unequivocal from the potential energy distribution.

Deformation vibrations of CCC in alkanes and of CCP in trialkylphosphines were found to fall in the 500–400-cm^{-1} region.[19,20] The compound in this study has no such puzzling modes and the 600–300-cm^{-1} region is completely clear aside from the 376-cm^{-1} band (solid $(CH_3)_3PTe$). Consequently the 376-cm^{-1} band has been confidently assigned to the P–Te stretching vibration. As expected from the heavier mass of tellurium, the P–Te frequency is lower than the P–Se frequency (441 cm^{-1} for $(CH_3)_3PSe$[6]). No bands were found in the region corresponding to ones around 400 and 450 cm^{-1} assigned to the P–Te stretching mode in trialkylphosphine tellurides[3] and at 519 cm^{-1} assigned to the P–Te stretch in tris(dimethylamino)phosphine telluride.[4]

The P–Te stretching force constant was found to have a value of 2.20 mdyn/Å. The P–X force constants (7.04 (P–O), 3.73 (P–S), and 2.84 mdyn/Å (P–Se)[6]) in the trimethylphosphine chalcogenides decrease in the order from O to Se. As anticipated from this trend, the calculated P–Te force constant is smaller than the P–Se constant. Zingaro et al.[2] have estimated the force constant and frequency of a P–Te bond by Gordy's rule,[21] using estimated bond distances upon an approximation of an isolated harmonic oscillator, as 1.6 mdyn/Å and 331 cm^{-1} for a single bond or 3.2 mdyn/Å and 472 cm^{-1} for a double bond. The observed frequency of 376 cm^{-1} for the P–Te stretch is close to the estimated single-bond frequency, but the force constant is approximately an average of the single- and double-bond values.

Trimethylphosphine telluride is so unstable that, in the air and at room temperature, trimethylphosphine is released from the solid complex, leaving tellurium behind. Trimethylarsine selenide has a similar tendency, but dissociation rate is small enough to be able to make a KBr pellet for infrared measurement. The As–Se force constant has been calculated to be 2.55 mdyn/Å.[22] The P–Te force constant is smaller than the As–Se constant, suggesting that the P–Te bond is weaker than the As–Se bond in accord with chemical evidence.

Registry No. $(CH_3)_3PTe$, 76773-16-5; $(CD_3)_3PTe$, 76773-17-6.

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X-ray Photoelectron Spectroscopic Study of Organometallic Nitrosyl Compounds of Chromium, Molybdenum, and Tungsten

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Gas-phase core electron binding energies of organometallic nitrosyl complexes of chromium, molybdenum, and tungsten are reported. On going from Cr to W in the series $CpM(NO)_2Cl$ (M = Cr, Mo, W), back-bonding to the NO groups increases and electron density is withdrawn from the Cl atoms. The data for $CpM(NO)_2Cl$ and $CpM(CO)_2NO$ (M = Cr, Mo, W) indicate that the back-bonding in the Mo and W compounds is significantly different from that in first-row transition-metal nitrosyls. Electron density is mainly transferred to the nitrosyl oxygen atom, whereas, in first-row nitrosyls, approximately equal amounts of electron density are transferred to the oxygen and nitrogen atoms.

Previous X-ray photoelectron spectroscopic (XPS) studies of transition-metal nitrosyls and carbonyls in the gas phase have established that NO groups are stronger π acceptors than CO groups[2] and that the 1s binding energies of the atoms of these ligands are linearly related to the corresponding N–O or C–O stretching force constants.[3-5] We now report the results of a gas-phase XPS study of a series of organometallic nitrosyl complexes of chromium, molybdenum, and tungsten. The measured core binding energies, listed in Table I, allow us to compare the π-donor and σ-acceptor properties of the group 6 transition-metal atoms. The data also allow us to compare the donor and acceptor properties of the nitrosyl group with those of other groups such as the carbonyl group, the cyclopentadienyl group, and the chloro group.

Spectra

The carbon 1s spectrum of $CpCr(CO)_2NO$ (Cp = η^5-C_5H_5) is shown in Figure 1. The spectrum is readily deconvoluted into two peaks, separated by 1.7 eV. An unrestricted least-squares fit of the spectrum yields an intensity ratio of 3.8:1, although the ratio of Cp to CO carbon atoms in the compound is 2.5:1. This result is not unexpected; the C 1s and O 1s peaks of carbonyl groups usually lose considerable intensity to shake up peaks at higher binding energy.

