the isomeric alkenes as the neutral reactants.[15] However, product distributions and the behavior of cross sections with kinetic energy distinguish the cyclic from the acyclic systems. Most striking are the differences in reactivity of cyclopropane and propene (for which no reactions were detected at low energies) and the multiple dehydrogenation of cyclopentane, reaction 10, and cyclohexane, reactions 17 and 18, a process not observed for any pentene or hexene isomer. Interestingly, Allison and Ridge[21] have observed such multiple dehydrogenations in the reactions of Ti^+ and $TiCl^+$ with alkenes. They speculate that dehydrocyclization reactions result in the production of metal ion–cyclic alkene complexes. No carbon–carbon bond cleavage reactions were observed in those studies in contrast to the present results.

Conclusion

While the case for the intermediacy of cobaltacycle ions in the reactions of Co^+ with cyclic alkanes is equivocal, the observations made in the present study are consistent with such a mechanism. Unfortunately, no conclusions can be drawn concerning the relative rates of metallacycle decomposition via ring cleavage processes vs. reductive elimination reactions yielding the reactant cyclic alkane or an isomerized alkene. The present results do suggest, however, that of the ring cleavage reactions, symmetric or nearly symmetric C–C bond cleavage is preferred. Cleavage at all positions does occur, however.

As in previous studies,[14,15] the structure of the reactant hydrocarbon is an important factor determining product distributions. Thus, reactions of the cyclic alkanes differ appreciably from those of the isomeric alkenes. Since the product ions $CoC_5H_6^+$, $CoC_6H_8^+$, and $CoC_6H_6^+$ are observed in the cyclopentane and cyclohexane systems but not in acyclic alkene[15] or alkane[14] systems, dehydrocyclization of the latter hdyrocarbons is regarded as improbable.

In studies related to the present experiments, reactions of $CpNi^+$ ions, where $Cp \equiv (\eta^5\text{-}C_5H_5)$, with cyclic alkanes have been examined.[22,23] While no cleavage reactions occur, dehydrogenation of cyclobutane and multiple dehydrogenations of cyclopentane and cyclohexane, all exothermic, are observed. In another study,[24] the product ions $CpCo(C_6H_{10})^+$, $CpCo(C_6H_8)^+$, and $CpCo(C_6H_6)^+$ were observed in an ionized mixture of $CpCo(CO)_2$ and cyclohexane. From a comparison of these results with the present study it is apparent that the cyclopentadienyl ligand can greatly affect the chemistry of the metal center. Specifically, the processes initiated by insertion into a C–C bond are not observed.

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Negative Ion States of d^6 Transition-Metal Hexacarbonyls

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Abstract: The energies of the low-lying unstable negative ion states of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have been obtained by electron transmission spectroscopy. Calculations employing the SCF Xα method indicate that these compounds possess a number of stable negative ion states and that the observed unstable states arise from electron capture into the antibonding ligand field orbitals and other empty orbitals correlating with the 2π and 6σ orbitals of free CO.

The study of the electronic structure of organometallic compounds has enjoyed a renaissance over the past few years. In particular the transition-metal carbonyl complexes have received a good deal of attention. This is not surprising since the CO–metal bond is quite common in organometallic chemistry. Additionally, an understanding of the CO–metal bond is fundamental to the study of CO chemisorption as well as catalytic reactions at metal surfaces.

Ultraviolet photoelectron spectroscopy (UPS), first extensively applied to studies of hydrocarbons, has recently been employed to measure the ionization potentials of organometallics in order to learn about the energies of the occupied valence orbitals of these compounds.[2] However, a complete picture of the electronic structure requires information on the low-lying unoccupied orbitals. Much of this information is available from electron transmission spectroscopy[3] (ETS), the experiment conjugate to UPS. Whereas UPS measures the energy required to remove an electron from an occupied orbital, ETS measures the energy of a negative ion state arising from electron capture into an unoccupied orbital. A limitation to ETS is that only the energies associated with unstable negative ions are accessible. That is, only negative electron affinities can be determined by ETS. This technique was first applied in studies of atoms and di- and triatomics.[4] Subsequently, ETS has been applied in investigations of the properties of π^* orbitals of unsaturated hydrocarbons.[3] We report here the first extension of the technique to transition-metal complexes.

