reagents also catalyze these and related reactions.[1,12]

As would be expected, deuteride delivered from Li[DBEt$_3$] adds to the η^2-allene complex at the allene ligand (the η^2-ethylene complex reacts in a similar fashion). This contrasts our earlier work[3] that shows that this same reagent adds to the η^5-C_5H_5 ring in [CpFeCO[P(OPh)$_3$](η^2-alkyne)]BF$_4$ for alkyne = $PhC\equiv CMe$ and $MeC\equiv CCO_2Me$, an unexpected result.[13] A possible reason for this difference is the perturbation to the electronic levels of the iron–alkyne complexes by the unfavorable four-electron, two-center $d\pi$–$\pi_\perp$ interaction that has recently been invoked[14] to explain the fact that d^4 alkyne complexes are more stable than the d^6 alkyne complexes that are being used in this work. The situation is even further complicated by the facts (Scheme II) that Li[HB(*sec*-Bu)$_3$] also adds hydride to the η^5-C_5H_5 ring for alkyne = $MeC\equiv CMe$ but Li[DBEt$_3$] (or Li[HBEt$_3$]) adds at both locations in about even amounts. Steric effects, the degree of distortion of the η^2-alkyne toward an η^1-geometry, and the nature of the transition state (whether reactant-like or product-like) have all been used to explain other trends in nucleophilic addition reactions[15] with π-coordinated unsaturated ligand complexes and could all have an effect on the above results. For example, steric differences in the two reagents used in Scheme II could explain the differing results for those two reactions, but in the absence of more detailed information about the probable reaction mechanism, such speculation seems unwarranted.

This work and our earlier work in this area clearly point out that nucleophilic addition reactions with alkynes do not simply parallel those with alkenes or allenes.[16] Also, one must be very careful in the study of metal–alkenyl complexes because of the possibility of rearrangement reactions that can be induced by standard purification techniques or typical NMR solvents.

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Registry No. 1, 92421-57-3; 2, 92421-58-4; 3, 92366-24-0; 4, 92421-59-5; 5, 92421-60-8; 6, 92421-61-9; 7, 86563-32-8; 8, 92421-62-0; 9, 92421-63-1; 10, 92421-64-2; 11, 92421-65-3; 11-d_1, 92421-66-4; 12, 92471-24-4; 12-d_1, 92421-67-5; [CpFe(CO)[P(OPh)$_3$][η^2-$MeC\equiv CMe$)]BF$_4$, 87556-47-6; [CpFeCO[P(OPh)$_3$](η^2-$CH_2=C=CH_2$)]BF$_4$, 71359-49-4; CpFeCO[P(OPh)$_3$]I, 31988-05-3.

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Transition Metal–Isocyanide Bonding: A Photoelectron Spectroscopic Study of Iron Tetracarbonyl Isocyanide Complexes

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The He I and X-ray photoelectron spectra of the iron tetracarbonyl complexes of methyl, *tert*-butyl, trimethylsilyl, and phenyl isocyanide have been obtained. The bonding properties of these isocyanides are compared with those of carbon monoxide by using the core-binding energy data to interpret the valence ionization energies. The data show that all the isocyanides have comparable σ-donor ability and that, in the Fe(CO)$_4$CNR complexes, they are significantly weaker σ donors than carbon monoxide. The stronger σ-donor character of the coordinated CO ligands is presumably due to the σ–π synergism of the Fe–CO bonding. The net interaction of an isocyanide ligand with the iron d orbitals leaves the energy of the d orbitals destabilized relative to Fe(CO)$_5$. The data indicate that the relative energies of interaction of the d orbitals with the filled ligand π orbitals and the empty ligand π^* orbitals are different in Fe–CO and Fe–CNR bonds, with the interactions of the filled ligand π orbitals being relatively more important in Fe–CNR bonds than in Fe–CO bonds. The net electron withdrawal by a coordinated isocyanide ligand, although significant, is much lower than that by a coordinated carbonyl ligand. It is clear that the interactions of transition metals with isocyanides (and probably also with other ligands with similar electronic structures) cannot be adequately described without considering the combined σ-donor, π-acceptor, and π-donor characters of the ligands.

