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Directional Effects of CO π Bonding in Group 6 Pentacarbonyl Amines

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Carbon-13 and oxygen-17 NMR spin−lattice relaxation time measurements were used to investigate π bonding in the following group 6 transition metal pentacarbonyl amines: WL(CO)$_5$, L = pyrazine, pyridine, quinuclidine, trimethylamine; M(quinuclidine)(CO)$_5$, M = Cr, Mo. Values of $T_1(^{17}O)$ and $T_1(^{13}C)$ [at two field strengths] of axial and radial carbonyls permitted calculation of the ^{17}O quadrupole coupling constants (χ) and the CO π antibonding orbital populations ($[2\pi]_\chi$) at both sites. It was observed that the ratio of increases of the axial/radial orbital populations (relative to the metal hexacarbonyls) was substantially greater than the theoretical maximum of 2 and approximately independent of ligand, indicating that CO π bond strength enhancements induced by the amine ligands are (a) very strongly trans directed and (b) virtually independent of the amine's σ basicity. The above conclusions were supported by the results of Fenske−Hall MO calculations. Both experimental and calculated values of the 2π orbital populations of the two aromatic amines, pyrazine and pyridine, were virtually identical to results for the aliphatic ligands, from which it was concluded that, in contrast to some other reports, the π^* orbital systems in these aromatic amines are **not** capable of accepting electrons from the metal d$_\pi$ orbitals.

Introduction

When a CO in a transition metal carbonyl is replaced by a ligand which is a stronger σ donor, such as an amine, the conventional picture is that the ligand will donate additional electron density to the metal, raising the energy of its filled d$_\pi$ orbitals which will, in turn, interact more effectively with the antibonding orbitals of the remaining carbonyls, increasing their populations, $[2\pi]$. One might expect this effect to be isotropic, affecting axial and radial orbital populations equally.[2] An alternative view, supported by both experimental[3] and theoretical[4,5] evidence is that the 2π orbital populations of the radial carbonyls may be enhanced preferentially via direct through-space donation from the amine's σ-bonding orbital.

At the same time, replacement of a carbonyl by a non-π-accepting amine ligand is expected to increase the π bond strength of the axial carbonyl by twice as much as radial CO's, since the axial CO interacts with the ligand through twice the number of metal d$_\pi$ orbitals as do the radial carbonyls.[6]

It is straightforward to show that the net enhancement of the 2π orbital population of the axial CO resulting from the sum of the above effects should be no greater than twice the increase in the radial carbonyls, independent of whether the σ donicity induces an isotropic or cis-directed enhancement; i.e., one expects that $\Delta[2\pi]^{ax} \leq 2\Delta[2\pi]^{rad}$.

In a recent experimental investigation[7] of 2π orbital occupations in several tungsten pentacarbonyl complexes derived from NMR relaxation time measurements, the results on W[NMe$_3$](CO)$_5$ were rather unusual, with $\Delta[2\pi]^{ax} \approx 3{\cdot}\Delta[2\pi]^{rad}$, in conflict with the above simple picture of CO π bond enhancements by amine ligands.

In an effort to probe further the directional effects of CO π bond enhancements due to amine ligands, we have performed NMR relaxation time measurements of 2π orbital populations in three additional tungsten pentacarbonyls, WL(CO)$_5$, L = quinuclidine, pyridine, pyrazine, whose ligands encompass an extremely broad range of σ basicity, as measured by their pK_a's [pK_a(quin) = 10.7, pK_a(NMe$_3$) = 9.8, pK_a(py) = 5.2, pK_a(pyrazine) = 0.7].[8] Measurements have also been performed on the quinuclidine complexes of the molybdenum and chromium pentacarbonyls.

The results of these measurements are discussed below and compared with orbital populations predicted from semiempirical MO calculations. The results on the pyridine and pyrazine complexes are also used to address the question of whether aromatic amine ligands can function as π acids via back-donation to their antibonding π^* systems.