The transition-metal hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were chosen for their volatility and their simple and symmetrical geometry and because of their d^6 electronic configuration. Simple ligand field theory suggests that the first unoccupied orbital is the antibonding σ molecular orbital of e_g symmetry and that the splitting in the octahedral ligand field is sufficiently large that occupation of this orbital may give rise to an unstable temporary negative ion state. Gray and Beach[5] point out that a number of antibonding π orbitals, mainly localized on the ligands, can be expected at energies comparable to that of the

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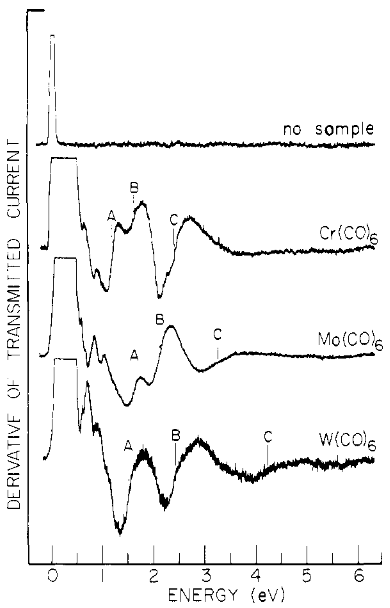

Figure 1. Derivative electron transmission spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. The attachment energies corresponding to the three features above 1 eV are marked A, B, and C. The spectrum taken with no sample illustrates the sharp onset of transmitted current which is observed in the absence of attachment processes near 0 eV.

e_g ligand field orbital. Therefore it was expected that a number of negative ion states corresponding to slightly negative electron affinities would be observable in the electron transmission spectrum. In addition it is possible that occupation of strongly antibonding orbitals, located primarily on the exterior of the molecule, will give negative ion states at higher energies. As explained below, a theoretical analysis of our ETS data confirms these expectations.

Experimental Section

Electron transmission spectroscopy is a technique for measuring the energy of a temporary negative ion formed by electron capture into an unoccupied orbital of a molecule. The experiment involves the measurement of the transparency of a gas to an electron beam as a function of energy. The transparency depends in an inverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with large cross section only over a narrow energy range. Since the negative ion promptly decays by giving up the trapped electron, the formation and decay process appears as a sharp fluctuation in the electron-scattering cross section. The process, as well as the corresponding feature in the transmission vs. electron energy spectrum, is referred to as a "resonance".

The electron spectrometer[6] consists of an electron source followed by an electron monochromator, a gas cell, and an electron collector. In practice the first derivative of the transmitted current as a function of energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.[7] The energy associated with a resonance is known as an "attachment energy" (AE) and, with respect to the derivative spectrum, is defined as the point vertically midway between the minimum and maximum which characterize the resonance. For the present purposes an attachment energy may be identified with the negative of the corresponding electron affinity (EA).[8]

Results

The derivative electron transmission spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are shown in Figure 1 along with the trace obtained with no gas in the target cell. The only feature in this latter trace is a sharp spike corresponding to the derivative of the sudden onset of electron current near zero electron energy. This "turn-on" feature is considerably broader in the sample spectra, implying the occurrence of an attachment process for electrons of nearly zero kinetic energy. Following this feature in each spectrum there are at least two more features below 1 eV. Above these are three persistent features—two resonances in the 1–2.4-eV range (marked A and B in Figure 1) and a third in the 2.4–5-eV range (C in Figure 1). The attachment energies corresponding to these three features are presented in Table I.

Table I. Attachment Energies (eV) of Prominent Features (Marked A, B, and C in Figure 1) in the Electron Transmission Spectra of Transition-Metal Hexacarbonyls[a]

	A	B	C
$Cr(CO)_6$	1.23	1.64	2.42
$Mo(CO)_6$	1.65	2.14	3.29
$W(CO)_6$	1.53	2.46	4.26

[a] The uncertainty is 0.05 eV.

The electron transmission spectra in Figure 1 are far more complex than any spectra of this type previously presented. Although the spectra roughly conform to the expectations expressed above, the assignment of each feature to a negative ion state is certainly a much more difficult problem than previously encountered. Even a knowledge of the ordering of negative ion states in these compounds is not adequate to assign the observed features because of the strong possibility of the occurrence of stable negative ion states below the range of ETS. Certainly the Koopman's theorem approach employed in the past will not serve in this case. Accordingly, we have undertaken some approximate quantum mechanical calculations which consider explicitly the electronic properties of the negative ion.

