Table III. Bond Distances and Angles for the $Ir(NO)(PPh_3)(O_2C_6Br_4)$ Molecule

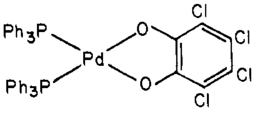
Distances (Å)

Ir–P	2.281 (6)	C3–C4	1.392 (30)
Ir–N	1.676 (22)	C4–C5	1.359 (28)
Ir–O2	2.008 (14)	C5–C6	1.381 (31)
Ir–O3	1.905 (14)	C6–C1	1.427 (30)
N–O1	1.186 (23)	C3–Br1	1.855 (22)
O2–C1	1.329 (24)	C4–Br2	1.845 (22)
O3–C2	1.345 (25)	C5–Br3	1.885 (21)
C1–C2	1.358 (28)	C6–Br4	1.833 (22)
C2–C3	1.367 (29)		

Selected Angles (Deg)

P–Ir–N	93.4 (6)	Ir–O2–C1	110.9 (13)
P–Ir–O2	168.8 (4)	Ir–O3–C2	114.9 (12)
P–Ir–O3	88.4 (4)	O2–C1–C2	117.6 (21)
N–Ir–O2	97.2 (7)	O2–C1–C6	123.8 (20)
N–Ir–O3	176.0 (8)	O3–C2–C1	115.3 (21)
O2–Ir–O3	81.2 (6)	O3–C2–C3	124.1 (19)
Ir–N–O1	177.8 (21)		

(2) Å for the Ir^- complexes $Ir(NO)_2(PPh_3)_2^+$, $Ir(NO)(CO)(PPh_3)_2$, and $Ir(NO)(PPh_3)_3$.[6-8] A length of 1.76 (2) Å was found for the Ir(0) complex $[Ir_2(NO)_2(PPh_3)_2]O$,[9] and a length of 1.68 (3) Å has been reported for the five-coordinate Ir(I) cation $Ir(H)(NO)(PPh_3)_3^+$.[10] The value of 1.676 (22) Å which we find for $Ir(NO)(PPh_3)(O_2C_6Br_4)$ is among the shortest lengths of this series. The Ir–P length of 2.281 (6) Å is also relatively short. Values found in the nitrosyl complexes above all exceed 2.31 Å and average to a length of 2.33 Å. Square-planar Ir(I) complexes with trans phosphine ligands also have values in this range.[11] The closely related palladium(II)–catecholate complex $Pd(PPh_3)(O_2C_6Cl_4)$ (III) has



III

Pd–P lengths which average to 2.286 (2) Å, a value which is nearly identical with the present length.[12] The Pd–O lengths of this structure are also closely related to the Ir–O length trans to the phosphine ligand. Palladium–oxygen lengths in this structure average to 2.033 (5) Å while the Ir–O2 length in the present case is 2.008 (14) Å. At the site trans to the nitrosyl ligand of $Ir(NO)(PPh_3)(O_2C_6Br_4)$ we find the Ir–O3 length to be 1.905 (14) Å, 0.10 Å *shorter* than the value for O2. This value is shorter than the Ir–O length of 1.941 (10) Å to the bridging oxo ligand of $[Ir_2(NO)_2(PPh_3)_2]O$ which is also located trans to a linear nitrosyl.[9]

The trend in Ir–O lengths found in this structure is contrary to what might be expected from the relative trans influences of the NO^+ and PPh_3 ligands. It can be understood if the catecholate ligand is viewed to be a strong π donor. Both the NO^+ and catecholate oxygens are strong σ donors, and the strong Ir–N bond would destabilize the trans Ir–O bond. The Ir–O3 length, however, appears anomalously short. As a strong π donor trans to the nitrosyl ligand, the synergistic bonding effect would serve to strengthen both the Ir–N and Ir–O3 bonds. There is indirect evidence for the π-donor strength of catecholate ligands in their molybdenum chemistry. They effectively replace oxo ligands from molybdenum, giving a series of oxygen deficient Mo(VI) complexes which are surprisingly inert to hydrolysis.[13] The oxo ligand is an effective π donor in its bonding with d^0 metals, and this property seems to also be true of the catecholates.

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Registry No. $Ir(NO)(PPh_3)(O_2C_6Br_4)\cdot CH_2Cl_2$, 73178-92-4.