Introduction

The study of transition-metal complexes containing isocyanide ligands has developed into an important area of organometallic chemistry that has been the subject of recent reviews.[2,3] However, the interactions of the isocyanide and metal orbitals in such complexes have received little attention. Because photoelectron spectroscopy is the most direct method for measuring orbital interactions of

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Table I. Core Binding Energies (eV) of Iron Tetracarbonyl Isocyanide Complexes and Related Compounds

	Fe $2p_{3/2}$		C 1s		O 1s		N 1s	
	E_B	fwhm[a]	E_B	fwhm	E_B	fwhm	E_B	fwhm
$Fe(CO)_4CNCH_3$	714.98 (4)[b]	1.40 (12)	292.83 (3)[c]	1.88 (10)	539.14 (5)	1.63 (13)	405.95 (4)	1.53 (7)
$Fe(CO)_4CNC(CH_3)_3$	714.81 (2)	1.37 (7)	292.53 (7)[d]	1.85 (15)	539.03 (4)	1.81 (16)	405.54 (2)	1.45 (8)
			291.05 (7)[e]	1.21 (14)				
$Fe(CO)_4CNSi(CH_3)_3$	714.84 (2)	1.34 (8)	292.52 (3)[d]	1.73 (10)	539.03 (2)	1.65 (6)	404.88 (4)	1.35 (9)
			290.40 (3)[e]	1.65 (2)				
$Fe(CO)_4CNC_6H_5$	714.85 (2)	1.29 (6)	292.50 (3)[d]	1.61 (8)	539.05 (2)	1.54 (6)	406.02 (3)	1.33 (8)
			290.79 (3)[f]	1.29 (7)				
$Fe(CO)_5$[g]	715.79 (4)	1.25 (9)	293.71 (5)	1.27 (13)	539.96 (2)	1.38 (5)		
$CNCH_3$[h]			292.37 (10)[i]	1.38 (20)			406.67 (4)	1.33 (7)
			293.35 (10)[e]	1.30 (20)				
$CNC(CH_3)_3$[h]			291.83 (16)[i]	1.55 (20)			406.05 (2)	1.13 (9)
			292.84 (8)[j]	1.33 (14)				
			291.06 (3)[e]	1.20 (9)				
CNC_6H_5[h]			292.53 (6)[i]	1.35 (15)			406.50 (2)	1.24 (6)
			291.84 (8)[j]	1.10 (20)				
			290.84 (3)[f]	1.26 (8)				

[a] Full-width at half-maximum. [b] Uncertainty in last digit indicated parenthetically. [c] All carbon, see text. [d] Carbonyl carbon, isocyano carbon, and alkyl or aryl carbon attached to nitrogen. [e] Methyl carbon. [f] Phenyl carbon. [g] Reference 12. [h] Reference 8. [i] Isocyano carbon. [j] Alkyl or aryl carbon attached to nitrogen.

this type, we have undertaken a combined valence and core photoelectron study of the axially substituted iron pentacarbonyl derivatives $Fe(CO)_4CNR$ (where R = CH_3, $C(CH_3)_3$, $Si(CH_3)_3$, and C_6H_5). These isocyanide complexes were chosen because they are volatile and stable in the gas phase and because comparison with $Fe(CO)_5$ allows a direct comparison of the bonding properties of the isocyanides with those of carbon monoxide.

The only previously reported gas-phase photoelectron spectra of isocyanide complexes of transition metals were the He I spectra of $Cr(CO)_5CNCH_3$[4] and of $Mn(CO)_4(CNCH_3)Br$.[5] The valence[6,7] and core[8,9] photoelectron spectra of several free isocyanides have been reported.

Results

X-ray Spectra. Core-binding energies of the iron tetracarbonyl isocyanide complexes, $Fe(CO)_5$, and the free isocyanides are given in Table I.

The fact that the Fe $2p_{3/2}$ binding energies of the isocyanide complexes are almost 1 eV lower than that of $Fe(CO)_5$ indicates a large decrease in the positive charge on the iron atom when an axial CO group is replaced by an isocyanide. This charge decrease indicates that the net electron acceptor character of an isocyanide is considerably less than that of carbon monoxide. The magnitude of the decrease in Fe binding energy on going from $Fe(CO)_5$ to the isocyanide complexes is slightly less than that seen on going to $Fe(CO)_4P(CH_3)_3$ and $Fe(CO)_4NC_5H_5$,[10] indicating that isocyanides have acceptor properties slightly greater than those of trimethylphosphine and pyridine.

