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Article

Ligand Electronic Parameters as a Measure of the Polarization of the C≡O Bond in $[M(CO)_xL_y]^n$ Complexes and of the Relative Stabilization of $[M(CO)_xL_y]^{n/n+1}$ Species

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The electronic description of octahedral (*fac*-$[M(CO)_3L_3]^n$, with M = Re, Ru, and Mn, and $[Cr(CO)_5L]^n$), square-planar (*cis*-$[Pt(CO)_2L_2]^n$), and tetrahedral ($[Ni(CO)_3L]^n$) carbonyl complexes (where L = monodentate ligand) was obtained via density functional theory and natural population analyses in order to understand what effects are probed in these species by vibrational spectroscopy and electrochemistry as a function of the ligand electronic parameter of the associated L. The analysis indicates that while ligand electronic parameters may be considered as a measure of the net donor power of the ligand, the net transfer of the electron density (or charge) does not occur from the ligand to the metal ion. In $[M(CO)_xL_y]^n$ carbonyl species, the charge transfer occurs from the ligand L to the oxygen atom of the bound carbon monoxides. This charge transfer translates into changes of the polarization (or permanent dipole) and the covalency of the C≡O bonds, and it is this effect that is probed in IR spectroscopy. As the analysis shifts from IR radiations to electrochemical potentials, the parameters best describe the relative thermodynamic stability of the oxidized and reduced $[M(CO)_xL_y]^{n/n+1}$ species. No relationship is found between the metal natural charge of the $[M(CO)_xL_y]^n$ fragments analyzed and the parameters. Brief considerations are given on the possible design of CO-releasing molecules.

Introduction

The quantitative analysis and parametrization of the effects that ligands have on transition-metal ions have been employed in the last 30 years in inorganic and organometallic chemistry as a tool to "predict and tune" the properties of metal complexes. The foundations of the analysis are based on the idea that certain spectroscopic, physical, and structural properties of metal complexes can be expressed and understood in terms of the electronic (and/or steric) parameters assigned to the ligands involved in the primary coordination sphere of the metal ion. Several theoretical models aimed at relating ligands' effects to the properties of transition-metal complexes have appeared.[1−7]

The common basis of all of the studies is the concept of "average environment" or that ligands' effects are additive and, as such, can be parametrized. On the basis of the ligand additive model, we have also recently introduced a ligand parameter, $IR_P(L)$, which may be used to predict the symmetric C≡O stretching frequency of octahedral carbonyl complexes.[8] Our analysis yielded the following relationship:

$$\nu_{CO}{}^{cal} = S_R[\sum IR_P(L)] + I_R \qquad (1)$$

where $\nu_{CO}{}^{cal}$ is the calculated (or predicted) symmetric C≡O stretching frequency and S_R and I_R are constants that depend upon the metal, its oxidation state, and the number of CO ligands in its primary coordination sphere. One of the interesting outcomes of the study[8] was the realization that $IR_P(L)$ values linearly correlate with the well-established Lever's electronic parameter E_L.[9−13]

Extension of this observation to other ligand parameters yields the same result (see the Supporting Information, SI). These correlations, however, are not new. It has long been known that there is a linear correspondence between E_L and P_L (a parameter developed by Chatt, Leigh, Pickett, and coworkers).[3−5] It was also recently demonstrated that there

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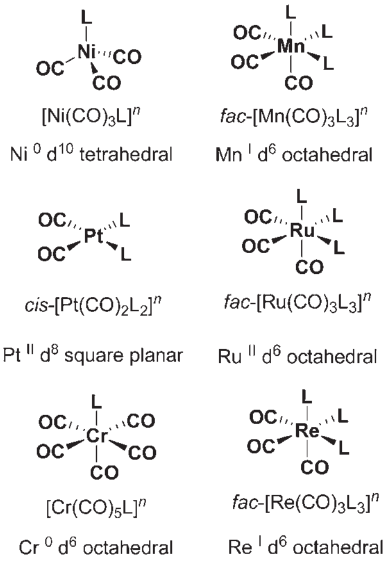
exists a "full transferability" between the so-called computed electronic ligand parameters (CEPs), E_L, and Tolman's electronic parameters (ν).[14] These linear relationships, however, suggest that all parameters presented to date may describe the same fundamental property of the ligands. The differences in the values and in the units of measure of the parameters consequently reflect only the different analytical techniques that were used to probe and reveal this property.

In this respect, it has been suggested that the ligand parameters (E_L, P_L, CEP, and ν) are a measure of the net donor power of the ligand, in terms of both σ and π contributions.[9,11,14] The argument is then often made, particularly when PR_3 ligands (PR_3 = phosphine or phosphite) are bound to a metal carbonyl fragment, that the σ basicity and π acidity of the ligands alter the electronic density of the metal ion, thereby directly influencing both the redox properties and the carbonyl stretching frequencies.[8,14–16]

It is, thus, generally accepted that the terminal carbonyl stretching frequencies are directly dependent on the electronic density of the metal ion to which the carbon monoxide is bound and that the net donor charge transfer of the ligand refers mainly to the central metal ion. A number of theoretical studies, however, have shown that the partial population of the CO π^* orbitals, due to the metal π back-donation, is not sufficient alone to account for variation of the CO stretching frequencies in metal carbonyl complexes.[17–23] Thus, some fundamental questions arise: (1) What exactly is probed in IR spectroscopy of metal carbonyl complexes as a function of the ligand parameters? (2) Why is there a linear correspondence between parameters derived from IR analysis and electrochemistry?

