state of the metal and the coordination of a dianion. In addition, the greater width of the lowest energy ionization of the ethylene complexes as compared to those of the carbonyl complexes, as shown in Table I and Figure 10, indicates a greater degree of bonding for these low ionization energy electrons in the metallacyclopropane systems. Also, this ionization of the ethylene–hydride complex is stabilized relative to the corresponding d^2 metal band of the carbonyl–hydride (0.14 eV) as a result of the electron delocalization over the metal

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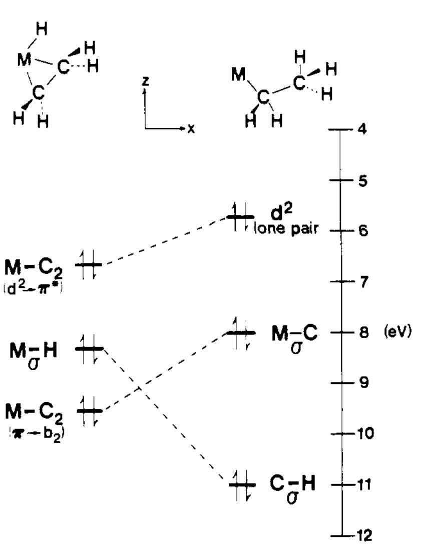

Figure 11. Ionization energy correlations for the olefin insertion reaction $Cp_2M(C_2H_4)H \rightarrow Cp_2M(C_2H_5)$. The relative ionization energies are to scale based on photoelectron studies of representative niobocene and tantalocene complexes with bound ethylene, hydride, methyl, and ethyl groups.

and two carbon atoms. Thus, this ionization is more like that of a delocalized $M-C_2$ σ bond, correlating to the orbital (**2b**). The ionization correlating to the symmetric orbital (**1b**) appears at approximately 9.5 eV and is partly obscured by the Cp π ionizations. The representation of the olefin as a dianion in the metallacyclopropane model is also supported by the ionizations. As mentioned in the results section, the substantial shifts of the C–H ionizations and the C–C π ionization to lower ionization energies reflect a large increase in negative charge potential on the olefin.

Metallacyclopropane–Hydride Stability. Insertion of an olefin into a metal–hydride bond is implicated in many important synthetic and catalytic reactions. Of course, insertion is the reverse of the familiar β-hydride elimination process. Lauher and Hoffmann[28] have discussed the surprising stability of these metal–ethylene–hydride complexes relative to the ethylene-inserted metal–alkyl complexes. They emphasized that, upon transformation from metal–ethylene–hydride to metal–alkyl, the loss of stabilizing metal d²-to-ethylene π^* back-donation was the primary electronic factor inhibiting the insertion. The fates of the M–H σ- and ethylene π-bonding orbitals, which correlate with C–H σ- and M–C σ-bonding orbitals in the alkyl complex, were not treated in any detail. However, the relative energies of these latter orbitals are crucial quantities for understanding the thermodynamic stability of the complex relative to the insertion product. For reasons based on the results of the previous section and the following discussion, it is more appropriate to describe the transformation discussed by Lauher and Hoffmann as a metallacyclopropane–hydride to metal–alkyl transformation.

A correlation diagram based on *experimental* valence ionization data, rather than theoretical orbital eigenvalues, of the metallacyclopropane–hydride to metal–alkyl transformation is shown in Figure 11. For the metallacyclopropane–hydrides, the lowest $M-C_2$ and M–H σ-ionization energies are taken directly from Table I. The higher $M-C_2$ ionization energy is in the vicinity of 9.5 eV and is partly obscured by the Cp π ionizations as discussed earlier. For the metal–alkyl, the metal–carbon σ-ionization energy is from data for $Cp_2Nb(CO)CH_3$ and $Cp_2Ta(C_2H_4)(C_2H_5)$. The metal–alkyl d² ionization is found from data on the related metallocene–allyl complexes, $Cp_2M(C_3H_5)$ (M = Nb, Ta),[31] in which metal–allyl π-back-bonding is minimal.

In comparing the metallacyclopropane–hydride to the olefin-inserted metal–alkyl, three factors play a role in deciding which structure is the most stable on the grounds of valence electronic structure. First, the electrons involved in the ($1_{a1} \rightarrow \pi^*$) $M-C_2$ bond of the metallocyclopropane become localized on the metal center in the metal alkyl. This localization and loss of bonding of electron density on the metal center destabilizes these electrons. The experimental observation of the shift in this ionization is the effect correctly predicted by Lauher and Hoffmann.[28] Second, the M–H σ bond in the metallacyclopropane–hydride correlates to a much more stable C–H σ bond in the metal–alkyl. These electrons are more stable in the metal–alkyl, and in fact the diagram shows this stabilization more than offsets the destabilization of the metal electron density mentioned by Lauher and Hoffmann and favors formation of the metal–alkyl. Finally, the ($\pi \rightarrow b_2$) $M-C_2$ bond in the metallacyclopropane correlates to a less stable, localized M–C σ bond in the metal–alkyl. Thus, formation of a very stable C–H σ bond favors the metal alkyl complex, but delocalized $M-C_2$ bonding favors the metallacyclopropane–hydride complex. The stabilization obtained upon C–H bond formation in the metal–alkyl is insufficient in this case to counter the loss of stabilization obtained from the favorable, delocalized metallacyclopropane $M-C_2$ σ bonding.