The C 1s spectra were not clearly resolved, and only limited meaningful deconvolution was possible. The C 1s spectrum of $Fe(CO)_4CNCH_3$ shows only one band, with a slight shoulder on the low binding energy side. Deconvolution of this band gave two peaks of relative intensity 5:1 at 292.9 and 292.2 eV, respectively, with an uncertainty of at least 0.1 eV in the peak positions. The peak at lower binding energy is reasonably assigned to the donor carbon atom of the isocyanide group, and the peak at higher binding energy is assigned to the methyl carbon atom and the carbonyl groups. This assignment indicates that the binding energy of the donor carbon atom of the isocyanide group decreases only slightly on coordination and implies that the electron flow from the isocyanide ligand is balanced by a flow of electron density back to the isocyanide and by an increase in the relaxation energy. The carbon binding energy of the methyl group of the isocyanide decreases by about 0.5 eV, a reasonable change when one considers that the binding energy of the nitrogen atom to which it is attached decreases by 0.7 eV. The binding energy of the carbonyl carbon atoms in $Fe(CO)_4CNCH_3$ is 0.8 eV lower than in $Fe(CO)_5$, partly due to the lower Fe charge (potential effect) and partly due to an increase in negative charge on the CO groups (increased back-bonding to CO because of relatively weak back-bonding to the CH_3NC ligand). In the case of the *tert*-butyl and phenyl isocyanide complexes, two peaks of relative intensity 6:3 and 6:5, respectively, were observed in the C 1s spectra. In both cases, the four carbonyl carbons and the two carbons attached to the N atom of the isocyanide group formed one band, and the three methyl or five phenyl carbons formed the other band. The C 1s spectrum of $Fe(CO)_4CNSi(CH_3)_3$ showed two peaks of relative intensity 5:3, with the isocyano carbon underneath the CO carbon peak, and the three methyl carbons well resolved at lower binding energy.

In general, the O 1s binding energy decreases about 0.9 eV on going from $Fe(CO)_5$ to $Fe(CO)_4CNR$. This decrease can be interpreted in the same way as that of the carbonyl carbon binding energy, i.e., in terms of the relatively weak back-bonding to the isocyanide ligands.[11,12] The decrease in O 1s binding energy on going from $Fe(CO)_5$ to $Fe(CO)_4P(CH_3)_3$ and $Fe(CO)_4NC_5H_5$ is about 1.2 eV, again indicating that the isocyanides are slightly better π acceptors than trimethylphosphine and pyridine.

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Table II. Ionization Energies (eV) of Iron Tetracarbonyl Isocyanide Complexes

$Fe(CO)_4CNCH_3$	$Fe(CO)_4CNC(CH_3)_3$	$Fe(CO)_4CNSi(CH_3)_3$	$Fe(CO)_4CNC_6H_5$
7.56, 7.79 ($d_{x^2-y^2}$, d_{xy})	7.49, 7.67 ($d_{x^2-y^2}$, d_{xy})	7.50, 7.69 ($d_{x^2-y^2}$, d_{xy})	7.49, 7.76 ($d_{x^2-y^2}$, d_{xy})
8.89 (d_{xz}, d_{yz})	8.74 (d_{xz}, d_{yz})	8.74 (d_{xz}, d_{yz})	8.83 (d_{xz}, d_{yz})
			9.79 (π C_6H_5, b_1)
			9.99 (π C_6H_5, a_2)
12.30 (σ Fe–CN)	11.76 (σ Fe–CN, σ C–C)	11.27 (σ Fe–CN, σ Si–C)	12.22 (σ Fe–CN)
12.98 (π C–N)	12.85 (π C–N)	12.62 (π C–N)	12.86 (π C–N, σ C_6H_5)

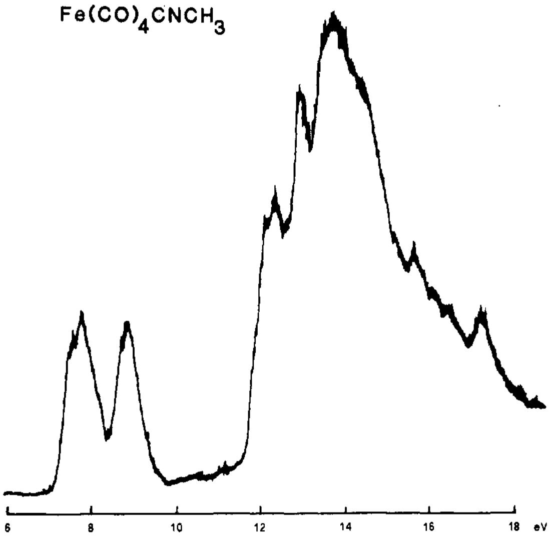

Figure 1. He I photoelectron spectrum of $Fe(CO)_4CNCH_3$.