The answers to these questions are important not just from a theoretical point of view. Understanding, for example, what effects ligands have on a given $[M(CO)_xL_y]^n$ fragment, in terms, e.g., of the M$-$CO bond, may help the design of CO-releasing molecules (CO-RMs), a newly emerging class of molecules with potential pharmaceutical applications.[24] It is ultimately in this subject that our interest resides. Specifically, the analysis herein described aims at understanding whether the effects brought about by certain ligands on a selected $[M(CO)_x]^n$ fragment can serve as a useful guide, or an indication, for the rational design of CO-RMs.

Chart 1. Metal Complexes Investigated in This Study



In order to address the issues above, we have carried out a density functional theory (DFT) analysis and natural population analysis (NPA) of the complexes, shown in Chart 1. The results will show that while the ligand electronic parameters may be considered as a measure of the net donor power of the ligand, contrary to what may be generally assumed, the net transfer of the electron density (or charge) does not occur from the ligand to the metal ion. Rather, in $[M(CO)_xL_y]^n$ carbonyl species, the charge transfer occurs from the ligand L to the oxygen atom of the bound carbon monoxides. This charge transfer translates into changes of the polarization (or permanent dipole) and the covalency of the C≡O bonds. It is this effect that is probed by IR radiations. As the analysis shifts from vibrational spectroscopy to electrochemical potentials, the parameters best describe the relative thermodynamic stability of the oxidized and reduced $[M(CO)_xL_y]^{n/n+1}$ species.[25] No relationship is found between the metal natural charge of the $[M(CO)_xL_y]^n$ fragments analyzed and the parameters. Brief considerations are finally given on the possible design of CO-RMs.

Experimental Section

Computational Details. Geometry optimizations as well as frequency calculations for all molecules were performed at the DFT level of theory with the *Gaussian03* program package[26] using the hybrid B3LYP functional[27] in conjunction with the LanL2DZ basis set.[28–30] Pure basis-set functions (5d7f) were used in all calculations. Geometries were fully optimized without symmetry restrictions prior to the frequency calculations and full NPA. For comparison with the ligand parameters, natural atomic charges were considered while bond orders were obtained from the Wiberg bond index matrix in the NAO basis set after the full NPA. The *Origin* program (version 6.1) was used to plot data and derive equations for the best linear fits.

Results and Discussion

Correlation of $IR_P(L)$ Parameters with the A_1 ν_{CO} Mode of $[M(CO)_xL_y]^n$ Complexes. In our previous analysis, ligand $IR_P(L)$ values were derived from *fac*-$[Re(CO)_3L_3]^n$ complexes and the validity of the model was tested only against other octahedral d^6 tris- and bis-carbonyl species.[8]

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For this reason, we considered an important first step in our discussion to test the $IR_P(L)$ values also against carbonyl complexes of different geometries. Thus, in order to verify the general validity of the $IR_P(L)$ parameters, we began our analysis by correlating $IR_P(L)$ values with the gas-phase A_1 ν_{CO} mode (ν_{CO}^{cal}) values of octahedral (*fac*-$[M(CO)_3L_3]^n$, with M = Re, Ru, and Mn, and $[Cr(CO)_5L]^n$), square-planar (*cis*-$[Pt(CO)_2L_2]^n$), and tetrahedral ($[Ni(CO)_3L]^n$) complexes. The selected metal carbonyl $[M(CO)_xL_y]^n$ fragments differ not only in their geometry but also in their d electronic configuration (i.e., d^6 for M = Cr, Re, Ru, and Mn, d^8 for M = Pt, and d^{10} for M = Ni) and the overall relative charge n of the species considered.

In this analysis, only monodentate ligands were considered in order to directly compare the DFT ν_{CO}^{cal} values with the corresponding ligand $IR_P(L)$ parameter. A total of 22 ligands were selected so as to encompass the widest possible range of $IR_P(L)$ values. These vary from hydride [$IR_P(H^-)$ = 295 cm^{-1}] to triphenylphosphite [$IR_P(P(OPh)_3]$ = 340 cm^{-1}) or carbon monoxide [$IR_P(CO)$ = 348 cm^{-1}]. Figure 1 shows a plot of $IR_P(L)$ against the DFT-calculated ν_{CO}^{cal} values for the corresponding complexes. We found a good linear relationship (R = 0.96−0.98) in all cases, indicating that the $IR_P(L)$ additive model may be considered to be generally valid for $[M(CO)_xL_y]^n$ species irrespective of the geometry, the metal M d electronic configuration, and the overall charge n of the complexes.

It should be mentioned, however, that while the linear correlation between $IR_P(L)$ and ν_{CO}^{cal} values of complexes of Re, Mn, and Ni gave excellent results ($R \geq 0.98$), greater scattering was observed when complexes of Ru, Cr, and Pt were analyzed. It was generally found that ν_{CO}^{cal} values of halides X (with $X \neq F^-$) were underestimated for the latter metal complexes. At this level of theory, the A_1 stretching frequencies of ruthenium, chromium, and platinum carbonyl complexes of halides were calculated all within a close range. This was an unexpected result considering that $IR_P(F^-)$ is considerably lower than the other $IR_P(X)$ values. All other ligand parameters (E_L, P_L, CEP, and ν) are in agreement with our IR_P(halide) assignments; thus, this discrepancy remains unclear at the moment.

