Table II. Deviations (Å) of Porphine Skeleton from Least-Squares Plane

Au	0.03	C7	0.54	C14	−0.27
N1	−0.05	C8	0.36	C15	0.21
C1	−0.28	C9	0.03	N4	0.05
C2	−0.41	C10	−0.17	C16	0.27
C3	−0.27	N3	0.04	C17	0.42
C4	−0.06	C11	−0.17	C18	0.35
C5	0.08	C12	−0.43	C19	0.05
N2	0.01	C13	−0.32	C20	−0.16
C6	0.16				

the chloroform carbon suggesting strongly that a weak hydrogen bond exists between the two atoms. The hydrogen of chloroform is highly acidic and is known to show such behavior in acetone solution.

Although the positions of the atoms of the porphine ring could not be determined with a high degree of certainty (±0.05 Å),[8] the standard deviation of the atoms from the least-squares plane was ±0.27 Å, with some atoms deviating up to 0.5 Å from the plane (Table II). Furthermore, the porphine ring shows a well-defined quasi S_4-$\bar{4}$ ruffling similar to that observed with (Cl)Mn(TPP),[6] (N_3)Mn(TPP),[7] and porphyrin diacids[9] where the pyrrole rings are tilted alternately up and down with respect to the $\bar{4}$ axis around the C_a–C_m bonds. Since the standard deviation from the plane is about 5 times the standard deviation in position, the ruffling and the symmetry of the porphine ring in (Cl)Au(TPP) are both highly significant. However, as with the Mn(TPP) structures, the underlying cause of the ruffling is not clear. The common feature of the central core region between the former covalent structures and the ionic (Cl)Au(TPP) is that both metals form strong interactions with the pyrrolic nitrogen atoms.

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Registry No. (Cl)Au(TPP), 61483-93-0.

Supplementary Material Available: Tables III and IV, listing the final atomic parameters of (Cl)Au(TPP) and chloroform of solvation (2 pages). Ordering information is given on any current masthead page.

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Substituent Effects on the Electronic Structure of Aryl Isocyanide–Transition Metal Complexes

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Hexakis(aryl isocyanide)manganese(I) compounds show a large variation in oxidation half-potential.[1,2] Members of the series $[Mn(CNC_6H_4R)_6]^+$ follow the sequence in $E_{1/2}$ values where R = p-OCH_3 < H ≈ o-, m-, p-CH_3 < p-NO_2. For a series of mixed methyl isocyanide–carbonyl complexes, we have previously shown a good correlation of $E_{1/2}$ value with the energy of the highest occupied molecular orbital (HOMO) of the complex which depends intimately on the nature of the π-bonded ligands.[3] The extent of π back-bonding will often be reflected in the stretching frequencies of the ligands,[3a,4] so one might expect to see variations in ν(CN) corresponding to the variations in $E_{1/2}$ for the series $[Mn(CNC_6H_4R)_6]^+$. Interestingly enough, ν(CN) is essentially invariant within the series, all having a strong CN stretch at 2089 ± 1 cm^{-1} (free-ligand values[1a] 2121 ± 4 cm^{-1}). In this note we reconcile the seemingly anomalous electrochemical and infrared data on the basis of nonempirical molecular calculations[5] on a series of aryl isocyanides, CNC_6H_4R (R = H, o-, m-, p-CH_3, p-OCH_3, p-NO_2).

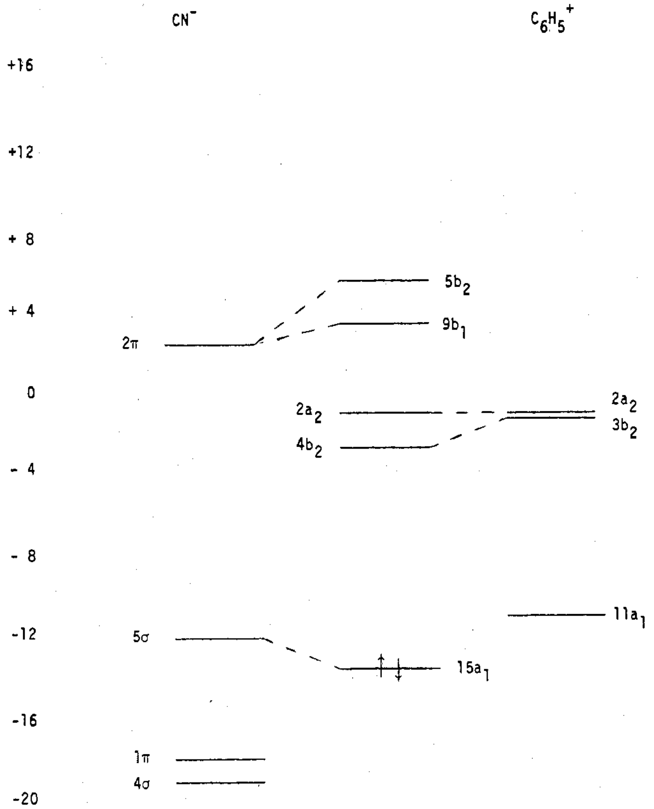

Figure 1. Bonding diagram of highest occupied and first four unoccupied molecular orbitals of CNC_6H_5. Contributions from the principal MO's of CN^- or $C_6H_5^+$ are shown. Energies are in eV.

The size of hexakis(aryl isocyanide) complexes has made their theoretical treatment difficult and studies to date have chiefly discussed the UV–visible spectra, on the basis of qualitative MO schemes for the complexes.[6] The theoretical treatment of the full complexes is further complicated by the lack of good structural data; the symmetry of such complexes is subject to much conjecture and spectral information does not provide an unambiguous answer.[6] Correlation of the UV–visible spectra also has been attempted on the basis of CNDO calculations on the free ligand.[7] The results of our calculations differ substantially from the CNDO results, particularly in the order of filled MO's. On the basis of what is reported by Fantucci et al., it is impossible to assess whether or not their calculations are consistent with the scheme presented here.

The MO scheme for CNC_6H_5 is representative of the entire series of substituted aryl isocyanides (Figure 1). Transformation into the canonical orbitals of CN^- and $C_6H_5^+$ was performed, which allows assessment of the bonding picture in terms of the molecular orbitals of the two fragments. In Table

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 dπ 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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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