Quantum Mechanical Calculations

Method. A series of calculations have been performed on CO and $Mo(CO)_6$ by using the scattered-wave Xα self-consistent field MO method.[9] This method has previously been applied to CO[10] and to $Cr(CO)_6$[11] Similar methods, using the statistical exchange or Xα approximation but employing an analytical basis set for expansion of the one-electron orbitals, have been applied to $Cr(CO)_6$[12] and to $Mo(CO)_6$ and $W(CO)_6$.[13] Finally, the scattered-wave model has also been used to calculate electron-scattering cross sections for free CO.[14]

In all cases agreement between calculated and observed energies has been reasonably good, with typical errors of about 1 eV. For example, the two calculations on $Cr(CO)_6$ give binding energies of 8.6[11] and 8.3 eV,[12] respectively, for the highest occupied (metal d, ligand field t_{2g}) orbital in good agreement with the experimental value of 8.5 eV.[15] The calculated UV absorption energies were also in the same range as those observed,[13] although the closeness in energy of a large number of different transitions make definitive assignments difficult. For free CO the scattered-wave calculation[14] reproduced the angular variation of the elastic electron-scattering cross section but gave a value for the energy of the resonance about 2 eV larger than experiment.

The scattered-wave Xα method suffers from the imposition of a "muffin-tin" form on the potential. However, it appears that this problem is not too serious for molecules of high symmetry such as $Mo(CO)_6$.[16] Even for nonspherical molecules such as CO, the problem can be overcome to some extent by use of overlapping atomic spheres.[10] For the case of excited states and negative ions this weakness of the method is counterbalanced by its great radial flexibility in the expansion of the orbitals. By numerically solving Schrodinger's equation within regions centered

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Table II. Calculated Orbital Energies (eV) for CO

orbital	ground-state[a]	ground-state with Watson sphere[b]
2π	−1.2	−11.5
5σ	−8.5	−18.8
1π	−10.8	−21.2
4σ	−14.7	−25.0

[a] From reference 11. [b] From present work.

on the nuclei, we can avoid the problem of basis set choice and can accommodate the expansion of electron density which accompanies negative ion formation.

For the present problem the important feature of both the scattered-wave and the analytical orbital Xα methods is that both utilize the transition-state procedure.[17] This approach takes account of the electronic relaxation which accompanys electron capture or electron ejection by performing a self-consistent field calculation on a "transition state" with orbital occupation numbers halfway between those in the initial and the final states. The transition energy is then given, accurate to terms of second order in the occupation numbers, by orbital eigenvalues or their differences. For example, to calculate the electron affinity associated with an orbital which is empty in the ground state, we add half of an electron to it and redo the calculation to self-consistency. The EA is then given as the negative of this transition-state orbital eigenvalue. Such a procedure has yielded accurate EA's for many stable negative ions.[18,19]

For free CO we employed a bond distance of 1.13 Å and sphere radii of 0.79 and 0.77 Å on C and O, respectively.[20] For $Mo(CO)_6$ we used a Mo–C bond distance of 2.063 Å and a C–O bond distance of 1.145 Å[20] and assumed O_h symmetry. Sphere radii used were 1.25, 0.81, and 0.82 Å for Mo, C, and O, respectively. All statistical exchange values (α) were taken from Schwarz's tabulation.[21] Since our program cannot treat orbitals with positive eigenvalues, we added in some cases a sphere of uniformily distributed positive charge (the "Watson sphere"[22]) to stabilize the empty levels. Our experience indicates that the Watson sphere shifts all levels by the same amount to within a few tenths of 1 eV. In all our calculations all electrons (including the metal core) were included in the self-consistent process.

CO. For free CO our ground-state calculations were identical with those of ref 10 except for the imposition of a Watson sphere of radius 2.70 Å and charge of 2+ electronic units. The sphere radius chosen was approximately twice as great as that of a sphere tangent to the C atomic sphere in order to ensure that almost all the electron density would be contained inside the Watson sphere. In Table II we list our calculated ground-state orbital energies. We find that the Watson sphere has stabilized all the orbitals by between 10.3 and 10.4 eV, a value very close to the electrostatic potential of 10.6 eV expected inside a charged sphere of radius 2.70 Å and charge +2. This suggests that orbital energies calculated for other states of CO can thus be corrected by the Watson sphere electrostatic potential without introducing serious error.