The relative stabilities of these complexes as indicated by this spectroscopic study agree well with the conclusions obtained from a kinetic study of the insertion of olefins into niobium–hydride and tantalum–hydride bonds.[32] One result from the kinetic study (¹H NMR coalescence and magnetization-transfer techniques) is that the insertion to form the metal–alkyl is more facile for the niobium complexes than for the tantalum complexes. We observed on the basis of the He I/He II comparisons that the bonding and electron distribution of the olefin to the metal tends more toward the metallacyclopropane limit in the case of tantalum compared to niobium, and the stability of the metallacycle is key to inhibiting the insertion process for a given olefin. Likewise, the kinetic studies showed that insertions for the corresponding pentamethylcyclopentadienyl complexes are slower than insertions for the cyclopentadienyl complexes (in the absence of steric effects). Although we have not included pentamethylcyclopentadienyl complexes in the present study, we know from previous work that the methyl groups substantially increase the electron-donor ability of the rings to the metal.[36] The metallacycle formation will be increasingly important for stabilization of the extra charge on the metal, and insertion will be inhibited.

In the comparison of substitution groups on the olefins, the kinetic study found that electron-withdrawing groups on the olefin favor stabilization of the ground state and increase the olefin binding constant. As Figure 10 shows, the electron withdrawing groups on the olefin will favor more complete formation of the metallacycle unit in contrast to a coordinated olefin and produce a more stable complex and ionizations. Electron-releasing groups on the endo position of the coordinated olefin (C_β position of the resulting alkyl) accelerate the insertion into the metal–hydride bond as expected on the basis of the decreased stability of the ground state. It might also be noted that the contribution of the endo carbon to the HOMO will increase with electron-releasing groups on this position, and this M–C(endo) bond will be preferably broken in proceeding to the transition state. Interestingly, electron-withdrawing groups at the exo carbon position apparently accelerate the insertion process. This trend does not follow from the stability of the ground-state complex as a whole but may similarly follow from the increased contribution of the endo carbon to the HOMO when the metallacycle bonding is polarized in this way, and again a preferable breaking of the M–C(endo) bond in proceeding to the transition state of the insertion.

Conclusions

This study illustrates that photoelectron spectral data can be extremely useful in revealing the relative stability of organometallic species both in terms of relative individual bond strengths (M–H vs M–C) and relative overall thermodynamic stability (metallacyclopropane–hydride vs metal–alkyl). Information regarding nonintuitive, subtle electronic factors, such as the role of relative bond strengths in metallacyclopropane–hydride stabilization and resistance to olefin insertion, can be obtained provided the ionization features of the investigated molecules are well understood in comparison to those of other known complexes. These data show that for these early transition metal bent metallocenes, metal–hydrogen σ bonds are slightly stronger than metal–carbon σ bonds. The metal–ethylene complexes, while often described similarly to metal–carbonyl complexes, actually have far different electron distributions and formal oxidation states. The results of this study give direct evidence that these systems are best described as metallacyclopropanes with formal M(V) oxidation states, in agreement with conclusions drawn from other investigations.[32]

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Experimental and Theoretical Studies of the Gas-Phase Protonation of Vinyl Ethers, Vinyl Sulfides, and Vinyl Selenides

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Abstract: A series of nine chalcogen-substituted ethylenes (chalcogen = O, S, Se) have been synthesized, and their gas-phase proton affinities (PA) were determined experimentally by measuring gas-phase basicities (GB) in an ion cyclotron resonance (ICR) spectrometer and theoretically by means of ab initio MO calculations at the STO-3G and 3-21G* levels. A satisfactory correlation ($r = 0.978$, slope = 1.41) has been obtained between the experimental and calculated 3-21G(*) values. In contrast with a number of previous reports, we consistently found that third- (SMe) and fourth-row (SeMe) substituents do not stabilize better the adjacent positive charge than does the second-row substituent OMe, even in the gas phase. In fact, comparison of experimental proton affinity value of ethylene with that of mono(methylchalco)ethylenes indicates that OMe, SMe, and SeMe groups stabilize the corresponding ethyl cations to very much the same extent. In 2-propyl cations the trend is O > S > Se, but the differences ($\delta\Delta$ in Table III) are quite small: 1.2 kcal mol^{-1} between O and S and 1.4 kcal mol^{-1} between S and Se. The superior ability of oxygen in carbenium ion stabilization appears the most clearly in the protonation of bis(methylchalco)ethylenes: dimethoxyethyl cation is more stable than the corresponding thio species by $\sim$5.5 kcal mol^{-1}, whereas dithio- and diselenocarbenium ions again have very similar stabilities. These conclusions are supported and extended by ab initio results on optimized geometries.

The effects of substituents on the stability of gas-phase ions are being increasingly studied in order to distinguish the intrinsic molecular properties from the effects of the surrounding medium (solvent, etc.). From an experimental point of view, the substituent effects can be evaluated by the determination of the gas-phase basicity (GB), and hence of the proton affinity (PA), in equilibrium proton-transfer reactions. The results of these studies have been recently reviewed.[2]

Another approach to the evaluation of the properties of isolated systems consists of the calculation of the total energy of the systems using molecular orbital methods. The results of the latter not only can be compared to experimental results but they also provide insights into the geometries of the ionized species. Furthermore, the energy–structure relationships of the less stable species can also be investigated by the MO methods.[3]

The present study addresses the problem of the stabilization of carbocations by substituents containing adjacent heteroatom(s). Except for the case of enamines,[4] these effects have been relatively little studied in the gas phase,[5] unlike the well-documented substituent effects of alkyl groups on the stability of, e.g., carbenium, oxonium, and ammonium ions.[2] Regarding the stabilizations of carbenium ions by group VI substituents, it has been admitted, essentially on the basis of kinetic data in solution[6] on one hand and mass spectrometric and ion cyclotron resonance studies[5] on the other hand, that α-oxygen-substituted carbenium ions are more stable in solution than their α-thio analogues, whereas the reverse holds in the gas phase. While early theoretical calculations[7] seemed to confirm the latter conclusion, higher level ab initio results obtained recently[8-10] have shown that second- and third-row

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