The nitrogen 1s spectrum of $CpCr(NO)_2NO_2$ (Figure 2) shows, on the high binding energy side, a strong band due to free nitric oxide from decomposition of the sample. A peak at approximately 407.7 eV due to $CpCr(NO)_2NO_2$ can be clearly resolved. Because there are twice as many NO groups as NO_2 groups and because the nitrogen binding energy of the analogous compound $CpCr(NO)_2Cl$ is fairly close to 407.7 eV, we believe that the binding energy of the NO groups in $CpCr(NO)_2NO_2$ is approximately 407.7 eV. The nitrogen of the NO_2 group either has about the same binding energy as the nitrogen of the NO group or, more likely, has a higher binding energy. Indeed it is possible to fit the spectrum quite well with peaks at 407.5 and 408.5 eV, having an intensity ratio of 2:1, respectively. However, because of the interference of the nitric oxide band, we have little faith in this deconvolution and prefer simply to conclude that the binding energy of the NO_2 group is probably greater than 407.7 eV.

The oxygen 1s spectrum of $CpCr(NO)_2NO_2$ (Figure 3) also shows a peak due to free nitric oxide; however in this case the nitric oxide peak is well separated from the peaks due to the

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Table I. Core Binding Energies and Full Widths at Half-Maximum for Nitrosyl Complexes (eV)

	O 1s		N 1s		C 1s		Cl $2p_{3/2}$		metal core level[a]	
compd	E_B	fwhm	E_B	fwhm	E_B	fwhm	E_B	fwhm	E_B	fwhm
$CpCr(CO)_2NO$	538.91 (4)[b]	1.59 (9)	406.84 (7)	1.26 (17)	290.82 (4)[c] 292.51 (12)[c]	1.27 (7) 1.47 (17)			581.77 (5)	1.30 (10)
$CpCr(NO)_2NO_2$	537.77 (10)[d] 539.46 (10)[e]	1.38 (17) 1.38 (17)	407.7 (2)[e]	1.6 (3)	291.08 (12)	1.53 (33)			582.57 (9)	1.34 (16)
$CpCr(NO)_2Cl$	539.45 (6)	1.39 (17)	407.47 (9)	1.35 (37)	291.25 (7)	1.47 (17)	203.38 (8)	1.21 (24)	582.67 (7)	1.30 (20)
$CpMo(CO)_2NO$	538.77 (3)	1.70 (13)	406.93 (9)	1.23 (22)	290.77 (3)[c] 292.52 (10)[c]	1.26 (7) 1.58 (18)			234.91 (4)	1.34 (10)
$CpMo(NO)_2Cl$	538.98 (8)	1.50 (32)	407.35 (8)	1.26 (20)	291.31 (6)	1.50 (17)	203.82 (13)	1.35 (42)	236.26 (9)	1.25 (24)
$CpW(CO)_2NO$	538.57 (5)	1.80 (14)	406.85 (8)	1.40 (18)	290.98 (10)[c] 292.52 (17)[c]	1.35 (11) 1.64 (27)			38.22 (12)	1.88 (22)
$CpW(NO)_2H$	538.33 (15)	1.50 (30)	407.05 (9)	1.35 (20)	291.14 (9)	1.44 (14)			38.79 (11)	1.20 (20)
$CpW(NO)_2Cl$	538.67 (7)	1.47 (21)	407.23 (10)	1.38 (31)	291.30 (5)	1.16 (20)	204.08 (7)	1.07 (23)	39.53 (7)	1.22 (18)

[a] Cr $2p_{3/2}$, Mo $3d_{5/2}$, or W $4f_{7/2}$. [b] Uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. [c] The lower E_B due to Cp carbons; the higher E_B due to CO carbons. [d] NO_2 group. [e] NO group.