Experimental Section

Relaxation Time Measurements and Experimental 2π Orbital Populations. All of the ML(CO)$_5$ complexes used in our studies were synthesized from M(THF)(CO)$_5$ and the appropriate amine ligand.[9] The

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Table 1. Relaxation Times and Quadrupole Coupling Constants[a,b]

complex[c]	T [°C]	site	T_{1Q} (^{17}O)[d] [ms]	T_{1A} (^{13}C)[d] [s]	T_{1B} (^{13}C)[e] [s]	T_{1CSA} (^{13}C) [s]	$\Delta\sigma$ [ppm]	τ_c [ps]	χ [MHz]
W[pyraz](CO)$_5$	11	axial	43.6 (5)	3.23 (0.2)	7.57 (0.4)	3.13	420.1	60.4	0.633
	21	axial	98.0 (4)	4.99 (0.1)	9.10 (0.3)	6.14		30.8	0.591
	11	radial	9.6 (0.1)	4.99 (0.1)	9.42 (0.4)	5.89	414.5	32.9	1.83
	21	radial	13.0 (0.4)	7.12 (0.1)	15.1 (0.2)	7.47		26.0	1.77
W[py](CO)$_5$	11	axial	148 (2)	5.35 (0.44)	10.7 (0.8)	5.96	421.1	31.6	0.475
	21	axial	170 (10)	5.92 (0.21)	12.6 (1.0)	6.21		30.3	0.453
	11	radial	16.8 (0.2)	8.06 (0.74)	15.3 (0.6)	9.46	415.5	20.4	1.75
	21	radial	19.9 (0.1)	8.31 (0.06)	18.3 (0.1)	8.47		22.8	1.53
W[quin][(CO)$_5$	11	axial	275 (38)	4.19 (0.15)	8.84 (0.68)	4.42	420.3	42.7	0.300
	21	axial	352 (31)	5.28 (0.42)	13.0 (1.6)	4.93		38.4	0.280
	11	radial	15.8 (0.0)	6.47 (0.15)	12.4 (0.1)	7.54	416.3	25.6	1.62
	21	radial	18.0 (0.5)	7.88 (0.22)	16.3 (0.9)	8.47		22.7	1.60
Mo[quin](CO)$_5$	11	axial	86 (7)	3.62 (0.06)	8.27 (0.08)	3.58	438.6	48.5	0.503
	21	axial	126 (01)	5.26 (0.69)	9.60 (1.81)	6.46		26.9	0.560
	11	radial	12.1 (0.2)	5.87 (0.3)	10.2 (0.3)	7.73	423.3	24.1	1.90
	21	radial	16.3 (0.2)	7.74 (0.63)	12.7 (0.1)	11.0		16.9	1.96
Cr[quin](CO)$_5$	11	axial	129 (8)	5.44 (0.07)	12.9 (1.0)	5.23	448.7	31.7	0.509
	21	axial	148 (12)	6.92 (0.48)	14.6 (1.1)	7.29		22.7	0.561
	11	radial	20.3 (0.5)	9.17 (0.40)	17.8 (0.4)	10.5	438.5	16.4	1.78
	21	radial	25.6 (1.5)	10.2 (0.1)	20.8 (0.3)	11.2		15.6	1.63

[a] Relaxation times are the average of three measurements at each temperature. [b] Quantities in parentheses represent the mean deviation between measurements. [c] pyraz = pyrazine; py = pyridine; quin = quinuclidine. [d] Measurements performed at B_0 = 7.05 T. [e] Measurements performed at B_0 = 4.70 T.

Table 2. Experimental 2π Orbital Populations and C−K Force Constants

no.	complex[a]	$[2\pi]^{ax}_{\chi}$	$[2\pi]^{rad}_{\chi}$	$\Delta[2\pi]^{ax}_{\chi}$,[b]	$\Delta[2\pi]^{rad}_{\chi}$,[b]	$-\Delta k_{ax}$[c]	$-\Delta k_{rad}$[c]
1	W[pyraz](CO)$_5$	0.585 (0.003)[d]	0.403 (0.005)[d]	0.21	0.02	1.13	0.58
2	W[py](CO)$_5$	0.61 (0.002)[d]	0.43 (0.017)[d]	0.23	0.05	1.23	0.57
3	W[quin](CO)$_5$	0.64 (0.002)	0.43 (0.001)	0.26	0.05	1.29	0.64
4	Mo[quin](CO)$_5$	0.60 (0.004)	0.38 (0.004)	0.25	0.03	1.40	0.63
5	Cr[quin](CO)$_5$	0.60 (0.007)	0.42 (0.012)	0.22	0.04	1.43	0.72
6	W[NMe$_3$](CO)$_5$	0.63 (0.001)	0.46 (0.007)	0.25	0.08	1.30	0.63
7	W[PMe$_3$](CO)$_5$	0.53 (0.009)	0.46 (0.011)	0.15	0.08	0.82	0.56
8	W[P(OMe)$_3$](CO)$_5$	0.47 (0.007)	0.42 (0.005)	0.09	0.04	0.53	0.36