Supplementary Material Available: A listing of structure factor amplitudes (×10) (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Theoretical Study of Vibrational Interaction Coordinates and π Bonding in Chromium Hexacarbonyl. Comparison with Cobalt Hexacyanide and Nickel Tetracarbonyl

David E. Sherwood, Jr., and Michael B. Hall*

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Chromium hexacarbonyl has been extensively studied, both experimentally and theoretically, as a model system for transition-metal–carbon monoxide bonding. The near-zero-valent carbonyl complexes known suggest a synergistic effect, i.e., L → M σ donation balanced by M → L π acceptance. Values for these parameters are not readily accessible experimentally, and their magnitudes and relative importance are still being argued in the literature today.

Klemperer and Johnson have recently reported the results of scattered-wave Xα calculations (SW–Xα) for $Cr(CO)_6$.[1] Their results indicate that σ donation is the only important interaction for the metal–carbon bond and that the Cr 3dπ → CO 2π back-bonding strongly affects only the carbon–oxygen bonds. This is in direct conflict with earlier molecular orbital (MO) studies such as self-consistent charge and configuration (SCCC),[2] Hartree–Fock–Roothaan (HFR),[3] discreet variational Xα (DV–Xα),[4] and Fenske–Hall[5] MO calculations, which have been successfully used to interpret the ultraviolet adsorption spectrum[2] and low-energy photoelectron spectrum[3-5] of $Cr(CO)_6$, as has the more recent SW–Xα results. Unique to the SW–Xα study was its ability to rationalize the interaction coordinate analysis of the vibrational spectrum of $Cr(CO)_6$ by Jones et al.,[6] where it was shown that stretching a single metal–carbon bond ($Cr–C_0$, Figure 1) significantly affects only the trans metal–carbon bond ($Cr–C_t$). The cis metal–carbon bonds ($Cr–C_c$) are essentially unchanged. Although no attempt was made to calculate the interaction coordinates, this trans effect was used as confirmation of the SW–Xα σ-only bonding scheme. However, stretching the $C_0–O_0$ bond also causes changes in chromium–carbon bonding,

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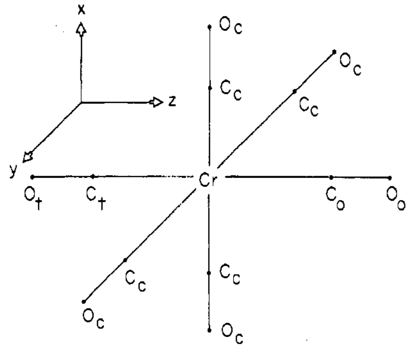

Figure 1. Coordinate system and atom labels for chromium hexacarbonyl.

and these changes are expected to be π dominated. This study will show that the interaction coordinates can best be interpreted in a framework of moderately strong Cr–C π bonding by quantitatively predicting the changes in all the bonds of $Cr(CO)_6$ for both the Cr–C_0 and C_0–O_0 stretches.

We have also considered the interaction coordinate response of two additional systems: cobalt hexacyanide ($Co(CN)_6^{3-}$) and nickel tetracarbonyl ($Ni(CO)_4$). The cobalt hexacyanide, which is isoelectronic with $Cr(CO)_6$, represents a system with weaker π acceptors, and its interaction coordinates should be even more strongly σ dominated. The major difference between $Ni(CO)_4$ and $Cr(CO)_6$ should arise from the changes in coordination geometry. The degree of π back-bonding in this system has also been the subject of considerable controversy. Johnson and Wahlgren have stated that π back-bonding is unimportant for the Ni–C bond, on the basis of results of their interpretation of SW–Xα calculations on $Ni(CO)_4$.[7] Recently, Bursten et al.[8] have projected the SW–Xα electron densities on to atomic orbital representations and have found considerable occupancy of CO 2π molecular orbitals and therefore strong $3d\pi \rightarrow$ CO 2π back-bonding. This compares well with other types of calculations[3,4] and with a recent reinterpretation of the SW–Xα by Larsson and Braga.[9]

Theory

The interaction coordinate $(j)_i$ is defined as the response of the jth bond when the ith bond is perturbed by a unit displacement.[10] The interaction coordinates are unitless quantities, and, hence, the response of the jth bond when the ith bond is stretched is of equal magnitude but of opposite sign to the response of the jth bond when the ith bond is compressed. In order to calculate the $(j)_i$ values, we have made use of the electron-preceding principle,[11] i.e., if one performs a molecular orbital calculation with a geometry perturbed from the ground state (in this case stretching or compressing the ith bond), changes in overlap populations will indicate how the individual atoms of a molecule would move if the geometry were allowed to relax. For the ith bond the negative of the change in overlap population represents the density change needed to restore the ith bond to its equilibrium position. To simplify our model, we have assumed a linear relationship between the calculated change in overlap populations and the expected change in geometry (interaction coordinates $(j)_i$). For an increase in numerical accuracy (some changes in overlap populations being quite small), all values computed are differences between stretched and compressed geometries. For purpose of discussion, positive values of $(j)_i$ indicate that the jth bond stretches, while negative values indicate that the jth bond compresses, when the ith bond is stretched.