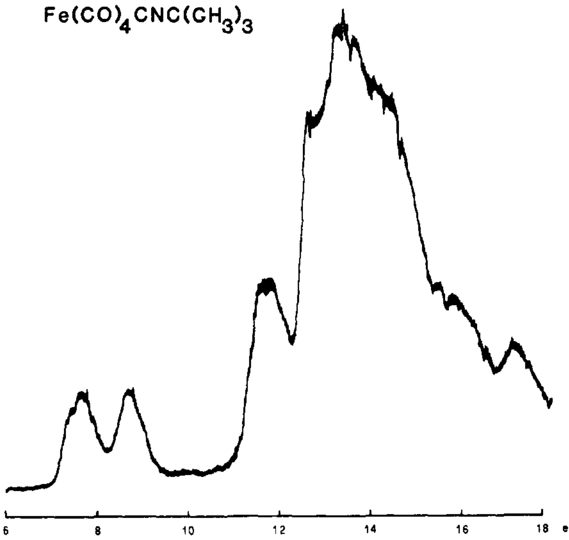

Figure 2. He I photoelectron spectrum of $Fe(CO)_4CNC(CH_3)_3$.

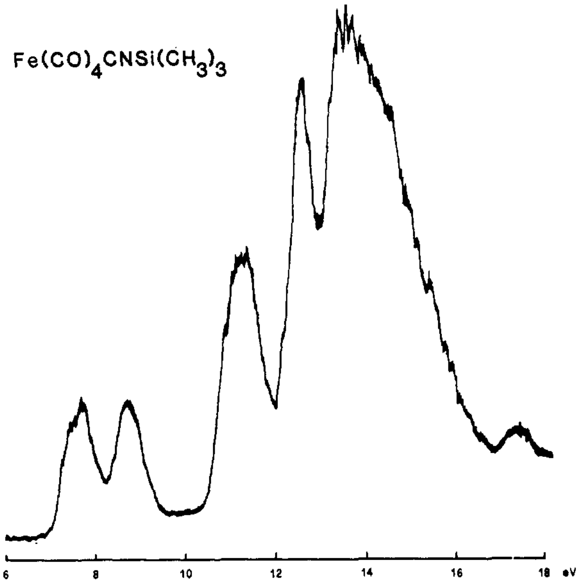

Figure 3. He I photoelectron spectrum of $Fe(CO)_4CNSi(CH_3)_3$.

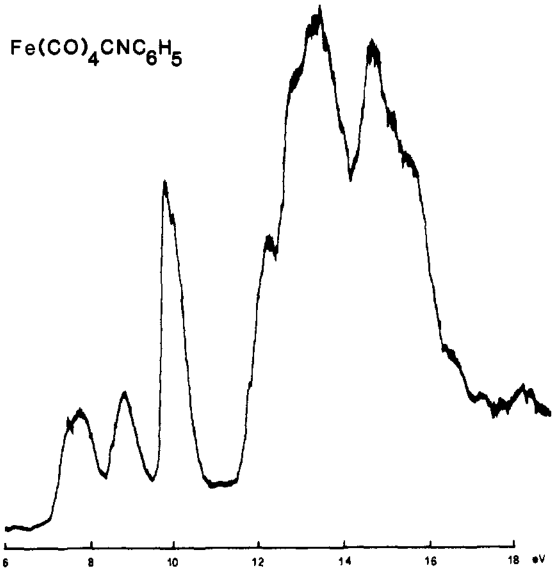

Figure 4. He I photoelectron spectrum of $Fe(CO)_4CNC_6H_5$.

The N 1s binding energy decreases on going from the free ligands to the complexes. This decrease may be partly due to an increase in relaxation energy on coordination, but it is probably mainly due to a flow of electron density from the iron atom to the isocyanide. When methyl isocyanide is coordinated to a BH_3 group to form BH_3CNCH_3 (in which we have previously found no net π interaction),[13] the N 1s binding energy *increases* by 0.5 eV. Thus the *decrease* of 0.7 eV in the N 1s binding energy on going from $CNCH_3$ to $Fe(CO)_4CNCH_3$ is strong evidence for back-bonding in the iron complex.

Although we did not thoroughly study shake-up in the spectra of these isocyanide complexes, we did not observe intense satellite structure (I_s/I_p greater than 0.1) in any of the spectra. Shake-up peaks have been observed in the C 1s and N 1s spectra of several homoleptic alkyl and aryl isocyanide complexes of second- and third-row transition metals.[14]

Ultraviolet Spectra. The He I photoelectron spectra of the four isocyanide iron tetracarbonyl complexes are shown in Figures 1–4. The lowest ionization energies in the complexes are given in Table II.

