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An analysis of the bonding in some 'nonclassical' d^0 and d^{10} metal carbonyl complexes ☆

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Abstract

The bonding in nonclassical carbonyl complexes, those with unusually high CO stretching frequencies, is analyzed via Fenske–Hall molecular orbital calculations. The systems analyzed include nonclassical carbonyl complexes of d^{10} Ag(I) and of d^0 Zr(IV); these are compared to classical carbonyl complexes of Zr(II) and Mo(0). The Cotton–Kraihanzel CO-stretch force constants are correlated to the Mulliken populations of the 5σ and 2π molecular orbitals of the CO ligands.

Keywords: Metal carbonyl complexes; Molecular orbital calculations; Backbonding

1. Introduction

The CO ligand is arguably the most important ligand in low-valent transition metal chemistry, in large part because of the ease with which CO ligands are detected in vibrational spectroscopy. The analysis of the bonding in metal–carbonyl complexes has been aided enormously by the simplified energy-factored force field developed by Cotton and Kraihanzel [1]. The tenets of the Cotton–Kraihanzel (C–K) method allow for the easy calculation of C–O stretching force constants in monocarbonyl complexes and in polycarbonyl complexes in which the CO ligands are approximately 90° or 180° apart.

Most applications of the C–K method have focused on 'classical' metal carbonyls, predominantly involving metal centers with from 2 to 8 metal-localized electrons (d^2 through d^8 electron configurations). These complexes generally exhibit CO stretching frequencies that are lowered by more than 100 cm^{-1} from the 2143 cm^{-1} frequency of free CO. This reduction in CO stretching frequency is generally taken as evidence for M → CO backbonding: the donation of electron density from the metal *n*d orbitals into the antibonding 2π orbital of CO. This backbonding weakens the C–O bond and lowers the stretching frequency, which is reflected in lower C–K force constants relative to that of free CO. A multitude of quantitative relationships between the C–K force constants for coordinated CO and the ligand environment about the metal atom has been advanced [2].

Several recent reports have expanded the number of 'nonclassical' carbonyl complexes, i.e., those in which the CO stretching frequency is close to or even higher than that in free CO. Strauss and co-workers [3–5] have isolated and structurally characterized the first silver carbonyl complexes, $[Ag(CO)_n][B(OTeF_5)_4]$ (**1**, $n=1$; **2**, $n=2$), d^{10} Ag(I) complexes that possess 'normal' linear carbonyl ligands ($\angle Ag–C–O > 176°$). These complexes are at one extreme of nonclassical carbonyls, namely complexes of closed-d-shell atoms. As expected, the IR spectrum of **1** shows one CO stretch; surprisingly, however, the frequency of the stretch, 2204 cm^{-1}, is considerably higher than that of free CO, an indication that no significant Ag → CO backbonding occurs even though there is a surfeit of d-electron density available. The other extreme of nonclassical carbonyl complexes is carbonyl adducts of d^0 metals, complexes that have been observed for some time as fragile intermediates in carbonylation reactions of d^0 complexes [6]. Two very recent papers report the first thermally stable carbonyl adducts of d^0 Zr(IV). Stryker and co-workers isolated $[Cp^*{}_2Zr(\eta^3\text{-}C_3H_5)CO]^+[BPh_4]^-$ (**3**; $Cp^* = \eta^5\text{-}C_5Me_5$) [7]. This complex, which has not yet been structurally characterized by X-ray diffraction, exhibits a CO stretch at 2079 cm^{-1}. Jordan and co-workers have synthesized $[(\eta^5\text{-}C_5R_5)_2Zr(\eta^2\text{-}COMe)(CO)]^+[BMe(C_6F_5)_3]^-$ (**4**, R = H; **5**, R = Me) [8]. Complexes

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☆ Dedicated to Professor F.A. Cotton, mentor, colleague, and friend, on the occasion of his 65th birthday.