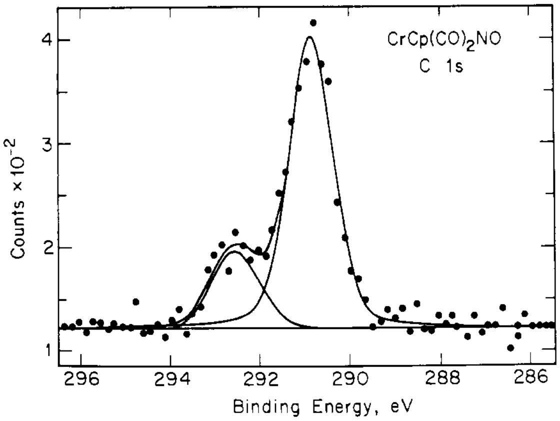


Figure 1. Carbon 1s spectrum of $CpCr(CO)_2NO$. The more intense peak, at 290.82 eV, corresponds to the cyclopentadienyl group; the weaker peak, at 292.51 eV, corresponds to the C groups.

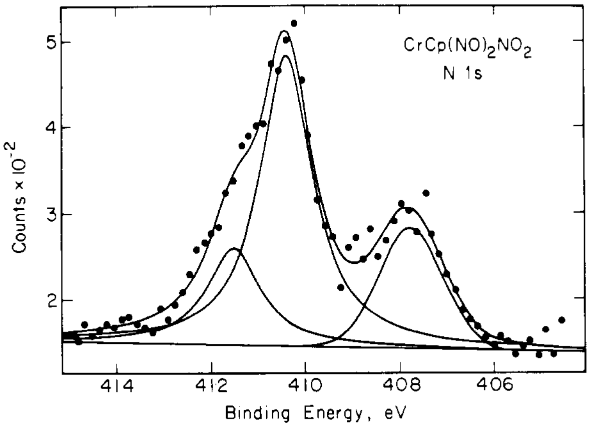


Figure 2. Nitrogen 1s spectrum of $CpCr(NO)_2NO_2$. The peaks at higher binding energy correspond to free NO from partial decompsotion of the sample; the unresolved band at lower binding energy corresponds to the NO and NO_2 groups of the complex.

coordinated NO_2 and NO groups at 537.77 and 539.46 eV. By comparison with the oxygen binding energy of $CpCr(NO)_2Cl$, the peak at 539.46 eV is readily assigned to the NO group.

Binding Energy Trends

Consider the binding energies of the mononuclear chromium compounds. On going from $CpCr(CO)_2NO$ to $CpCr(NO)_2NO_2$, the chromium, cyclopentadienyl carbon, nitrosyl nitrogen, and nitrosyl oxygen binding energies all increase, indicating that the combined electron-withdrawing ability of one NO group and one NO_2 group is greater than that of the two CO groups that they replace. This result is not surprising in view of the great electron-withdrawing ability of the NO_2 group and the fact that the nitrosyl group is a better π acceptor than the carbonyl group. On going from $CpCr(NO)_2NO_2$ to $CpCr(NO)_2Cl$, similar but smaller binding energy increases occur, except in the case of the nitrosyl nitrogen binding energy (which has an uncertainty of ~0.2 eV in the former compound), indicating that the Cl group is slightly more electron withdrawing than the NO_2 group.

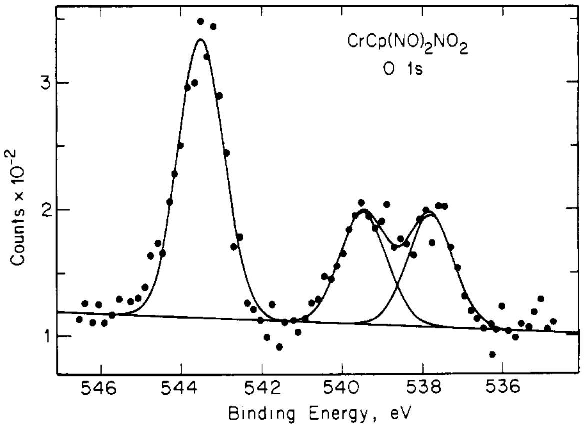
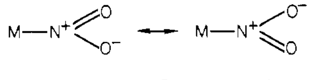


Figure 3. Oxygen 1s spectrum of $CpCr(NO)_2NO_2$. The intense peak at high binding energy corresponds to free NO from partial decomposition of the sample; the peaks at low binding energy correspond to the NO and NO_2 groups of the complex.