To determine the energy for addition of 1 electron to the empty 2π orbital of CO, we then added half of an electron to the 2π orbital and reiterated to self-consistency. The 2π orbital eigenvalue in this transition state was −7.4 eV, which when corrected for the Watson sphere stabilization of about 10.6 eV gives an eigenvalue of +3.2 eV and thus an electron affinity of −3.2 eV. This value is in reasonable agreement with the experimental value of about −2 eV.[3,4] Note that the CO 2π orbital energy changed by 4.1 eV between the ground state and the electron attachment transition state, an important factor in the high energy of the unstable negative ion.

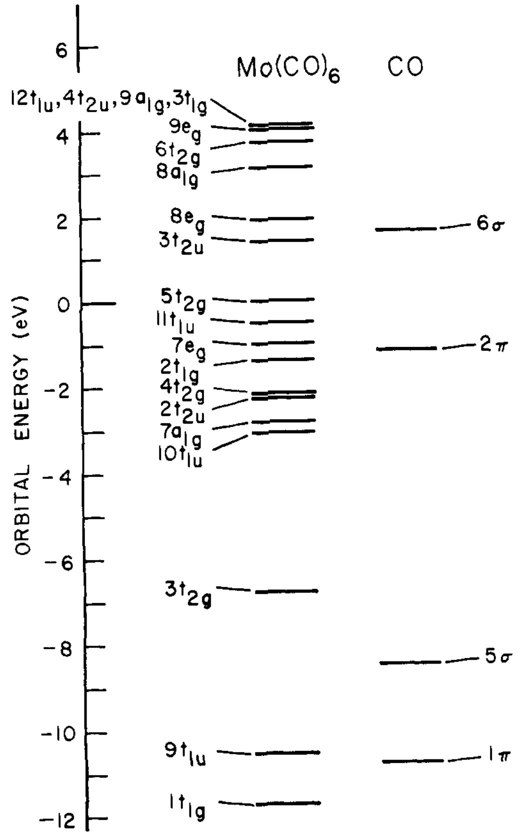

Figure 2. Calculated orbital energies in the ground states of neutral $Mo(CO)_6$ and CO. The highest occupied orbitals are $3t_{2g}$ and 5σ, respectively.

Table III. Orbital Energies (eV) of Highest Occupied and Empty Orbitals in the Ground State of Neutral $Mo(CO)_6$

$12t_{1u}$	4.1	$11t_{1u}$	−0.5
$4t_{2u}$	4.1	$7e_g$	−1.0
$9a_{1g}$	4.1	$2t_{1g}$	−1.4[a]
$3t_{1g}$	4.1	$4t_{2g}$	−2.16
$9e_g$	4.0	$2t_{2u}$	−2.29
$6t_{2g}$	3.7	$7a_{1g}$	−2.85
$8a_{1g}$	3.1	$10t_{1u}$	−3.10
$8e_g$	1.9	$3t_{2g}$[b]	−6.86
$3t_{2u}$	1.4	$9t_{1u}$	−10.56
$5t_{2g}$	0.0	$1t_{1g}$	−11.77

[a] Orbital energies at and above this level estimated from energies in stabilized $3t_{2g}$ transition state. [b] Highest occupied orbital.

In our calculation, the CO negative ion state has been treated as an ordinary bound state, satisfying the same boundary conditions as the stable states of the molecule. In essence we have employed what is known as a "stabilization method".[23] This method has yielded reasonable results in several cases and is probably the only approach presently possible for molecules as complex as those treated here. The 2π state we calculate is higher in energy than the 2π state corresponding to the neutral molecule plus free electron. However, the state we have located shows little tendency to adopt the extremely diffuse electron density expected for a free electron. Only 29% of the 2π orbital electron density is found in the outer-sphere region in our scattered-wave calculation, a figure no larger than that found for the 5σ-bound orbital. Thus, our self-consistent field procedure has apparently found a local energy minimum corresponding to a well-localized, quasi-bound 2π state.

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Table IV. Estimated Electron Affinities (eV) for Unstable Negative Ions and Orbital Compositions[a]

		M	C	O	int	outs
$3t_{1g}$	−5.0	0	0	2	21	76
$9e_g$	−5.0	0	2	0	1	97
$6t_{2g}$	−4.6	0	0	0	4	95
$8a_{1g}$	−4.0	0	0	0	4	95
$8e_g$	−2.8	13	7	3	10	67
$3t_{2u}$	−2.3	0	5	1	47	47
$5t_{2g}$	−0.8	8	25	2	35	30
$7e_g$	−0.7	40	8	3	29	20
$11t_{1u}$	−0.3	1	17	7	42	34

[a] Percentage distribution of electron density among regions of the molecule in $5t_{2g}$ electron attachment transition state; M, C, and O = atomic spheres, int = interatomic region, outs = extramolecular region.

