Table I. Highest Occupied and Lowest Four Unoccupied Molecular Orbitals of CNC_6H_5, with Percent Character Analysis in Terms of CN^- Canonical Orbitals and CN Atomic Orbitals[a]

		% CN^- MO's				% CN AO's			
MO	E, eV	4σ	1π	5σ	2π	C_s	C_p	N_s	N_p
$15a_1$	−13.24	31	0	67	0	40	56	1	1
$4b_2$	−2.44	0	3	0	29	0	27	0	5
$2a_2$	−0.84	0	0	0	0	0	0	0	0
$9b_1$	3.58	0	0	0	97	0	58	0	38
$5b_2$	5.84	0	0	0	54	0	29	0	25

[a] Symmetry labels are according to Cotton,[8] with the molecule lying in the xz plane.

Table II. Energy Levels of CNC_6H_4R as a Function of Substituents[a]

	Ring-π^*(CN)			π^*(CN)		
R	E	% C	% N	E	% C	% N
H	−2.44	27	5	3.58	58	38
o-CH_3	−2.28	26	5	3.71	58	39
m-CH_3	−2.37	28	5	3.60	58	38
p-CH_3	−2.06	28	5	3.73	58	39
p-CH_3O	−0.97	26	6	4.12	58	39
p-NO_2	−5.69	14	1	2.74	50	38
	0.43	28	12			

[a] Energies are in eV. r(CN) = 1.12 Å; other coordinates and conformations are from ref 9.

I the important MO's of CNC_6H_5 are expressed as percent characters of the CN^- fragment as well as the C and N atomic orbitals.

Several features of the MO's of CNC_6H_5 should be noted. The $15a_1$ orbital is essentially a lone pair on the CN carbon composed primarily of the 5σ orbital of CN^-. The interaction of the $3b_2$ orbital of the $C_6H_5^+$ fragment with the out-of-plane CN^- 2π (and, to a lesser extent, the 1π) produces the bonding and antibonding combinations $4b_2$ and $5b_2$. The $4b_2$ orbital has a greater amount of ring character than CN character and will be denoted a ring-π^*(CN) orbital. The $2a_2$ orbital is the unperturbed $2a_2$ orbital of $C_6H_5^+$. It is localized on the ring and will have negligible interaction with a metal center. The $9b_1$ orbital is essentially the in-plane 2π orbital of CN^-, perturbed slightly by the σ framework of the aryl ring, and is denoted a π^*(CN) orbital. As in CN^-, it is localized chiefly on the carbon and is strongly antibonding between the carbon and nitrogen.

In Table II the effects on the ring-π^*(CN) and π^*(CN) orbitals of changing the substituents on the aryl ring can be seen. As would be expected, a more electron-donating substituent on the ring, for example p-CH_3O, destabilizes the MO's relative to CNC_6H_5 while a more electron-withdrawing substituent, such as p-NO_2, stabilizes the MO's (the analysis of p-$CNC_6H_4NO_5$ is further complicated by interaction of the π system of the nitro group with that of the rest of the molecule, which results in two ring-π^*(CN) orbitals). It is important to note the relative insensitivity of the π^*(CN) orbital energy compared to that of the ring-π^*(CN) orbital. The insensitivity of the π^*(CN) level to change in substituent in conjunction with a constant gross ligand environment around the metal (and hence approximately the same atomic 3d level) indicates that the π^*(CN) levels should back-accept to about the same degree regardless of ring substituent. The extent of back-bonding to the π^*(CN) orbital will have a great effect on ν(CN) due to its strongly antibonding character. The ring-π^*(CN) orbitals, however, have essentially no nitrogen character and are therefore nonbonding between the carbon and nitrogen of the CN group. If one makes the reasonable assumption that contributions to a nonbonding orbital will not significantly affect the stretching frequency, then it follows that ν(CN) for the complex will primarily be a function of the π donation to the π^*(CN) orbitals. However, as indicated, such donation is expected to be constant and hence the values of ν(CN) are expected to be constant, as is observed. In contrast, the ring-π^*(CN) are energetically much closer to the metal $d\pi$ orbitals, and their interaction with the metal will determine the HOMO energy of the complex. Because of the energetics, the energy of the HOMO will be quite sensitive to large substituent-induced changes in the ring-π^* energy level, as reflected in the electrochemical data. It is appropriate to note that the σ-donating lone pair ($15a_1$ in CNC_6H_5) is almost entirely localized on the CN fragment (97–98% throughout the series) and is essentially invariant to ring substituents. This is reflected in the constancy of the σ eigenvalues (−13.4 ± 0.6 eV) for the entire series. Based upon this, σ donation is expected to remain constant throughout the series and should have little or no effect on the experimental differences within it. Thus it is the conjugation of the aryl ring with the π system of the CN group which produces two π-accepting ligand orbitals of very different character, which, in turn, have different effects on the experimental observables in aryl isocyanide–metal complexes.[10]

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Registry No. CNC_6H_5, 931-54-4; CNC_6H_4-o-CH_3, 10468-64-1; CNC_6H_4-m-CH_3, 20600-54-8; CNC_6H_4-p-CH_3, 7175-47-5; CNC_6H_4-p-CH_3O, 10349-38-9; CNC_6H_4-p-NO_2, 1984-23-2.

