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Semiempirical Quantum Mechanics and the Quantification of Ligand Electronic Parameters

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Semiempirical Quantum Mechanics and the Quantification of Ligand Electronic Parameters[#]

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Abstract

Motivation. Quantification of electronic effects in organometallic chemistry has received little attention in the literature despite their importance in the control of catalytic processes. It is well recognized that the A_1 CO vibration for $Ni(CO)_3L$ is a good measure of electronic effects. Recently, Crabtree has used density functional theory to compute the A_1 CO vibration for $Ni(CO)_3L$ complexes and found good agreement with experiment. In this paper, a more rapid computational method for the derivation of a general quantitative measure of ligand electronic effects is presented. With semiempirical quantum mechanics (PM3(tm) Hamiltonian in Spartan 5.0 or 02), the A_1 CO vibrations for $Mo(CO)_5L$, $W(CO)_5L$, and $[CpRh(CO)(L)]$ are computed, which is termed the semiempirical quantum mechanics electronic parameter, SEP. The SEP values are compared with measures of electronic effects in the experimental and computational literature and are found to be robust, general measures of the electronic nature of a ligand.

Method. Semiempirical quantum mechanics was used to geometry optimize the $Mo(CO)_5L$, $W(CO)_5L$, and $[CpRh(CO)(L)]$ complexes. Spartan 5.0 or Spartan 02 was used to compute the vibrational frequencies of $Mo(CO)_5L$, $W(CO)_5L$, and $[CpRh(CO)(L)]$ with the PM3(tm) Hamiltonian.

Results. The newly defined SEP was found to correlate well with Tolman's experimental ν_{CO} parameter, Lever's electrochemical parameter, as well as Crabtree's computed parameter.

Conclusions. The SEP values are a robust, easy to compute computational measure of the electronic nature of a wide variety of different ligands.

Keywords. Electronic parameter; semiempirical quantum mechanics, PM3; Spartan; electronic effects; Tolman.

Abbreviations and notations

CEP, Crabtree's electronic parameter based on ν_{CO} computed for $Ni(CO)_3L$ with DFT	SEP, our semiempirical quantum mechanics electronic parameter
CpRhCO, $[(\eta^5-C_5H_5)Rh(CO)]$	SEQM, Semiempirical quantum mechanics
DFT, Density functional theory	TEP, Tolman's electronic parameter (ν_{CO} measured on $Ni(CO)_3L$ complexes)
LEP, Lever's electronic parameter measured from Ru(II)/Ru(III) redox couples	

1 INTRODUCTION

Organometallic reactions are dominated by the subtle interplay between steric and electronic effects expressed by ligands at the metal center. Phosphines are extremely important in organometallic chemistry since the 1940s and are often used in homogeneous catalysis [1]. Phosphines are known to stabilize the low oxidation states of transition metals, which are characteristic of organometallic catalysts [2]. Phosphines can be used to alter the steric and electronic environment about the metal in a systematic and predictable fashion, thus tuning a catalytic system. Quantification of steric effects in organometallic chemistry, particularly the steric demand of phosphines, dates back to the 1970s with Tolman's definition of the cone angle, θ [3]. Subsequently, solid angles, Ω, have been used as a geometric measure of steric effects [4,5], as have the angular deformation constant, S_4' [6]. Computational measures of steric effects are dominated by Brown's ligand repulsive energy parameter, E_R [7–17].

The development of a quantitative electronic parameter for phosphines, and other ligands, has been somewhat more difficult. At the same time as defining the cone angle, Tolman introduced the Tolman Electronic Parameter (TEP) [3]. Tolman recognized that the electronic nature of a P–donor ligand, L, is expressed in the symmetric A_1 CO stretch in $Ni(CO)_3L$ complexes. Using back–bonding arguments, Tolman reasoned that the A_1 v_{CO} is a sensitive and quantitative measure of the electron density at the metal. However, in order to use the TEP, the $Ni(CO)_3L$ complex must be prepared from the toxic $Ni(CO)_4$ starting material. In addition, the complex must be stable enough for an IR spectrum to be recorded. These two facts make the TEP cumbersome to work with for a generalized ligand. Furthermore, there is no capacity for *a priori* measurement of TEP (or Lever Electronic Parameter, LEP, see below) for novel ligands, and hence a computational procedure would be of interest in the context of molecular design.