$Mo(CO)_6$. In Table III and Figure 2 we give the energies for the highest occupied and several empty orbitals in the ground state of $Mo(CO)_6$. Since the high energy orbitals ($2t_{1g}$ and above) have positive eigenvalues in the ground state of the neutral molecule, a stabilization method was employed to approximate these energies. The low energy empty orbitals ($10t_{1u}$ through $4t_{2g}$) were first located for the neutral molecule. Then self-consistency was obtained for the $3t_{2g}$ photoionization transition state (5.5 electrons in the $3t_{2g}$) stabilized by a Watson sphere of radius 4.03 Å and +1 charge. All the low- and high-energy empty orbitals were then found for this state. The low-energy empty orbitals were stabilized between 4.86 and 5.36 eV. For an approximation of the energies of the high-energy orbitals of the ground-state neutral molecule, the energy difference between each high energy orbital and the $10t_{1u}$ orbital in the transition state was added to the energy of the $10t_{1u}$ orbital in the ground-state neutral.

To assess the accuracy of the calculation, we calculated the $3t_{2g}$ (Mo 4d ligand field) orbital binding energy (transition state without Watson sphere) obtaining a value of 8.8 eV, which compares favorably with the experimental value of 8.4 eV.[14] Our calculated transition-state energy of 4.14 eV for the $3t_{2g} \rightarrow 10t_{1u}$ transition is in good agreement with the experimental value of 4.32 eV as well as with previous calculations.[13] However, our calculated energy for the $3t_{2g} \rightarrow 7e_g$ transition is 6.07 eV, much larger than that obtained from a previous assignment of the UV absorption spectrum[5] but consistent with the negative electron affinity predicted for electrn capture into the $7e_g$ orbital (see below).

In Figure 2 we include calculated CO orbital energies (with that for the 6σ orbital from the calculation with a Watson sphere). A previous study[11] of $Cr(CO)_6$ indicates that in terms of symmetry, energy, and charge distribution, the 5σ of CO correlates most strongly with the $6a_{1g}$, $9t_{1u}$, and $6e_g$ orbitals of $Mo(CO)_6$ (of which only the $9t_{1u}$ is shown) while the 1π correlates with the $2t_{2g}$, $8t_{1u}$, $1t_{2u}$, and $1t_{1g}$ occupied orbitals of $Mo(CO)_6$ (of which only the $1t_{1g}$ is shown). We find the highest occupied orbital ($3t_{2g}$) to be essentially a nonbonding ligand field orbital with about 60% of the electron density within the Mo atomic sphere.

By symmetry, σ orbitals on CO give rise to a_{1g}, e_g, and t_{1u} molecular orbitals on $Mo(CO)_6$, while π orbitals correlate with orbitals of t_{1g}, t_{1u}, t_{2g}, and t_{2u} symmetry on $Mo(CO)_6$. On the basis of energetics it appears that the empty orbitals from $10t_{1u}$ through at least $8e_g$ correlate with the 2π and 6σ orbitals of CO. In particular, the t_{1g} and t_{2u} orbitals have only high angular momentum components on the Mo and no CO σ character. They are of pure CO π character with antibonding interactions between adjacent ligands. We found the $7e_g$ antibonding ligand field orbital to have about 50% of its electron density on the metal atom.

We then performed a calculation on the transition state for electron attachment to the $10t_{1u}$ orbital, obtaining an electron affinity of 1.8 eV (orbital eigenvalue equals −1.8 eV), corresponding to a stable negative ion. With the assumption that the other CO-concentrated empty orbitals are affected by the transition state procedure in a way similar to that for the $10t_{1u}$ there will be a number of stable negative ion states based on the relative orbital energies in Table III. The primary reason for the low energies of these negative ions is not that they have highly negative eigenvalues in the neutral molecule. Rather, it is because they are only slightly destabilized in the electron attachment transition state. For the $10t_{1u}$ orbital this destabilization is only about 1.3 eV, compared to a 4.2-eV destabilization in the 2π negative ion of CO. The lower destabilization for the $Mo(CO)_6$ case is a simple consequence of the dispersal of electron charge onto the six CO ligands. Thus, we might expect multiligand transition-metal compounds to generally have stable negative ions in which the excess charge is spread over all the ligands.[25]