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(10) The expected MO scheme for the full complex will be similar to the qualitative scheme proposed by Mann et al.[6]

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Use of Oxygen 1s Binding Energies and Multiplicity-Weighted C–O Stretching Frequencies to Measure Back-Bonding in Transition Metal–Carbonyl Complexes

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Back-bonding in a transition metal carbonyl involves a decrease in the C–O bond order of the carbon monoxide ligand

$$^-M{-}C{\equiv}O^+ \longleftrightarrow M{=}C{=}O$$

Because a decrease of bond order corresponds to a decrease

Table I. Correlation of Oxygen 1s Binding Energies of Carbonyl Complexes with Back-Bonding

Carbonyl compd	E_B(O 1s), eV	$\langle\nu_{CO}\rangle$, cm^{-1}	$n_V + n_{CO}$	$\langle\nu_{CO}\rangle$ ref
$C_6H_6Cr(CO)_3$	538.23	1938	10	6
$C_7H_7V(CO)_3$	538.6	1935	10	7
$C_5H_5V(CO)_4$	538.7	1963	10	8
$C_5H_5(CH_3)Mo(CO)_3$	538.8	1971	10	9
$C_5H_5Mn(CO)_3$	538.85	1974	11	10
$Mn_2(CO)_{10}$	538.89	2017	12	10
$C_7H_8Fe(CO)_3$	539.09	2004	12	11
$CH_3(OCH_3)CCr(CO)_5$	539.1	1984	12	12
$C_4H_6Fe(CO)_3$	539.29	2005	12	13
$W(CO)_6$	539.52	2017	12	10
$Mo(CO)_6$	539.61	2021	12	10
$CH_3Re(CO)_5$	539.64	2033	12	14
$Cr(CO)_6$	539.66	2018	12	10
$HMn(CO)_5$	539.84	2039	12	15
$CH_3Mn(CO)_5$	539.87	2032	12	16
$V(CO)_6$	539.9		11	
$CH_3COMn(CO)_5$	539.92	2038	12.5	17
$Fe(CO)_5$	540.00	2035	13	10
$Ni(CO)_4$	540.11	2066	14	10
$Cl_3SiMn(CO)_5$	540.31	2058	13	18

of bond strength, the C–O stretching frequencies (or the derived force constants) of transition metal carbonyls have commonly been used to measure the degree of back-bonding. Unfortunately there are very few other physical properties which can be used to measure back-bonding and which are correlated with the stretching frequencies or force constants. Carbon-13 NMR chemical shifts have been shown to be related to the degree of back-bonding in carbonyls,[1] but good correlations with C–O stretching frequencies have been obtained only for restricted sets of compounds, in which the structures are very similar.[2]

Because back-bonding in a carbonyl involves a shift of negative charge from the metal atom to the oxygen atoms of the CO ligands, we anticipated that O 1s binding energies would be closely correlated with back-bonding. During the last few years we have measured these binding energies for a wide variety of transition metal–carbonyl complexes in which the CO ligands are terminally bound.[3-5] The data are given in Table I. One would expect a correlation of the O 1s binding energies with the corresponding C–O stretching force constants. Unfortunately the force constants have not been calculated for all the molecules in Table I and could not be readily calculated without making some rather poor approximations. As an alternative to the use of force constants, we have used the multiplicity-weighted averages of the C–O stretching frequencies,[6-18] $\langle\nu_{CO}\rangle$. These values, also listed in Table I, were calculated from literature assignments of the frequencies by giving a weight of 1 to those of A or B symmetry, a weight of 2 to those of E symmetry, and a weight of 3 to those of T symmetry. A plot of E_B(O 1s) vs. $\langle\nu_{CO}\rangle$, given in Figure 1, shows that these quantities are closely correlated.[19] The straight line through the points corresponds to the equation $E_B(\text{O 1s}) = 0.0146\langle\nu_{CO}\rangle + 510.00$. We believe that this correlation is strong evidence that both E_B(O 1s) and $\langle\nu_{CO}\rangle$ can be used to measure back-bonding in carbonyl complexes.