The first two ionizations are due to iron-localized orbitals. The lowest ionization energy band is split and is centered at ~7.6 eV. This ionization is from an e orbital which has primarily Fe $d_{x^2-y^2}$, d_{xy} character, with significant carbonyl σ-antibonding character (Hoffmann has extensively discussed the bonding properties of the metal or-

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Table III. Experimental Ionization Energies (eV) and Calculated Localized Orbital Ionization Potentials of the Metal Orbitals of Iron Tetracarbonyl Isocyanide Complexes

	$d_{x^2-y^2}$, d_{xy}			d_{xz}, d_{yz}		
	IE	LOIP	IE - LOIP	IE	LOIP	IE - LOIP
$Fe(CO)_5$[a]	8.53	(8.53)		9.85	(9.85)	
$Fe(CO)_4CNCH_3$	7.68	7.88	−0.20	8.89	9.20	−0.31
$Fe(CO)_4CNC(CH_3)_3$	7.58	7.75	−0.17	8.74	9.07	−0.33
$Fe(CO)_4CNSi(CH_3)_3$	7.60	7.77	−0.17	8.74	9.09	−0.35
$Fe(CO)_4CNC_6H_5$	7.63	7.78	−0.15	8.83	9.10	−0.27

[a] Reference 17.

bitals of the $Fe(CO)_4$ fragment[15,16]), and the splitting of this e band is undoubtedly due to the Jahn–Teller effect. Hubbard and Lichtenberger[17] have discussed the Jahn–Teller splitting in the corresponding band of $Fe(CO)_5$. Their conclusion, that OC–Fe–CO bending in the equatorial plane is responsible for the breaking of the degeneracy, is consistent with the splitting observed in the axially substituted compounds of this study. The next band, at about 8.8 eV, is from an e orbital which is primarily Fe d_{xz}, d_{yz} in character. As in $Fe(CO)_5$, this band does not show Jahn–Teller splitting.

The next two bands in all of the complexes are due to isocyanide ligand orbitals. The metal–ligand σ-bonding orbital, corresponding to the carbon lone pair in the free isocyanide, has the lower ionization energy, whereas the C–N π orbital has the higher ionization energy. The bands at 11.76 eV in $Fe(CO)_4CNC(CH_3)_3$ and 11.27 in $Fe(CO)_4CNSi(CH_3)_3$ also correspond to ionizations from pseudo-π C–C or Si–C bonding orbitals (Table II). The iron–isocyanide σ-bond ionization energy steadily decreases from 12.30 to 11.27 eV on going from the methyl to the trimethylsilyl isocyanide complex. This inductive effect is also shown by the C–N π-ionization energies, but the changes are less marked.

In the spectrum of $Fe(CO)_4CNC_6H_5$, bands due to the ionization of the phenyl ring orbitals were observed at 9.79 and 9.99 eV. These ionizations correspond to the b_1 and a_2 ionizations which, in free phenyl isocyanide, occur at 9.50 and 10.15 eV, respectively.[7] The decrease of the $b_1 - a_2$ splitting in the complex is indicative of a reduced mesomeric interaction between the isocyanide and phenyl π orbitals. The rest of the spectrum is assigned by analogy to the spectrum of the methyl isocyanide adduct, because it appears that a methyl group and a phenyl group have about the same effective inductive effect.[18]

At ionization energies greater than 13 eV, a broad band is observed in all of the complexes. This band corresponds to ionization of CO $\sigma + \pi$ orbitals and ionization of the isocyanide group orbitals. Because of the lack of resolution of this band, detailed assignment was not possible.

Interpreting Valence Ionization Potentials Using Core-Binding Energies

The shift in the ionization energy of the donor orbital of a ligand on going from the free ligand to the transition-metal complex gives information about the ligand–metal σ bonding in the complex. The corresponding shifts in the ionization energies of the transition-metal dπ orbitals potentially give information about the π-donor/acceptor character of the ligand. Unfortunately, the direct interpretation of shifts in valence ionization energies in terms of chemical bonding is seldom reliable, because shifts in ionization energy are influenced not only by changes in bonding but also by changes in atomic charge and electronic relaxation energy. In organometallic compounds, charge and relaxation effects may be so large as to obscure the effects of changes in bonding.[19]

To minimize these difficulties, we use core-binding energies to correct for changes in charge and relaxation energy.[20] This method is based on the approximation that shifts in valence orbital ionization energies caused by differences in charge and relaxation energy are eight-tenths of the corresponding shifts in core-binding energy.[21] The method can be illustrated by examining the changes in π bonding when an axial CO group in $Fe(CO)_5$ is replaced by $CNCH_3$ to form $Fe(CO)_4CNCH_3$.