To obtain approximate electron affinities for the unstable negative ions of $Mo(CO)_6$, we performed calculations in which half of 1 electron was added to either the $7e_g$ or the $5t_{2g}$ orbital and the charge density reiterated to self-consistency with a Watson sphere imposed. The transition-state eigenvalue of the $5t_{2g}$ orbital was −2.73 eV, which when corrected for the potential from the Watson sphere[26] yielded an approximate electron affinity of −0.8 eV corresponding to an unstable negative ion state. For the $7e_g$ orbital the calculated EA was −0.7 eV. Assuming that the transition-state destabilizations for the other empty orbitals, all of which are concentrated on CO, will be similar to that for the $5t_{2g}$, we estimate the electron affinities shown in Table IV. The larger transition-state destabilization experienced by the $7e_g$ orbital is a consequence of its substantial localization on the Mo.

As the negative ion becomes more unstable, its lifetime decreases and the resonance broadens. In addition to the calculated energy we expect the lifetime of the state to be reflected in its spatial distribution. As shown in Table IV the amount of charge in the extramolecular or outer-sphere region increases substantially as the energy of the state rises. In fact, most of the states with estimated orbital energies of 4.0 eV or above are 95% in the extramolecular region. The boundary conditions imposed in our scattered-wave program require the orbitals to go to zero at infinity. Such a boundary condition is unrealistic for a state like the $8a_{1g}$ and alternative boundary conditions have been employed in scattering calculations.[14] Nonetheless, those orbitals with very diffuse electron densities and short lifetimes can probably be identified by using our method by their concentration in the extramolecular region.

Conclusions

We can use the results in Table IV to make a tentative assignment of features in the electron transmission spectra. The calculations suggest that the peaks below 1 eV can be attributed to negative ion states arising from electron capture into the $11t_{1u}$, $5t_{2g}$, and $7e_g$ orbitals: the two clear features (A and B in Figure 1) in the range of 1.4–2.2 eV may be assigned to capture into the $3t_{2u}$ and $8e_g$ orbitals and the broad feature (C in Figure 1) at about 3.3 eV to capture into the $6t_{2g}$ and perhaps other states of slightly higher energy. This last feature is not attributed to electron capture into the $8a_{1g}$ orbital since the resulting negative ion state would have appreciable s-wave character and would thus be unobservable by ETS because of its extremely short lifetime.[3] It is conceivable that the structure below 1 eV is a vibrational progression in a single anion state since the CO stretching fre-

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(25) In ionization processes the transition-state stabilization of orbitals delocalized over the six CO ligands is small. For example, in $Cr(CO)_6$ the stabilization of the $1t_{1g}$ orbital in going from the ground state to photoionization transition state is only 2.2 eV[10] compared to 5.4 for the 1π orbital of the free CO. It also has been observed that the calculated binding energies of the predominantly CO-type orbits are too small by about 2–3 eV.[11] This discrepancy was eliminated for the case of $Cr(CO)_6$ when a calculation was performed on an ion with the valence electron hole localized on one of the ligands,[24] the state with the localized hole was about 2 eV more stable than that with the hole forced to delocalize over all six CO ligands by symmetry constraints. In our calculations we have not considered the possibility of charge localization on one of the CO groups in the ion. However, a simple qualitative argument suggests that if cations of the hexacarbonyls are stabilized by hole localization, the hexacarbonyl negative ions will be stabilized by charge dispersal. Therefore, states with the added electron localized on one CO will be less stable than those in which the extra charge is spread over all the CO's.

(26) We have found that doubling the size and charge of the Watson sphere and reiterating to self-consistency changed this value by only 0.1 eV.

quency in hexacarbonyls is about 0.25 eV.[27] However, such vibrational structure is weak in the CO molecule itself,[3] and since the added electron in the $Mo(CO)_6$ anion is distributed over six ligands, we would expect the C–O distance change to be smaller and the vibrational structure even weaker.