A second experimentally based quantitative measure of electronic effects is Lever's electronic parameter, LEP [18,19]. The LEP was developed to create an electrochemical series based on the redox potentials of Ru(II)/Ru(III) couples. Consider a $[Ru(bipy)_nL_{6-2n}]^{m+}$ complex that shows a potential E_{obs} relative to the normal hydrogen electrode. Then, LEP is defined as

$$E_{obs} = 2n \times 0.255 + (6 - 2n)\text{LEP} \qquad (1)$$

The 0.255 in equation (1) comes from the Ru(II)/Ru(III) potential of $[Ru(bipy)_6]^{2+}$ ($E_{obs} = 1.53$ V vs. NHE in acetonitrile), which contains six identical Ru–N bonds. Therefore, the LEP of 2,2′–dipyridine is 1.53/6 = 0.255 V. The degree to which the ligand, L, adds or removes electron density from the Ru is reflected in the E_{obs} that is measured. As with the TEP, the LEP is limited by the preparation of the required Ru(II) and Ru(III) complexes. Moreover, the potentials are solvent dependent, which prevents the LEP from being a completely general measure of electronic effects.

Ideally, quantitative measures of the electronic nature of ligands are needed that are based on

computational methods, which are fast, general and do not rely on experimental data. Crabtree recently computed ν_{CO} for a variety of $Ni(CO)_3L$ complexes using density functional theory with the B3PW91 functional and a mixture of 6–31G(d,p) and 6–31G basis sets [20]. Excellent correlations were observed between Crabtree's computational electronic parameter, CEP, and both TEP and LEP. The only disadvantage to the CEP is the computational intensity of the DFT method that limited it to very small phosphines such as PH_3, PH_2F, PHF_2, and PF_3.

Semiempirical quantum mechanical (SEQM) are significantly faster than DFT methods, and Cundari has clearly demonstrated that SEQM methods are capable of predicting accurate geometries for transition metal complexes [21]. Therefore, SEQM methods have the potential of providing an accurate electronic parameter, called SEP, which can be computed expeditiously. Moreover, SEQM methods are capable of expediently modeling large, experimentally relevant ligand systems. The amount of computer time required to compute ν_{CO} for $Ni(CO)_3(PPh_3)$, for example, at the DFT level is substantial, on the order of days with typical software and hardware. The analogous computation with PM3(tm) takes a matter of minutes. To our knowledge, no systematic evaluation of PM3(tm) for vibrational analysis of TM complexes has been reported. In this paper, we report on the computation of SEP values and their performance relative to TEP, LEP, and CEP.

2 COMPUTATIONAL METHODS

All calculations were carried out on an SGI Octane2 or O^2 workstation running the Spartan 5.0 or Spartan 02 software obtained from Wavefunction [22]. All $Mo(CO)_5L$, $W(CO)_5L$, and $CpRh(CO)(L)$ complexes were built in Spartan and were initially geometry optimized using the Merck Molecular Force Field, MMFF. Subsequently, the PM3(tm) Hamiltonian was employed for geometry optimization on each complex with appropriate molecular charge and multiplicity [21]. The SCF energy convergence was set to the default of 1.0×10^{-10} kcal/mol for both geometry optimizations and frequency determinations. In a few cases, problems determining achieving SCF convergence were found, and the SCF convergence energy was altered to 1.0×10^{-7} kcal/mol. In some cases of very poor SCF convergence, it was necessary to employ the GRADUAL keyword.
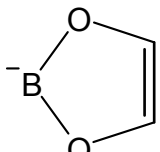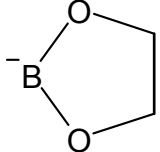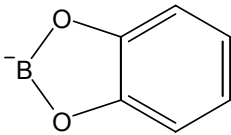
Once the optimized geometry was found, vibrational frequency calculations were performed. All of the normal modes of the complexes were visualized to identify the highest frequency A_1 mode, which occurred between approximately 2135 and 2162 cm^{-1}.