[a] pyraz = pyrazine; py = pyridine; quin = quinuclidine. [b] $\Delta[2\pi]_{\chi} = [2\pi]_{\chi}\{\text{complex}\} - [2\pi]_{\chi}\{M(CO)_6, M = Cr, Mo, W\}$; metal hexacarbonyl orbital populations are from ref 14. [c] $\Delta k = k_{CO}\{\text{complex}\} - k_{CO}\{M(CO)_6, M = Cr, Mo, W\}$; C−K force constants for the metal hexacarbonyls are from: Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349. [d] Quantities in parentheses represent the average error between runs.

NMR samples were prepared under argon in CDCl$_3$ (*ca.* 0.3 M) using Schlenk techniques.[10] The samples were subjected to three freeze−pump−thaw cycles, after which the tubes were flame-sealed.

Axial and radial ^{13}C (T_{1A}) and ^{17}O (T_{1Q}) spin−lattice relaxation times were determined on a Varian VXR-300 FT-NMR spectrometer at B_0 = 7.05 T (75.4 MHz for ^{13}C and 40.7 MHz for ^{17}O), using the standard IRFT pulse sequence.[11] T_1's were calculated, via nonlinear regression, from a fit of the data by a three-parameter magnetization equation.[12] Each relaxation time was determined three times; the results in Table 1 represent the average of the runs. In addition, ^{13}C (T_{1B}) relaxation times were measured at a second field strength, B_0 = 4.70 T (50.3 MHz for ^{13}C), on a Varian Gemini-200 spectrometer.

^{13}C T_1's at the two fields were used to evaluate the contributions of chemical shift anisotropy (T_{1CSA} in Table 1) to the relaxation times at 7.05 T, from which the rotational correlation times, τ_c, of the CO vectors were determined. Values of the anisotropy, $\Delta\sigma$, required for this calculation, were estimated using methods described elsewhere.[13] The ^{17}O relaxation times were used with measured values of τ_c to calculate the QCC's of axial and radial oxygens in each complex. Details of the above calculations have been presented in an earlier investigation.[14] The results are presented in the last column of Table 1.

Recently, we developed a semiquantitative relationship between an oxygen's QCC, χ, and the carbonyl's 2π orbital population.[15] This expression was used to calculate antibonding orbital populations of both axial and radial carbonyls in each complex. The results, $[2\pi]^{ax}_{\chi}$ and $[2\pi]^{rad}_{\chi}$, are presented in Table 2; the subscript indicates that the values were derived from QCC data.

To ascertain the reproducibility of quadrupole coupling constants (χ) and 2π orbital populations derived from the NMR data, all series of measurements were performed at two temperatures (11 and 21 °C).

For comparison purposes, experimental 2π populations reported recently for three additional tungsten carbonyl complexes,[7] are also contained in Table 2 (**6**−**8**).

Theoretical 2π Orbital Populations. To afford a comparison with

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(15) Equation 4 in ref 14.