The fact that the oxygen 1s binding energy of the coordinated NO_2 group is more negative than that of the coordinated NO group can be rationalized by simple valence-bond considerations. In the coordinated NO_2 group, the oxygen atoms have a negative formal charge



$$M{-}N^{+}{\genfrac{}{}{0pt}{}{=O}{-O^{-}}} \longleftrightarrow M{-}N^{+}{\genfrac{}{}{0pt}{}{-O^{-}}{=O}}$$

whereas in the coordinated NO group, the oxygen atom has a positive formal charge

$$^{-}M{-}N^{+}{\equiv}O^{+} \leftrightarrow M{=}N^{+}{=}O$$

Thus we would expect the oxygen atoms of the coordinated NO_2 group to be more negatively charged than that of the coordinated NO group. Although no peak corresponding to the NO_2 nitrogen could be reliably deconvoluted from the N 1s spectrum, the data suggest that the N 1s binding energy of the NO_2 group is greater than that of the NO group. Simple valence-bond considerations show that the nitrogen atoms of these groups have the same formal charge. However, the back-bonding to the NO group is probably greater than that to any other ligand (except perhaps NS and NSe groups), and therefore one would expect the nitrogen atom charge to be more negative in the coordinated NO group than in the coordinated NO_2 group.

The binding energy shifts of the molybdenum and tungsten compounds are similar to those of the chromium compounds. Thus, on going from $CpW(CO)_2NO$ to $CpW(NO)_2H$, the nitrogen cyclopentadienyl carbon, and tungsten binding energies increase, indicating that the combination of an NO group and an H group is more electron withdrawing than two CO groups. Although the hydrogen atom is an electron-withdrawing group,[6-8] replacement of the hydrogen atom by a chlorine atom causes all the binding energies to increase further, because of the greater electronegativity of chlorine.

Effect of NO Back-Bonding on σ Donation of Cl. In the series of compounds $CpM(NO)_2Cl$ (M = Cr, Mo, W), the carbon binding energy is essentially constant. However, on going from the chromium compound to the tungsten compound, the oxygen and nitrogen binding energies markedly *decrease* and the chlorine binding energy *increases*. We believe these data are consistent with the general observation that, on descending a transition-metal family, the π-donor ability of the metal increases. Thus on going from the chromium compound to the tungsten compound, π-donor bonding to the NO groups increases, and for compensation of the increased metal atom charge, σ-donor bonding from the chlorine atoms increases. These bonding changes are also manifest in the solid-state molecular structures of the chromium and tungsten complexes: the W–Cl bond length is short (relatively strong σ bonding), whereas the Cr–Cl bond length is more characteristic of ionic bonding.[9] Apparently the σ and π parts of the metal–cyclopentadienyl bonding are of comparable importance, and thus the opposite effects of the changes in σ and π bonding cancel, resulting in essentially no change in the charge on the cyclopentadienyl group.

We have interpreted the increase in chlorine bonding energy in the series $CpM(NO)_2Cl$ on going from Cr to W as evidence for a corresponding decrease in negative charge on the chlorine atom. This is an important result, representing direct evidence of ligand charge compensation for back-bonding in a series of compounds. However, it is conceivable that the increase in chlorine binding energy is not due to a decrease in negative charge on the chlorine but rather to an increase in potential at the chlorine atom due to an increase in positive charge on the metal atom. To eliminate doubt, we have used the binding energy data to calculate the changes in charge on the N, O, Cl, and metal atoms on going from the chromium compound to the molybdenum compound and from the chromium compound to the tungsten compound. In each case we solved four equations in four unknowns. The four unknowns were the changes in the four atomic charges.[10] Three of the equations were potential equations[11] of the type

$$\Delta E_B(A) = k\Delta Q_A + \sum_{i \neq A} (14.4\Delta Q_i/r_i)$$

where k is the average value of the reciprocal of the valence-electron radius,[12,13] Q_i is the charge on atom i, and r_i is the distance between atom i and atom A.[14] One of the equations was $\sum \Delta Q_i = 0$. The results of the calculations, shown in Table II, confirm the fact that the increase in chlorine binding energy do indeed correspond to increases in charge (measured as positive charge) on the chlorine atoms.