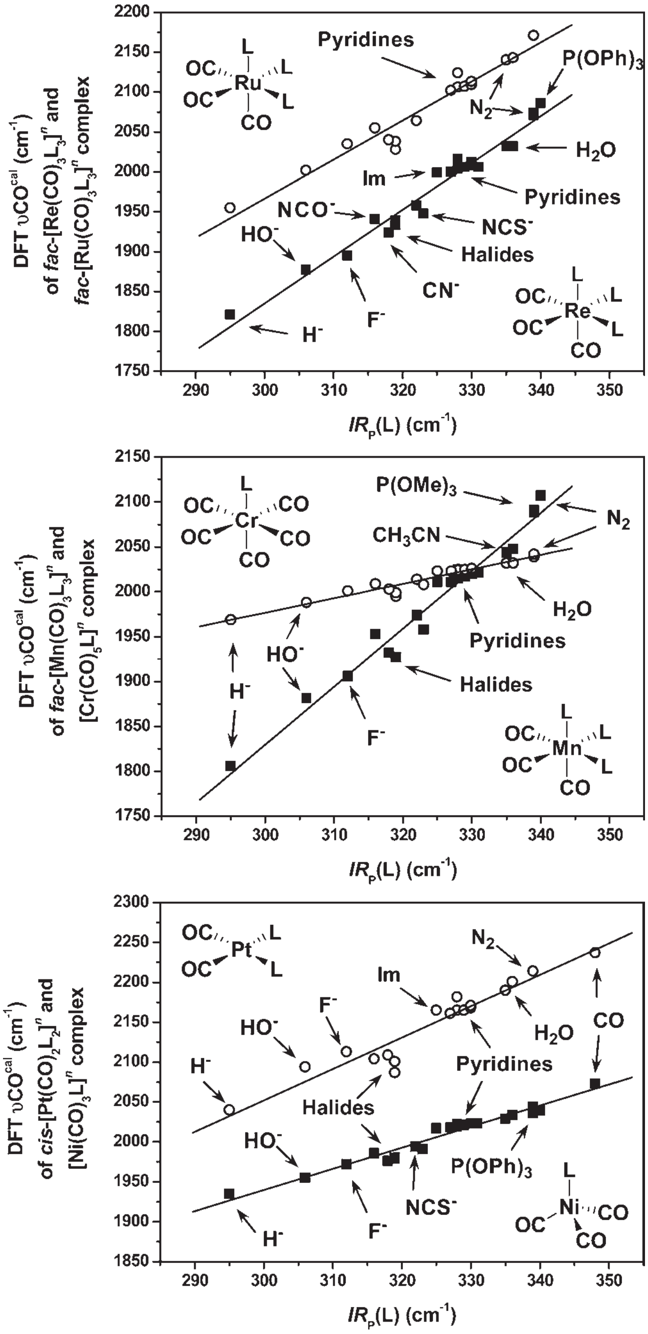

Figure 1. Plot of DFT-calculated symmetric C≡O stretching frequency (A_1 mode, DFT ν_{CO}^{cal}, y axis, cm^{-1}) against the corresponding $IR_P(L)$ value (x axis, cm^{-1}) of (top to bottom) octahedral *fac*-$[Ru(CO)_3L_3]^n$ (○) and *fac*-$[Re(CO)_3L_3]^n$ (■) complexes, octahedral $[Cr(CO)_5L]^n$ (○) and *fac*-$[Mn(CO)_3L_3]^n$ (■) complexes, square-planar *cis*-$[Pt(CO)_2L_2]^n$ (○), and tetrahedral $[Ni(CO)_3L]^n$ (■) complexes. The plots show the linear relationship between DFT ν_{CO}^{cal} and $IR_P(L)$ of 22 complexes.

Analysis of the Charge Distribution of $[M(CO)_xL_y]^n$ Complexes as a Function of the $IR_P(L)$ Parameters. As was mentioned in the Introduction, it has often been suggested that ligand electronic parameters (E_L, P_L, CEP, and ν) are a measure of the net donor power of the ligand, in terms of both σ and π contributions. By the net donor power, the net transfer of the electron density (or charge) from the ligand L to the metal complex (here $[M(CO)_xL_y]^n$) is understood. While this assumption might be considered intuitively obvious, it remains unclear to what part of a metal carbonyl fragment the ligand L donates its electronic charge. Lever et al. have recently demonstrated that in *o*-benzoquinonediimine (bqdi) complexes of Ru the E_L parameters linearly relate to the net charge residing on bqdi,[31] but we are not aware of any studies that have dealt with this particular question in the case of $[M(CO)_xL_y]^n$ species. In this case there are, in principle, three possibilities to consider. The net transfer of the electron density from the ligand L may result in (i) an increased charge on the central metal ion M, (ii) an increased charge on the carbonyl ligands comprising the coordination sphere of the metal fragment considered (possibly via M−CO π back-bonding), or (iii) a combination of both.