Before discussing the molecular orbital approach used in predicting the $(j)_i$ values, we will briefly mention how these values are derived from the experimental data (IR frequencies). The values of $(j)_i$ are ratios of compliance constants,[12] $(j)_i = C_{ij}/C_{ii}$, where the compliance constant matrix (**C**) is the inverse of the force matrix (**F**). One can either use the **G** matrix method to find **F** and invert this to produce **C** or use the $\mathbf{G}^{-1}$ matrix method to solve directly for **C**. Both will yield identical results if all the parameters are known; however, often one has less information available than the number of unknowns, and certain simplifying assumptions must be made. Certain interactions may be set to zero or based on similar molecules. Ionic corrections must also be made for charged species. The results of refining the experimental frequencies are, thus, only a model thermselves, and their statistical accuracy may be misleading because other solutions with different assumptions may fit the experimental frequencies as closely yet yield somewhat different values for $(j)_i$.

As an alternative to our approach of estimating the interaction coordinates from overlap polulations, one could attempt to calculate the potential energy surface and to solve directly for the force constant matrix.[13] This method has successfully been used recently to predict the interaction coordinates for several molecules of main group elements.[14] This direct method may or may not give better values for interaction coordinates; its accuracy will depend on the type of calculation. The size and expense of studying large systems limit us to a more approximate technique which works reasonably well for transition-metal complexes.

Parameter-free, Fenske–Hall MO calculations[15] have been carried out on $Cr(CO)_6$, $[Co(CN)_6]^{3-}$, and $Ni(CO)_4$. The atomic basis set of Clementi was used for the C, O, and N,[16] and the *s* functions were reduced to a single exponent.[17] Richardson's atomic functions were used for the Cr, Co, and Ni,[18] and the 4s and 4p exponents were all 2.0.[19] This basis set has been successfully used in several previous force constant analyses.[20] The experimental bond lengths for $Cr(CO)_6$[21] and $[Co(CN)_6^{3-}]$[22] were used with perfect octahedral coordination. The bond lengths for $Ni(CO)_4$ were those used by Mitcheson and Hillier[23] with perfect tetrahedral coordination. Metal–carbon bond strength was approximated by summing the overlap populations between the M 3d and C 2s, 2p orbitals. Carbon–X bond strength (X = O or N) was approximated by summing the C 2s, 2p and X 2s, 2p overlap populations. For the carbonyl complexes basis-set transformations, based on free CO at the same internuclear distance, were used for direct calculations of the Mulliken polulations of each carbonyl's 5σ and 2π molecular orbitals.

Results and Discussion

$Cr(CO)_6$. To simulate a chromium–carbonyl stretch, we

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Table I. Change in Overlap Populations and Interaction Coordinates for $Cr(CO)_6$

	change in overlap pop.			predicted change in bond lengths, A	predicted interacn coordinates $(l)_k$	exptl interactn coordinates[a] $(l)_k$
	σ	π	total			
$(\mathrm{Cr-C_0})_{\mathrm{Cr-C_0}}$	−0.035 60	−0.071 52	−0.107 12	0.3828	1.0	1.0
$(\mathrm{Cr-C_t})_{\mathrm{Cr-C_0}}$	0.012 17	0.010 62	0.022 79	−0.0814	−0.213	−0.228
$(\mathrm{Cr-C_c})_{\mathrm{Cr-C_0}}$	−0.001 92	0.005 73	0.003 81	−0.0136	−0.035	−0.005[b]
$(\mathrm{C_0-O_0})_{\mathrm{Cr-C_0}}$	−0.020 93	0.045 54	0.024 61	−0.0319	−0.083	−0.045
$(\mathrm{C_t-O_t})_{\mathrm{Cr-C_0}}$	0.000 92	−0.009 42	−0.008 50	0.0110	0.029	0.019
$(\mathrm{C_c-O_c})_{\mathrm{Cr-C_0}}$	−0.000 68	−0.003 98	−0.004 66	0.0061	0.016	0.004
$(\mathrm{Cr-C_0})_{\mathrm{C_0-O_0}}$	0.002 67	0.039 59	0.042 26	−0.1510	−0.659	−0.401
$(\mathrm{Cr-C_t})_{\mathrm{C_0-O_0}}$	−0.000 90	−0.009 82	−0.010 72	0.0383	0.167	0.164
$(\mathrm{Cr-C_c})_{\mathrm{C_0-O_0}}$	0.000 16	−0.006 46	−0.006 30	0.0225	0.098	0.037
$(\mathrm{C_0-O_0})_{\mathrm{C_0-O_0}}$	−0.017 97	−0.158 44	−0.176 41	0.2290	1.0	1.0
$(\mathrm{C_t-O_t})_{\mathrm{C_0-O_0}}$	−0.000 04	0.009 47	0.009 43	−0.0122	−0.053	−0.011
$(\mathrm{C_c-O_c})_{\mathrm{C_0-O_0}}$	0.000 82	0.004 39	0.005 21	−0.0068	−0.029	−0.013