Table 3. Calculated 2π and 5σ Orbital Populations

no.	complex[a]	$\Delta[2\pi]^{ax}_{FH}$ [b]	$\Delta[2\pi]^{rad}_{FH}$ [b]	$\Delta[5\sigma]^{ax}_{FH}$ [c]	$\Delta[5\sigma]^{rad}_{FH}$ [c]
1	W[pyraz]$(CO)_5$	0.20	0.04	−0.07	−0.01
2	W[py]$(CO)_5$	0.21	0.04	−0.07	−0.01
3	W[quin]$(CO)_5$	0.22	0.04	−0.07	−0.01
4	Mo[quin]$(CO)_5$	0.17	0.00	−0.05	+0.02
5	Cr[quin]$(CO)_5$	0.23	0.05	−0.00	−0.01
6	W[NMe_3]$(CO)_5$	0.22	0.04	−0.07	−0.01
7	W[PMe_3]$(CO)_5$	0.08	0.03	−0.05	−0.01
8	W[$P(OMe)_3$]$(CO)_5$	0.09	0.03	−0.04	−0.01

[a] pyraz = pyrazine; py = pyridine; quin = quinuclidine. [b] $\Delta[2\pi]_{FH} = [2\pi]_{FH}\{complex\} - [2\pi]_{FH}\{M(CO)_6, M = Cr, Mo, W\}$. Calculated $M(CO)_6$ 2π orbital calculations: Cr, 0.49; Mo, 0.54; W, 0.52. [c] $\Delta[5\sigma]_{FH} = [5\sigma]_{FH}\{complex\} - [5\sigma]_{FH}\{M(CO)_6, M = Cr, Mo, W\}$. Calculated $M(CO)_6$ 2σ orbital calculations: Cr, 1.51; Mo, 1.48; W, 1.48.

experimental results, orbital occupancies were calculated using the semiempirical molecular orbital method developed by Fenske and Hall.[5,16] The calculations were performed on a Digital Equipment Corp. VAX 6310 minicomputer using the FORTRAN program Fenhall.[17] The methodology and computational details have been presented by the original authors.[5,16]

Application of the program to calculate orbital populations requires an assumed structure of the complex. Reported experimental structures of the metal hexacarbonyls[18a,b] were used in the calculations. Crystal structures of most of the substituted complexes have not yet been reported. Therefore, M−C, M−O, and M−L distances were taken from reported structures of similar complexes.[18c−e] The structures of the ligands were calculated using the semiempirical MNDO-PM3 technique[19] to obtain optimized equilibrium (minimum energy) ligand geometries.

Calculated 2π and 5σ orbital populations of both axial and radial carbonyls, relative to the hexacarbonyls, are presented in Table 3. For comparison, calculated populations on three tungsten carbonyl complexes (compounds **6**−**8**), for which experimental results were reported recently,[7] are also presented in the table.

The Directionality of π Bonding

Shown in the first two columns of Table 2 are the antibonding orbital populations of the axial and radial carbonyls in the substituted metal carbonyls; a larger value of $[2\pi]_{\chi}$ indicates a stronger M−C π bond. The deviations in values calculated at the two temperatures (given in parentheses) are satisfyingly low and provide evidence of the precision of this method of estimating π bond strengths.

Of greater significance than the absolute orbital populations are the enhancements effected in the remaining CO's by replacement of one carbonyl by an alternate ligand. $\Delta[2\pi]^{ax}_{\chi}$ and $\Delta[2\pi]^{rad}_{\chi}$ in this table represent increases in $[2\pi]$ relative to populations earlier reported for the respective metal hexacarbonyls.[14] It is quite clear from the table that for all of the amine-substituted complexes (**1**−**6**), $\Delta[2\pi]^{ax}_{\chi} \gg \Delta[2\pi]^{rad}_{\chi}$, indicating that these ligands induce a much greater enhancement in π bond strengths of the trans carbonyls.

Comparative π bond changes at the two sites are best illustrated in Figure 1, in which we have plotted increases in the radial vs axial orbital populations. As discussed in the Introduction, current models of metal carbonyl bonding yield the prediction that $\Delta[2\pi]^{ax}_{\chi}/\Delta[2\pi]^{rad}_{\chi} \leq 2$. This ratio is represented by the solid line in the figure.