3 RESULTS AND DISCUSSION

Cundari has demonstrated that the PM3(tm) Hamiltonian is not ideally suited for optimization of nickel–based systems [21]. Therefore, we employed the $Mo(CO)_5$, $W(CO)_5$, and $CpRh(CO)$

fragments in these computations since PM3(tm) is known to provide accurate geometries for these metals. The Cambridge Crystallographic Database [23] was searched for all monomeric and mononuclear $Mo(CO)_5L$ and $W(CO)_5L$ (L = phosphine or phosphite) complexes that showed no errors (R < 10%) and no disorder. These complexes were imported into Spartan and geometry optimized with the PM3(tm) Hamiltonian and vibrations computed. The substituents on the ligands were modified to generate structures that were not found in the Cambridge database. The results of SEP computations are summarized in Table 1.

Table 1. Semiempirical Quantum Mechanics Electronic Parameter Computed in the $Mo(CO)_5$ Environment (SEP in cm^{-1}), Tolman's Electronic Parameter (TEP in cm^{-1}), Crabtree's DFT Electronic Parameter (CEP in cm^{-1}), and Lever's Electronic Parameter (LEP in V) for a Variety of Ligands, L.

Ligand, L	SEP	TEP	CEP[a]	LEP
CO	2202.57	2120.0	2210.6	0.99
PH_3	2166.13	2083.2	2170.8	0.43
PH_2Me	2166.17	2075.3	2164.3	0.35
$PHMe_2$	2166.37	2069.6	2158.1	0.28
PMe_3	2165.58	2064.1	2152.4	0.33
$P(i–Pr)_3$	2167.01	2059.2	**2147.0**	
$P(CH=CH_2)_3$	2165.71	2069.5	**2155.4**	0.24
$P(p–tol)_3$	2166.59	2066.7	**2154.8**	
$P(o–tol)_3$	2168.83	2066.6	**2154.7**	
PHF_2	2179.03	2100.8	2190.0	0.67
PH_2F	2172.80	2090.9	2179.6	0.54
PF_3	2184.20	2110.8	2201.2	0.81
PMe_2CF_3	2178.49	2080.9	2169.7	0.42
PCl_3	2194.62	2107.0	2197.0	
$P(NMe_2)_3$	2172.01	2061.9	2151.0	0.19
$P(OMe)_3$	2176.50	2079.5	2171.3	0.42
Br^-	2153.76	2033.5	2120.2	−0.22
F^-	2153.54	2016.8	2102.7	−0.42
SiH_3^-	2118.67	2005.2	2085.8	
BH_2^-	2118.25			
	2137.37	1991.0	2075.8	−0.74
	2135.96	1986.6	2071.3	−0.80
	2140.98			
$B(OH)^{2-}$	2133.01	1980.6	2065.0	−0.88

[a] CEP values of complexes in bold were obtained by extrapolation of the CEP–versus–TEP least–squares line obtained from smaller phosphine models