Table II. Calculated Changes in Atomic Charge in $CpM(NO)_2Cl$ (M = Cr, Mo, W)

	Cr → Mo	Cr → W
ΔQ_N	−0.0019	−0.0060
ΔQ_O	−0.016	−0.026
ΔQ_{Cl}	0.022	0.034
ΔQ_M	0.014	0.030

Change in Nature of Back-Bonding in Molybdenum and Tungsten. Evidence for an increase in back-bonding on going from a chromium compound to a corresponding tungsten compound is also apparent from the decrease in oxygen binding energy on descending the series $CpM(CO)_2NO$ (M = Cr, Mo, W). However it is significant that the carbonyl carbon and nitrosyl nitrogen binding energies are essentially constant in this series. This sort of result was also observed in the $CpM(NO)_2Cl$ series; from Table II it can be seen that the changes in the nitrogen atom charge are much lower than the changes in the oxygen atom charge. The data indicate that, at least for nitrosyl groups, the oxygen atom recieves most of the electron density when back-bonding increases by descending the Cr, Mo, W family. Previous work[5] has shown that the nitrogen and oxygen atoms recieve comparable amounts of electron density when back-bonding increases in nitrosyls of the first-row transition metals. Thus the present data suggest that back-bonding of second- and third-row transition metals is different in character from that of first-row transition metals. Some data[5] for carbonyls support this idea. On going from $CH_3Mn(CO)_5$ to $CH_3Re(CO)_5$, E_B(C 1s) is unchanged, whereas E_B(O 1s) decreases by 0.27 eV. However, in the cases of $M(CO)_5PF_3$ (M = Cr, Mo), $M(CO)_5CS$ (M = Cr, W), and $M(CO)_6$ (M = Cr, Mo, W), the changes in both E_B(C 1s) and E_B(O 1s) are very small, indicating no significant change in back-bonding.

The effect which we have observed in the case of nitrosyl compounds may be rationalized by assuming that, on descending a transition-metal family, σ donation by the NO group increases because of the large increase in nuclear charge of the metal, and the resultant improved dπ–π* overlap causes an increase in back-bonding. The stronger σ bonding between the nitrogen and metal atom causes a shift of electron density from nitrogen to metal which compensates for the increase in π* electron density due to increased back-bonding. Thus the nitrogen atom charge is almost unchanged although the oxygen atom becomes more negative.

Experimental Section

The spectra were obtained with use of procedures described previously.[6] Some of the C 1s, N 1s, and O 1s binding energies have been reported previously.[5] The $CpM(CO)_2NO$ complexes and $CpW(NO)_2H$ are volatile enough that we were able to obtain their spectra at room temperature. However, it was necessary to hold $CpCr(NO)_2NO_2$ at 50 °C and the $CpM(NO)_2Cl$ complexes at 80 °C in order to obtain satisfactory spectra. In the elevated-temperature runs, the entire spectrometer (except for the pumps, the detector preamplifier, and a few control valves) was enclosed in a thermostated

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(10) We assumed, as a good approximation, that the atomic charges of the cyclopetadienyl groups are constant in this series. Thus we were only concerned with the $M(NO)_2Cl$ groups.

(11) The application of this potential equation to a similar problem is described in ref 6.

(12) Values of $\langle 1/r \rangle$ were calculated from data in ref 13. The k values, in units of electronic charge per eV, were 27.9 for nitrogen (assuming 25% s character), 32.5 for oxygen (20% s character), and 21.7 for chlorine (10% s character).

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(14) The structural data were taken from ref 9. The parameters for $CpMo(NO)_2Cl$ were assumed to be the average of those for the Cr and W compounds.

oven. This technique prevents condensation of sample in the analyzer chamber, and thus possible deterioration of electron focussing is avoided. Most of the binding energies are based on spectrometer calibrations with the N_2 1s, Ne 1s, and Ne 2s lines. However, in the case of the O 1s and N 1s spectra of $CpCr(NO)_2NO_2$, it was possible to measure the binding energies relative to the decomposition product nitric oxide, NO. In a separate run, we determined the binding energies of a commercial sample of nitric oxide (Matheson) as follows: E_B(O 1s) = 543.32 (6) eV (strong line), 544.13 (16) eV (weak line), 543.52 (8) eV (weighted average), fwhm(O 1s) = 1.06 (12) eV (strong line), 1.07 (33) eV (weak line); E_B(N 1s, deconvoluted strong line) = 410.32 (4) eV, fwhm(N 1s, deconvoluted strong line) = 1.29 (12) eV; E_B(N 1s, deconvoluted weak line) = 411.68 (13) eV, fwhm(N 1s, deconvoluted weak line) = 1.40 (24) eV.

