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The Transition Metal–Isocyanide Bond. An Approximate Molecular Orbital Study

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The bonding properties of methyl isocyanide in transition metal complexes are examined *via* approximate molecular orbital calculations on the series of complexes $Mn(CO)_{5-n}(CNCH_3)_nBr$, n = 0–4, $Mn(CO)_{6-n}(CNCH_3)_n^+$, n = 0–6, and $Fe(CNCH_3)_6^{2+}$. A force constant analysis is presented which, in conjunction with the molecular orbital results, shows that both σ- and π-bonding changes in the metal to isocyanide bond can influence observed stretching frequencies. The antibonding behavior of the $7a_1$ orbital, the carbon "lone pair" in methyl isocyanide, helps explain the observed increase in ν_{CN} values for bound methyl isocyanide compared to the free ligand in many metal complexes even though there is significant back-bonding to the ligand. We also find that for the cationic manganese species electrochemical potentials for the $+1 \rightarrow +2$ oxidation process correlate extremely well with calculated highest occupied molecular orbital (HOMO) energies. These results confirm the importance of including near-neighbor interactions in an approximate molecular orbital scheme.

Introduction

In the past few years there has been considerable research in the field of isocyanides as ligands in transition metal complexes.[1,2] In such complexes isocyanides are generally thought of as being capable of extensive back-bonding in a manner analogous to that of carbonyl.[3] Recently we published the results of an X-ray diffraction and molecular orbital study on $Mn(CO)_3(CNCH_3)_2Br$, which showed that significant back-bonding to the methyl isocyanide ligand does occur, even in competition with carbonyl.[4] In order better to understand the consequences of the bonding of methyl isocyanide to a transition metal and the physical and chemical properties of the resulting complexes we have undertaken molecular orbital studies on the series of complexes $Mn(CO)_{5-n}(CNCH_3)_nBr$, n = 0–4, $Mn(CO)_{6-n}(CNCH_3)_n^+$, n = 0–6, and $Fe(CNCH_3)_6^{2+}$. These complexes allow comparison of carbonyl and isocyanide ligands competing in varied molecular environments. In addition, comparison of some of these complexes with their carbonyl or cyanide analogs, for example $Mn(CO)_6^+$, $Mn(CN)_6^{5-}$, $Mn(CO)_5CN$, and $Mn(CO)_5CNCH_3^+$, provides an opportunity to contrast carbonyl, cyanide, and isocyanide bonding.

Molecular Orbital Calculations

Method. The approximate, nonparameterized molecular orbital method has been described previously.[5] Choice of wave functions and bond distances is described below. All calculations were carried out using the MEDIEVAL series of programs written in these laboratories for the Univac 1108 computer at the Academic Computing Center, Madison, Wis.[6]

Basis Functions. Clementi's double-ζ functions for neutral atoms were used for carbon, oxygen, and nitrogen,[7] except that the N(−1) functions were used for cyanide nitrogen.[8] Choice of wave functions is made consistent with the resulting atomic charges calculated *via* a Mulliken population analysis[9] in all cases. The 1s and 2s functions were curve-fit to single ζ using the maximum-overlap criterion, while maintaining their orthogonality.[10] For bromine the "best atom" functions of Clementi and Raimondi were used,[11] after Schmidt orthogonalization to ensure that all one-center overlaps are zero. For hydrogen, an exponent of 1.16 was used, which corresponds to the minimum energy exponent for methane.[12]

For manganese the 1s–3d functions were taken from the results of Richardson, *et al.*[13] For the 3d case we used the function corresponding to the Mn^+ ($3d^6$) configuration. 4s and 4p orbitals for manganese were constructed in a manner described previously by maximizing their overlap with the carbonyl carbon atom.[14] Iron functions were chosen in the same way. A more detailed discussion of the method for obtaining the basis functions, including the list of orbital exponents and coefficients for the various functions, is available.[15]

Table I. Bond Distances and Angles

Distances, Å

Mn–Co	1.79 (trans to Br only)	C≡O	1.128
Mn–CO	1.83 (all others)	C≡N(isocyanide)	1.166
$Mn–CNCH_3$	1.97	$N–CH_3$	1.424
Mn–Br	2.537	C–H	1.102
$Fe–CNCH_3$	1.90	C≡N(cyanide)	1.16
Mn–CN	1.97		

Angles

C–N–C	180°	N–C–H	109° 28′

Bond Parameters. Free-ligand bond distances for $CNCH_3$[16] and CO[17] were used in this work. For cyanide a value of 1.16 Å was used as in previous work.[18,19] Structural studies confirm that the ligand values for the bound case differ only slightly from the free values. The metal to ligand distances were chosen as follows. For the manganese complexes we referred to the crystal structure results for $Mn(CO)_3(CNCH_3)_2Br$.[4] Thus, the Mn–CO distance for a carbonyl trans to bromine was taken as 1.79 Å, while for all other cases Mn–CO was maintained at 1.83 Å, the average of the equatorial carbonyl distances in the crystal structure. Manganese to methyl isocyanide distances were maintained at 1.97 Å, also the average value. The Mn–Br distance was taken as 2.537 Å.

For the $Fe(CNCH_3)_6^{2+}$ calculation we took note of our previous observation that there is a correspondence of metal to methyl isocyanide bond lengths and metal to cyanide bond lengths.[4] Therefore we chose an $Fe–CNCH_3$ distance equal to the Fe–CN distance of 1.90 Å in $Na_2Fe(CN)_5NO \cdot 2H_2O$.[20]

For the manganese cyanide complexes, the Mn–CN distance was taken as 1.97 Å, the same value as for the $Mn–CNCH_3$ distance. An advantage of maintaining the Mn–CN value the same as the $Mn–CNCH_3$ distance is that differences in bonding observed for the two ligands can be attributed to electronic changes within the complex, rather than apparently minor bond distance changes. The value of 1.97 Å compares favorably to the mean manganese to carbon distance of 1.98 Å in $K_3Mn(CN)_5NO \cdot 2H_2O$.[21] Table I summarizes all the bond distances used.