[a] Reference 6. [b] The value for $Cr(CO)_6$ is statistically different from those of Mo and W analogues, where for Cr the value is 0.004 and for Mo and W the value is −0.013. The value in this table is the average of these two values.

increased the $Cr–C_0$ bond length ($d_{Cr–C_0}$) 10% of its equilibrium bond length, keeping the $C_0–O_0$ and $Cr(CO)_5$ geometry fixed. To simulate a carbon–oxygen stretch, we increased the $C_0–O_0$ bond length ($d_{C_0–O_0}$) 10% of its equilibrium bond length, keeping the $(CO)_5$ $Cr–C_0$ geometry fixed. Bond compressions were done in a similar way. The calculated changes in the overlap populations are based on the stretched minus the compressed states and are shown in Table I. For a check on the linearity of this system, calculations were performed at several different distances and the overlap populations of all the bonds were remarkably linear over a wide range of stretches (±5%, ±10%, ±15%). Although stretches that occur upon IR irradiation are very small, the value of 10% was chosen as a standard for this study as it is in the linear region and gives reasonably large values for changes in overlap populations. The coordinate response to a change in bond order for Cr–C and C–O bonds are different, the carbon–oxygen internuclear distance changing only slightly with change in bond order for multiply bonded CO.[24] For a chromium–carbon bond the calculated response factor was −3.57 Å for a unit increase in overlap populations (on the basis of change in the $Cr–C_0$ overlap populations when $d_{Cr–C_0}$ was increased). For a carbon–oxygen bond this response factor was −1.30 Å for a unit increase in overlap populations (on the basis of change in the $C_0–O_0$ overlap populations when $d_{C_0–O_0}$ was increased). With the coordinate response factors the change in overlap population for each bond of $Cr(CO)_6$ was converted into a corresponding change in bond distance (Table I). Interaction coordinates (Table I) were predicted by putting these changes in bond distances relative to the change in bond distance of the stretched moiety.

Overlap population analysis for the Cr–C bonds of $Cr(CO)_6$ in the ground state was symmetry factored into σ (55%) and π (45%) contributions. The $Cr–C_c$ σ bonds which are in the xy plane (see Figure 1) are 75% with the Cr $d_{x^2-y^2}$ orbital and 25% with the Cr d_{z^2} ring.[25] For $Cr–C_0$ and $Cr–C_t$ the σ bonds are 100% with the d_{z^2} orbital. Table I shows the overlap populations and resultant interaction coordinates for a chromium–carbon (subscript $Cr–C_0$) stretch. When the $Cr–C_0$ bond is stretched, the largest bond change is that of the $Cr–C_0$ bond itself (i.e., the interaction coordinates are at least 0.2 times smaller). The next largest effect is the strengthening of the $Cr–C_t$ bond and the third largest is the strengthening of the $C_0–O_0$ bond. These theoretical predictions are in complete accord with the experimental results.

Table II. Mulliken Population Analysis for Carbonyl Molecular Orbitals of $Cr(CO)_6$

carbonyl MO		ground state	$Cr–C_0$ str[a]	$\Delta(Cr–C_0)$	$C_0–O_0$ str[a]	$\Delta(C_0–O_0)$
$C_t–O_t$	5σ	1.524 84	1.516 26	−0.008 58	1.525 69	0.000 85
$C_t–O_t$	2π	0.509 37	0.533 31	0.023 94	0.485 78	−0.024 59
$C_c–O_c$	5σ	1.524 84	1.531 73	0.006 89	1.518 75	−0.006 09
$C_c–O_c$	2π	0.509 37	0.515 49	0.006 12	0.503 29	−0.006 08

[a] 10% of the equilibrium bond distance.