It is of considerable interest to know what structural and electronic factors are important in determining that one carbonyl has a large amount of back-bonding and that another has a relatively small amount of back-bonding. One would expect, other things being equal,[20] that a low effective nuclear charge on the metal atom would be conducive to back-bonding. The effective nuclear charge of the metal atoms in carbonyl complexes probably increases fairly regularly as the position of the metal in the periodic table moves from left to right. Hence we can use n_V, the number of valence electrons on the *free* metal atom, as a parameter linearly related to the effective nuclear charge of the metal in a carbonyl complex.

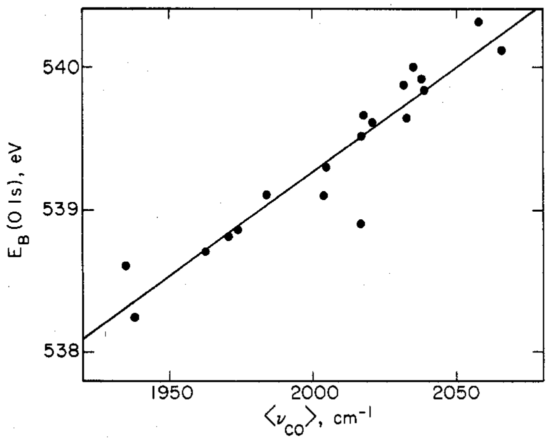

Figure 1. Oxygen 1s binding energies for carbonyl complexes vs. the multiplicity-weighted C–O stretching frequencies. Data are given in Table I.

Another factor expected to influence the degree of back-bonding in a metal–carbon monoxide linkage is the competition for metal dπ electrons due to other carbonyl groups bonded to the metal and due to other back-bonding ligands. The back-bonding in a carbonyl linkage should decrease with an increase in n_{CO}, defined as the total number of coordinated carbonyl groups and groups equivalent to carbonyl groups. In the case of carbonyl complexes containing ligands other than CO, we assume somewhat arbitrarily (although in fair agreement with prevailing opinions[21] regarding the back-bonding abilities of ligands) that each of the following ligands is equivalent, as a π acceptor, to one CO group: C_7H_8 (η^4), C_6H_6, C_5H_5, C_4H_6, $CH_3(OCH_3)C$, $SiCl_3$. We also assume that the C_7H_7 ligand is equivalent to two CO's, that the CH_3CO ligand is equivalent to one-half CO, and that the H atom and CH_3 group have no π-acceptor character.

Back-bonding should decrease with an increase in either n_V or n_{CO}. Although it is not clear that the terms should be weighted equally, we have used the simple sum $n_V + n_{CO}$ as a parameter which is expected to correlate with E_B(O 1s). The values of the parameter ($n_V + n_{CO}$) are given in Table I. It can be seen that there is a definite correlation[22] between ($n_V + n_{CO}$) and E_B(O 1s). Although the correlation is not as good as that between $\langle\nu_{CO}\rangle$ and E_B(O 1s), it is clear that our ideas regarding the fundamental nature of back-bonding are qualitatively sound. The ($n_V + n_{CO}$) value for $V(CO)_6$ is out of line perhaps because the vanadium atom in this compound is one electron short of the krypton effective atomic number. This electron deficiency would be expected to make the vanadium atom a relatively poor dπ donor.

When the appropriate XPS data become available, it will be of interest to test the correlations which we have observed with data for bridging carbonyl groups.

Experimental Section

All spectra were obtained with samples in the gas phase. Except in the case of $Fe(CO)_5$, the old Berkeley iron-free magnetic spectrometer and previously described procedures were used.[23,24] Differences between some of the data of Table I and previously published data are due to a spectrometer recalibration and the present use of the value 248.62 eV for the Ar $2p_{3/2}$ reference.[25] The spectrum of $Fe(CO)_5$ was obtained using the Uppsala high-resolution spectrometer;[26] the O 1s binding energy was measured relative to that for CO, 542.57 eV. The binding energies given to two decimal places have probable errors of ±0.05 eV; those given to one decimal place have probable errors of ±0.1 eV.

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Registry No. $C_6H_6Cr(CO)_3$, 12082-08-5; $C_7H_7V(CO)_3$, 12083-16-8; $C_5H_5V(CO)_4$, 12108-04-2; $C_5H_5(CH_3)Mo(CO)_3$, 12082-25-6; $C_5H_5Mn(CO)_3$, 12079-65-1; $Mn_2(CO)_{10}$, 10170-69-1; $C_7H_8Fe(CO)_3$, 12145-94-7; $CH_3(OCH_3)CCr(CO)_5$, 20540-69-6; $C_4H_6Fe(CO)_3$, 12078-32-9; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; $CH_3Re(CO)_5$, 14524-92-6; $Cr(CO)_6$, 13007-92-6; $HMn(CO)_5$, 16972-33-1; $CH_3Mn(CO)_5$, 13601-24-6; $V(CO)_6$, 14024-00-1; $CH_3COMn(CO)_5$, 13963-91-2; $Fe(CO)_5$, 13463-40-6; $Ni(CO)_4$, 13463-39-3; $Cl_3SiMn(CO)_5$, 15488-10-5.