The two lowest ionization energies of both complexes correspond to molecular orbitals which are primarily Fe 3d atomic orbitals. The orbital that is primarily Fe $d_{x^2-y^2}$, d_{xy} in character has the lower ionization energy and is assigned the symmetry designation e′ in $Fe(CO)_5$ and e in $Fe(CO)_4CNCH_3$. The orbital of higher ionization energy is primarily Fe d_{xz}, d_{yz} in character, of e″ symmetry in $Fe(CO)_5$ and e symmetry in $Fe(CO)_4CNCH_3$. In order to compare the bonding characters of these orbitals in the two complexes, it is necessary to use the Fe $2p_{3/2}$ binding energy difference to correct for the decreased positive charge on the Fe atom and any change in relaxation energy on going from $Fe(CO)_5$ to $Fe(CO)_4CNCH_3$. Eight-tenths of the Fe binding energy difference is 0.64 eV. When this quantity is subtracted from the ionization energies of the corresponding e′ and e″ orbitals of $Fe(CO)_5$, one obtains "localized orbital ionization potential" (LOIP) values that correspond to the ionization energies that the e orbitals in $Fe(CO)_4CNCH_3$ would have if they had bonding character identical with that of the corresponding e′ and e″ orbitals in $Fe(CO)_5$. When the calculated LOIP values are subtracted from the experimental ionization energies of $Fe(CO)_4CNCH_3$, the magnitude and sign of the differences give a reliable measure of the change in bonding character of the metal orbitals caused by the substitution of a $CNCH_3$ ligand for a CO ligand. The results of these calculations for the metal orbitals of all of the iron tetracarbonyl isocyanide complexes are presented in Table III.

The metal orbitals of all of the isocyanide complexes are destabilized relative to $Fe(CO)_5$. This destabilization is probably due to interaction with a lower lying orbital of the same symmetry, in this case, the filled C–N π-bonding isocyanide orbital. In $CNCH_3$, the 2e C–N π level (IP = 12.46 eV[6]) is energetically situated to have a much stronger interaction with the filled metal e orbitals than its CO 1π

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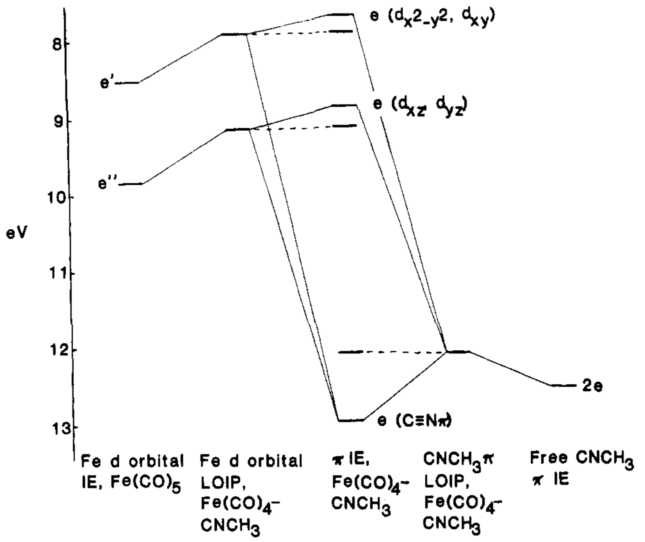

Figure 5. High-lying occupied π orbital interactions in $Fe(CO)_4CNCH_3$.

counterpart (IP = 16.91 eV[6]). In addition, the 2e orbital has greater electron density at the carbon atom than does the CO 1π orbital.

This destabilization of the metal orbitals should be accompanied by a stabilization of the isocyanide C–N π orbital of the complex relative to the free isocyanide. In the case of $Fe(CO)_4CNCH_3$, the stabilization of the methyl isocyanide C–N orbital can be determined, because the appropriate C 1s binding energies are known. This orbital is located mainly on the isocyano carbon and nitrogen atoms, so that an average of the C 1s and N 1s binding energy differences between $Fe(CO)_4CNCH_3$ and $CNCH_3$ should provide the necessary correction for differences in charge and relaxation energy. Eight-tenths of the average C–N binding energy difference is 0.37 eV, and when this amount is subtracted from the ionization energy of the free ligand, an LOIP value of 12.1 eV is obtained. Comparison of the LOIP value with the observed C–N π ionization energy of $Fe(CO)_4CNCH_3$ indicates a stabilization of 0.8 eV. Although the C 1s binding energy of the isocyano carbon of $Fe(CO)_4CNCH_3$ is not known with great certainty, we do not believe that it increases on coordination (the only result which could change the conclusion that this orbital is significantly stabilized on coordination). In previous X-ray photoelectron studies, we have always observed that the binding energies of all the atoms in a ligand shift in the same direction when the ligand is coordinated to a metal atom. Because the N 1s binding energy of $CNCH_3$ decreases on forming $Fe(CO)_4CNCH_3$, it is reasonable to assume that the isocyano C 1s binding energy also decreases. In either case, the C–N π orbital would be expected to have a greater contribution from the N 2p atomic orbitals than from the C 2p atomic orbitals, so that it would probably be acceptable to use only the N 1s binding energy when calculating the LOIP; such calculation gives a stabilization of 1.0 eV for the C–N π orbital of the complex.