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4 and **5** each exist as mixtures of 'O-outside' (**4a** and **5a**) and 'O-inside' (**4b** and **5b**) isomers. The four species have CO stretching frequencies that range from 2105 to 2176 cm^{-1}. The authors were able to obtain a crystal structure of **5a**, and the Zr–C–O linkage is essentially linear.

In this contribution, we shall report Fenske–Hall approximate molecular orbital calculations [9] on some of the above nonclassical carbonyl complexes and some closely related classical carbonyls. The Fenske–Hall method is ideally suited to allow us to analyze the synergistic metal–carbonyl bonding in order to compare σ-donation and π-acceptance by the carbonyl ligands [10]. Finally, we will correlate the MO results with the calculated C–K force constants, using a notion first developed by Hall and Fenske [11].

2. Computational details

Molecular orbital calculations were performed on a Silicon Graphics IRIS Indigo computer system using the Fenske–Hall method [9].

In all relevant calculations, the cyclopentadienyl (Cp) rings have local D_{5h} symmetry with C–C and C–H bond lengths of 1.42 and 1.08 Å, respectively. In compounds with Cp* ligands, the C–Me distance was set at 1.50 Å. The C–O distances in all carbonyl ligands have been set to 1.13 Å. The molecular geometries of $[Ag(CO)_n][B(OTeF_5)_4]$ and $Mo(CO)_6$ were taken from their crystal structures deposited in the Cambridge Structural Database [12] and were idealized to C_s and O_h symmetry, respectively. The molecular geometry of the O-outside isomer of $[Cp_2Zr(\eta^2\text{-}COCH_3)CO]^+$ (**4a**) was taken from the crystal structure of the corresponding Cp* complex [8] and was idealized to C_s symmetry. An assumed C_s geometry for the O-inside isomer, **4b**, was obtained by rotating the COMe group by 90° about the line that bisects the C–Zr–O angle. The geometry of $Cp^*_2Zr(CO)_2$ was obtained from its crystal structures [13], and was idealized to C_{2v} symmetry. A crystal structure of $Cp_2Zr(CO)(PMe_3)$ is not available in the literature. Therefore, the Zr–P distance was set at 2.693 Å [14], the P–Zr–C(carbonyl) angle was set at 92.2° [15], and the P–C bond lengths were fixed at 1.824 Å [16]. A tetrahedral geometry was assumed about the P atom and the entire molecule was idealized to C_s symmetry. The assumed geometry for the $Cp_2Zr(CO)^{q+}$ ($q=0$, 1, 2) fragments was taken from the metric parameters for **5a** [8], and this geometry was fixed regardless of overall charge.

Atomic basis functions were generated by using the method of Bursten, Jensen, and Fenske [17]. Contracted double-ζ functions were used for the metal nd AOs, for the C, O, F, and B 2p AOs, for the P 3p AOs, and for the Te 5p AOs. Basis functions for silver, zirconium, and molybdenum were derived from the +1, +2, and neutral oxidation states, respectively.

The calculations were performed using a fragment analysis in which the transformed molecular orbitals of $C_5R_5^-$, CO, $B(OTeF_5)_4^-$, $COCH_3^-$, and PMe_3 were allowed to interact with the metal atomic orbitals. In all calculations, the carbonyl 3σ and 6σ and the first three occupied C_5H_5 orbitals were deleted from the basis transformation set [18].

3. Results and discussion

Our approach to correlating the MO calculations with vibrational force constants is the one pioneered by Hall and Fenske [11]. These authors assumed that the C–K force constants could be correlated to the Mulliken populations of the CO 5σ and 2π molecular orbitals. In free CO, the populations of these MOs are 2.0 and 0.0, respectively, and both the 5σ and 2π molecular orbitals are C–O antibonding. Therefore, forward-donation ($5\sigma \rightarrow M$), which depopulates the 5σ MO, serves to strengthen the C–O bond relative to free CO, and back-donation ($M \rightarrow 2\pi$), which populates the 2π MO, will weaken the C–O bond. Thus, the two major bonding interactions in metal carbonyls oppose one another with respect to the C–O force constants. Hall and Fenske demonstrated a nice linear relationship between the C–K force constant k_{CO} and the 5σ and 2π populations:

$$k_{CO}=a(5\sigma)+b(2\pi)+c \qquad (1)$$

where (5σ) and (2π) are the total 5σ and 2π Mulliken populations of the CO ligand.