Free-Ligand Results. While the calculations are carried out in an atomic basis set, it is more useful for the interpretation

Table II. Free-Ligand Orbitals Used in Bonding

		% character					
		s(C)	p(C)	s(O)	p(O)	Eigenvalue, eV	Overlap population[a]
CO	5σ	34.4	47.8	1.0	16.7	−13.79	−0.128
	2π		66.8		33.3	+0.29	−0.478

		% character					
		$s(C_1)$	p(C)	s(N)	p(N)	Eigenvalue, eV	Overlap population
CN^-	5σ	20.7	53.0	3.0	23.3	+2.45	−0.277
	2π		62.6		37.4	+17.49	−0.723

		% character								
		$s(C_1)$	$p(C_1)$	s(N)	p(N)	$s(C_2)$	$p(C_2)$	H total	Eigenvalue, eV	Overlap population[b]
$C^1NC^2H_3$	$7a_1$	40.7	56.0	0.7	0.8	0.0	1.7	0.1	−13.39	−0.032
	3e		59.3		36.6		0.1	4.0	+3.17	−0.536

[a] This is on a per electron basis. [b] Expressed in the $C^1{\equiv}N$ region.

Table III. Eigenvalues for $CNCH_3$ in (eV)

Orbital	Present method	*Ab initio*[a]	Orbital	Present method	*Ab initio*[a]
$4a_1$	−36.80	−35.02	1e	−23.43	−17.45
$5a_1$	−31.45	−28.13	2e	−17.30	−13.00
$6a_1$	−25.09	−20.06	$7a_1$	−13.39	−12.63

[a] See ref 22.

of bonding trends in the complexes to transform the results into basis sets comprised of the free-ligand molecular orbitals. The results of the calculations for the free carbonyl, cyanide, and methyl isocyanide ligands are presented in Table II. The table lists the per cent atomic orbital character of those molecular orbitals that are found by our calculation to be involved in bonding to the transition metal, *i.e.*, the 5σ and 2π orbitals in the carbonyl and cyanide ligands and the $7a_1$ and 3e orbitals in methyl isocyanide. Since this is the first study on $CNCH_3$ using our method, Table III contains a comparison of eigenvalues with those obtained from *ab initio* studies by Liskow, *et al.*[22] The comparison is limited to the $4a_1$ through $7a_1$ levels since our SCF procedure places the 1s orbitals of carbon and nitrogen in the "core" with the atomic nuclei and the *ab initio* paper does not report the virtual eigenvalues. The comparisons are quite reasonable, particularly in consideration of the approximations intrinsic to our method and the restricted basis sets employed in both calculations. The very good accord for the eigenvalue of the $7a_1$ orbital is especially gratifying since this orbital plays an important role in discussions to come.

The formation of methyl isocyanide may be pictured as the hypothetical methylation of cyanide

$$CN^- + CH_3^+ \rightarrow CNCH_3$$

The bond between the two moieties essentially involves the sp^3 hybrid of the methyl cation and the 4σ "lone pair" on the nitrogen atom of the cyanide anion. The orbital counterparts in methyl isocyanide of the 5σ and 2π in cyanide now carry the labels $7a_1$ and 3e, respectively. The results in Table II display the two principal effects of the hypothetical reaction. First, there is a substantial stabilization of the $7a_1$ and 3e eigenvalues of $CNCH_3$ relative to the 5σ and 2π eigenvalues of CN^-. Second, the $7a_1$ orbital appears to be even more localized on the carbon atom that will ultimately interact with the metal. One notes, however, that the overlap population[23] of the $7a_1$ orbital indicates that the orbital is somewhat antibonding in the $C{\equiv}N$ region. Thus, one can expect analogies to occur in comparing the interactions of the $7a_1$ orbital of methyl isocyanide with those of the 5σ orbitals in the carbonyl and cyanide ligands, which are also found to be antibonding.

The 3e orbitals of the methyl isocyanide moiety are strongly antibonding in the $C{\equiv}N$ region as indicated by the overlap population in Table II. Since these orbitals are virtual in the free ligand, an occupation greater than zero upon bonding to a transition metal represents the amount of back-bonding from the metal 3d orbitals to the methyl isocyanide ligand. In this way the 3e orbitals are analogous to the 2π orbitals in carbonyl and cyanide.

Force Constant Study

We have calculated carbonyl and isocyanide force constants for the mixed carbonyl and isocyanide complexes. The stretching frequencies used for the analysis were taken from the literature, and the band assignments were made by us, on the basis of reported intensities and by consideration of the infrared selection rules. The ir data are presented in Table IV. Using these data we have applied the method of Cotton and Kraihanzel (CK)[24] to derive a set of approximate force constants since insufficient experimental data are available to render a more rigorous treatment possible. The derived carbonyl and isocyanide force constants are given in Table V. Although there are several well-founded criticisms of the CK method[25,26] it has been maintained that the trends in force