In order to address this issue, we carried out a full analysis of the electronic description of all of the $[M(CO)_xL_y]^n$ complexes shown in Chart 1. We first considered the charge on the central metal ion obtained from the NPA

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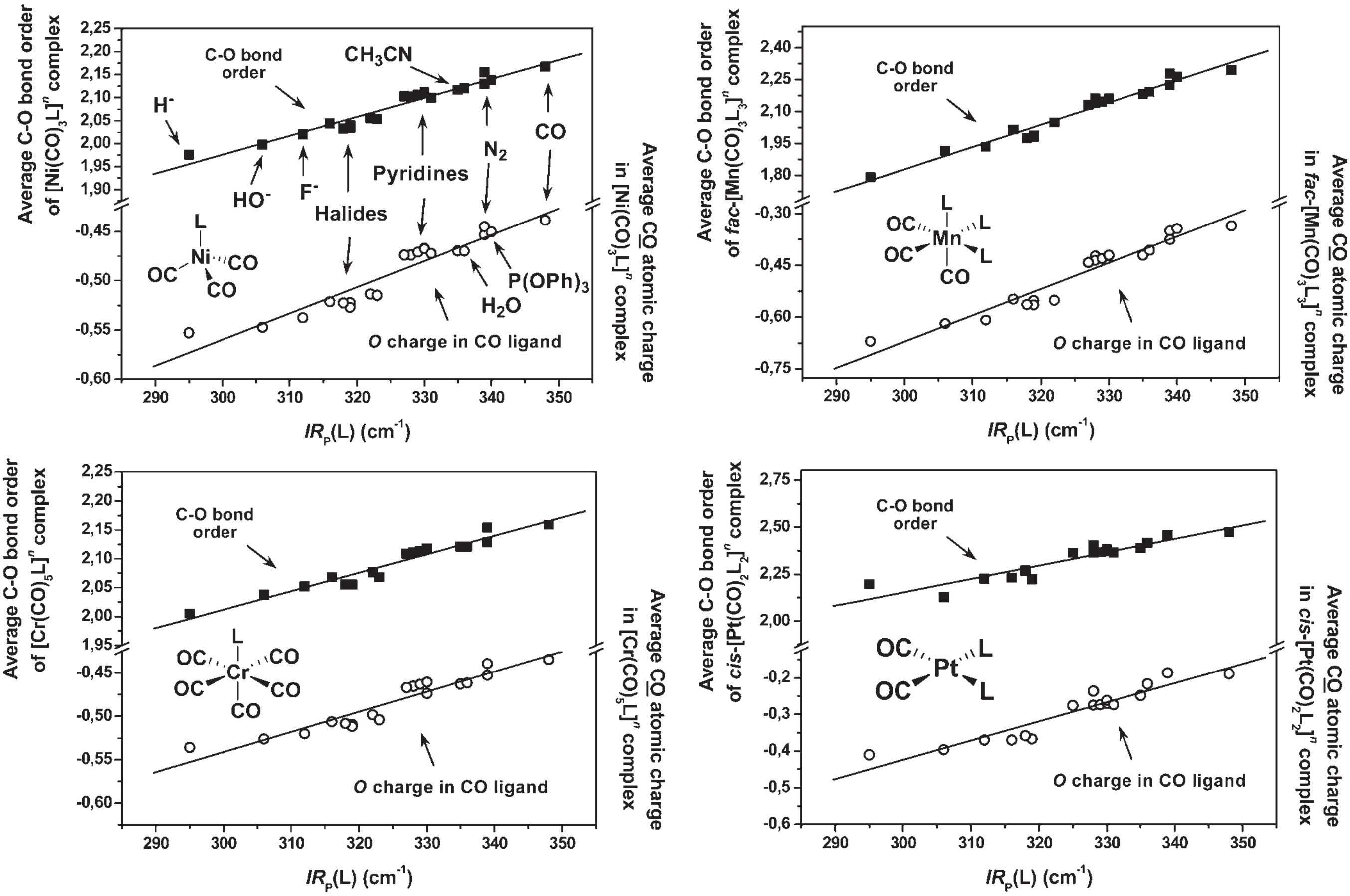

Figure 2. Plot of DFT-calculated average C−O bond orders (y axis, top left, ■) and average natural atomic charge on oxygen atoms of CO ligands (y axis, bottom right, ○) of tetrahedral $[Ni(CO)_3L]^n$ complexes, octahedral *fac*-$[Mn(CO)_3L_3]^n$ complexes, octahedral $[Cr(CO)_5L]^n$ complexes, and square-planar *cis*-$[Pt(CO)_2L_2]^n$ complexes against the corresponding $IR_P(L)$ value (x axis, cm^{-1}). The identity of selected ligands is shown in the top-left graph. The same ligands were used in all calculations.

of the DFT-calculated wave functions and correlated this with the $IR_P(L)$ values of the associated ligand L. We found no relationship between the metal natural charge and the $IR_P(L)$ parameters (see the SI). Moreover, we found that at this level of theory the electronic density on the metal ion of complexes of strong π-acceptor ligands [e.g., N_2, CO, or $P(OR)_3$] was often similar to that of the corresponding hydride (H^-) species (see the SI).

