Computed Ligand Electronic Parameters from Quantum Chemistry and Their Relation to Tolman Parameters, Lever Parameters, and Hammett Constants

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The calculated (DFT, B3PW91) A_1 ν(CO) frequency in $LNi(CO)_3$ defines an electronic parameter that reliably predicts the relative donor powers of a wide variety of cationic, neutral, and negatively charged ligands. These calculated parameters correlate very well with the available Tolman and Lever parameters, and also with Hammett's σ_m, where available. The method avoids any experimental limitations and, in particular, can be used for proposed ligands not yet experimentally available.

Introduction

The properties observed in a series of transition metal complexes can vary widely and are mainly determined by the electronic and steric effects of the ligands L. Ideally, one would like to be able to estimate these effects, not just for known ligands but also for ones that are merely being considered for future work. In this paper, we propose a computational method for estimating the electronic parameters of ligands, applicable whether or not they are available for experimental study.

Two widely used sets of parameters seem to measure ligand electronic effects satisfactorily. The best known is Tolman's electronic parameter (TEP) for phosphines, R_3P, based on the position of the A_1 ν(CO) vibration of $(R_3P)Ni(CO)_3$ in the IR spectrum. The better the donor power of R_3P, the lower the ν(CO) vibration becomes as a result of back-donation into CO π^* orbitals. A steric parameter, also available but not discussed further here, is estimated from the cone angle of the Ni−L fragment, measured from a space-filling model, taking care to fold back any dangling groups on the ligand. The resulting Tolman parameters have been of the greatest help in understanding the role of electronic and steric effects of phosphines in organometallic chemistry and homogeneous catalysis. As a measure of its importance to the field, the key Tolman review[1] has been cited more than 1700 times and is the third most cited chemical review of the 1945−95 period.[2] The data are normally incorporated into a "Tolman map", which shows the location of each phosphine ligand and therefore the relative steric and electronic effects of each ligand.

The Tolman approach has a few limitations, however. While the steric parameter of a new ligand—even one that is planned but not yet synthesized—is relatively easy to obtain using molecular models, finding the electronic parameter relies on the synthesis first of L and then of $LNi(CO)_3$ (**1**), followed by spectroscopic study of **1**. The notorious toxicity of a common precursor, $Ni(CO)_4$, makes the procedure troublesome. Some important ligands, like pyridine, NO, H_2O, H_2S, and all anions, do not give the required stable $L-Ni(CO)_3$ complex. The mixed ligands in series of theoretical interest, such as PH_3, PH_2F, PHF_2, and PF_3, are not commonly available or easily studied experimentally, but empirical substituent parameters do allow the Tolman electronic parameter (TEP) to be reliably estimated for substituted phosphines.[3] TEP values for bidentate or polydentate ligands are not directly obtainable from $LNi(CO)_3$. However, for bidentate ligands, IR data for *cis*-$[L_2Mo(CO)_4]$ (**2**) were previously shown[4] to correlate very well with the TEP, and reliable data can be obtained for monodentate and bidentate ligands with this convenient system.

An alternative series of electronic parameters, found by Lever,[5,6] is based on the electrochemical E_0 value for various redox couples, notably Ru(III)/Ru(II), in series of complexes containing the ligands of interest. The data are deconvoluted into Lever electronic parameters (LEP) for individual ligands. Lever parameters have the advantage of covering a much wider set of ligands than Tolman parameters, including anionic and O- and N-donor ligands. One limitation is that the measurement requires the use of an electrochemical apparatus, not available in as many laboratories as is IR spectroscopy. In addition, electrochemical irreversibility can degrade the quality of the data for certain ligands and solvation and ion-pairing effects might interfere to some extent.

Both TEP and LEP are believed to measure the net donor power of ligand L toward the probe Ni(0) or Ru(II). Net donor power refers to the net transfer of electron density from ligand to metal fragment, counting both σ and π effects. Relatively few ligands appear in both series, so the quality of any correlation between TEPs and LEPs has been hard to judge. This may reflect the specific experience of the investigators: the TEP tends to be measured by organometallic chemists and the LEP by coordination chemists. In principle, there is no reason to expect a very precise correlation between the two parameters. Of course, differences between the probes Ni(0) or Ru(II), and possibly also differences between the ways the ligands and complexes behave in the IR and electrochemical

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assays, might easily lead to differences in the order of ligands in the TEP vs the LEP listing.