Table IV. Stretching Frequencies for Mixed Carbonyl and Isocyanide Complexes

Compd	Ref	Solvent	ν_{CN}, cm^{-1}	ν_{CO}, cm^{-1}
$BrMn(CO)_4(CNCH_3)$	*a*	$CHCl_3$	2226 m	2105 m (A′), 2033 vs (A″, A′), 1980 s, br (A′)
$BrMn(CO)_3(CNCH_3)_2$	*a*	$CHCl_3$	2220 m (A′), 2202 m (A″)	2048 vs (A′), 1997 (A″), 1949 s (A′)
$BrMn(CO)_2(CNCH_3)_3$	*a*	$CHCl_3$	2212 m (A′), 2182 sh (A′), 2166 vs (A″)	1993 s (A′), 1913 s (A′)
$BrMn(CO)(CNCH_3)_4$	*a*	$CHCl_3$	2142 vs, br (E)	1881 s, br
$Mn(CO)_6^+$	*b*	Nujol		2101 vs (T_{1u})
$Mn(CO)_5(CNCH_3)^+$	*a*	CH_2Cl_2	2264 m	2158 m (A_1), 2075 vs, br (E + A_1)
$Mn(CO)_4(CNCH_3)_2^+$	*a*	CH_2Cl_2	2249 m, br (A_1), 2221 sh (B_1)	2125 m ($A_1^{(1)}$), 2064 sh ($A_1^{(2)}$), 2051 vs (B_1), 2036 sh (B_2)
$Mn(CO)_3(CNCH_3)_3^+$	*a*	CH_2Cl_2	2245 m (A_1), 2220 sh (A_1), 2202 s (B_1)	2090 m (A_1), 2020 vs, br (A_1, B_1)
$Mn(CO)_2(CNCH_3)_4^+$	*a*	CH_2Cl_2	2177 vs, br (E_u)	1985 vs (A_{2u})
$Mn(CO)(CNCH_3)_5^+$	*a*	CH_2Cl_2	2226 w (A_1), 2180 sh (A_1), 2156 vs (E)	1956 s
$Mn(CNCH_3)_6^+$	*c*	CH_2Cl_2	2129 (T_{1u})	
$Fe(CNCH_3)_6^+$	*d*	Nujol	2234 vs (T_{1u}), 2197 w (?)	

[a] M. Treichel, G. E. Dirreen, and H. J. Mueh, *J. Organometal. Chem.*, 44, 339 (1972). [b] R. W. Cattrall and R. J. H. Clark, *ibid.*, 6, 167 (1966). [c] F. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, **83**, 351 (1961). [d] L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley-Interscience, London, 1969, p 116.

Table V. Carbonyl Force Constants (mdyn/Å) and Populations (electrons)

	k_1	k_2	k_3	k_i	2π	5σ
		Cations				
$Mn(CO)_6^+$	18.33			(0.25)[a]	0.420	1.329
$Mn(CO)_5(CNCH_3)^+$	17.53			0.21	0.456	1.338
		17.82		0.21	0.435	1.349
$Mn(CO)_4(CNCH_3)_2^+$	17.24			0.24	0.473	1.357
		17.47		0.24	0.450	1.369
$Mn(CO)_3(CNCH_3)_3^+$	16.63			0.26	0.492	1.374
		16.99		0.26	0.466	1.388
$Mn(CO)_2(CNCH_3)_4^+$	16.41			(0.25)[a]	0.482	1.406
$Mn(CO)(CNCH_3)_5^+$	15.45				0.528	1.409
		Halides				
$Mn(CO)_5Br$[b]	16.32			0.22	0.558	1.340
		17.39		0.22	0.476	1.365
$Mn(CO)_4(CNCH_3)Br$	15.93			0.25	0.578	1.357
		17.19		0.25	0.489	1.385
			16.80	0.25	0.512	1.372
$Mn(CO)_3(CNCH_3)_2Br$	15.50			0.34	0.598	1.373
		16.44		0.34	0.527	1.390
$Mn(CO)_2(CNCH_3)_3Br$	14.83			(0.25)[a]	0.622	1.388
		15.99		(0.25)[a]	0.543	1.407
$Mn(CO)(CNCH_3)_4Br$	14.29				0.647	1.403

[a] Values in parentheses are estimated. [b] Values for k_i and k_1 from E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, **63**, 45 (1967).

constants calculated in this manner do reflect those that would be observed with more rigorous force fields, provided that the compounds under consideration are related.[27] The compounds we have considered are all six-coordinate d^6 complexes. The value of using force constants is that, unlike stretching frequencies, they allow us to assign to the CO or CN oscillator a single quantity that is presumed to be directly related to the bond strength.

In deriving force constants for mixed complexes the limited experimental data require one to make further simplifications in the CK method. Thus, the force constants for the methyl isocyanide oscillator and those of the carbonyl oscillator were treated using separate sets of CK equations for each type of ligand. This kind of approximation is reasonably justified as long as there are no fundamental vibrations in the molecule with frequencies near those of interest.[28] However, Table IV shows that the CO and CN stretching frequencies are close enough that coupling could occur between these oscillators, and hence our neglect of such interactions undoubtedly introduces some errors in the force constant determinations. We have carried out trial calculations which indicate that inclusion of reasonable values for the interaction force constants between carbonyl and methyl isocyanide would not affect the principal force constants by much more than 0.1 mdyn/Å.

Within a particular ligand type, CO or $CNCH_3$, we have included coupling between the oscillators as outlined by the CK method. Neglect of these terms, which one reasonably expects to have substantial effects on the principal force constants, would be difficult to justify. In a few cases, identified in Table V, the paucity of experimental data required the assignment of an assumed value for the interaction constant, k_i. As the table illustrates, where such choices were necessary, the constants chosen were consistent with the values derived for other compounds of the same type.

Carbonyl Results. A previous molecular orbital study from these laboratories on a series of d^6 carbonyl halides and dihalides demonstrated that, for the carbonyl ligand, trends in force constants could be accounted for when changes in both the 5σ and 2π orbital occupations were considered.[29] In particular, that study emphasized that donation of electron density from the 5σ orbital resulted in a strengthening of the CO bond consistent with the antibonding character of the orbital.