Additional analysis of the bond orders and the electronic description of the complexes obtained from the DFT-calculated wave functions has revealed, however, a good linear relationship between the $IR_P(L)$ parameters and the C−O bond orders and between the $IR_P(L)$ parameters and the atomic charges on the oxygen atoms of carbonyl groups (Figure 2).[32] A similar tendency was observed when the M−C bonds [i.e., a decrease in the M−C bond order vs $IR_P(L)$] and atomic charges on the carbon atoms of carbonyl groups were analyzed, but the regression coefficients were generally too far from unity to draw any accurate relationship. Thus, it appears that in the $[M(CO)_xL_y]^n$ complexes considered the ligands L transfer electronic charge onto the oxygen atoms of carbonyl groups and not onto the metal ion. The net ligand transfer of the electron density to the CO's decreases linearly as the $IR_P(L)$ values increase. Concurrent with higher $IR_P(L)$ values, a linear increase of the C−O bond orders is observed. These changes are plotted in Figure 2 for some selected complexes. In the case of *fac*-$[Re(CO)_3L_3]^n$ complexes, a similar partial analysis was previously carried out,[8] while *fac*-$[Ru(CO)_3L_3]^n$ complexes show results virtually identical with those of the *fac*-$[Mn(CO)_3L_3]^n$ species and are omitted to avoid redundancy.

Our results are in agreement with several theoretical works that have analyzed the nature of the CO and M−CO bonds.[17−20,22] The fundamental picture that has emerged from these studies is that the partial population of the CO π^* orbitals, due to the metal π back-donation, is not sufficient alone to account for variation of the CO stretching frequencies in metal carbonyl complexes. Electrostatic effects also play a fundamental role. Goldman and Krogh-Jespersen, for example, have demonstrated that changes in the CO bond distance and stretching frequencies are nearly identical whether CO is bound to H^+ or a positive point charge.[20] In their analysis, these authors concluded that CO bond lengthening and stretching may be mainly attributed to polarization of the CO bonding orbitals, which, in turn, affects the covalency of the bond.[20]

In our case, we found a very similar result. The linear correlation between the $IR_P(L)$ values and the CO stretching frequencies (ν_{CO}^{cal}; Figure 1) of the $[M(CO)_xL_y]^n$ fragments and the atomic charges on the oxygen atoms of the

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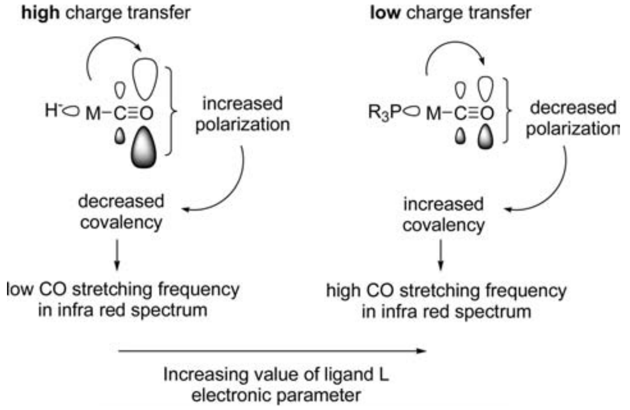

Figure 3. Schematic representation of the effects of changes in the polarization of the CO bond of $[M(CO)_xL_y]^n$ complexes as a function of the increasing value of the ligand electronic parameter. The shape of the orbitals is purely illustrative, and the size is intended as a measure of the atomic charge.

carbonyl groups (CO^{δ}; Figure 2) points consequently at a linear relationship between ν_{CO}^{cal} and CO^{δ}. In other words, the net transfer of the electron density (or charge) from the ligand to the metal fragment induces an increase in the polarization (and thus the permanent dipole) of the CO bonds due to an increase of CO^{δ} (i.e., the charge on the oxygen atoms of the carbonyl groups). This effect is more pronounced with ligands characterized by low $IR_P(L)$ values (e.g., H^-), while strong π-acceptor ligands [e.g., N_2, CO, or $P(OR)_3$] decrease the polarization of the CO bonds, making CO more "N_2-like". The electronic field induced by the latter ligands increases the covalency of the CO bond [as shown by the relationship between $IR_P(L)$ and the C−O bond order; Figure 2], and thus the CO stretching frequency increases (i.e., ν_{CO}^{cal} increases; Figure 1). It may thus be stated that, in $[M(CO)_xL_y]^n$ species, the ligand electronic parameters are a measure of the polarization of the C≡O bonds and not of the electronic density of the metal ion. Changes in the polarization (or permanent dipole) of the CO bonds translate into changes of the covalency of the bonds, and it is this effect that is probed by IR radiations. Figure 3 schematically represents these results. It should be mentioned here that what it is probed via IR spectroscopy as a function of the parameters is only the final charge density and not the mechanism by which the final state is reached.

NPA and Molecular Orbital (MO) Analysis of $[Ni(CO)_3L]^n$ and $[Cr(CO)_5L]^n$ Complexes as a Function of the Electronic Parameters. It was previously mentioned that there exists a linear relationship between the ligand electronic parameters derived from the analysis of ν_{CO} stretching frequencies of $[M(CO)_xL_y]^n$ complexes [i.e., $IR_P(L)$, CEP, and ν] and the parameters derived from the analysis of $M(n)/M(n+1)$ redox potentials (i.e., E_L and P_L). A final question that we wanted to address relates to this linear relationship. We have just shown that the ligand parameters may be considered as describing the polarization of the C≡O bonds in carbonyl complexes and that there is no correlation with the central metal charge. Thus, how can the parameters linearly relate to the redox potential of $M(n)/M(n+1)$ couples? In other words, what effect is probed in the $[M(CO)_xL_y]^n$ complexes as a function of the parameters as the analysis shifts from IR radiations to electrochemical potentials?