We have noted that the computed steric effect of a ligand is sensitive to the conformation of that ligand [15–17,24,25]. Therefore, it is possible that the SEP will change with ligand conformation. The SEP values for a number of substantially different conformations of PPh$_3$ and PMe$_2$Ph ligands were computed, all of which yielded the same value for SEP. Therefore, SEP is relatively independent of ligand conformation and rigorous conformational analyses were not included. There are good correlations between the two computed electronic parameters and Tolman's experimental ν_{CO} values (Figure 1).
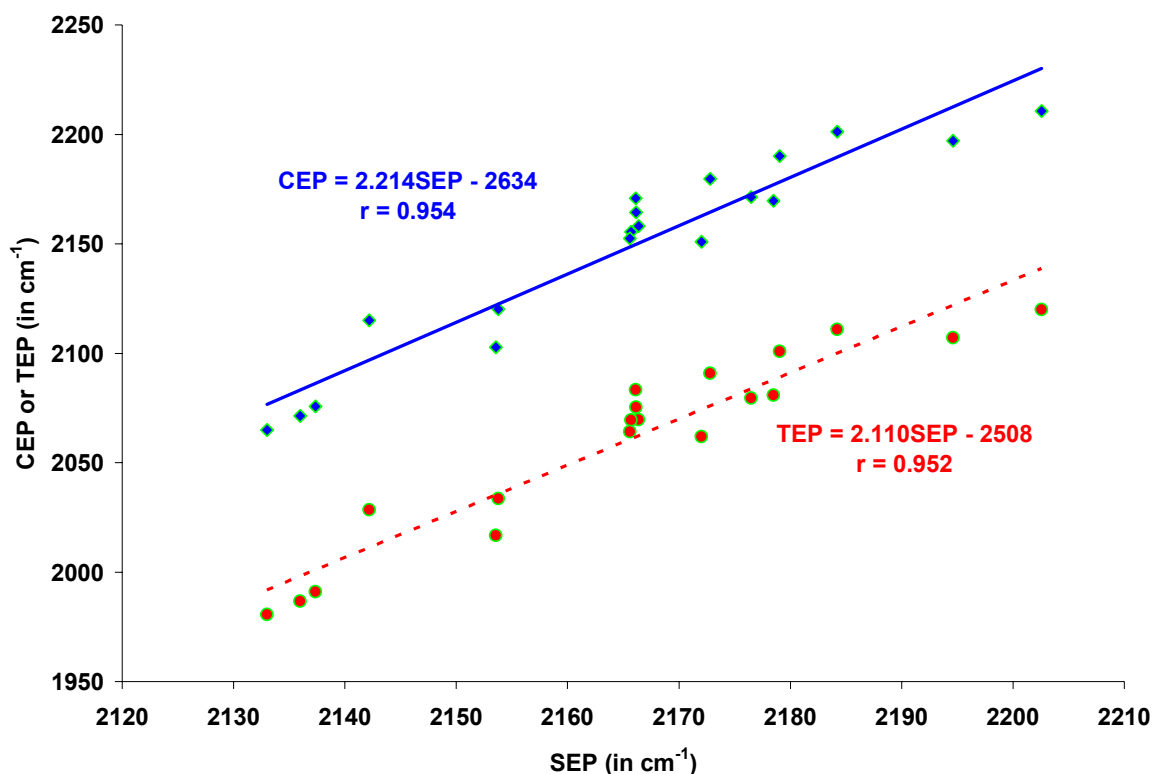

Figure 1. Plot of Tolman's Electronic Parameter, TEP, and Crabtree's Electronic Parameter, CEP, versus our Semiempirical quantum mechanics Electronic Parameter (SEP) for all the ligands listed in Table 1.