A third common series, mainly used in organic chemistry, the Hammett substituent constants σ, needs to be considered.[7] These were defined from the ionization constants of the appropriately substituted benzoic acids as shown in eq 1, where K_H is the ionization constant for benzoic acid in water at 25 °C and K_X is the corresponding constant for a *meta*- (σ_m) or a *para*-substituted (σ_p) benzoic acid. We use the σ_m because it gives the best correlation (vide infra). In addition, the electronic influence of a *meta* substituent does not involve any resonance effects. However, not all the required substituted benzoic acids are available, and essentially only anionic X-type ligands have σ_m values.

$$\sigma(X) = \log K_X - \log K_H \quad (1)$$

By computing electronic parameters, we avoid many of the limitations described above. We no longer need to have the ligand in hand or to make a Ni or Ru derivative, and we can use the broadest range of ligands. Many different approaches can be envisaged, but we felt that we needed the calculation to be rapid and easy, and we wanted the result to have a close relation to an existing electronic parameter for ease of interpretation. Computation of an LEP is not straightforward because of solvent effects and because Ru(III) is an open shell system; both are likely to be difficult to model. Computation of a σ_m value could be as difficult because solvent and temperature effects must be important in the ionization process and would be very difficult to reproduce accurately. In addition, the proton is not the most appropriate probe. Computing a TEP, which relies only on the determination of a vibrational frequency, seemed to be a much more promising approach.

In this paper, we use quantum chemical methods to calculate the predicted A_1 ν(CO) vibration of (L)Ni(CO)$_3$ for a wide variety of L (68 ligands).[8] The resulting computationally derived ligand electronic parameter (CEP) is shown to correlate extremely well with the experimental TEPs, LEPs, and σ_m constants where available. The method therefore provides a powerful and convenient way to estimate electronic parameters for any ligand L, even at the design stage of an investigation before the ligand has been synthesized.

Computational Details

All calculations were performed with the Gaussian 98 set of programs.[10] The complex LNi(CO)$_3$ was optimized without any symmetry constraint within the framework of density functional theory at the B3PW91 level.[11] The nickel atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group and its associated basis set.[12] The phosphorus atoms were also treated with Stuttgart's RECPs and the associated basis set,[13] augmented by a polarization d function ($\alpha = 0.387$). A 6-31G(d,p)[14] basis set was used for all non-phosphorus atoms in L. However, for some big ligands (PMe$_3$, P(OMe)$_3$, P(NMe$_2$)$_3$, SMe$_2$, OMe$_2$, SiMe$_3$, and CMe$_3$), the atom directly bonded to Ni was represented by a 6-31G(d,p) basis set whereas the remainder of the ligand was treated with a 6-31G basis set. An analogous methodology gave very good results for various M(CO)$_n$ complexes.[15]

Each local extremum was verified as a minimum by an analytical frequency calculation. The highest ν(CO) vibrational frequency without any scaling factor defines the computed electronic parameter (CEP). To eliminate the vibrational coupling between L and the Ni(CO)$_3$ fragment, the results from the frequency calculations are saved in a formatted checkpoint file from Gaussian 98. A new formatted checkpoint file is created where only the geometry of the Ni(CO)$_3$ fragment, as optimized in LNi(CO)$_3$, is included. Also given is the Hessian submatrix in Cartesian coordinates for the Ni(CO)$_3$ fragment where the contributions of all the atoms in L have been deleted from the full Hessian matrix. The vibrational frequencies of this hypothetical Ni(CO)$_3$ fragment within the "field" created by L are obtained with the freqchk[8] utility of Gaussian 98. The highest ν(CO) vibrational frequency without any scaling factor defines the computed electronic parameter, devoid of any vibrational coupling (CEP*).

Table 1. CEP (cm^{-1}) and TEP (cm^{-1})[1] for Selected Ligands

ligand	TEP	CEP	ligand	TEP	CEP
PF_3	2110.8	2201.2	PH_2Me	2075.3	2164.3
PHF_2	2100.9	2190.0	$PHMe_2$	2069.6	2158.1
PH_2F	2090.9	2179.6	$P(CH{=}CH_2)_3$	2069.5	2155.4
$P(OMe)_3$	2079.5	2171.3	PMe_3	2064.1	2152.4
PH_3	2083.2	2170.8	$P(NMe_2)_3$	2061.9	2151.0
$PMe_2(CF_3)$	2080.9	2169.7	PCl_3	2097.0	2197.0

Table 2. Coupled CEP (cm^{-1}) and Uncoupled CEP* (cm^{-1})

ligand	CEP	CEP*	Δ^a	ligand	CEP	CEP*	Δ^a
NO^+	2287.4	2281.5	5.9	NCH	2167.7	2172.9	−5.2
CO	2210.6	2193.2	17.4	CCH^-	2106.7	2103.0	3.7
CS	2187.3	2186.2	1.1	SiH_3^-	2090.7	2081.2	9.5
CF_2	2186.7	2185.3	1.4	H^-	2074.3	2072.2	2.1
N_2	2185.8	2188.1	−2.3	NO^-	2075.2	2070.6	4.6
AsH_3	2169.4	2171.9	−2.5				

[a] Δ = CEP − CEP*.