In the following discussion, we will report the results of Fenske–Hall calculations on some of the nonclassical carbonyl complexes discussed above and compare the results to those of some classical complexes. Brief descriptions of the bonding will be provided. We will then test the applicability of Eq. (1) to these systems.

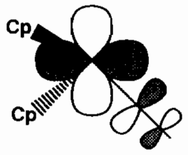
3.1. Classical and nonclassical zirconium carbonyls

We have recently used the Fenske–Hall method to investigate linear relationships in d^0 Cp'_2TiXX' complexes [19]. In the present study, we believe that Cp_2ZrLL' complexes provide an excellent opportunity to apply a similar analysis to classical and nonclassical carbonyls. In addition to the d^0 Zr(IV) nonclassical carbonyl complexes **4** and **5** discussed above [7,8], there are classical d^2 Zr(II) carbonyls of the type $Cp'_2Zr(CO)L$ (**6**, $Cp'=\eta^5\text{-}C_5H_5$, L=CO [20]; **7**, $Cp'=\eta^5\text{-}C_5H_5$, $L=PMe_3$ [21]; **8**, $Cp'=\eta^5\text{-}C_5Me_5$, L=CO [20]). In the simplest sense, the d^0 complexes should be incapable of π-backbonding. In actuality, charge is shuttled from the donor Cp ligands to the Zr center, which in turn can be backbonded to the CO. In addition, the ancillary anionic ligand has been proposed as a significant source of charge for backbonding from d^0 metals [22]. Because complexes **4**–**7** share a common $Cp_2Zr(CO)$ fragment, we have explored some of these effects by performing MO calculations on $Cp_2Zr(CO)^{q+}$ ($q=0, 1, 2$) under a fixed geometry that corresponds to that used for complexes **4a** and **4b**.

The electronic structure of the d^0 fragment $Cp_2Zr(CO)^{2+}$ is straightforward. The filled valence orbitals include the C–C and C–H σ-bonding orbitals and the 3σ, 4σ, and 1π orbitals of the CO, none of which interact to any extent with the Zr atom. The lowest π MO of the Cp ligands (a_2'' under D_{5h}) interacts very slightly with the Zr orbitals, donating a total of only 0.06e per Cp ligand. The e_1'' HOMOs of the Cp^- ligands act as significant donors to the Zr 4d and 5s AOs, donating 0.62e per Cp. Formation of the Zr–CO σ bond effects the transfer of 0.47e from the CO 5σ MO to the Zr center.

As expected, the interaction of the CO 2π MOs in the filled orbitals of $Cp_2Zr(CO)^{2+}$ is small. The $Cp_2Zr(CO)^{2+}$ fragment has C_s symmetry and the CO ligand lies in the mirror plane of the molecule. As such, the two 2π MOs belong to different irreducible representations, namely an in-plane orbital of a′ symmetry ($2\pi_{\|}$) and an out-of-plane orbital of a″ symmetry ($2\pi_{\perp}$). Enough charge is 'shuttled' from the donor ligands through the Zr atom to allow the transfer of 0.16e back to the CO 2π orbitals.