In Figure 1, the regression lines are almost parallel (slope of 2.214 for CEP vs. SEP and slope of 2.110 for TEP vs. SEP). SEQM methods accurately compute vibrational frequencies for organic molecules since there is one predominant type of bonding that is present. However, there is a systematic overstatement of vibrational frequencies for organometallic species with SEQM and DFT methods as seen in Table 1. This theory–experiment deviation in vibrational frequencies is a consequence of the neglect of anharmonic effects in the calculations and the many different types of bonds present in organometallic compounds (covalent, σ–donors/π–acceptors, π–donors/π–acceptors, etc.) [26]. Most importantly, the relative ranking of ligand electronic effects is independent of computational methodology employed; see Table 1 and Figure 1. Therefore, the more expedient SEQM method is capable of reproducing the same trend in ligand electronic effect as CEP. There is a similarly good correlation between SEP and LEP ($r = 0.960$; Figure 2).
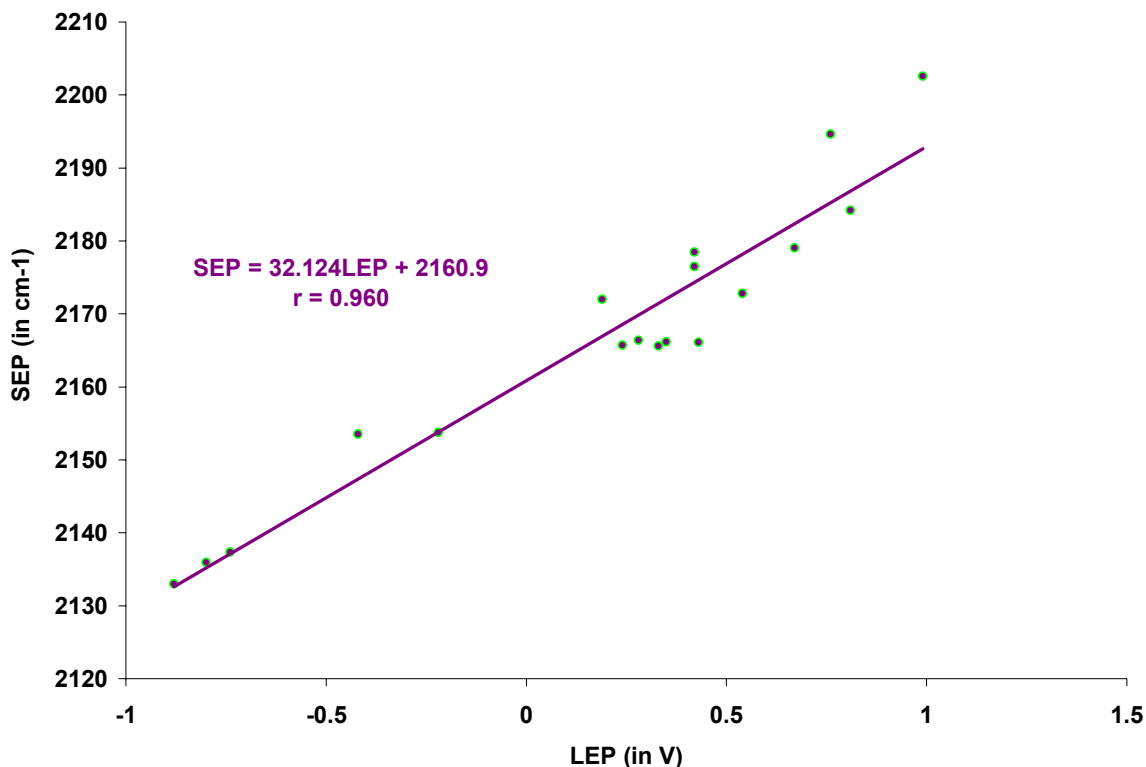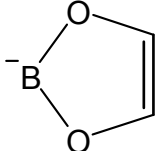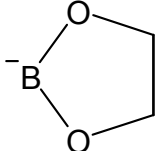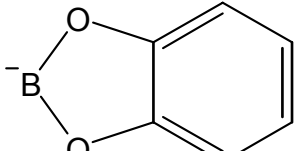
Figure 2. Plot of Lever's Electronic Parameter, LEP, versus the Semiempirical quantum mechanics Electronic Parameter (SEP) for the ligands listed in Table 1.