Table VI. Carbonyl Force Constant Linear Regression Analysis

Variable	Coeff	Partial F value	Significance level, %
	Neutral Complexes Only[a]		
2π	−16.45	1398.74	99.9
5σ	−8.88	54.97	99.9
Const	37.44	537.28	99.9
	Cations Only[b]		
2π	−18.92	112.56	99.9
5σ	−9.78	23.57	99.7
Const	39.32	336.33	99.9
	Combined Data[c]		
2π	−13.42	212.20	99.9
5σ	−12.12	25.19	99.9
Const	40.10	162.55	99.9

[a] Standard error of estimate 0.07 mdyn/Å. [b] Standard error of estimate 0.10 mdyn/Å. [c] Standard error of estimate 0.23 mdyn/Å.

The mixed isocyanide–carbonyl complexes in the present study provide a test of the previous conclusions for carbonyl in a quite different molecular environment. Here the carbonyl is competing for electron density with another good π-electron acceptor, the isocyanide ligand. The 5σ and 2π orbital occupations are listed with the corresponding force constants in Table V. We have tabulated data for the cationic compounds and the neutral bromine containing compounds separately, for reasons to be discussed below.

A test of the relation between carbonyl 5σ and 2π occupations *vs.* the force constant was carried out *via* a linear regression analysis. The force constant, k, is expressed in terms of orbital occupations

$$k = a(5\sigma) + b(2\pi) + c \tag{1}$$

where (5σ) and (2π) are the total occupations for the respective orbitals. The data were treated in three blocks: neutral complexes only, cations only, and all data combined. The results are presented in Table VI. Several important observations can be made from the table. First, the significance level of all the regression coefficients is greater than 99%, indicating the importance of both the 5σ and 2π orbital occupations in accounting for the observed force constant changes. Also, the negative signs for the regression coefficients of both the orbitals are in accord with previous results[29] and with the antibonding character of these orbitals. Thus, as the occupation of either orbital increases, the effect is a lowering in the force constant. Note, however, that the standard error of estimate for the combined data is more than twice that for the cations and neutral complexes treated separately. The reason for this behavior is most easily visualized in the following way. A two-dimensional plot of the force constant *vs.* orbital occupation can be accomplished if we define an "effective occupation" according to

$$(\mathrm{occ}) = (2\pi) + (a/b)(5\sigma) \tag{2}$$

Then the equation for the combined data

$$k = 40.10 - 13.42(2\pi) - 12.12(5\sigma) \tag{3}$$

reduces to

$$k = 40.10 - 13.42(\mathrm{occ}) \tag{4}$$

The result is presented in Figure 1. It is apparent from the figure that the values for the neutral halogen-containing compounds and the cation fall on two parallel lines. This results in an improved fit when the data are treated separately, while the regression analysis attempts to force a fit of the parallel lines with a single line when the data are treated together.

Several explanations may be offered for the observed displacement of these lines. One is that the very application

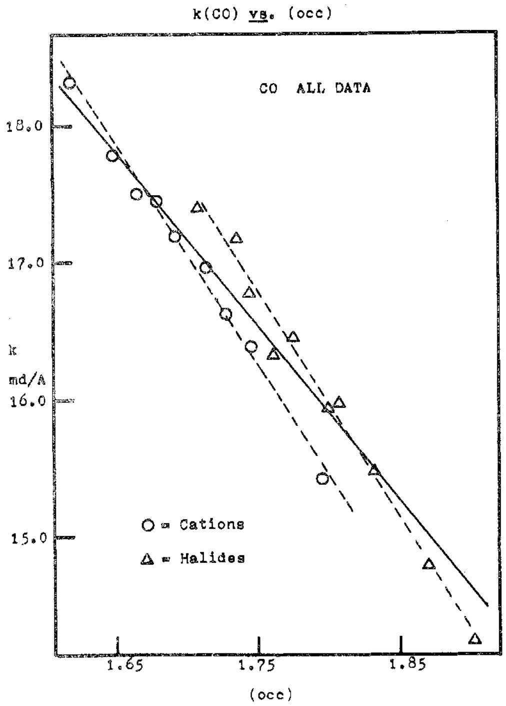

Figure 1. Carbonyl force constant *vs.* effective occupation.

of a CK analysis is dependent on the assumptions that interaction terms neglected remain nearly constant for the compounds under consideration. It is not unreasonable to suppose that such terms may be different for cationic complexes containing carbonyl and methyl isocyanide only compared to those neutral complexes containing halogen as well. Another possible explanation is revealed by examination of the ir data in Table IV. The data for the halide complexes were measured in chloroform, while most of the cation data were determined in dichloromethane. Solvent effects are known to cause shifts in ir frequencies, particularly for isocyanides in chlorinated hydrocarbons.[30] A final possible explanation is that the molecular orbital calculations do not properly account for electronic changes that occur on going from one set of compounds to the other. Such an effect could arise from the approximations we make to the HFR operator or as a result of our choice of bond distance. While it is not expected that there are radical bond distance differences between the two sets of compounds, the possibility of differences great enough to cause the observed shift cannot be ruled out.

Without a more rigorous force constant analysis it is not possible to determine with certainty which of the above possible explanations is correct. Nevertheless, the fact that *within* each group of compounds the proper trends in force constants are almost exactly accounted for is encouraging. The fit is within expected experimental error for both sets of compounds and for both the CO and $CNCH_3$ oscillators.

In light of the above discussion it was deemed desirable to compare the results of the carbonyl force constant analysis of the present study with an equation relating the force constant to 2π and 5σ occupations derived in a previous study of d^6 pentacarbonyl halides and tetracarbonyl dihalides.[29] The root mean square of the residuals of the k observed and k calculated for the combined data was 0.312 mdyn/Å. Therefore it was concluded that the previously derived equation should not be applied to the present series of molecules. Thus, the generality of our approach for the study of σ and π changes affecting bond strength in a closely related series of molecules is demonstrated, while the possibility of deriving a single equation to correlate accurately such changes for the carbonyl group in all molecules is made less certain.