The $(Cr–C_c)_{Cr–C_0}$ interaction coordinate is negligible experimentally, and our value, while somewhat large, is an order of magnitude smaller than $(Cr–C_t)_{Cr–C_0}$. This small discrepency arises, in part, because the total change in overlap populations for the $Cr–C_c$ bond is the smallest calculated and hence the most uncertain. The cis and trans CO bonds are slightly weakened and the small, positive interaction coordinates are in good agreement with those predicted.

When the $Cr–C_0$ bond is stretched, the $C_0–O_0$ moiety becomes both a poorer σ donor and a poorer π acceptor. Both of these effects reduce the $Cr–C_0$ bond order which loses more π (61%) than σ (39%) interaction, as expected, since the π overlap integral will be reduced more drastically than the σ when stretching a bond. This decrease in Cr $3d\pi \rightarrow C_0–O_0$ 2π donation causes a large increase in the $C_0–O_0$ overlap population, but its relatively small coordinate response to this change produces a smaller interaction coordinate (still the second largest). The loss of $Cr–C_0$ π interaction on stretching this bond is compensated for by an increase in π interaction with both the cis and trans carbonyls. The π change for the $Cr–C_c$ bond is about half as much as for the $Cr–C_t$ bond, as expected, since both $3d\pi$ orbitals interact with the trans carbonyl whereas only one $3d\pi$ orbital interacts with each cis carbonyl. The σ interactions are somewhat more complicated. The occupied 3d metal–carbon-bonding orbital ($3d_{z^2} + 5\sigma$) is 36.0% d_{z^2} and 13.9% C (each) in $Cr(CO)_6$ at the equilibrium geometry. On stretching of the $Cr–C_0$ bond the character changes to 33.6% d_{z^2}, 12.6% C_0, 13.1% C_c, and 21.1% C_t. These changes result in a large increase in the $Cr–C_t$ overlap population and a small decrease in the $Cr–C_c$ overlap population. Our calculations show that, for the $Cr–C_t$ bond, increased σ interaction accounts for 53% of the bond order increase, the remainder being accounted for by increased π interactions. For the $Cr–C_c$ bond, the negative change in σ interaction counterbalances the gain in π bonding, leading to a small change in bond strength and a small interaction coordinate. The interaction coordinates for cis and trans C–O bonds, when $Cr–C_0$ is stretched, are easily understood in light of the changes in Mulliken populations (Table II). The

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Table III. Change in Overlap Populations and Interaction Coordinates for $Co(CN)_6^{3-}$

	change in overlap pop.			predicted change in bond lengths, Å	predicted interacn coordinates $(l)_k$	exptl interacn coordinates[a] $(l)_k$
	σ	π	total			
$(Co–C_0)_{Co–C_0}$	−0.026 96	−0.040 96	−0.067 92	0.3780	1.0	1.0
$(Co–C_t)_{Co–C_0}$	0.010 01	0.002 76	0.012 77	−0.0711	−0.188	−0.23
$(Co–C_c)_{Co–C_0}$	−0.000 97	0.001 73	0.000 76	−0.0042	−0.011	−0.008
$(C_0–N_0)_{Co–C_0}$	−0.014 99	0.025 92	0.010 93	−0.0163	−0.043	−0.011
$(C_t–N_t)_{Co–C_0}$	0.001 45	−0.001 92	−0.000 47	0.0007	0.002	−0.002
$(C_c–N_c)_{Co–C_0}$	−0.000 97	−0.000 86	−0.001 83	0.0027	0.007	−0.001
$(Co–C_0)_{C_0–N_0}$	−0.002 00	0.016 38	0.014 38	−0.0800	−0.345	−0.104
$(Co–C_t)_{C_0–N_0}$	0.000 69	−0.001 78	−0.001 09	0.0061	0.026	−0.017
$(Co–C_c)_{C_0–N_0}$	−0.000 25	−0.001 92	−0.002 17	0.0121	0.052	−0.007
$(C_0–N_0)_{C_0–N_0}$	−0.020 41	−0.135 27	−0.155 68	0.2320	1.0	1.0
$(C_t–N_t)_{C_0–N_0}$	0.000 54	0.001 76	0.002 30	−0.0032	−0.017	0.005
$(C_c–N_c)_{C_0–N_0}$	0.000 84	0.001 73	0.002 57	−0.0038	−0.014	−0.003

[a] Reference 26.

changes are π dominated for both cis and trans carbonyls, with increased 2π occupation weakening the bonds, more so for the C_t–O_t bond.