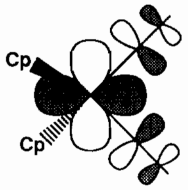
The LUMO of $Cp_2Zr(CO)^{2+}$ is, expectedly, the first MO that predominantly contains Zr 4d AO character. As shown in Scheme 1, this MO corresponds to an in-plane 4d orbital stabilized by backbonding to the $2\pi_{\|}$ orbital of CO. The addition of one and two more electrons to give $Cp_2Zr(CO)^+$ and $Cp_2Zr(CO)$, respectively, should therefore be accompanied by substantial increases in the population of the $2\pi_{\|}$ orbital, with little change to the $2\pi_{\perp}$ population. The population analysis given in Table 1 demonstrates that this is indeed the case. Each additional electron causes an increase of more than 0.16e in the population of the $2\pi_{\|}$ MO with very little change in the $2\pi_{\perp}$ population. Consistent with the primarily Zr $4d\pi$ nature of the orbital, the CO 5σ population is largely unaffected by the change in charge.



LUMO of $Cp_2Zr(CO)^{2+}$

Scheme 1.

We now add a second CO ligand to $Cp_2Zr(CO)$ to yield the classical carbonyl complex $Cp_2Zr(CO)_2$ (**6**), for which population analysis is also presented in Table 1. We find that each CO in **6** acts as a donor and acceptor to nearly the same extent as the single carbonyl in $Cp_2Zr(CO)$. This somewhat counterintuitive result is consistent with ligand additivity, wherein the total donation/acceptance is nearly linear with the number of CO ligands [2]. The low CO stretching frequencies in **6** are largely the consequence of the substantial back-donation to the CO 2π orbitals. The HOMO of **6** is an a_1 orbital that involves substantial backbonding from the in-plane $4d\pi$ AO to the CO $2\pi_{\|}$ orbitals of both CO ligands, as shown in Scheme 2.



HOMO of $Cp_2Zr(CO)_2$

Scheme 2.

When a strongly donating PMe_3 ligand is added to $Cp_2Zr(CO)$ to give compound **7**, the amount of backbonding to the CO 2π orbital increases substantially, to 0.58e, while the CO 5σ population is about the same as in $Cp_2Zr(CO)$. The CO stretching frequency in **7** is correspondingly ca. 80 cm^{-1} lower than the average of the two frequencies in **6**. The replacement of the Cp ligands of **6** with Cp* ligands, to generate **8**, leads to slightly greater π-backbonding. The change in 2π population is not nearly as great as that between **6** and **7**, which is consistent with the smaller shift in CO stretch from **6** to **8** (ca. 30 cm^{-1}).

Jordan and co-workers reported extended Hückel calculations on the nonclassical Zr(IV) carbonyls **4a** and **4b** [8]. They viewed the molecules as the addition of a CO ligand to a $Cp_2Zr(\eta^2\text{-COMe})^+$ moiety in either its O-inside or O-outside conformation. Consistent with our discussion above, we will view **4a** and **4b** slightly differently, namely as the addition of an anionic acetyl ligand to $Cp_2Zr(CO)^{2+}$. This approach allows us to focus on the changes in the CO populations as the acetyl ligand is added. We shall see that the results we obtain for **4a** and **4b** are in excellent accord with those obtained by Jordan and co-workers.

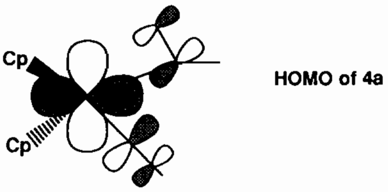
The $COMe^-$ ligand forms a Zr–C σ bond via donation from its HOMO, which is a largely C-localized 'lone pair' that has a small π-antibonding contribution from the O atom. The molecular orbital that represents this Zr--C σ interaction is the HOMO of both **4a** and **4b**. The O-outside isomer **4a** exhibits $\nu(CO)=2123$ cm^{-1}, which is slightly lower than that of free CO. For **4a** we have assumed a C(acetyl)–Zr–C(carbonyl) angle of 75°, which is that observed in **5a** [8]. At this acute angle, the same Zr 4d orbital that is used to form the Zr–C σ interaction can also be involved in Zr–CO π-

Table 1
Cotton–Kraihanzel force constants and CO Mulliken populations for some systems that contain the $Cp_2Zr(CO)$ fragment