Table VII. Methyl Isocyanide Force Constants (mdyn/Å) and Orbital Occupations (electrons)

	k_1	k_2	k_i	3e	$7a_1$
		Cations			
$Mn(CO)_5(CNCH_3)^+$	19.51			0.212	1.390
$Fe(CNCH_3)_6^{2+}$	19.41		$(0.20)^a$	0.218	1.376
$Mn(CO)_4(CNCH_3)_2^+$	19.03		0.24	0.222	1.416
$Mn(CO)_3(CNCH_3)_3^+$	18.92		0.14	0.234	1.441
$Mn(CO)_3(CNCH_3)_3^+$		18.75	0.14	0.251	1.430
$Mn(CO)_2(CNCH_3)_4^+$	18.45		$(0.20)^a$	0.266	1.452
$Mn(CO)(CNCH_3)_5^+$	18.29		0.16	0.259	1.488
$Mn(CO)(CNCH_3)_5^+$		18.02	0.16	0.280	1.476
$Mn(CNCH_3)_6^+$	17.66		$(0.20)^a$	0.295	1.496
		Halides			
$Mn(CNCH_3)(CO)_4Br$	18.87			0.257	1.440
$Mn(CNCH_3)_2(CO)_3Br$	18.62		0.15	0.267	1.465
$Mn(CNCH_3)_3(CO)_2Br$	18.28		0.16	0.278	1.487
$Mn(CNCH_3)_3(CO)_2Br$		18.18	0.16	0.298	1.475
$Mn(CNCH_3)_4(CO)Br$	17.77		$(0.15)^a$	0.313	1.496

[a] Values in parentheses are estimated.

Methyl Isocyanide Results. Table VII lists the 3e and $7a_1$ orbital occupations and force constants for the isocyanide groups in the complexes studied. The nonzero 3e orbital occupations indicate that for all these compounds the methyl isocyanide to metal bond involves significant π-bond character. Increasing occupation of the 3e orbital in these complexes ought to lead to a weaker CN bond, due to its antibonding character. Examination of the table reveals that while this is generally true, it is not always the case. For example, the four equivalent CN oscillators in $Mn(CO)_2(CNCH_3)_4^+$ have a force constant of 18.45 mdyn/Å and a 3e occupation of 0.266 electron. The isocyanide trans to the carbonyl in $Mn(CO)(CNCH_3)_5^+$ has a force constant of 18.29 mdyn/Å, but the 3e orbital occupation, 0.259 electron, is actually lower. Thus the greater 3e occupation in this example would appear to correspond to the greater force constant. An explanation for the apparent anomaly is offered by examination of the $7a_1$ occupations. In the case of $Mn(CO)_2(CNCH_3)_4^+$ the $7a_1$ occupation is 1.452 electrons, while for the methyl isocyanide of interest in $Mn(CO)(CNCH_3)_5^+$ it is 1.488 electrons. Recalling that Table II shows that the $7a_1$ orbital is *antibonding* in the CN region, the trends for the two cases can be explained. As the $7a_1$ occupation decreases from 1.488 to 1.452 electrons, the CN bond strength will be increased since electrons are being removed from an antibonding orbital. This increase in bond strength due to σ effects is apparently sufficient to overcome the bond weakening which results from the increase in 3e occupation. To test this hypothesis better we carried out a linear regression analysis in the same manner as was done for carbonyl. The results of this analysis are presented in Table VIII. The form of the equation relating the isocyanide force constant to 3e and $7a_1$ orbital occupations is

$$k = a(7a_1) + b(3e) + c \qquad (5)$$

where $(7a_1)$ and (3e) are the occupations of the respective orbitals. As for the carbonyl ligand in these complexes the data were treated in three blocks: cations, halogen-containing neutral compounds, and combined.

The results of the analysis are very informative. First, as occurred in the carbonyl force constant analysis, the fit of the combined data is not quite so good as for the cations or the neutral halogen-containing compounds alone. Figure 2 displays the combined data and again the two sets of compounds lie on nearly parallel lines with the neutral compounds above the cationic species. Hence, the comments previously made concerning the correlations for carbonyl hold for the methyl isocyanide ligand as well.

Second, the high significance levels of the regression coefficients and low standard error of estimate indicate that,

Table VIII. Methyl Isocyanide Force Constant Linear Regression Analysis

Variable	Coeff	Partial F value	Significance level, %
	Neutral Complexes Only[a]		
3e	−11.98	43.03	97.7
$7a_1$	−7.66	15.88	94.2
Const	33.00	186.00	99.5
	Cations Only[b]		
3e	−13.71	33.06	99.8
$7a_1$	−5.54	11.30	98.5
Const	30.06	262.24	99.9
	Combined Data[c]		
3e	−8.82	8.04	98.4
$7a_1$	−7.45	8.82	98.7
Const	31.66	116.34	99.9

[a] Standard error of estimate 0.05 mdyn/Å. [b] Standard error of estimate 0.08 mdyn/Å. [c] Standard error of estimate 0.15 mdyn/Å.