The filled orbital π interactions that occur when an $Fe(CO)_4$ fragment bonds to a $CNCH_3$ ligand are shown in an energy level diagram in Figure 5. The metal orbital ionization energies of $Fe(CO)_5$ are corrected for the differences in charge and relaxation energy on forming the isocyanide complex. Similarly, the C–N π orbital ionization energy of $CNCH_3$ is corrected for differences in charge and relaxation energy. Comparison of the LOIP values with the actual ionization energies of the complex allows one to assess quantitatively the destabilization of the metal orbitals and the stabilization of the isocyanide C–N π orbital. The equatorial metal orbital of $Fe(CO)_4CNCH_3$ which is Fe $d_{x^2-y^2}$, d_{xy} and CO σ in character is destabilized less than the metal orbital which is d_{xz}, d_{yz} in character, as would be expected from the orientation of these orbitals relative to the axial isocyanide group. The amount of destabilization of the d_{xz}, d_{yz} orbital is 0.3 eV and is the same in all of the isocyanide complexes (Table III). This is also the amount of destabilization observed for this orbital in equatorially coordinated olefins, where the d_{xz}, d_{yz} orbital is orthogonal to the olefin π* acceptor orbital. Also, in our earlier study of the iron tetracarbonyl complexes of trimethylphosphine and pyridine, we concluded that these ligands were not acting as π acceptors, because they caused a destabilization of 0.3 eV of the d_{xz}, d_{yz} orbital.

However, in this case, the destabilization cannot be taken as evidence that the isocyanides are not engaged in any back-bonding, because the observed destabilization may be the resultant of a stabilizing interaction with the π* orbital and an even greater destabilizing interaction with the π orbital. In view of the net electron acceptor character of the isocyanide group in $Fe(CO)_4CNR$ complexes as shown by the binding energy shifts, we believe that the isocyanides do act as π acceptors, even in competition with carbon monoxide, but that filled orbital π interactions are relatively greater for isocyanides than for carbon monoxide. In this respect isocyanides are similar in their ligating properties to CS and NS, which Hubbard and Lichtenberger[22] have shown to have relatively strongly interacting filled π orbitals.

Finally we consider the relative σ-bonding capabilities of isocyanides and carbon monoxide. Once again, this is possible only in the case of $Fe(CO)_4CNCH_3$, for which we know the isocyano carbon binding energy. Using the isocyano C 1s binding energy difference between $CNCH_3$ and $Fe(CO)_4CNCH_3$, an LOIP value of 11.1 eV is obtained for the carbon "lone-pair" orbital of $CNCH_3$ in the complex. Comparison with the ionization energy of the Fe–CNR σ orbital indicates a stabilization of 1.2 eV. An analogous calculation for CO in $Fe(CO)_4CNCH_3$ gives an LOIP value of 11.4 eV for the CO carbon "lone pair" in the complex. Comparison with the ionization energy of the Fe–CO σ orbital is difficult because of the overlap of the Fe–CO σ orbital bands with the CO π orbital bands. These overlapping bands extend from 13 to 15 eV. If one conservatively chooses an ionization energy on the low ionization energy side of this group of bands, say 13.5 eV, for the ionization energy of the Fe–CO σ orbital, comparison with the LOIP value indicates a lower limit for the stabilization of 2.1 eV. A molecular orbital energy diagram illustrating the stabilization of the CO and $CNCH_3$ σ "lone-pair" orbitals in $Fe(CO)_4CNCH_3$ (corrected for potential and relaxation energy effects) is shown in Figure 6. This diagram graphically illustrates the greater net stabilization of the CO lone pair relative to the $CNCH_3$ lone pair.