Results

CEP for Phosphine Ligands. DFT (B3PW91) calculations were carried out on LNi(CO)$_3$ for a wide variety of L (see Table 5). A frequency calculation on the fully optimized structure for LNi(CO)$_3$ yielded the predicted A_1 ν(CO) vibrational frequency, which serves as a definition for the computed electronic parameter (CEP). These provide information about the net donor/acceptor character of the ligands L, following Tolman's proposal. Other parameters, E_B and C_B, have been derived by Drago et al.[16] and have been shown to apply to phosphine ligands. Giering et al.[17] have proposed electrochemical parameters for phosphines and some other ligands in order to estimate relative σ and π contributions to the bonding.

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Table 3. CEP (cm^{-1}) and LEP (V)[5] for Various Ligands

ligand	LEP	CEP	ligand	LEP	CEP
NO^+	1.9[a]	2287.4	I^-	−0.24	2120.4
CO	0.99	2210.6	Br^-	−0.22	2120.2
H_2	0.80[a]	2192.4	F^-	−0.42	2102.7
N_2	0.68	2185.8	OH^-	−0.59	2091.9
C_2H_4	0.76	2172.6	CN^-	0.02	2115.0
$P(OMe)_3$	0.42	2171.3	NH_3	0.07	2161.8
NCMe	0.34	2167.3	H_2O	0.04	2174.4
SMe_2	0.31	2161.3	H^-	−0.30	2074.3
PMe_3	0.33	2152.4	NO^-	0.02	2075.2
Cl^-	−0.24	2120.8			

[a] From ref 24.

Table 4. CEP (cm^{-1}) and σ_m[7] for Various Ligands

ligand	σ_m	CEP	ligand	σ_m	CEP
Br^-	0.39	2120.2	CCH^-	0.21	2106.7
Cl^-	0.37	2120.8	$CH{=}CH_2^-$	0.06	2080.0
F^-	0.34	2102.7	$SiMe_3^-$	−0.04	2063.4
I^-	0.35	2120.4	*t*-Bu^-	−0.10	2062.8
H^-	0.00	2074.3	NH_3	0.86	2161.8
OH^-	0.12	2091.9	SMe_2	1.00	2161.3
SH^-	0.25	2102.5	PMe_3	0.74	2152.4
SiH_3^-	0.05	2090.7	N_2	1.76	2185.8
Me^-	−0.07	2065.7	$-CN^-$	0.56	2115.0
OMe^-	0.12	2099.0	$-NC^-$	0.48	2121.9
SMe^-	0.15	2097.1			

As a first test of our methodology, we compared CEPs for phosphine ligands with experimental IR spectroscopic measurements (Table 1 and Figure 1). When all data are used in the regression, the correlation coefficient is an excellent 0.982. However, from Figure 1, the point for PCl_3 seems to be an outlier; when discarded from the regression, the correlation coefficient becomes 0.996. The experimental value for PCl_3 may be less accurate as the Ni complex is rather unstable.[3]

From the regression analysis, we obtain the following equation (eq 2) relating calculated CEPs (cm^{-1}) to experimental TEPs (cm^{-1}):

$$\mathrm{TEP} = 0.9572\mathrm{CEP} + 4.081 \qquad (2)$$

This relation can be used to estimate a TEP for the few ligands, other than PR_3, where experimental values are available. The ν(CO) frequency for $Ni(CO)_4$ in CCl_4 solution, 2125 cm^{-1},[18] compares well with the TEP value of 2120 cm^{-1} as deduced from the CEP value of 2210.6 cm^{-1} (Table 5) in eq 2.

$(N_2)Ni(CO)_3$, observed by Turner et al.,[19] shows an A_1 ν(CO) frequency at 2101 cm^{-1} in liquid krypton. Using a CEP of 2185.8 cm^{-1} (Table 5) in eq 2, we obtain a predicted TEP of 2096.2 cm^{-1}, in excellent agreement with experiment. Moreover, a measurement in solid N_2 yielded a value of 2098 cm^{-1} for the TEP.[20]

Finally, *cis*-$[(NMe_3)_2Mo(CO)_4]$ has a ν(CO) of 2017 cm^{-1}.[21] Anton and Crabtree[4] have shown that a very good correlation exists between ν(CO) frequencies for *cis*-$[L_2Mo(CO)_4]$ and $LNi(CO)_3$ systems and have established eq 3:

$$\nu_{Ni} = 0.593\nu_{Mo} + 871 \qquad (3)$$

The predicted experimental frequency for the hypothetical $(NMe_3)Ni(CO)_3$ thus becomes 2067.1 cm^{-1}. Using a CEP value of 2155.9 cm^{-1} for NMe_3 (Table 5), we predict a TEP of 2067.6 cm^{-1}, in excellent agreement with experiment.