$CpCr(NO)_2NO_2$,[15] $CpW(NO)_2H$,[8] $CpM(CO)_2NO$,[16] and $CpM(NO)_2Cl$[16] (M = Cr, Mo, W) were prepared according to published procedures.

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Registry No. $CpCr(CO)_2NO$, 36312-04-6; $CpCr(NO)_2NO_2$, 68013-60-5; $CpCr(NO)_2Cl$, 12071-51-1; $CpMo(CO)_2NO$, 12128-13-1; $CpMo(NO)_2Cl$, 12305-00-9; $CpW(CO)_2NO$, 12128-14-2; $CpW(NO)_2H$, 69532-01-0; $CpW(NO)_2Cl$, 53419-14-0.

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Metal Vapor–Acetylene Cryochemistry: Vibrational, Optical, and SCF-Xα-SW Investigations of $M(\pi\text{-}C_2H_2)_n$ (Where M = Ni or Cu; n = 1 or 2). Comparison with Chemisorbed Acetylene

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Nickel and copper vapor cocondensation reactions, with pure acetylene and acetylene/inert gas matrices, have been investigated over a range of temperatures upward from 10–12 K, by infrared and ultraviolet–visible spectroscopy. A combination of ligand concentration, bulk thermal annealing, and mixed isotopic $^{12}C_2H_2/^{13}C_2H_2$ substitution experiments under mononuclear reaction conditions established the existence of two acetylene complexes of the type $M(C_2H_2)_n$ (where M = Cu or Ni, n = 1 or 2). The vibrational data favored simple π-acetylene bonding in all cases, thereby supporting the conclusions drawn from recent ESR observations for the copper–acetylene system. Thermal stability studies in solid acetylene established decomposition temperatures around 150 and 80 K for the $Ni(C_2H_2)_2$ and $Cu(C_2H_2)_2$ species, respectively, following the similar order observed for $Ni(C_2H_4)_3$ and $Cu(C_2H_4)_3$ and paralleling the trend observed for acetylene chemisorbed on Ni and Cu surfaces. The optical spectroscopic properties and bonding schemes for the $M(C_2H_2)$ complexes were probed by the SCF-Xα-SW molecular orbital method. A Dewar–Chatt–Duncanson bonding picture emerged for both complexes but with minimal π delocalization of charge from the metal to the ligand for $Cu(C_2H_2)$. A $^2A_1$ electronic ground state configuration was predicted for $Cu(C_2H_2)$, which was in agreement with predictions based on an analysis of ESR data. Calculated electronic properties and optical trends were found to be well represented for $Cu(C_2H_2)$ and $Ni(C_2H_2)$ and proved to be helpful in discussing the interrelationships between the acetylene data and the corresponding ethylene data. The various modes of bonding observed for chemisorbed acetylene were briefly surveyed, and, in the case of $Ni(C_2H_2)$, the problems inherent in localized bonding discussions of chemisorbed acetylene were examined in light of recent high-resolution electron energy loss spectroscopy studies of the extensively rehybridized, di-σ form of acetylene on metal surfaces.

Introduction

The determination of the molecular geometry and electronic structure of hydrocarbon molecules adsorbed on transition-metal surfaces is a problem of central concern to those involved in unravelling fundamental processes in heterogeneous catalysis. Information of this kind may not only reveal details of the nature and strength of the chemisorption bond but may also provide an insight into surface-molecule transformations and surface-catalyzed reactions.

The hydrocarbon chemisorption problem has been probed by both semiempirical and ab initio molecular orbital techniques using, for example, $M_n(C_2H_2)$ and $M_n(C_2H_4)$ localized bonding models in which the metal and metal cluster size are varied in an attempt to examine the convergence behavior of these finite molecular systems toward the corresponding bulk experimental and/or theoretical data.[2–14] With use of metal atom matrix spectroscopic methods, species such as $M_n(C_2H_4)$, where M = Co,[15] Ni[16b], or Cu[17] and n = 1 or 2, have recently

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