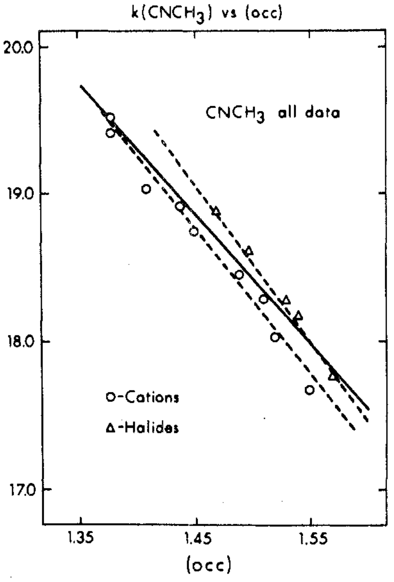

Figure 2. CN in $CNCH_3$ force constants *vs.* effective occupation.

as anticipated, both the 3e and $7a_1$ occupations are affecting the observed force constant changes and that the orbital occupations are both found to enter the resulting force constant equation with *negative* coefficients. This is in line with the calculated antibonding character of these orbitals in the CN region.

The traditional notion that comparison of the C≡N stretching frequency of the bound $CNCH_3$ ligand to that of the free ligand is a measure of π back-bonding only[31,32] must be modified in the light of the present study. σ donation out of the $7a_1$ orbital may increase the bond strength in the C≡N region enough that even fairly extensive π back-bonding will not lower it sufficiently to bring the frequency below that of the free ligand. For example, the two C≡N stretching frequencies observed in $Mn(CO)_3(CNCH_3)_2Br$ at 2220 and 2202 cm^{-1} are *higher* than the free ligand value of 2166 cm^{-1}. Yet both the crystal structure data and the molecular orbital results[4] for this compound indicate that π back-bonding is definitely taking place to the methyl isocyanide ligands. Even in $Mn(CO)_5(CNCH_3)^+$, a cationic compound with five competing carbonyls, the molecular orbital results indicate a significant π back-bonding to the isocyanide, although ν_{CN} for this compound is 2264 cm^{-1}. While it has been argued that kinematic coupling may account for some of the increase,[33] our results show that most of the observed increase should be attributed to σ donation out of the antibonding $7a_1$ orbitals.

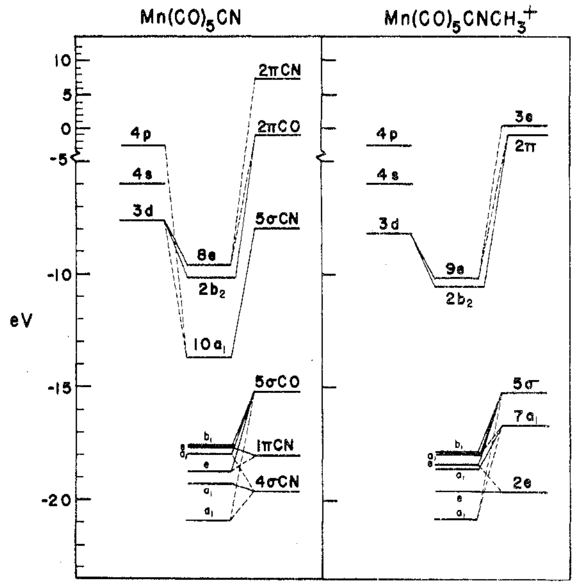

Figure 3. MO diagrams for $Mn(CO)_5CN$ and $Mn(CO)_5CNCH_3^+$.

Table IX. Ligand Orbital Occupations

		$Mn(CO)_6^+$	$Mn(CO)_5CNCH_3^+$	$Mn(CO)_5CN$	$Mn(CNCH_3)_6^+$	$Mn(CN)_6^{5-}$
cis CO	5σ	1.329	1.349	1.352		
	2π	0.420	0.435	0.470		
trans CO	5σ	1.329	1.338	1.344		
	2π	0.420	0.456	0.510		
CN	5σ			1.179		1.333
	2π			0.112		0.302
$CNCH_3$	$7a_1$		1.390		1.496	
	3e		0.212		0.296	
3d total		5.913	5.894	5.933	5.860	6.289
Metal total		7.510	7.419	7.586	7.005	8.221

Comparison of the Bonding Behavior of CN^-, $CNCH_3$, and CO

Cyanide and Isocyanide. The present study permits a close examination of certain traditional views concerning the bonding of cyanide, isocyanide, and carbonyl ligands. For example, the two compounds, $Mn(CO)_5CN$ and $Mn(CO)_5(CNCH_3)^+$ provide ready comparison of cyanide and isocyanide in identical molecular environments. Figure 3 presents molecular orbital diagrams for the two species. Since the compounds differ in charge, the eigenvalues for the 1+ species have been scaled to a higher energy by 3.88 eV. This scale factor brings the $1a_2$ molecular orbitals for the two complexes into line. The $1a_2$ orbital is a nonbonding linear combination of 1π orbitals in the *xy* plane.

Figure 3 shows that in the two complexes the metal orbitals and carbonyl MO's are very similar in relative energy. Note, however, that the 3e and $7a_1$ levels for methyl isocyanide in $Mn(CO)_5(CNCH_3)^+$ are considerably lower in energy than the 5σ and 2π cyanide levels in $Mn(CO)_5CN$. Since the metal levels have remained essentially unchanged, the net effect is that the 3e orbital is drawn closer to the metal levels, while the $7a_1$ orbital is drawn away. Hence, one might anticipate on the basis of energetics alone, that the methyl isocyanide is a weaker σ donor and a stronger π acceptor than cyanide. Indeed this is the case, as indicated by the orbital occupations given in Table IX. The cyanide in $Mn(CO)_5CN$ donates 0.821 electron and back-accepts 0.112 electron, while the methyl isocyanide group in $Mn(CO)_5(CNCH_3)^+$ donates 0.710 electron and back-accepts 0.212 electron.