Vibrational Coupling between L and $Ni(CO)_3$. It is well-known that some ligands L show vibrational coupling between L and $Ni(CO)_3$.[22] By defining an electronic ligand parameter from computation, we were concerned that this vibrational coupling could alter the apparent electronic influence of the ligand L. We have thus devised a simple scheme to estimate the magnitude of the coupling. With the Hessian matrix of the complex $LNi(CO)_3$ in hand, it is possible to extract the submatrix of the $Ni(CO)_3$ fragment. The diagonalization of this matrix yields the ν(CO) frequency of an "isolated" $Ni(CO)_3$ fragment in the field created by the ligand L. This frequency defines an uncoupled computed electronic parameter CEP*. Among the 68 ligands, we have considered (Table 5) only 11 to have a CEP* differing from the CEP by more than 1 cm^{-1} (Table 2).

The highest difference is observed, as expected, for CO with 17.4 cm^{-1}. Ligands with stretching frequencies and reduced masses close to that for CO also exhibit a significant shift: e.g., SiH_3^- (9.5 cm^{-1}) and NO^+ (5.9 cm^{-1}).

Whether we consider CEP or CEP* as the appropriate measure of the overall electronic effect of the ligand L, the two scales do not differ significantly. The main difference concerns CO, one of the most electron-accepting ligands of all on the CEP scale, although it is less accepting than QF_3 (Q = Bi, As, Sb, P) on the CEP* scale (Table 5). On the CEP* scale vs the CEP, N_2 becomes more accepting than CS and CF_2, and SiH_3^- becomes more donating than Ph^-.

Despite these small differences, the order is essentially the same for the two scales (Table 5). Even if CEP* might ideally be considered as the best measure of the intrinsic donor power of the ligand L, barring any vibrational coupling, we have chosen to adopt the CEP scale as a working data set for further comparison because of the greater ease of the CEP calculation.

Transferability between CEP and LEP. CEPs are available for a broad range of ligand types, and there is a good overlap of data points with LEPs. This allowed us to look for a correlation with all the ligands in Table 3 included, and the correlation coefficient is a modest 0.91.

For example, in $[Ru(bipy)_nL_{6-2n}]^{m+}$ ($n = 0-3$; bipy = 2,2′-dipyridyl), with an Ru(III)/Ru(II) potential E_{obs}, the LEP value for ligand L was derived[5] following eq 4:

$$E_{obs}(Ru^{III}/Ru^{II}) = 0.51n + (6 - 2n)\mathrm{LEP} \qquad (4)$$

In general, one may have data for complexes of the type $Ru(bipy)_2L_2$ and $Ru(bipy)L_4$, providing two independent evaluations of LEP, once a value for LEP(bipy) is assumed. This approach works very well for a wide range of ligands but is less satisfactory in certain specific cases.

For hydride, the predicted CEP is far out of line with the one usually adopted. However, the redox couples for Ru are not electrochemically reversible in this case, so the LEP(H^-) value of −0.3 V was derived from the P_L ligand parameter of Pickett and Pletcher[23] through the relationship derived by Lever (eq 5),[5] based on electrochemical measurements on chromium carbonyls (eq 6). The accuracy of $P_L(H^-)$ and hence of LEP(H^-)

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Table 5. CEP and CEP* Data for All Ligands Studied[a]