Table 2. Semiempirical Quantum Mechanics Electronic Parameter Computed in the $W(CO)_5$ and CpRhCO Environments (SEP in cm^{-1}), Tolman's Electronic Parameter (TEP in cm^{-1}), Crabtree's DFT Electronic Parameter (CEP in cm^{-1}), and Lever's Electronic Parameter (LEP in V) for a Variety of Ligands, L

Ligand, L	SEP $(WCO)_5$	SEP (CpRhCO)	TEP	CEP[a]	LEP
CO	2184.60	2161.09	2120.0	2210.6	0.99
PH_3	2143.62	2073.27	2083.2	2170.8	0.43
PH_2Me	2144.15	2076.18	2075.3	2164.3	0.35
$PHMe_2$	2143.91	2079.58	2069.6	2158.1	0.28
PMe_3	2143.86	2082.02	2064.1	2152.4	0.33
PEt_3	2142.86	2084.56	2061.7		0.34
$P(n–Pr)_3$	2142.84	2087.95			0.34
$P(i–Pr)_3$	2140.94	2081.95	2059.2	**2147.0**	
$P(n–Bu)_3$	2142.84	2083.10	2060.3		0.29
$P(t–Bu)_3$	2135.23	2088.67	2056.1		
PCy_3	2139.06	2086.08	2056.4		
$P(CH=CH_2)_3$	2142.95	2082.34	2069.5	2155.4	0.24
PMe_2Ph	2143.33	2087.42	2065.3		0.34
$PMePh_2$	2142.89	2086.93	2067.0		0.37
PPh_3	2142.48	2090.04	2068.9		0.39
$P(p–tol)_3$	2141.79	2089.28	2066.7	**2154.8**	
$P(o–tol)_3$	2142.12	2100.25	2066.6	**2154.7**	
$P(mes)_3$[b]	2137.10	2103.07	2064.2		
PBn_3[c]	2142.00	2093.08	2066.4		
$P(C_2H_4CN)_3$	2149.50	2108.54	2077.9		
PHF_2	2155.06	2104.38	2100.8	2190.0	0.67
PH_2F	2149.73	2085.62	2090.9	2179.6	0.54
PF_3	2158.98	2115.08	2110.8	2201.2	0.81
PCl_3	2170.30	2139.79	2107.0	2197.0	
PMe_2CF_3	2152.23	2102.97	2080.9	2169.7	0.42

Table 2. (Continued)

Ligand, L	SEP (WCO)$_5$)	SEP (CpRhCO)	TEP	CEP[a]	LEP
PMe(CF$_3$)$_2$	2163.82	2139.09	2097.9		
P(CF$_3$)$_3$	2174.53	2146.71	2114.9		
PPh$_2$CF$_3$	2152.06	2114.73	2084.3		
PPh(CF$_3$)$_2$	2162.29	2136.82	2099.6		
PMe$_2$(C$_6$F$_5$)	2148.84	2093.84	2071.3		
PMe(C$_6$F$_5$)$_2$	2154.12	2105.26	2081.1		
P(C$_6$F$_5$)$_3$	2156.97	2112.48	2090.9		
P(CF$_3$)$_2$(C$_6$F$_5$)	2164.10	2119.09	2106.5		
P(NMe$_2$)$_3$	2146.47	2101.00	2061.9	2151.0	0.19
P(OMe)$_3$	2152.92	2108.33	2079.5	2171.3	0.42
P(OEt)$_3$	2152.46	2107.95	2077.0		
P(OCH$_2$)$_3$Me	2153.63	2107.03	2087.3		
P(OPh)$_3$	2156.51	2110.99	2085.3		0.58
Br$^-$	2125.31	2033.53	2033.5	2120.2	−0.22
F$^-$	2118.18	2020.33	2016.8	2102.7	−0.42
SiH$_3^-$	2104.76	2002.26	2005.2	2085.8	
BH$_2^-$	2100.53	2000.95			
	2115.98	2027.28	1991.0	2075.8	−0.74
	2114.07	2027.09	1986.6	2071.3	−0.80
	2120.08	2038.60			
B(OH)$^{2-}$	1992.72	1870.70	1980.6	2065.0	−0.88

[a] CEP values of complexes in bold were obtained by extrapolation of the CEP–versus–TEP least–squares line obtained from smaller phosphine models

[b] mes = mesityl = 2,4,6–trimethylbenzene

[c] Bn = benzyl = CH$_2$Ph

To investigate the effect of metal complex on SEP, a number of W(CO)$_5$L and CpRh(CO)L complexes were also subjected to PM3(tm) optimization and vibrational frequency calculation, the results of which are summarized in Table 2.