While the foregoing discussion emphasizes the dissimilarities in bonding behavior of cyanide and isocyanide, a comparison of the results of calculations on $Mn(CNCH_3)_6^+$ and Mn-

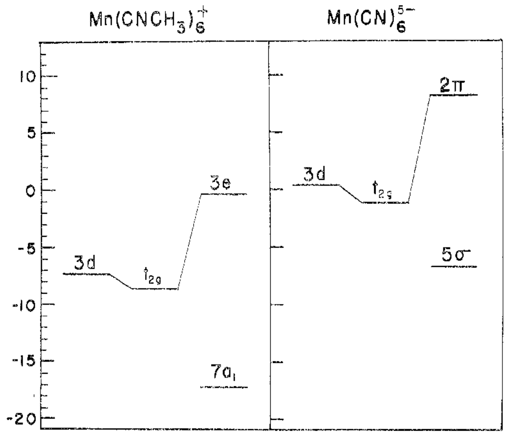

Figure 4. MO diagram for $Mn(CNCH_3)_6^+$ and $Mn(CN)_6^{5-}$.

$(CN)_6^{5-}$ illustrates the degree of caution required in making generalizations. Figure 4 displays the molecular orbital diagrams showing the placement of the metal 3d and relevant ligand orbitals for these two compounds. Because of the high negative charge on the cyanide species, the eigenvalues are shown stabilized by 21 eV to bring them onto approximately the same scale as $Mn(CNCH_3)_6^+$. This is for convenience only, as the relative placement of orbitals within each complex is what matters.

Note that the energy separation of the 3d–3e orbitals in the methyl isocyanide complex nearly equals the 3d–2π orbital energy difference in the cyanide case. The net result is that both ligands interact with the metal $3d\pi$ levels about equally. This results in nearly identical back-bonding to the two ligands, as the orbital populations in Table IX confirm. A major difference in the MO diagrams is that the 3d level in the cyanide complex seems considerably destabilized with respect to the isocyanide case. This increase in energy is a consequence of the increased σ donation by the cyanide 5σ orbital compared to that of the methyl isocyanide $7a_1$ orbital. The increased σ donation results in greater electron density being placed in the metal 3d orbitals, hence increasing their energy and bringing them into closer proximity to the 2π orbitals. The net result is that the cyanide and isocyanide ligands for these complexes are essentially the same in terms of back-bonding ability.

The foregoing emphasizes the importance of the *total* molecular environment on the relative bonding properties of ligands.[18,19] When the molecular environment consisted of five carbonyls, as in the $Mn(CO)_5X$ case, X = CN or $CNCH_3$, the methyl isocyanide was clearly a better π acceptor than cyanide. However, in the MnX_6 case, the two ligands are the same in back-bonding ability, though the cyanide is still clearly the better σ donor. These examples point out the danger of assuming that bonding characteristics of a ligand are the same irrespective of the total molecular environment.

Carbonyl and Isocyanide. A generally accepted view has been that carbonyl is a better π acceptor and a weaker σ donor than isocyanide. The greater σ donor strength of the CNR ligand has been given as the basis for the stabilization of higher oxidation states by this ligand. For example, this argument has been used to rationalize the existence of $Mn(CNCH_3)_6^{2+}$ while $Mn(CO)_6^{2+}$ is not known.[3] Further affirmation of the donor–acceptor characteristics of the two ligands appeared to be given by electrochemical studies on the series $Mn(CO)_x(CNCH_3)_{6-x}^+$ with $x = 1$–5.[34] The ease of oxidation for these complexes decreased as the number of carbonyl groups increased. Qualitatively, one might expect greater difficulty in removal of a metal electron as the effective positive charge on the metal is increased by the presence of more carbonyl groups.

Table X

Complex	Metal AO occupations: 3d only	Metal AO occupations: Total	HOMO energy, eV	$\frac{1}{2}[E_{p,c} + E_{p,a}]^a$
$Mn(CNCH_3)_6^+$	5.860	7.005	−8.65	0.38
$Mn(CNCH_3)_5CO^+$	5.859	7.080	−9.41	0.79
$Mn(CNCH_3)_4(CO)_2^+$	5.867	7.172	−10.19	1.12
$Mn(CNCH_3)_3(CO)_3^+$	5.871	7.248	−11.45	1.65
$Mn(CNCH_3)_2(CO)_4^+$	5.880	7.329	−12.74	2.14
$Mn(CNCH_3)(CO)_5^+$	5.894	7.419	−14.02	2.65
$Mn(CO)_6^+$	5.913	7.510	−15.35	

[a] These data are taken from ref 32 and are given in volts with respect to sce, for the +1 → +2 process. $Mn(CO)_6^+$ was not studied.

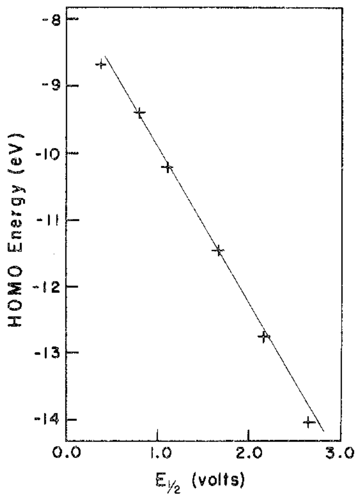

Figure 5. HOMO energies *vs.* oxidation potentials for $Mn(CNCH_3)_n(CO)_{6-n}^+$ complexes.

While our calculations are in accord with the generally accepted view of the relative π-acceptor abilities of carbonyl and isocyanide, we do not concur with the view as to the weaker σ donor ability of the carbonyl group. This is most easily illustrated by a comparison of the orbital occupations in Table IX of the carbonyl 5σ orbital in $Mn(CO)_6^+$ with that of the $7a_1$ orbital in $Mn(CNCH_3)_6^+$. The greater orbital occupation of the $7a_1$ orbital indicates that the methyl isocyanide is acting as the weaker σ donor. The net result is that the 3d orbitals of manganese in $Mn(CO)_6^+$ contain 0.05 more electron than the counterpart orbitals in $Mn(CNCH_3)_6^+$. Since this latter observation contradicts the qualitative interpretation for the electrochemical studies mentioned in the previous paragraph, a different explanation for the experimental observations seems necessary. Our calculations provide us with an appropriate alternative.