ligand	CEP (cm^{-1})	CEP* (cm^{-1})	TEP (cm^{-1})	LEP (V)	σ_m	ligand	CEP (cm^{-1})	CEP* (cm^{-1})	TEP (cm^{-1})	LEP (V)	σ_m
NO^+	2287.4	2281.5	2193.5	**1.9**	2.12	NMe_3	2155.9	2155.9	2067.6	0.25	0.80
CH^+	2283.2	2283.2	2189.5	1.84	2.08	$SbMe_3$	2155.9	2155.7	2067.6	0.25	0.80
CO	2210.6	2193.2	2120.0	**0.99**	1.35	$P(CH{=}CH_2)_3$	2155.4	2155.2	**2069.5**	0.24	0.79
BiF_3	2207.3	2207.2	2116.8	0.89	1.32	$AsMe_3$	2155.2	2154.9	2067.0	0.24	0.79
AsF_3	2205.1	2205.0	2114.7	0.86	1.30	G1	2155.0	2154.0	2066.8	0.24	0.79
SbF_3	2202.9	2202.9	2112.6	0.83	1.27	G5	2153.6	2153.0	2065.4	0.22	0.78
PF_3	2201.2	2200.7	**2110.8**	0.81	1.26	PMe_3	2152.4	2152.0	**2064.1**	**0.33**	**0.74**
PCl_3	2197.0	2196.6	2107 (**2097**)[b]	0.76	1.21	$P(NMe_2)_3$	2151.0	2150.5	**2061.9**	0.19	0.75
η^2-H_2	2192.4	2192.4	2102.6	**0.8**	1.17	G6	2150.1	2149.6	2062.1	0.18	0.74
PHF_2	2190.0	2189.9	**2100.8**	0.67	1.14	G2	2142.8	2142.3	2055.1	0.09	0.67
NF_3	2189.9	2189.1	2100.2	0.67	1.14	G3	2142.1	2141.7	2054.4	0.08	0.66
CS	2187.3	2186.2	2097.7	0.64	1.12	G4	2137.6	2136.9	2050.1	0.02	0.62
CF_2	2186.7	2185.3	2097.1	0.63	1.11	NC^-	2121.9	2121.9	2035.1	−0.18	**0.48**
σ-N_2	2185.8	2188.1	2096.3	**0.68**	1.10 (**1.76**)[b]	Cl^-	2120.8	2120.8	2034.0	**−0.24**	**0.37**
CCH_2	2183.5	2182.6	2094.1	0.59	1.08	I^-	2120.4	2120.4	2033.6	**−0.24**	**0.35**
PH_2F	2179.6	2179.6	**2090.9**	0.54	1.04	Br^-	2120.2	2120.2	2033.5	**−0.22**	**0.39**
CH_2	2178.5	2178.2	2089.3	0.53	1.03	CN^-	2115.0	2115.8	2028.5	**0.02**	**0.56**
BiH_3	2176.7	2175.8	2087.5	0.51	1.01	HCC^-	2106.7	2103.0	2020.5	−0.36	**0.21**
H_2O	2174.4	2174.4	2085.3	**0.04**	0.99	F^-	2102.7	2102.6	2016.8	−0.42	**0.34**
C_2H_4	2172.6	2172.5	2083.6	**0.76**	0.97	HS^-	2102.5	2102.5	2016.5	**−0.42**	**0.25**
SbH_3	2172.5	2171.2	2083.5	0.46	0.97	MeO^-	2099.0	2098.8	2013.2	−0.46	**0.12**
Me_2O	2171.9	2171.9	2082.9	0.45	0.96	MeS^-	2097.1	2097.0	2011.3	−0.48	**0.15**
$P(OMe)_3$	2171.3	2170.9	**2079.5**	**0.42**	0.96	OH^-	2091.9	2091.9	2006.4	**−0.59**	**0.12**
PH_3	2170.8	2170.9	**2083.2**	0.43	0.95	SiH_3^-	2090.7	2081.2	2005.2	−0.56	**0.05**
H_2S	2170.2	2170.2	2081.3	0.43	0.94	Ph^-	2085.8	2085.5	2000.5	−0.62	0.09
PMe_2CF_3	2169.7	2169.3	**2080.9**	0.42	0.94	σ-$(CH{=}CH_2)$	2080.0	2079.3	1995.0	−0.70	**0.06**
AsH_3	2169.4	2171.9	2080.6	0.42	0.94	$B(O_2C_2H_2)^-$	2075.8	2075.2	1991.0	−0.74	−0.01
NCH	2167.7	2172.9	2078.9	0.40	0.92	NO^-	2075.2	2070.6	1990.4	−0.75 (**0.02**)[b]	−0.01
NCMe	2167.3	2167.8	2078.5	**0.34**	0.91	H^-	2074.3	2072.2	1989.5	−0.76 (**−0.30**)[b]	**0.00**
PH_2Me	2164.3	2164.2	**2075.3**	0.35	0.88	$B(O_2C_2H_4)^-$	2071.3	2070.7	1986.6	−0.80	−0.05
NH_3	2161.8	2161.8	2073.3	**0.07**	**0.86**	CH_3^-	2065.7	2065.3	1981.3	−0.87	**−0.07**
Me_2S	2161.3	2161.2	2072.8	**0.31**	**1.0**	$B(OH)_2^-$	2065.0	2065.0	1980.6	−0.88	−0.11
$BiMe_3$	2160.4	2160.3	2071.9	0.30	0.85	$SiMe_3^-$	2063.4	2062.8	1979.1	−0.90	**−0.04**
$PHMe_2$	2158.1	2157.9	**2069.6**	0.28	0.82	t-Bu^-	2062.8	2062.6	1978.5	−0.90	**−0.10**

[a] Values in bold for TEP (cm^{-1}),[1] LEP (V),[5] and σ_m[7] have been used in the regression analysis; the other values have been determined via eq 2 (TEP), eq 7 (LEP), and eq 9 (σ_m). [b] Values in parentheses are experimental values excluded from the regression.

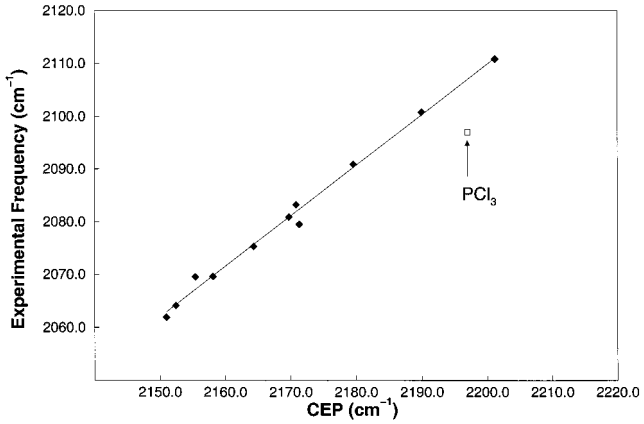


Figure 1. Correlation between CEP (cm^{-1}) and TEP[1] (cm^{-1}). PCl_3 has been excluded from the regression and is shown as an open symbol.