Compound	k_{CO} (mdyn $Å^{-1}$) [a]	5σ population	$2\pi_{\parallel}$ population	$2\pi_{\perp}$ population
$Cp_2Zr(CO)^{2+}$	–	1.48e	0.06e	0.11e
$Cp_2Zr(CO)^{+}$	–	1.51	0.22	0.10
$Cp_2Zr(CO)$	–	1.53	0.42	0.08
$Cp_2Zr(CO)_2$, **6**	15.05	1.52	0.40	0.08
$Cp_2Zr(CO)(PMe_3)$, **7**	13.87	1.51	0.51	0.07
$Cp_2Zr(CO)(COMe)^{+}$, **4a**	18.20	1.50	0.20	0.11
$Cp_2Zr(CO)(COMe)^{+}$, **4b**	19.12	1.52	0.11	0.11

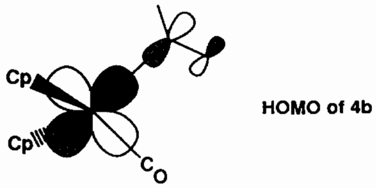
[a] Cotton–Kraihanzel force constant, calculated from available experimental vibrational data.

backbonding, as shown in Scheme 3. In essence, the LUMO of $Cp_2Zr(CO)^{2+}$ can be used as a σ-acceptor orbital for $COMe^-$ with only a small amount of mixing from other Zr 4d orbitals. As a result, there is a significant contribution from the CO $2\pi_{\parallel}$ MO in the HOMO of **4a**. The population of this orbital thereby increases by 0.14e relative to the value for $Cp_2Zr(CO)^{2+}$ owing to the 'shuttling' of charge from the $COMe^-$ ligand to the CO (Table 1).



Scheme 3.

The situation is slightly different for the O-inside isomer **4b**, which has a CO stretching frequency of 2176 cm^{-1}, higher than that of free CO. We have assumed a geometry that is related to that of **4a** via rotation of the COMe ligand about the bisector of the C(acetyl)–Zr–O(acetyl) angle. This change has a profound effect on the Zr 4d contribution in the HOMO of **4b** compared with that of **4a**. The Zr 4d orbital that is used as a σ-acceptor from $COMe^-$ is now poorly oriented to participate in Zr–CO backbonding, as shown in Scheme 4. Because charge cannot be shuttled effectively from the acetyl ligand to the CO $2\pi_{\parallel}$ MO, this orbital shows a much smaller population increase in **4b** relative to $Cp_2Zr(CO)^{2+}$ than was observed for **4a** (Table 1).



Scheme 4.

Table 1 shows that for the four 'real' Zr complexes discussed above (**6**, **7**, **4a**, and **4b**), the CO 5σ population is remarkably constant ($1.51 \pm 0.01e$). For these complexes, therefore, the value of k_{CO} will be largely a linear function of the total 2π population per CO ligand (Eq. (1)). Fig. 1 shows a plot of k_{CO} versus (2π) for the four complexes. The excellent linear fit indicates that the CO stretching frequency in both classical and nonclassical Zr carbonyls is governed by the extent of Zr→CO backbonding. Interestingly, we can use this linear fit to extrapolate the CO stretching frequency of an isolated $Cp_2Zr(CO)^{2+}$ fragment (ignoring its somewhat greater variance in CO 5σ population). The extrapolated value, 2227 cm^{-1}, is nearly 100 cm^{-1} higher than that of free CO.

3.2. Nonclassical silver carbonyls

The Ag(I) carbonyl complexes **1** and **2** reported by Strauss and co-workers [3–5] pose a very different situation from that of the Zr(IV) complexes discussed above. **1** and **2** contain a d^{10} metal center that would seem able to participate in significant π-backbonding. Instead, these complexes exhibit values of $\nu(CO)$ that are even higher than those in the d^0 complexes **3**–**5**. We have performed Fenske–Hall calculations on **1** and **2**, including the weakly coordinating anion, to examine whether they fit the same trends as the Zr complexes. The electronic structures of isolated $Ag(CO)_n^+$ ions have previously been investigated using ab initio methodology by Bauschlicher and co-workers [23] and by Veldkamp and Frenking [24].