Strictly speaking, the oxidation potential is a measure of the energy difference between the reduced and oxidized species including solvent effects and other variables. Nevertheless, since the electron removed comes out of the highest occupied molecular orbital (HOMO), it is reasonable to infer that, for a series of related species, the oxidation potential should show a correlation with the energy of the HOMO, with the more stable orbitals requiring greater energy for electron removal. Table X lists the HOMO energies *vs.* the oxidation potential for these species. Figure 5 displays a plot of these data. The correlation is excellent, with the negative slope in the figure indicating that the greater stability of the HOMO is responsible for the increased difficulty of oxidation as carbonyls are substituted for methyl isocyanides across the series. As we have already noted, this HOMO stabilization is not due to a greater positive charge on the metal since the electron density on the metal increases slightly through the series. We propose, therefore, that the existence of $Mn(CNCH_3)_6^{2+}$ and nonexistence of $Mn(CO)_6^{2+}$ is not a consequence of reduced σ-donating ability of carbonyl but rather is a result of the much greater HOMO stabilization in the carbonyl parent species with a resultant increased difficulty of oxidation.

A careful examination of our calculations indicates that the origin of the HOMO stabilization lies in the electron distributions within the ligand moieties. In the series, the electron population on a carbonyl carbon atom is less than that on the carbon atom of the methyl isocyanide adjacent to the metal. Consequently, the carbonyl carbon atoms carry greater positive charges than do their methyl isocyanide counterparts. Such positive charges in proximity to the transition metal have a stabilizing effect upon its 3d electrons and the resultant HOMO. Thus, the positive charge stabilization is not a direct one in the sense of having a higher charge on the metal but is indirect, through its near-neighbor interactions. Identification of this phenomenon is particularly relevant since there are computational methods in the literature which do not include such interactions in their calculational procedure.

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Registry No. $Mn(CO)_6^+$, 21331-06-6; $Mn(CO)_5(CNCH_3)^+$, 45113-87-9; $Mn(CO)_4(CNCH_3)_2^+$, 45146-17-6; $Mn(CO)_3(CNCH_3)_3^+$, 45167-07-5; $Mn(CO)_2(CNCH_3)_4^+$, 45186-22-9; $Mn(CO)(CNCH_3)_5^+$, 45211-82-3; $Mn(CO)_5Br$, 14516-54-2; $Mn(CO)_4(CNCH_3)Br$, 39048-79-8; $Mn(CO)_3(CNCH_3)_2Br$, 38833-18-0; $Mn(CO)_2(CNCH_3)_3Br$, 39043-33-9; $Mn(CO)(CNCH_3)_4Br$, 38833-19-1; $Fe(CNCH_3)_6^{2+}$, 17455-63-9; $Mn(CNCH_3)_6^+$, 45228-39-5; $Mn(CO)_5CN$, 15602-37-6; $Mn(CN)_6^{5-}$, 19567-57-8; $CNCH_3$, 593-75-9.

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The Ylide–Metal Complex. Preparations and Structures of Palladium(II) Complexes with a Stable Sulfur or a Nitrogen Ylide

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Palladium(II) complexes with a stable sulfur ylide, $PdCl_2L(Scy)$, $Pd_2Cl_4(PPhMe_2)_2(Scy)$, and $PdCl_2(Scy)_2$ [L = PPh_3, PPh_2Me, $AsPh_3$; Scy = $(CH_3)_2SC(CN)_2$], and with a nitrogen ylide, $PdCl_2L(Ncy)$ and $Pd_2Cl_4(Ncy)_2$ [L = PPh_3, PPh_2Me, $PPhMe_2$; Ncy = 3-$CH_3C_5H_4NC(CN)_2$], were prepared. Three types of coordination sites were found in Scy; Scy acts as a monodentate ligand through one nitrile group and the dimethylsulfonium sulfur and as a bidentate one through two nitrile groups to give the Scy-bridged dimer. The configurations of the complexes are elucidated on the basis of the analogy of Scy to tricyanomethanide anion and dimethyl sulfoxide. The difference of nucleophilicity between Scy and Ncy is discussed from their structures.

Introduction

To date, several publications have reported the reactions of various ylides with transition metal compounds, especially metal carbonyls, which are of interest in organometallic and organic reactions.[1-8] These studies primarily concern the use of ylides as a substrate in organometallic reactions. On the other hand, there have been few reports on metal complexes with ylides as ligand molecules.[9-12] Recently, we prepared some palladium(II) and platinum(II) halide complexes with stable sulfonium phenacylide $CH_3(C_6H_5)SCHC(O)C_6H_4Cl$-*p* and discussed the bonding character of the metal–ylide carbon bond.[13] The Scy and Ncy ylides used in the present study involve two cyano groups, which have more electron-withdrawing power than the carbonyl in the phenacylide, and therefore they are expected to be less reactive at the ylide carbon.

This paper reports the isolation of palladium(II) complexes with Scy and Ncy and their configurations. The nucleophilicity of these ylides is also discussed.

Experimental Section

Dimethylsulfonium dicyanomethylide, $(CH_3)_2SC(CN)_2$ (Scy),[14] and 3-methylpyridinium dicyanomethylide, 3-$CH_3C_5H_4NC(CN)_2$ (Ncy),[15] were prepared according to the literature.

All manipulations for preparing the ylide complexes were carried out in air.

Preparation of μ-(Dimethylsulfonium dicyanomethylide)-bis(di-