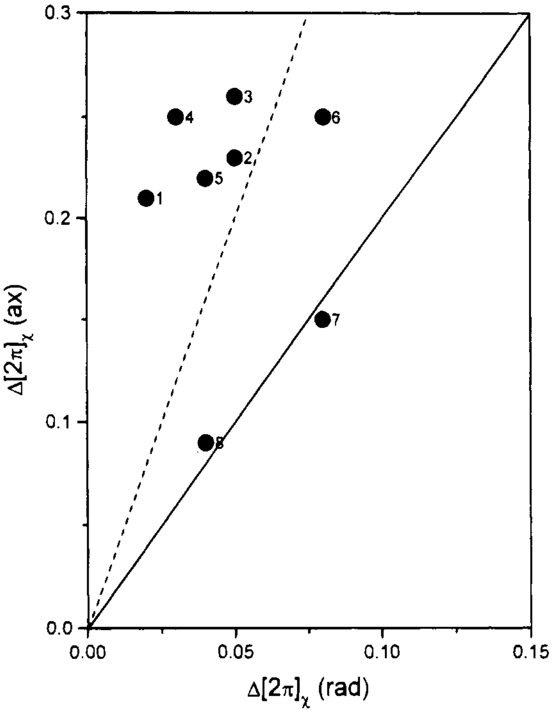

Figure 1. Experimental axial versus radial 2π orbital populations.

One observes that results for the phosphine and phosphite complexes (**7** and **8**) are, within experimental error, at the theoretical maximum ratio. In contrast, the ratios of trans/cis π bond enhancements in all of the amine complexes are substantially greater than 2 and, with only one exception (**6**), $\Delta[2\pi]^{ax}_{\chi}/\Delta[2\pi]^{rad}_{\chi} > 4$ (represented by the dashed line in the figure).

The amine ligands investigated here exhibit an extremely broad range of σ basicities, as measured by their pK_a's, which vary over 10 decades from 0.7 (pyrazine) to 10.7 (quin). Yet, from Table 2, the values of $\Delta[2\pi]^{ax}_{\chi}$ are remarkably constant, all lying in the range 0.22−0.26. There is a similarly narrow range of radial π bond enhancements.

From these results, we are compelled to conclude that (a) π bond strengths in amine-substituted metal carbonyls are almost independent of the ligand σ basicity and (b) in contrast to the standard models,[1−5] the increase in CO π bond strengths effected by amine substitution of a complex is very strongly trans directed.

Comparison with Theoretical π Bond Enhancements

The increase in 2π orbital populations of axial and radial carbonyls predicted from Fenske−Hall MO calculations[5−16] are presented in Table 3. To facilitate comparison with the experimental results, we have plotted the calculated vs experimental values of $[2\pi]$ in Figure 2; the solid and open circles represent the axial and radial data points, respectively.

The agreement between calculated and experimental π bond enhancements is quite reasonable. The two major sources of disagreement between the two sets of results are (a) approximations inherent in the method and (b) sensitivity of calculated orbital populations to the assumed molecular structure, particularly the M−C and M−L bond lengths.

One observes from the figure that the MO calculations correctly predict the moderate increases in axial orbital populations of the phosphine and phosphite complexes (**7** and **8**). Most significantly, the theoretical values are in complete agreement

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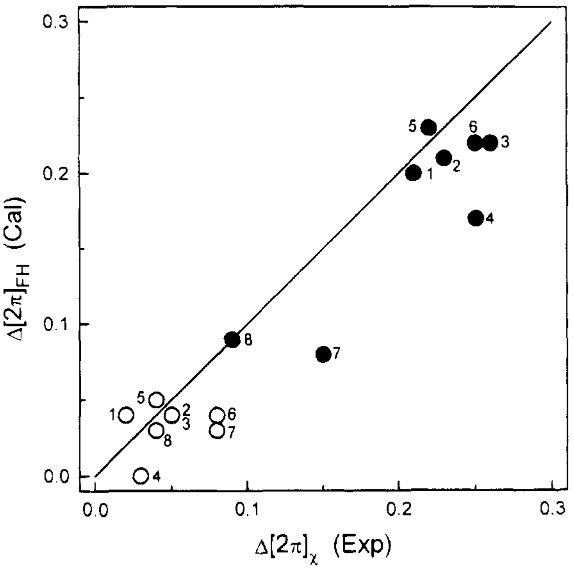

Figure 2. Theoretical versus experimental 2π orbital populations: (●) axial; (○) equatorial.

with the experimental results on all of the amine complexes, predicting very high and roughly constant values of $[2\pi]^{ax}$ and very low values of $[2\pi]^{rad}$. Thus, orbital populations calculated with the Fenske–Hall technique provide further supporting evidence for our conclusions that π bond strength increases in the amine complexes are strongly trans directed and approximately independent of ligand basicity.