Complex **1** contains an essentially linear $AgCO^+$ cation coordinated in bidentate fashion to $B(OTeF_5)_4^-$ anion. The $B(OTeF_5)_4^-$ ion is very large and weakly coordinating, properties that Strauss and co-workers consider crucial to the stability of complexes **1** and **2**. In order to determine whether the $B(OTeF_5)_4^-$ imparted unusual electronic properties, we performed calculations on **1** in which the actual ligand was used and in which the ligand was modeled as $B(OH)_4^-$ but with the same Ag–O distance as in **1**. We saw only minor differences in the electron distribution in the $AgCO^+$ fragment between these two calculations. The results we report here are those using the $B(OTeF_5)_4^-$ ion.

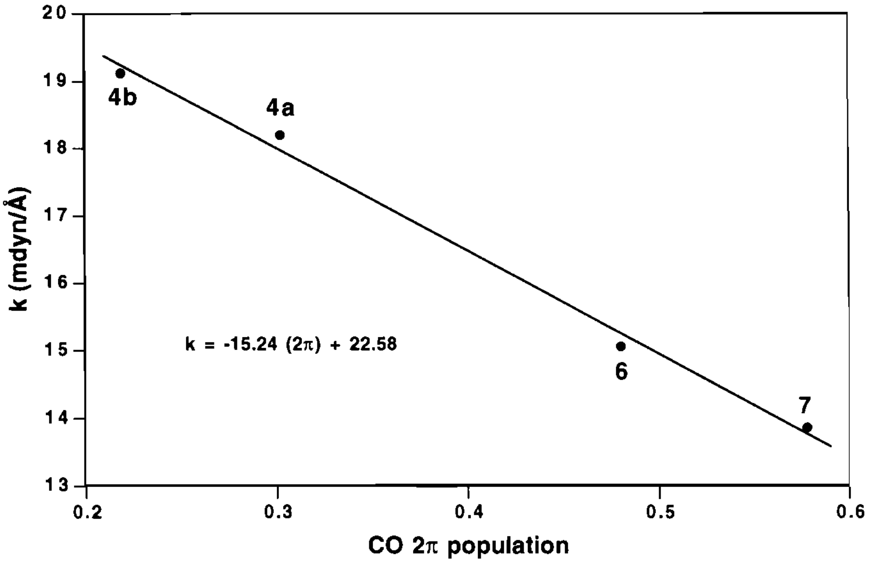


Fig. 1. Plot of k_{CO} vs. CO 2π population for a series of zirconium carbonyl complexes: 'O-out' $Cp_2Zr(CO)(COMe)^+$ (**4a**), 'O-in' $Cp_2Zr(CO)(COMe)^+$ (**4b**), $Cp_2Zr(CO)_2$ (**6**), and $Cp_2Zr(CO)(PMe_3)$ (**7**).

The 5σ population for the CO in **1** is 1.58e, somewhat higher than that in the Zr complexes. This higher population indicates that the CO is less σ-basic toward Ag than Zr, an observation consistent with the formally filled 4d subshell of Ag(I). The CO 2π population is only 0.13e, indicating that the Ag^+ ion is an exceedingly poor π donor toward CO. Trial calculations with a variety of Ag 5s and 5p orbital exponents led to the same result. The extremely low 2π population is largely responsible for the high value of ν(CO) exhibited by **1**.

In order to compare the results for **1** with those for a classical carbonyl complex, we have undertaken companion calculations on $Mo(CO)_6$ (**9**). The Mo 4d, 5s, and 5p AOs were generated in a fashion entirely analogous to that used to generate the Ag AOs. The CO ligands in **9** show 5σ and 2π populations of 1.45e and 0.50e, respectively, values that are in accord with strong σ donation and π acceptance by the CO ligands.