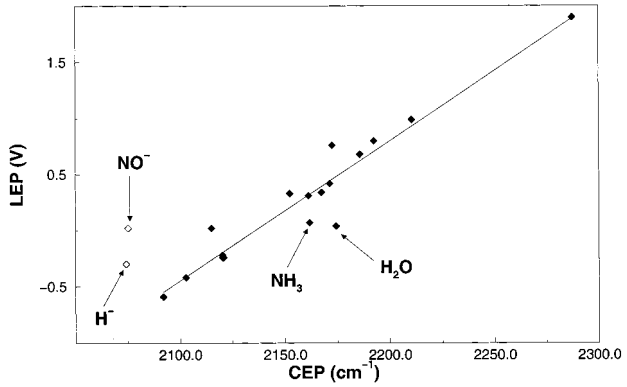


Figure 2. Correlation between CEP (cm^{-1}) and LEP[5] (V). NO^- and H^- have been excluded from the regression and are shown as open symbols.

is not high, and Morris has suggested that an LEP value of −0.4 V is more appropriate.[24]

$$P_L = 1.17\text{LEP} - 0.86 \quad (5)$$

$$P_L = E_{1/2}[Cr(CO)_6] - E_{1/2}[Cr(CO)_5L] \quad (6)$$

The nitrosyl ligand is unusual in having linear and bent forms, implying a 2*e* redox change at the metal. For $L = NO^+$, the nitrosyl ligand is linear in both oxidation states and the charge transfer from Ru to NO is expected to be similar in both. For $L = NO^-$, on the other hand, the structure might change, in which case differences in charge transfer to the metal could occur upon oxidation, and the LEP would be perturbed.[5,25] Finally, water and ammonia show some variability in LEP, possibly as a result of hydrogen bonding with solvent.[5]

To improve the correlation, we have thus excluded H^- and NO^- from the data set. Figure 2 shows the resulting linear fit with the excluded data represented with open symbols. The excellent correlation coefficient of 0.960 allows us to express the linear relationship between CEPs and LEPs (eq 7)

(24) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471.

(25) Dodsworth, E. S.; Vlcek, A. A.; Lever, A. B. P. *Inorg. Chem.* **1994**, *33*, 1045.

$$\text{LEP (V)} = (1.246 \times 10^{-2})\text{CEP (cm}^{-1}) - 26.619 \quad (7)$$

If the data for NH_3 and H_2O, also shown in Figure 2, had also been excluded, the correlation coefficient would have been 0.985.

Equation 7 enables us to derive LEPs for ligands where experimental values were not available (Table 5). Moreover, we can use the relationship to propose new LEPs for H^- (−0.76 V) and NO^- (−0.75 V). The agreement between the appropriate CEPs and both TEPs and LEPs has the further consequence that TEPs and LEPs are mutually related despite the difference in probe, Ni(0) vs Ru(II), and the difference in method, IR spectroscopy vs electrochemistry. This implies a full transferability between LEP and TEP as embodied in the relationship of eq 8:

$$\text{TEP (cm}^{-1}) = 76.82\text{LEP (V)} + 2.049 \times 10^3 \quad (8)$$

Transferability between CEP and σ_m. Hammett σ parameters have been shown to correlate with metal-centered electrochemical potentials in complexes of a variety of ligands.[26] We have therefore looked for relationships between Hammett parameters and our CEPs. From a practical point of view, correlations with σ_m or σ_p are preferred since there is a large database for each.[7] We have chosen to use σ_m values because these give the best correlation ($R = 0.967$ for σ_m vs $R = 0.844$ for σ_p).

In Table 4, we report the 21 cases for which experimental σ_m values are available among our 68 ligands (Table 5). Figure 3 shows the linear correlation between experimental σ_m and CEP; when the value for N_2 is excluded from the regression, an excellent correlation coefficient is found ($R = 0.967$). The value for N_2 is believed to be an outlier because the partial multiple C−N bond in the diazobenzoic acid used is very different from the essentially single bonds that occur for the other cases.

We thus obtain a linear relationship between σ_m and CEP (eq 9). This relation enables us to express any experimental parameter (LEP, TEP, or σ_m) as a function of any other through the intermediacy of the computed CEP (eqs 10 and 11).

$$\sigma_m = (10.08 \times 10^{-3})\text{CEP (cm}^{-1}) - 20.934 \quad (9)$$

$$\sigma_m = (10.53 \times 10^{-3})\text{TEP (cm}^{-1}) - 20.977 \quad (10)$$

$$\sigma_m = 0.819\text{LEP (V)} + 0.602 \quad (11)$$

It is possible to use the Hammett constant σ_m to derive LEP values for a large variety of ligands not covered by electrochemical measurements.[26] Further, electrochemically generated LEP values can be used to obtain σ_m values for new substituents.