In order to address this issue, a full optimization and electronic description (NPA) of the $[M(CO)_xL_y]^n$ species shown in Figure 2 (singlet state), together with their oxidized forms (i.e., $[M(CO)_xL_y]^{n+1}$, doublet state), was carried out. The analysis of these species was then related to the E_L parameters for a total of 20 ligands. Ligands were once again selected so as to encompass the widest possible range of E_L values, varying from hydroxide ($E_L = -0.59$ V) to carbon monoxide ($E_L = +0.99$ V).

Several authors in the past have shown that in a homologous series of compounds the highest occupied molecular orbital (HOMO) [or lowest unoccupied molecular orbital (LUMO)] energy linearly relates to the redox potentials of the complexes.[33−35] This notion is widely accepted, and undisputed, but it should be mentioned that only octahedral complexes of the type $[M(CO)_{6-x}(L)_x]^n$ and $[M(Cl)_{6-x}(L)_x]^n$ (where L = nitrile ligand) have been shown to obey this relationship.[33−35] We found that the linear correlation between the HOMO (or LUMO) energy still holds true for the $[M(CO)_xL_y]^n$ species shown in Figure 2, provided that the complexes are divided into groups according to their net charge n and that some ligands (particularly H^-, H_2O, and NH_3, which are variable in E_L) are not included in the final regression analysis (see the SI). This relationship (i.e., HOMO or LUMO energy vs E_L) gives the best results for octahedral $[M(CO)_xL_y]^n$ species ($R \geq 0.97$), while greater scattering is observed in tetrahedral and square-planar complexes particularly with anionic ligands (R = ca. 0.88−0.94; see the SI). The correlation appears to fail if the oxidized $[M(CO)_xL_y]^{n+1}$ complexes are considered.

It is still not yet clear why the HOMO (or LUMO) energy of one component alone should linearly correlate with the ligand parameter. As Lever et al. pointed out,[11] redox potentials are thermodynamic properties that depend on the relative binding energies of both the oxidized and reduced species. Indeed, when the relative ground-state energy difference of the two oxidation states (i.e., DFT-calculated energy of $[M(CO)_xL_y]^{n+1}$ − energy of $[M(CO)_xL_y]^n$) is plotted against the E_L values, an excellent correlation with the parameters ($R \geq 0.97$) is observed. As an example Figure 4 shows the analysis for $[Cr(CO)_5L]^{n/n+1}$ and $[Ni(CO)_3L]^{n/n+1}$ species. A clear separation between the negatively charged and neutral ligands is observed. The correlation between the two sets of ligands and the E_L values gives two nearly parallel lines. In the two $[M(CO)_xL_y]^n$ complexes considered, the relative energy difference between the oxidized and reduced forms of the species linearly increases as the E_L value of the associated ligand L increases.

In general, correlations with ligand parameters give a single straight line. In this case, the separation of the two lines is attributed to the relative difference of the charge n of the complexes, while the small difference in the slopes may be due to the experimental error of the parameter values. The only two ligands that showed a consistent deviation from the correlation (and were thus not included in the regression analysis) are water and ammonia.

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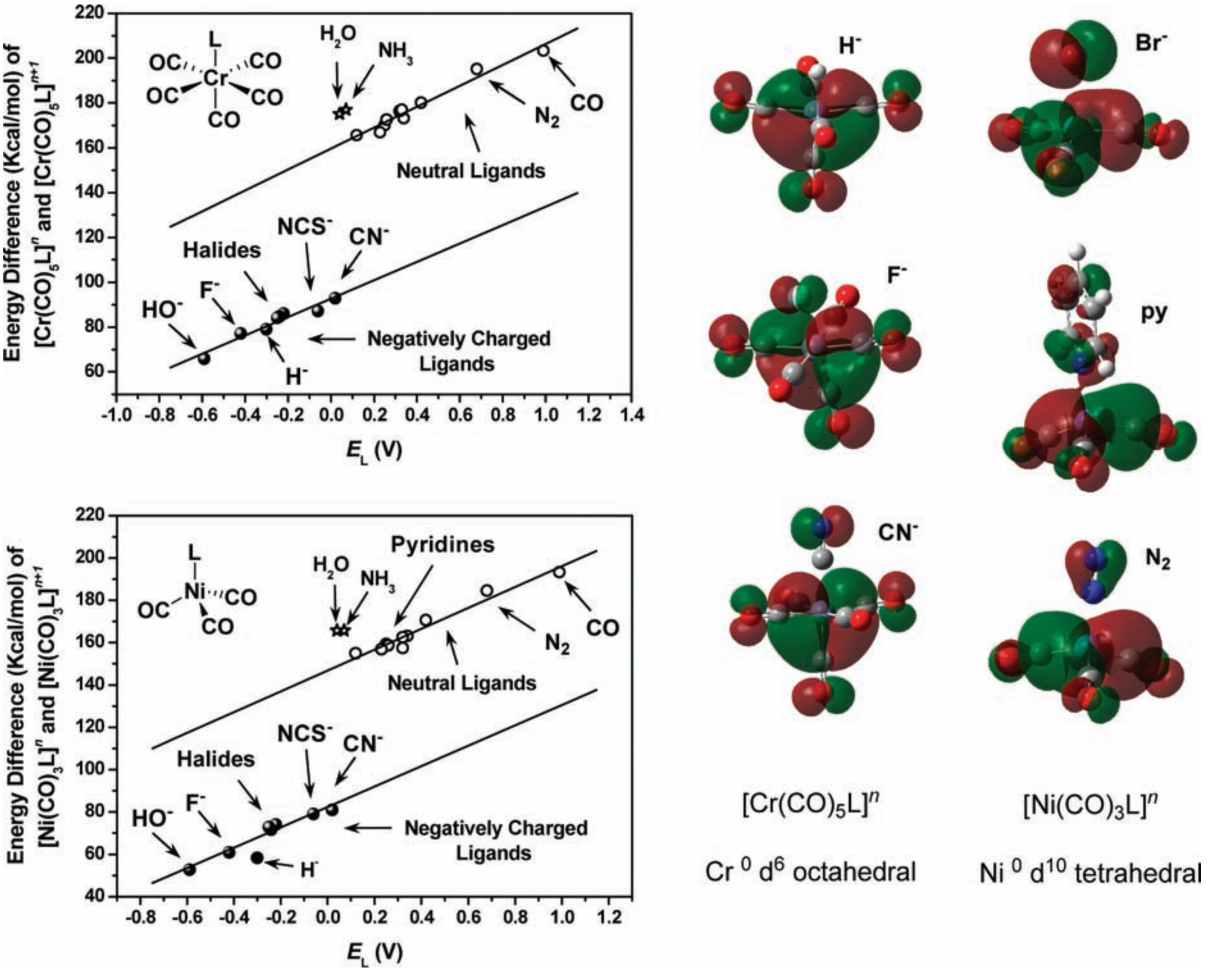