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Reactions of Coordinated Ligands. Selective Hydrogenation of α-Diimine Linkages in Complexes of Cobalt(III) with Macrocyclic Ligands

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The rapid expansion in the field of complexes of synthetic macrocyclic ligands can be traced to the application of novel chemical reactions to the synthesis of these materials. Thus, coordination template reactions,[1-3] metal ion promoted oxidative dehydrogenation reactions,[4-6] hydrogenation reactions of the free[7] and coordinated macrocycles,[1,3] and oxidation reactions of the chelate rings[8] have all led to new and important complexes; and for some macrocyclic ligands, these techniques remain as their only mode of preparation.

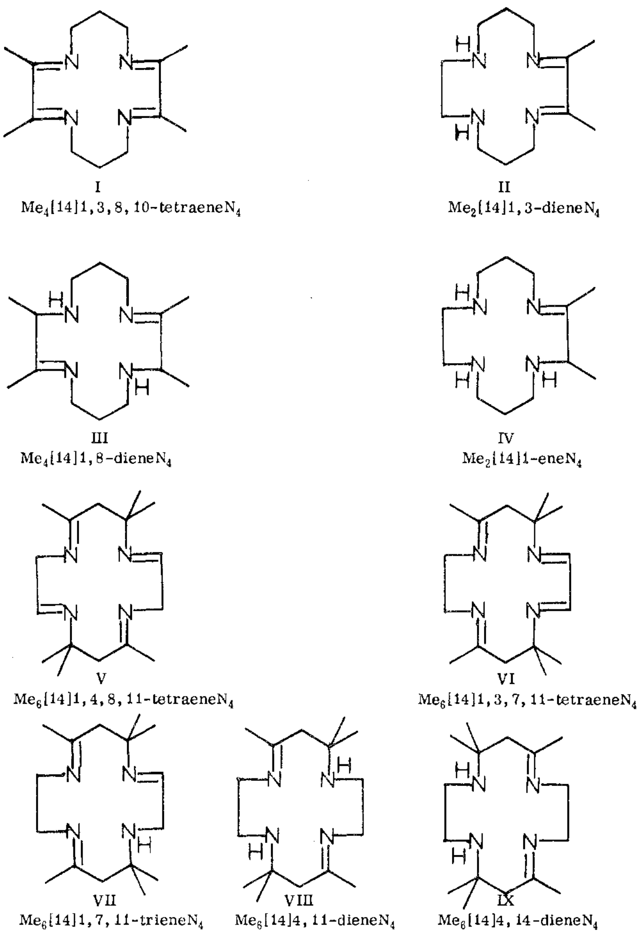

Figure 1. The macrocyclic ligands, showing the number of methyl substituents, the ring size in brackets, and the number and positions of unsaturation.[18,22]

We report here a structure-specific reduction which has led to the synthesis and characterization of new 14-membered macrocyclic complexes of cobalt(III), in which the macrocyclic ligands contain either one or two coordinated azomethine functions in the five-membered chelate rings. Hypophosphorous acid has been used as the reducing agent and it has been found to be specific for hydrogenation of one of a pair of coordinated conjugated imine double bonds. Addition of the acid to the cobalt(III) complexes (Figure 1) of $Me_4[14]1,3,8,10$-tetraeneN_4 (I) and $Me_2[14]1,3$-dieneN_4 (II) yields the cobalt(III) complexes of $Me_4[14]1,8$-dieneN_4 (III) and $Me_2[14]1$-eneN_4 (IV), respectively, as the only products. Unlike other common reducing agents, such as $NaBH_4$,[6,7,9,10] H_2/Pt,[11-13] or NaOH/Ni–Al,[11,14] which readily hydrogenate all of the imine functions present, hypophosphorous acid will not reduce isolated imine functions under our experimental conditions.

The results of electrochemical studies on broad series of complexes with macrocyclic ligands suggested that suitable reagents might lead to selective reductions of the kinds reported here.[15,16] In the case of nickel(II) complexes with macrocyclic ligands, one-electron reduction generally produces species that have been identified by ESR spectroscopy as nickel(I) derivatives.[16] In contrast, one-electron reduction of nickel(II) complexes of ligands that contain α-diimine linkages proceeds at relatively moderate potentials and the reduction products exhibit ESR spectra that signal the presence of free radicals. This has been explained as involving electron addition to the relatively low-energy π* orbital of the conjugated α-diimine moiety. It is reasonable to extend this reasoning to explain