Table 5 reports the results for all the ligands considered. The values in bold are the experimental data used to establish the correlation with calculated CEPs (eqs 2, 7, and 9). The other parameters (TEP, LEP, or σ_m) have been calculated using the appropriate equation. For cases where the data have been discarded from the regression analysis, both values are given.

Discussion

A general correlation between TEP and LEP is not too surprising in that both Ni(0) and Ru(II) are π-back-bonding metals, but the quality of the correlation is unexpected because of the possible differences between the probes and methods. In the Ni(0) system, believed to be effective in back-bonding to a suitable L, a π-acceptor L is expected to lower the electron density on Ni and raise the ν(CO) and therefore also the TEP directly. In the LEP method, Ru(II) is expected to be a much more effective back-bonding metal than Ru(III). As a result, a π-acceptor L is expected to stabilize Ru(II) relative to Ru(III) and hence affect the E_0 and the resulting LEP. The observed transferability between the TEP and LEP suggests that π effects are comparable in importance in these two commonly used probes.

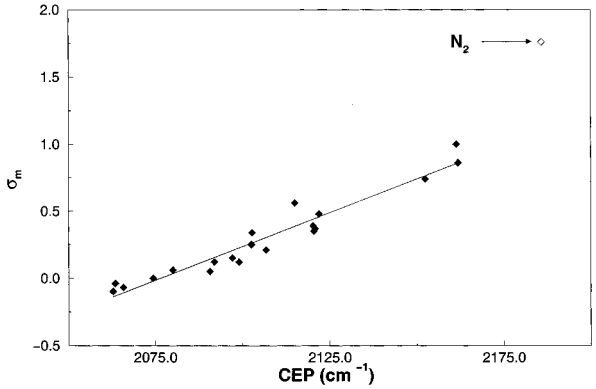


Figure 3. Correlation between CEP (cm^{-1}) and σ_m.[7] N_2 has been excluded from the regression and is shown as an open symbol.

The good correlation ($R = 0.967$) between σ_m and CEP is surprising because no metal at all is involved in the σ_m determination. Instead, the acidity of benzoic acid is affected by the presence of a substituent. Because of practical limitations on the type of benzoic acids that are known, the substituents are all anionic except for N_2, which was an outlier excluded from the correlation. Using σ_m, we avoid organic resonance contributions in the benzoic acid as occur for σ_p.

In discussing trends in the CEP data, we are unable to quantitatively determine the relative contributions of σ and π effects to the overall M− L bonding, so we restrict our discussion to the relative ordering. In qualitative discussions of the positions of individual ligands, however, we refer to traditional σ and π effects. Likewise, there is no reliable baseline that allows us to say where a ligand having no net donor power would come, since free $Ni(CO)_3$ is trigonal planar and therefore not strictly comparable with the pyramidal $Ni(CO)_3$ fragment in the tetrahedral $LNi(CO)_3$. Nevertheless, the value for H_2O, a relatively weakly bound ligand, 2174.4 cm^{-1}, gives an acceptable approximation of the baseline case.

Trends in CEPs. The data of Table 5 are shown in order of decreasing CEP value so that the weakest net donors appear early and the strongest net donors appear late in the list. The clearest trend involves ligand charge, which directly translates to net ionic charge of the $[LNi(CO)_3]$ complex. For example, NO^+ gives $[(ON)Ni(CO)_3]^+$, CO gives $[Ni(CO)_4]$, and CN^- gives $[(NC)Ni(CO)_3]^-$. The net donor power of the ligands increases as cationic L < neutral L < anionic L. This trend is so strong that even the weakest and strongest net donor neutrals do not overlap with either the cationic or anionic ligands. Such a result is reasonable and consistent with LEP data, but other than for sandwich ligands,[27] this point has not been emphasized in the past.

The neutral ligands, denoted as L, constitute the only series where we have extensive experimental TEP data for comparison.

(26) Masui, H.; Lever, A. B. P. *Inorg. Chem.* **1993**, *32*, 2199 and references therein.

(27) Lu, S. X.; Strelets, V. V.; Ryan, M. F.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chem.* **1996**, *35*, 1013.