Figure 4. Left: plot of the DFT-calculated ground-state energy difference (*y* axis, kcal/mol) between $[Cr(CO)_5L]^n$ (Cr^0, d^6, singlet) and $[Cr(CO)_5L]^{n+1}$ (Cr^I, d^5, doublet) (top graph) and between $[Ni(CO)_3L]^n$ (Ni^0, d^{10}, singlet) and $[Ni(CO)_3L]^{n+1}$ (Ni^I, d^9, doublet) (bottom graph) against the corresponding E_L values (*x* axis, V) for a total of 20 ligands. Right: HOMO shapes of $[Cr(CO)_5L]^n$ and $[Ni(CO)_3L]^n$ complexes for some selected ligands.

As was mentioned above, the values of both H_2O and NH_3 are variable in E_L. Perrin et al. has suggested that this variability may possibly be a result of hydrogen-bonding interactions of the ligands with solvent molecules.[14] In the case of the nickel complexes, H^- also appears out of line. This discrepancy for $[Ni(CO)_3L]^n$ species was already previously noted.[14] Furthermore, the E_L value for hydride was indirectly derived by Lever.[9]

Analysis of the calculated MOs (both in chromium and nickel complexes; see Figure 4) shows that in all cases the HOMOs have mainly a metal character and are generally antibonding (sometime nonbonding) in character with respect to the ligand L. Electrochemical oxidation processes involving $[Cr(CO)_5L]^n$ and $[Ni(CO)_3L]^n$ may thus be considered as referring to the oxidation of an electron mainly localized on the central metal ion. This observation posed the question as to whether the ligand parameters also described the relative metal charge density ($\Delta\delta$) of the oxidized and reduced $[M(CO)_xL_y]^{n/n+1}$ species. We found, however, no linear relationship between E_L values and the relative difference of the metal ion charges in the two oxidations (i.e., $\Delta\delta = \delta\ M^n - \delta\ M^{n+1}$, where δ = charge on the metal ion vs E_L values; see the SI). A relative increase of $\Delta\delta$ is calculated as the E_L value increases, but here one may speak of a tendency rather than a linear relationship (see the SI). We note here in passing that a good linear relationship ($R \geq 0.95$) between the $IR_P(L)$ values and the C−O bond orders and between the parameters and the atomic charges on the oxygen atoms of the carbonyl groups is still observed in the two different oxidation states of the complexes.

The results argue in favor of the fact that in metal carbonyl species, the effect that is probed via electrochemical potentials as a function of the ligand parameters is best described as the ability of the ligand to stabilize the ground-state energy of the oxidized form of the complex versus its reduced form. The lower the E_L value, the smaller the ground-state energy difference between the two different oxidation states. The previous IR analysis has shown that the ligand electronic parameters may be considered as a measure of the net donor power of the ligand. However, the charge transfer occurs mainly from the ligand to the bound CO's. This relationship holds true irrespective of the oxidation state of the $[M(CO)_xL_y]^n$ species and appears to have little to do with the charge on the metal ion. Figure 5 schematically represents these results.