The large difference in the results for **1** and **9** can be traced to the fundamental tenets that govern the extent of interaction between two interacting orbitals: (1) in general, the extent of interaction increases as the overlap of the interacting orbitals increases, and (2) in general, the extent of interaction decreases as the energetic separation between the interacting orbitals increases. Table 2 compares the overlaps and energetic separations of the metal 4dπ AOs and the CO 2π MOs in **1** and **9**. We see that Mo–CO backbonding is strongly favored over Ag–CO backbonding on both overlap and energetic considerations.

The influence of the $B(OTeF_5)_4^-$ ion on the backbonding in **1** is made clear by a separate calculation on $Ag(CO)^+$ in a geometry that corresponds to removal of the anion from the structure of **1**. The CO 2π population decreases to 0.10 for the isolated cation, indicating that even the coordination of a weak anion will increase the density available for Ag–CO backbonding. This calculation is also helpful in viewing the bonding in the dicarbonyl **2**, which consists of essentially free linear $Ag(CO)_2^+$ ions with largely noninteracting $B(OTeF_5)_4^-$ ions. The CO 5σ and 2π populations in $Ag(CO)_2^+$ are 1.55e and 0.08e, respectively. Unlike the Zr systems, the competition between the two CO ligands apparently leads to lower backbonding to each. The IR spectrum of **2** shows that the antisymmetric stretch of the two CO ligands occurs at 2198 cm^{-1}, and according

Table 2
Comparison of the overlaps and energetic separations of the metal 4dπ AOs and the CO 2π MOs in $Ag(CO)B(OTeF_5)_4$ (**1**) and $Mo(CO)_6$ (**9**)

Compound	4dπ/2π overlap [a]	ε(2π) − ε(4dπ) [b]	CO 2π population
$Ag(CO)B(OTeF_5)_4$	0.072	9.89 eV	0.13e
$Mo(CO)_6$	0.161	4.97 eV	0.50e

[a] Defined in the usual way, as the overlap integral between the appropriate 4d AO and the CO 2π MO in the transformed basis.
[b] Defined as the difference in the diagonal elements of the converged self-consistent-field matrix in the transformed basis.

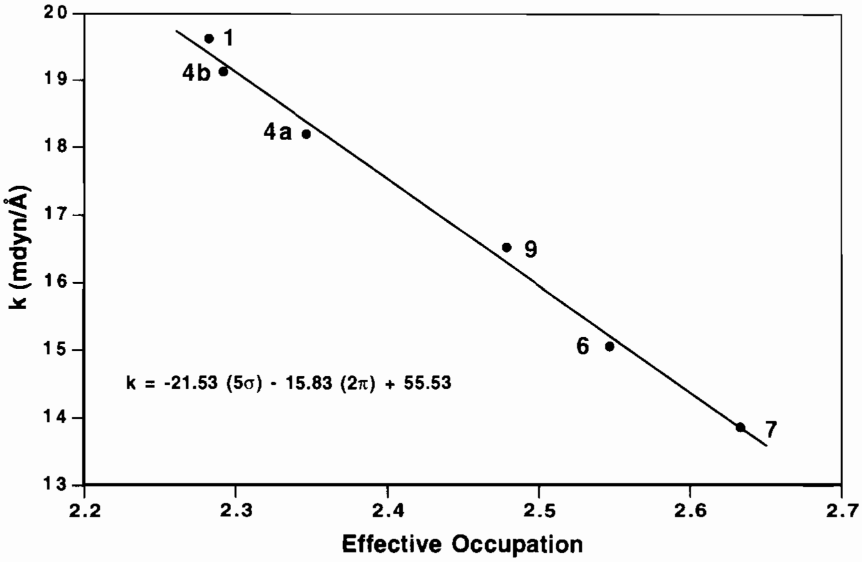


Fig. 2. Plot of k_{CO} vs. effective occupation for the following carbonyl complexes: $Ag(CO)[B(OTeF_5)_4]$ (**1**), 'O-out' $Cp_2Zr(CO)(COMe)^+$ (**4a**), 'O-in' $Cp_2Zr(CO)(COMe)^+$ (**4b**), $Cp_2Zr(CO)_2$ (**6**), $Cp_2Zr(CO)(PMe_3)$ (**7**), and $Mo(CO)_6$ (**9**).