A plot of SEP(CpRhCO) versus SEP(W(CO)$_5$) shows a linear correlation indicating that the choice of fragment for the SEP computation does not significantly affect the data (Figure 3). The two fragments, CpRh(CO) and W(CO)$_5$, have very different electronic environments at the metal. Therefore, the good correlation of SEPs computed in these two different environments strongly suggests that the SEP is a robust measure of ligand electronic effects that are fragment– independent. In addition, the good correlation between CEP (computed in the Ni(CO)$_3$ environment) and SEP (computed in the Mo(CO)$_5$, W(CO)$_5$, or CpRhCO environments) further

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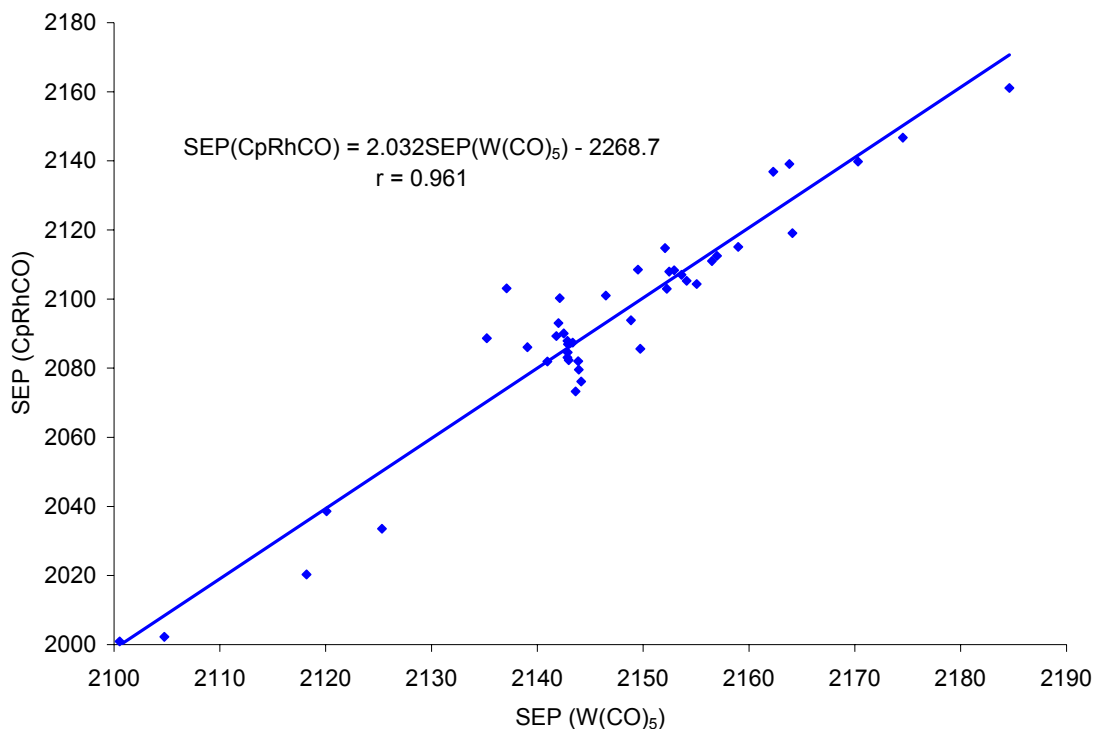reinforce the fragment independent nature of the SEP.