The greater σ-donor character of CO relative to $CNCH_3$ in $Fe(CO)_4CNCH_3$ is undoubtedly a result of the σ–π synergism of the Fe–CO bond. The proton affinities of CO and $CNCH_3$ and our earlier study of borane adducts[13] indicate that, in non-transition-metal complexes, methyl isocyanide is a stronger σ donor than carbon monoxide. Clearly, our results confirm the common picture of transition metal–carbonyl bonding, in which the removal of negative charge by the π* orbitals of CO is so great, that a very strong σ bond is formed between the metal atom

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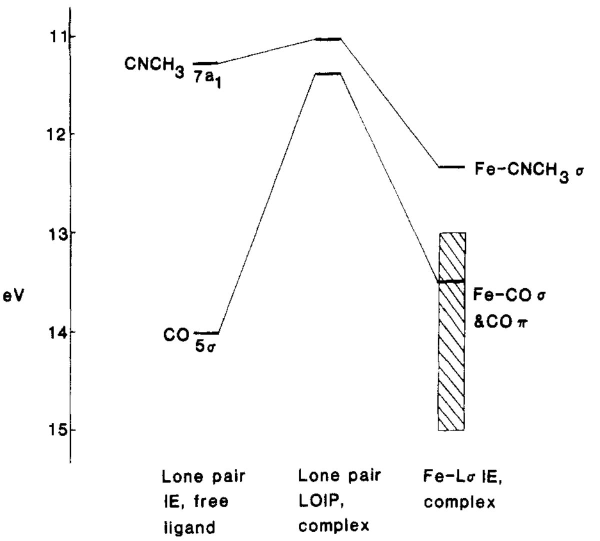

Figure 6. High-lying occupied σ orbital interactions in $Fe(CO)_4CNCH_3$.

and carbon monoxide, a ligand generally thought of as a weak σ donor.

Experimental Section

Methyl, *tert*-butyl, and phenyl isocyanide were prepared by standard methods.[23,24] Trimethylsilyl cyanide was prepared by the reaction of $(CH_3)_3SiBr$ and AgCN.[25] The iron tetracarbonyl complexes were prepared by sealed tube reactions of $Fe(CO)_5$ with the appropriate isocyanides (or cyanide).[26–28] Tetracarbonyl(methyl isocyanide)iron was purified by fractional condensation on the vacuum line, with the desired product collected in a 0 °C trap. The other products were purified by sublimation, and the melting points and infrared spectra of all of the products agreed with the literature.[29]

X-ray photoelectron spectra were obtained by using a GCA/McPherson ESCA-36 spectrometer with a Mg anode. Spectra were calibrated by using the N_2 1s (409.93 eV), Ne 1s (870.31 eV), and Ne 2s (48.47 eV) lines by a method described previously.[30] Samples were introduced through a large diameter (1.5-cm) inlet system with the flow regulated by cooling of the external sample reservoir.

He I excited spectra were recorded on a Perkin-Elmer PS-18 spectrometer using a heated inlet probe system. The ionization energy scale was calibrated by reference to peaks of admixed inert gases (Xe, Ar, He).

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Registry No. $Fe(CO)_4CNCH_3$, 14741-64-1; $Fe(CO)_4CNC(CH_3)_3$, 56448-44-3; $Fe(CO)_4CNCSi(CH_3)_3$, 19333-12-1; $Fe(CO)_4CNC_6H_5$, 17595-21-0.

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Bridged Ferrocenes. 12.[1] Metalation and Subsequent Reactions of Ferrocene Derivatives with Two or Three Trimethylene Bridges

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Reaction of 1,1′,2,2′-bis(trimethylene)ferrocene, I, 1,1′,3,3′-bis(trimethylene)ferrocene, II, and 1,1′,2,2′,4,4′-tris(trimethylene)ferrocene, III, with *n*-butyllithium (*n*-BuLi) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) or potassium *tert*-butoxide (KO-*t*-Bu) gave metal derivatives which were converted to the corresponding mono- and dicarboxylic acids and their methyl esters and in the case of III to the 3,3′-dibromo derivative. With a few modifications due to the peculiarities of the individual compounds, the explanation for the selectivity of the metalation reactions is essentially that given[2] for the metalation of 1,1′-trimethyleneferrocene, IV. The crystal structure of the dibromide was determined.

Introduction

The lithiation of ferrocene,[3] V (compounds I through XIV are illustrated in Figure 1; XV is in Figure 2), and[2] of IV with *n*-BuLi and TMEDA were found to give dilithio derivatives with the two lithium atoms situated on the corresponding positions of each cyclopentadienyl ring. In the case of V, this was determined[3] by means of a crystal structure of a related dilithio derivative; for IV the products from further reactions of the dilithio derivatives were

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