Table I also shows the overlap populations and resultant interaction coordinates for the carbon–oxygen (subscript C_0–O_0) stretch. Weakening the C_0–O_0 bond causes a large Cr–C_0 bond order increase as shown by the large $(Cr–C_0)_{C_0–O_0}$ interaction coordinate. The resultant weakening of the other chromium–carbon bonds shows the trend, trans > cis, for both the predicted and experimental interaction coordinates. The C_t–O_t and C_c–O_c bonds are both strengthened. Because interactions of coordinates separated from the primary stretching coordinates are expected to occur to some extent via the rearrangement of the intermediate coordinates,[6] the predicted values for the cis and trans carbonyls are somewhat too large.

The bond order changes for $Cr(CO)_6$ upon stretching the C_0–O_0 bond are π dominated (i.e., the change in π overlap populations are all an order of magnitude greater than the σ changes). The large interaction coordinates found for the Cr–C bonds arise from π interactions and demonstrate the importance of chromium–carbon π bonding. If the strength of the chromium–carbon bond were totally σ dominated, the $(Cr–C)_{C_0–O_0}$ values would all be lowered by a factor of 5.0, which would be in very poor agreement with the experimental evidence. The increased Cr $3d\pi$ to C_0 donation leaves less Cr $3d\pi$-electron density available for bonding with the other carbonyls, and both the Cr–C_t and Cr–C_c bond orders decrease. The loss of 2π character causes both C_c–O_c and C_t–O_t bond orders to increase.

$Co(CN)_6^{3-}$. Calculations for the cobalt complex were done in the same manner as for $Cr(CO)_6$ (i.e., stretching or compressing the bond of interest and keeping the rest of the geometry fixed). The calculated changes in overlap population, based on the stretched minus the compressed geometries, are given in Table III. The overlap populations of $Co(CN)_6^{3-}$ were not as well behaved as those of $Cr(CO)_6$ particularly for the cis and trans CN bonds. Whereas the changes in overlap population were linear with respect to a stretch or a compression, the changes were very small and occasionally of the same sign for both a stretch and a compression. This indicates that a particular CN bond distance is extremely stable with respect to changes in bond lengths far removed from it in the complex. The coordinate response factor for the cobalt–carbon bond was −5.56 Å for a unit increase in overlap populations (based on the change in Co–C_0 overlap populations when $d_{Co–C_0}$ was increased). This value which is higher than that for $Cr(CO)_6$ is indicative of more ionic character in the Co–CN bond. For the carbon–nitrogen bond, the response factor was −1.49 Å for a unit increase in overlap population (based on the change in C_0–N_0 overlap populations when $d_{C_0–N_0}$ was increased). This value is close to the carbonyl value and again reflects the fact that the internuclear distance of triply bonded systems responds less to a change in bond order.

Bond order analysis for the Co–C bonds of $Co(CN)_6^{3-}$ was symmetry factored into σ (74%) and π (26%) contributions. This is consistent with the reduced ability of the CN ligand to accept π electrons from the metal atom compared to the CO ligand. Table III shows the overlap populations, predicted interaction coordinates, and the experimental ones[26] for the cobalt–carbon (subscript Co–C_0) stretch. Comparing the experimental values for $Co(CN)_6^{3-}$ with $Cr(CO)_6$, we see similar behavior for the cis and trans metal–carbon bonds with M–C stretch, but the values are smaller for the cyanide. Whereas the Co–C_0 bond exhibits less π character, when the Co–C_0 bond is stretched the reduction in bond order arises in the same manner as in $Cr(CO)_6$, i.e., loss of π bonding (60%) and loss of σ bonding (40%). The loss of Co–C_0 π interaction on stretching this bond is compensated for by an increase in π bonding with the cis and trans cyanides. Again the π change for the Co–C_c bond is about half as much as for the Cr–C_t bond. The σ changes of the cis and trans cobalt–carbon bonds are similar to $Cr(CO)_6$. In this case, however, the $(Co–C_t)_{Co–C_0}$ value is more σ dominated (78%) than the $(Cr–C_t)_{Cr–C_0}$ (53%). The change in σ bonding for the $(Co–C_c)_{Co–C_0}$ is again positive and cancels the increase in π bonding to give a small value for the $(Co–C_c)_{Co–C_0}$ interaction coordinate. Hence, even with the small π bonding expected for the cyanide complex, changes in bond strength must take into account changes in π bonding, because the π overlaps are reduced more drastically than σ overlaps when a bond is stretched. The changes in the cyanide responses to its own Co–C_0 stretch are expected to be π dominated since populating or depopulating the CN 2π orbitals will be the primary cause for changes in CN bond lengths. Comparing the predicted values for $Cr(CO)_6$ and $Co(CN)_6^{3-}$, we find that $(C_0–O_0)_{Cr–C_0} \simeq 2(C_0–N_0)_{Co–C_0}$, because stretching the CN away from the metal causes a much smaller 2π loss. The experimental values show an even larger change in the same direction. The trans and cis cyanides remain virtually unchanged for both the predicted and experimental values when a cobalt–carbon bond is stretched. These results indicate a reduction in the transmission of π effects for the $Co(CN)_6^{3-}$ compared with $Cr(CO)_6$.