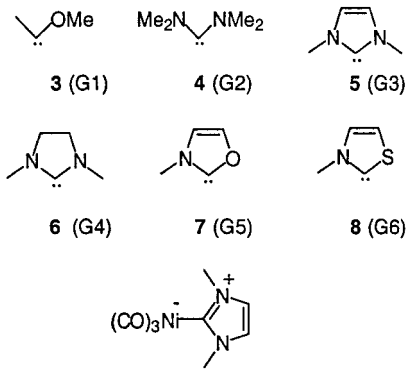
It is therefore here that we see how closely the CEP values track the experimental TEP data (Table 1 and Figure 1). QF_3s are among the weakest donor ligands, in line with the proposal that QF_3s are effective π-acceptors via the Q−X σ* orbitals.[22] Alternatively, the F substitution may simply decrease the σ-donor power of the donor atom. The trend as Q changes (Bi < As < Sb < P < N) is somewhat irregular; however, as the electronegativity of Q increases (Bi > Sb > As > P > N), we expect to see the Q−X σ* orbital become less polarized toward Q, and the Ni−Q π overlap, together with the π-back-bonding, would be expected to decrease. Variation in the Ni−Q distances could also affect the outcome. The same idea applied to X, decreasing the electronegativity of X leads to decreasing σ* polarization (or simply that a more electronegative X decreases the donor power of Q) , explains the CEP order $PF_3 > PCl_3$.

CO is also a very weak net donor. It is in the CO case that we see the largest effect of suppressing (CEP*) or including (CEP) the vibrational coupling: the shift is a very large 17.4 cm^{-1}, showing one advantage of the computational approach for this ligand. While the TEP and CEP both make CO the least donor neutral ligand, the CEP* gives an assessment more in line with chemical experience, putting it just above PCl_3 in donor power.

A surprise is the very weak net donation of H_2, presumably due to a combination of relatively weak σ-donation with a significant degree of π-back-donation. A related ligand, N_2, has an even lower CEP. Since neither ligand is a strong σ-donor, this ordering presumably arises because N_2 is a weaker π-acceptor than H_2. That back-donation is important for both cases can be seen by comparison with the CEP for the weak donor H_2O, 2174.4 cm^{-1}, where the ligand is generally considered as a predominantly σ-donor with only very weak π effects.

Again as expected, in each QR_3 series (Q = P, As, Sb, or Bi), the ligand becomes less of an acceptor as we go from R = F to H to Me. The effect of going from P to As, Sb, and Bi is rather small with a trend toward slightly more acceptor ligands as we descend the periodic table. In the series PF_3, $P(OMe)_3$, $P(NMe_2)_3$, and PMe_3, we see the expected trend toward increasing donor strength, except that the last two members of the series are very similar in CEP, no doubt because π-donation from the N lone pair into the P−N′ σ* orbital competes with back-donation from the metal.

A particularly interesting class of ligands is the carbenes denoted G1−6 and illustrated as **3**−**8**. They all tend to be strong donors, as expected from the predominant canonical resonance form, **9**, that puts a negative charge on the $Ni(CO)_3$ fragment; as we have seen above, this charge has a strong effect on the CEP. The methoxy carbene, G1, is comparable to $P(CH{=}CH_2)_3$ in donor power, but the other carbenes, G2−6, have CEPs that put them at the extreme donor end of the formally neutral ligands. Since these ligands are one of the few ligand series other than PR_3 to have proved to be exceptionally useful in catalysis, the fact that they have electronic parameters outside the range found for PR_3 may make them ligands of choice where strong donors are required. As the number of the heteroatom substituents in the aliphatic carbenes rises and their electronegativity falls, the CEP tends to fall as the ligands become better donors, giving G1 > G2 > G4. The aromatic G3 is a weaker donor than its aliphatic analogue, G4, presumably because the backbone C=C bond is a π-acceptor. Pombeiro et al. have discussed electrochemical data in relation to properties of carbene ligands.[28]



Among the anionic ligands, we find electronegative π-donors, such as halides and pseudohalides, high in the list. Isocyanide (M−NC) comes first, perhaps because it is a poorer σ-donor than cyanide (M−CN); in the same range come the weak π-donor halides. These are followed by the stronger π-donors RS^- and RO^- (R = H, Me). Finally, we have the strongly donating, less electronegative anions, such as Ph, H, and Me as well as the boryls.

Structural Trends. In principle, the Ni−C and C−O distances should also be good indicators of the electronic character of L. Experimentally, however, crystal structures are not sufficiently broadly available for the $LNi(CO)_3$ series, nor does the X-ray method locate the O and C atoms sufficiently accurately for reliable conclusions to be drawn. The present computation work predicts the structures of the series, so we looked at the averaged Ni−C and C−O distances as an indicator. The changes proved to be small and did not give a useful electronic parameter, the vibrational frequency being a far more sensitive indicator in the computational work, just as is the case for the experimental data.

Conclusions

The calculated A_1 ν(CO) frequency for $LNi(CO)_3$ yields a useful scale for defining the electronic parameters of a wide variety of cationic, neutral, and anionic ligands. These parameters (CEP) correlate very well with the Tolman and Lever electronic parameters. For certain anionic ligands, they also correlate very well with Hammett's σ_m. Thus, the CEP appears to be an efficient and reliable way to obtain electronic parameters for any ligand without experimental limitations.

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(28) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carbajo, R. J.; Lopez-Ortiz, F.; da Silva, M. F. C. G.; Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2000**, *2*, 341 and references therein.