CO-RMs Design and Concluding Remarks. It should be stated at this point that the results and discussion presented above refer exclusively to metal carbonyl species and

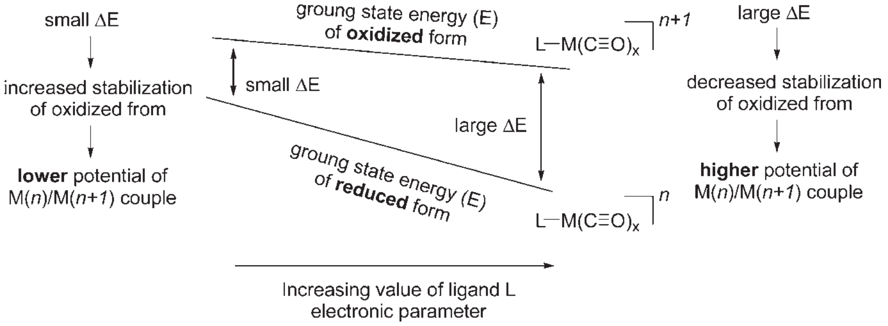

Figure 5. Schematic representation of the effects of changes of the ground-state energies of $[M(CO)_xL_y]^{n/n+1}$ complexes as a function of the increasing value of the ligand electronic parameter. The ground-state energies are purely illustrative and do not obey a linear relationship with the ligand parameters. The important value to consider is ΔE.

may not be generalized to other metal complexes. The nature of the probe, here CO, obviously has a critical influence on the final electronic density of the metal species. Our results do not imply that, e.g., in a catalytic transformation, when other metal complexes are involved, the donating power of L does not linearly increase the density at the metal as a function of the ligand parameter. As was briefly mentioned in the Introduction, our ultimate interest in understanding what effects ligands have on carbonyl species resides in the possibility of a convenient and rational design of CO-RMs. For example, it has been suggested that from a purely thermodynamic point of view, high CO stretching frequencies in the IR spectrum of metal carbonyl complexes may be the result of a weak M−CO bond.[36] Our analysis, however, indicates that the effect probed by high CO stretching frequencies in the IR spectrum of $[M(CO)_xL_y]^n$ species relates primarily to a decreased polarization of the C≡O bonds. The calculations show that the M−C bond orders tend to decrease as a function of increasing ligand parameter values but one may not necessarily take this effect as an indication of a favorable thermodynamic release of CO.

In terms of possible CO-RM design, it is interesting to note that the relative ground-state energy difference between the oxidized and reduced forms of a given metal carbonyl complex (i.e., ΔE in Figure 5) becomes progressively smaller as the ligand parameter decreases. This observation provides, in our view, a working hypothesis for the rational design of CO-RMs. Consider a water-soluble $[M(CO)_xL_y]^n$ carbonyl species with the metal ion in a relatively high formal oxidation state (a loose definition clearly depending on the nature of the metal ion M) where L = labile ligand with a low parameter (e.g., halides). Relative to the reduced form of the carbonyl species, substitution of L for water molecules is expected to destabilize the complex to a greater extent. Water has a very high $IR_P(L)$ value (336), closer to $P(OMe)_3$ and N_2 (339) than NH_3 (328).[8] The substitution of L by water molecules could then lead to decomposition of the $[M(CO)_xL_y]^n$ species and/or CO release. Indeed, coordination of H_2O to transition-metal-based CO-RMs has been sometimes indicated as the first step in the mechanism of CO release of these species.[37,38] Whether the CO release of some of the above-mentioned CO-RMs is a result of a redox process is not known, but it might explain why, for example, d^5 *cis*-$[Re^{II}(CO)_2L_4]^n$ species release CO, while similar d^6 *cis*-$[Re^{I}(CO)_2L_4]^n$ complexes do not.[39−42]

In summary, ligand electronic parameters may be considered as a measure of the net donor power of the ligand. However, contrary to what may be generally assumed, the net transfer of the electron density (or charge) does not occur from the ligand to the metal ion. In $[M(CO)_xL_y]^n$ carbonyl species, the net charge transfer occurs from the ligand L to the oxygen atoms of the bound carbon monoxides. In metal carbonyl complexes, the ligand electronic parameters may be considered as a measure of the polarization of the C≡O bonds and not of the electronic density of the metal ion. Changes in the polarization (and thus the permanent dipole) of the CO bonds translate into changes of the covalency of the bonds, and it is this effect that is probed by IR radiations. Consequently, high CO stretching frequencies in the IR spectrum of metal carbonyl complexes cannot be taken as a measure of a weak M−CO bond or as an indication of a thermodynamically favorable release of CO.

For $[M(CO)_xL_y]^n$ species, as the analysis shifts from IR radiations to electrochemical potentials, the effect that is probed as a function of the ligand parameters is best described as the ability of the ligand to stabilize the ground-state energy of the oxidized form of the complex versus its reduced form. The net transfer of the electron density still occurs from the ligand to the bound CO's in the two different oxidation states and appears to have little to do with the charge on the central metal ion. The analysis provides a working hypothesis for the rational design of CO-RMs. It is here suggested that, e.g., carbonyl complexes with the metal ion in a relatively high formal oxidation state (clearly depending on the nature of the metal ion M) and comprising labile anionic ligands should be destabilized by the substitution of these ligands by water or other biomolecules. This destabilization could then

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lead to decomposition of the $[M(CO)_xL_y]^n$ species and CO release.

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Supporting Information Available: Correlation between IRP(L) parameters and computationally derived electronic parameters, DFT-calculated natural atomic charge, relationship between the HOMO and LUMO energies of $[M(CO)_xL_y]_n$ species, and relationship between E_L values and the relative difference of the metal ion charges. This material is available free of charge via the Internet at http://pubs.acs.org.