This assignment yields a plausible explanation for the energy trends along the series Cr, Mo, W for the intermediate energy peaks. Since the $8e_g$ orbital has some metal d character, we expect it to change in energy as M is changed. The separation of the metal d ligand field t_{2g} and e_g orbitals ($3t_{2g}$ and $7e_g$ in $Mo(CO)_6$) is calculated to increase from 4.6 eV in $Cr(CO)_6$ to 5.9 eV in $Mo(CO)_6$ so that the antibonding e_g orbitals are apparently destabilized along the series. The $3t_{2u}$ orbital on the other hand is essentially a CO orbital, correlating with the 2π. Experimental studies suggest that the M–C distance is shorter in $Cr(CO)_6$ than in $Mo(CO)_6$ or $W(CO)_6$ and that the C–O distance is longer.[20] A larger C–O separation would be consistent with a lower energy $3t_{2u}$ orbital in $Cr(CO)_6$.

It is difficult to obtain from theory an accurate quantitative comparison between $Mo(CO)_6$ and the other hexacarbonyls due to inevitable computational artifacts resulting from the choice of sphere radii and other effects. However, we have found that electron affinities calculated for $Cr(CO)_6$ by using a previously employed parameter set[11] and the same stabilization method employed for $Mo(CO)_6$ are −0.2, −1.7, and −2.8 for the orbitals corresponding to $7e_g$, $3t_{2u}$, and $8e_g$, respedtively. Thus, the antibonding ligand field orbital (the $7e_g$ analogue) is more stable by about 0.5 eV in the Cr compound, and the analogue of the $3t_{2u}$ orbital is more stable by about 0.6 eV. The $8e_g$ analogue, however, is unchanged in energy. Although the electron attachment transition state has not been studied for the $Cr(CO)_6$ analogue of the $6t_{2g}$ orbital, its approximate ground-state orbital energy suggests that it is stabilized by about 0.7 eV in the Cr case as observed.

Our analysis therefore suggests that the d^6 transition-metal hexacarbonyls have a number of stable negative ions obtained from population of orbitals correlating with the 2π of CO. The lowest energy unstable negative ions arise from occupation of the e_g ligand field orbital, the highest energy 2π-type orbitals, and the 6σ-type orbitals. The scattered-wave $X\alpha$ method with a stabilizing Watson sphere yields electron affinities qualitatively consistent with those observed. In vieew of our results it is surprising that stable anions of these compounds have not been observed in solution although it is possible the hexacarbonyl anions give up CO to form a stable pentacarbonyl anion similar to the behavior of $Fe(CO)_5$ and $Ni(CO)_4$ upon electron capture.[28]

In summary then, we have made the first measurements of the energies of negative ion states of transition-metal complexes. We have in addition demonstrated that plausible state assignments can be made on the basis of SCF $X\alpha$ calculations employing the transition-state procedure to get electron affinities associated with electron capture into orbitals whose energies are obtained by means of a stabilization method.

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^{31}P NMR Spectra of Chelated (Diphosphine)rhodium Complexes in Solution

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Abstract: The $^{31}P\{^1H\}$ FT NMR spectra of Rh complexes that form in solution via ligand exchange of diphosphines with $HRh(CO)(PPh_3)_3$ have been scanned in order to characterize the complexes that form since with certain diphosphines such solutions catalyze selective olefin hydroformylation. It is shown that these diphosphines readily form Rh complexes under NMR conditions that exhibit 16-line multiplet spectra. The multiplets were simulated with AB_2X and ABCX (A, B, C = ^{31}P, X = ^{103}Rh) models and are attributed to approximately trigonal-bipyramid complexes of formula $HRh(CO)(P{\sim}P)(PR_3)$, $[HRh(CO)(P{\sim}P)_{1.5}]_2$, and $HRh(CO)(P{\sim}P)(P{\sim}P)^m$, where R = PPh_3 or $PEtPh_2$, m = monodentate, and P∼P = certain diphosphines including [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphine), diop, *trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane, *t*-bdcb, 1,1′-bis(diphenylphosphino)ferrocene, fdpp-1, and 1,1′-bis(bis(*p*-(trifluoromethyl)phenyl)phosphino)ferrocene, fdpp-2.

The complex $HRh(CO)(PPh_3)_3$ (**1**) is a well-known active catalyst for olefin hydroformylation.[1] In the presence of large excess concentrations of PPh_3 and under specific reaction conditions **1** confers a high selectivity in the conversion of α-olefins to linear (vs. branched) aldehydes.

It was recently shown[2] that certain diphosphines including *trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane, *t*-bdcb, [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(di-

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