Cotton–Krahainzel Force Constants

The spectroscopic technique most widely utilized to monitor pi bonding in metal carbonyl complexes has been the determination of vibrational CO force constants, k_{CO}, using the Cotton–Kraihanzel (C–K) π interaction force field.[20] Its basis lies in the fact that enhanced d_π–p_π back-bonding will increase $[2\pi]$, resulting in a diminished π bond order. However, it is now recognized that variation in pi bond strength is not the only factor influencing k_{CO}. There is substantial experimental[21] and theoretical[3,4,22,23] evidence that a weakened M–CO σ bond will also lower the force constant. This arises from an increase in the occupancy of the carbon's 5σ orbital. Like 2π, 5σ is also antibonding (negative overlap) relative to the CO framework.[3] Indeed, Hall and Fenske,[5] in MO calculations on metal carbonyl halides, have established an approximate relationship of the form $k_{CO} = A - B[2\pi] - C[5\sigma]$. The magnitudes of B and C are the similar, indicating that both σ and π orbital occupations have roughly comparable effects on k_{CO}.

Displayed in the last two columns of Table 2 are variations of the C–K force constants of both axial and radial carbonyls ($-\Delta k_{ax}$ and $-\Delta k_{rad}$) of the substituted complexes, relative to values in the metal hexacarbonyls. From these data, one calculates that the ratios, $-\Delta k_{ax}/-\Delta k_{rad}$, fall within the range 1.5–2.2, which is considerably lower than the ratios of $\Delta[2\pi]^{ax}_\chi/\Delta[2\pi]^{rad}_\chi$ found here. Therefore, at first it would appear that the vibrational force constants predict lower trans/cis π bond strength enhancements than found in our measurements.

This apparent anomaly can be explained, however, by inspection of σ bonding orbital populations of the carbonyls, $[5\sigma]$, as determined from the Fenske–Hall MO calculations.[5,16] The variations in these orbital occupancies relative to the hexacarbonyls are displayed in the last two columns of Table 3. One observes that $[5\sigma]$ of the axial carbonyls is, in general, diminished by amounts ranging from 0.04 to 0.07 electron. This decrease represents the synergistic **increase** in σ bonding of the trans CO's. In contrast, the radial carbonyls exhibit almost no change in the σ bond strengths. The lowered values of $[5\sigma]$ induce an increase in the net bond order and, therefore, in the C–K force constants of the axial carbonyls, relative to what their values would be based upon π bond effects alone. Hence, one sees that changes in k_{CO} are "buffered" by the synergistic variations in σ and π bond strengths and cannot be used as an accurate probe of π bonding alone.

π Acidity of Aromatic Amines

Whereas aliphatic amine ligands are clearly incapable of acting as π acids in metal carbonyl complexes, there has been much conflicting evidence in the literature[24] over whether the empty π^* orbital systems in aromatic amine complexes can function as effective π electron acceptors.

Two of the complexes studied here (**1** and **2**) contain the aromatic pyrazine and pyridine ligands. One observes from the experimental 2π orbital populations in Table 2 that the results found for these complexes are indistinguishable from those obtained for the systems with aliphatic amine ligands (**3**–**6**). These results are supported by the Fenske–Hall results (Table 3), which also predict the same values of $\Delta[2\pi]$ for all of the amines. We note, too, that performing the calculations with the ligand ring at angles of 0 and 45° to the radial CO's yielded the same values, to within less than 0.002 electron. Thus there is no evidence that the π^* orbitals in these ligands are capable of accepting electron density from the metal's d_π orbitals in these pentacarbonyl complexes.[25]

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[25] One reviewer has noted that, although there is no evidence of acidity in the systems studied here, one cannot exclude the possibility that the π^* system in aromatic amines might compete more effectively for electron density in complexes containing strong donor phosphine ligands in addition to CO's.