Consideration of the interaction coordinates when the C_0–N_0 bond is stretched will make this even more apparent. In $Cr(CO)_6$ the metal–carbon bonds have strong π bonding, and when the C_0–O_0 bond is stretched, the π changes are easily transmitted through the central Cr atom to the other Cr–C bonds and affect the cis and trans carbonyl bonds as well. This

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(26) Swanson, B. I.; Satija, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 987. There are some typographical errors in Table IV which have been corrected in our Table III (Swanson, B. I., private communication).

Table IV. Change in Overlap Population and Interaction Coordinates for $Ni(CO)_4$

	total change in overlap pop.	predicted interacn coordinates $(l)_k$	exptl interacn coordinates[a] $(l)_k$
$(Ni-C_0)_{Ni-C_0}$	−0.085 06	1.0	1.0
$(Ni-C_r)_{Ni-C_0}$	0.001 67	−0.019	−0.07
$(C_0-O_0)_{Ni-C_0}$	0.028 20	−0.108	−0.03
$(C_r-O_r)_{Ni-C_0}$	−0.005 29	0.020	0.01
$(Ni-C_0)_{C_0-O_0}$	0.019 50	−0.362	−0.30
$(Ni-C_r)_{C_0-O_0}$	−0.001 62	0.030	0.07
$(C_0-O_0)_{C_0-O_0}$	−0.164 72	1.0	1.0
$(C_r-O_r)_{C_0-O_0}$	0.007 29	−0.044	−0.01

[a] Reference 26.

is not the case in $Co(CN)_6^{3-}$. All of the calculated interaction coordinates are smaller by at least a factor of 2.0. The experimental numbers are even smaller. The effect on $(Co-C_0)$ when the (C_0-N_0) bond is stretched is to make the 2π orbital of CN more accessible to the central Co atom for π bonding. Cyanide, however, does not have the donor–acceptor properties of CO and, hence, this value is much smaller in the cyanide case. This small increase in π bonding in the $Co-C_0$ bond causes decreased π bonding with the cis and trans Co–C bonds; however because the π coupling is much smaller, $(Co-C_t)_{C_0-N_0}$ is reduced by an order of magnitude compared with $(Cr-C_t)_{C_0-O_0}$ in our calculations. This change is the largest single difference between $Cr(CO)_6$ and $Co(CN)_6^{3-}$ interaction coordinates. The experimental number for $(Co-C_t)_{C_0-N_0}$ is negative. This result suggests that the $Co-C_t$ bond, rather than being weakened as in $Cr(CO)_6$, is actually strengthened slightly, but the sign of this number has recently been called into question.[27] Again, the cis and trans CN responses to stretching C_0-N_0, both experimental and theoretical, are much smaller than the corresponding carbonyl responses.

A word of caution is in order for the interaction coordinates of $Co(CN)_6^{3-}$. Our calculated values show the same signs as the experimental ones for $Cr(CO)_6$. The signs for both the calculated and experimental values also obey the relationship $(l)_m = (l)_k(k)_m$. The values obtained from reducing the IR data for $Co(CN)_6^{3-}$ often do not fit such relationships. The cobalt cyanide values vary depending on the cations present. The solution of the force field requires estimation of ionic terms which can also depend on the particular salt studied. Error bars on the small values may be as large as ±2 times their actual value; hence, some small discrepancies may appear between the experimental values and our predicted ones. In summary, the large changes on going from $Cr(CO)_6$ to $Co(CN)_6^{3-}$ are the reduction of $(Co-C_t)_{C_0-N_0}$ by a factor of 10 and the reduction $(C_0-N_0)_{Co-C_0}$ and $(Co-C_0)_{C_0-N_0}$ which are found in the experimentally derived and our calculated values.