to the assumptions of the C–K method, this value will be a lower limit of the symmetric stretch frequency. It seems likely that the value of k_{CO} for $Ag(CO)_2^+$ will be greater than 20 mdyn $Å^{-1}$, as was recently observed in linear $Au(CO)_2^+$, which exhibits symmetric and antisymmetric CO stretches at 2254 and 2217 cm^{-1}, respectively [25]. We have not performed calculations on this cation, because of our reluctance to use the Fenske–Hall method for systems that contain relativistically influenced third-row transition metals. Nevertheless, we would expect to see the same general pattern of minimal backbonding owing to the contracted nature of the Au 5d AOs. To summarize, our studies are very supportive of the proposals of a near-complete lack of M→CO backbonding in the group 11 carbonyls, although our results indicate a greater degree of backbonding than do those of Veldkamp and Frenking [24].

3.3. *Analysis via Eq. (1)*

In Fig. 1 we demonstrated a linear relationship between k_{CO} and (2π) for the classical and nonclassical zirconium carbonyl complexes. This relationship follows from Eq. (1) because of the very small variation in (5σ) throughout the series. Throughout the entire series of compounds discussed here, including the nonclassical Zr and Ag carbonyls and the classical Zr and Mo carbonyls, there are significant variations in (5σ), however. Therefore, in order to attempt the correlation of all the results presented here, we must include both (5σ) and (2π) in our analysis according to Eq. (1).

Hall and Fenske used Eq. (1) to define an effective occupation, (occ), of the CO orbitals as

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

wherein Eq. (1) can be rewritten as

$$k_{CO} = b(\mathrm{occ}) + c \tag{3}$$

Fig. 2 shows the fit of the C–K k_{CO} values and calculated CO populations of compounds **1**, **4a**, **4b**, **6**, **7**, and **9** to Eq. (3). The fit is quite good, although the optimized values of a (-21.53 mdyn e^{-1} $Å^{-1}$) and b (-15.83 mdyn e^{-1} $Å^{-1}$) are somewhat curious in view of previous applications of Eq. (1). Both a and b are negative, consistent with the fact that both the 5σ and 2π orbitals of CO are antibonding. It is surprising, however, that the magnitude of a is greater than that of b, which implies that occupation of the 5σ orbital has a greater effect on k_{CO} than does occupation of the 2π orbital. Previous studies have found that $|b| > |a|$, although the range of specific values of a and b has been highly variable [9,26]. In the present study, we believe that specific magnitudes of a and b are greatly affected by the much smaller range for the 5σ population (1.45 to 1.58) than for the 2π population (0.13 to 0.58). As we have pointed out previously, the ranges in 5σ and 2π populations are consistent with the notion that the 2π orbitals are significantly more important than the 5σ orbital for determining the magnitude of k_{CO} [2].

4. Conclusions

The calculations reported above show that the unusual CO stretching frequencies of nonclassical carbonyl complexes can be treated via molecular orbital theory in a manner consistent with the treatment of classical carbonyls. All of the nonclassical carbonyls exhibit significantly less M→CO backbonding than do the classical carbonyls. The OC→M σ-donation in the nonclassical complexes is similar to that in classical carbonyls. Consistent with the conclusions of others, the high stretching frequencies exhibited by the nonclassical carbonyls (in many cases greater than that of free CO) are primarily the result of donation from the C–O antibonding 5σ orbital without compensating donation into the C–O antibonding 2π orbitals.

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