Figure 3. Plot of the semiempirical quantum mechanics electronic parameter computed in the CpRh(CO) environment plotted against SEP computed in the W(CO)$_5$ environment for the ligands listed in Table 2.
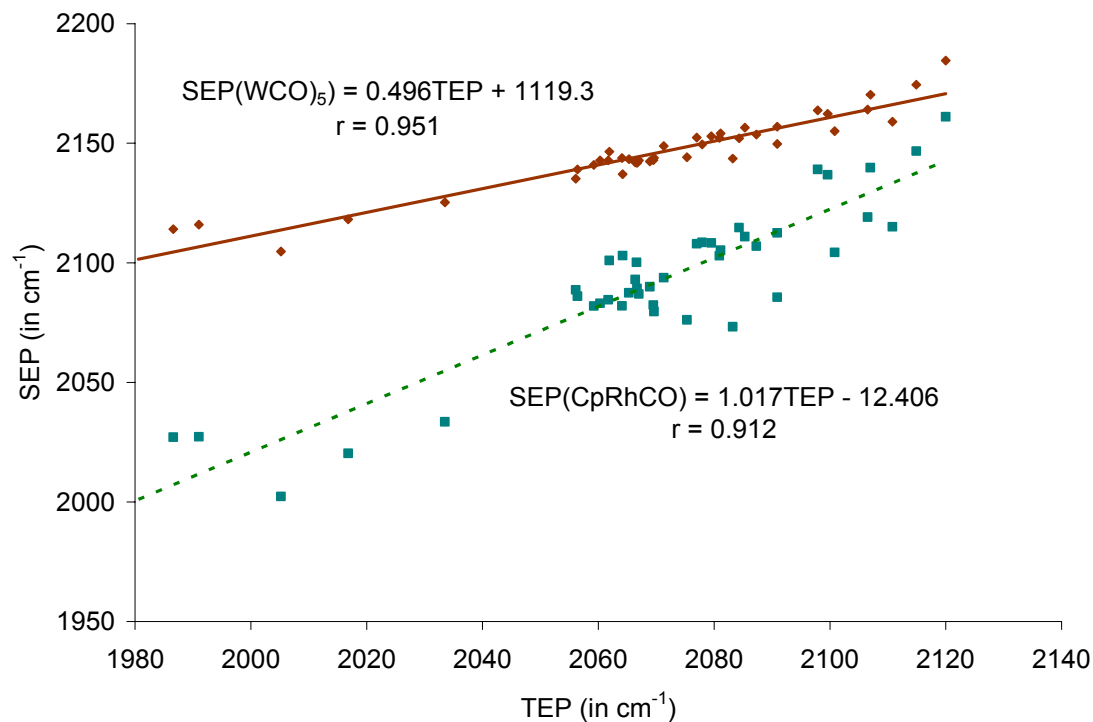

Figure 4. Plot of the semiempirical quantum mechanics electronic parameter SEP computed in the CpRh(CO) and W(CO)$_5$ environments plotted against the experimental TEP for the ligands listed in Table 2.

With the exception of the $B(OH)_2^-$ outlier, there are good correlations between SEP values in the two different environments and the experimental TEP (Figure 4).

The SEP values computed in the $W(CO)_5$ environment compare better with TEP than those computed in the CpRhCO environment. One possible reason is the electronic similarity between the all–carbonyl environments of $W(CO)_5$ and $Ni(CO)_3$ (for TEP) compared with the electronically dissimilar Cp ligand.

4 CONCLUSIONS

A semiempirical quantum mechanics metric of the electronic requirements of a variety of different ligands has been developed. This SEP correlates well with both experimental (TEP and LEP) and computational (CEP) measures of electronic effects reported in the literature. The new SEP has been shown to be relatively independent of the organometallic fragment to which the ligand is attached, as well as the conformation of the ligand. As a result, the SEP protocol provides an intuitive, easily calculated, yet powerful measure of the electronic profile of a ligand that can be used in the molecular design of novel organometallics for a variety of applications in catalysis and materials applications.

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