$Ni(CO)_4$. The nickel tetracarbonyl calculations, again, employed 10% stretches or compressions of the bond of interest, while keeping the rest of the geometry fixed. The calculated change in overlap populations and predicted interaction coordinates are given in Table IV. Due to the tetrahedral symmetry of $Ni(CO)_4$, when a single nickel–carbon $(Ni-C_0)$ or carbon–oxygen (C_0-O_0) bond is stretched, the remaining Ni–C bonds $(Ni-C_r)$ or C–O bonds (C_r-O_r) are equivalent. All the bonds in $Ni(CO)_4$ were found to be linear with respect to a wide range of stretch and compression values. Coordinate response values for nickel–carbon and carbon–oxygen were obtained as in the case of $Cr(CO)_6$ and $Co(CN)_6^{3-}$. For the Ni–C bond this value is −4.28 Å for a unit change in overlap population: a value closer to that of $Cr(CO)_6$ than $Co(CN)_6^{3-}$. For the C–O bond the response factor was −1.37 Å/unit change in overlap population, again close to the C–O response factor of $Cr(CO)_6$. The largest interaction coordinate $(Ni-C_0)_{C_0-O_0}$ arises mainly from π contributions (98%). This is transmitted to the other $Ni-C_r$ bonds and has a large effect on the other carbonyls. When the $Ni-C_0$ bond is stretched, the $(C_0-O_0)_{Ni-C_0}$ value is similar to the $(C_0-O_0)_{Cr-C_0}$ value of $Cr(CO)_6$ for both the calculated and experimental values in contrast with the $(C_0-N_0)_{Co-C_0}$ value of $Co(CN)_6^{3-}$. The other nickel carbon bonds are strengthened and the carbonyl bonds are weakened as in $Cr(CO)_6$ when this $Ni-C_0$ bond is stretched. Our predicted values for $(Ni-C_r)_{Ni-C_0}$ and $(Ni-C_r)_{C_0-O_0}$ are rather close to the values for the cis carbonyl bonds of $Cr(CO)_6$, while the experimental values are intermediate between the values for the cis and trans carbonyls. For the $(C_r-O_r)_{Ni-C_0}$ and $(C_r-O_r)_{C_0-O_0}$, both the predicted and experimental values are the average of the cis and trans values for $Cr(CO)_6$. In general the values for the Ni–C bonds are not as well reproduced as those for C–O bonds. In the case of $Ni(CO)_4$ there is significant population and bonding with the 4s and 4p functions. However, the diffuse nature of these atomic orbitals precludes their use in the calculation of overlap populations. Since the changes in M 4s and 4p bonding will be more important for the interaction coordinates of $Ni(CO)_4$, our predicted values are not as accurate as those in $Cr(CO)_6$ and $Co(CN)_6^{3-}$. Despite this problem, there is still fairly good agreement with the experimental values and π back-bonding is important in $Ni(CO)_4$ as it is in $Cr(CO)_6$.

π Bonding in $Cr(CO)_6$. Our calculations, which indicate moderately strong π chromium–carbon bonding in $Cr(CO)_6$, provide a theoretical model that may be used to interpret the interaction coordinates without invoking a σ-only-bonding model. Our results are also in general agreement with the low-temperature X-ray and neutron diffraction study of Rees and Mitchsler.[21] Population analysis showed 1.52 electrons in the 5σ orbitals and 0.51 electron in the 2π orbitals of each carbonyl, while the experimental values are 1.65 and 0.38, respectively. The gross atomic charge on Cr was 0.306 compared to the experimental value[21] of 0.15 ± 0.12.

While these calculations may over-emphasize the absolute magnitude of π-bonding character in transition-metal carbonyls, they show that the π bonding is important in these systems. We have been able to calculate accurate interaction coordinates and have shown that the results of vibrational studies can best be understood with a bonding model, which allows substantial metal–carbonyl π bonding. For those interaction coordinates which are expected to be π dominated, they are transmitted through the strong metal–carbon π system for $Cr(CO)_6$ but not for $Co(CN)_6^{3-}$. $Ni(CO)_4$, another system with extensive π back-bonding, has interaction coordinate responses like $Cr(CO)_6$. Our calculations have also shown that the interaction coordinates arise from complex changes in both π and σ bonding, which sometimes add to give a large effect and sometimes cancel to produce a small effect. With σ-only bonding as a model for the Cr–C bond, one would predict values of $(j)_i$ in poor agreement with experiment.

We believe the interpretation of bonding based on SW-Xα calculations of $Cr(CO)_6$ underestimates the importance of π bonding. Precise ab initio calculations, including configuration interaction, are currently in progress in order to obtain a more detailed picture of the bonding in $Cr(CO)_6$.

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(27) Swanson, B. I., private communication.