Carbonyl Substitution in β-Diketonatodicarbonyl-rhodium(I) by Cyclo-octadiene: Relationships with Experimental, Electronic and Calculated Parameters

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ABSTRACT

The substitution rate constant of the reaction between [Rh(β-diketonato)(CO)$_2$] and cyclo-octadiene is related to various empirical parameters and density functional theory calculated energies and charges, β-diketonato = R'COCHCOR. Results indicate that especially the Hammett meta substituent constants (σ), the Lever electronic parameters (E_L) and the density functional theory calculated energies and charges predict the substitution rate constant to a high degree of accuracy, for example: $\ln k_2 = 8.48\,(\sigma_R + \sigma_{R'}) - 2.24$ ($R^2 = 0.99$) $= 31.8\,\Sigma E_L - 63.0$ ($R^2 = 0.99$) $= -9.16\,E_{HOMO} - 52.1$ ($R^2 = 0.97$) $= 101\,\Sigma Q_{Mulliken}(Rh(CO)_2) - 49.9$ ($R^2 = 0.99$).

KEYWORDS

BETA-diketone, rhodium, substitution; dicarbonyl, cyclo-octadiene, DFT.

1. Introduction

The first [Rh(β-diketonato)(CO)$_2$] complexes were reported by Bonati and Wilkinson in 1964.[1] They showed that the carbon monoxide groups in [Rh(β-diketonato)(CO)$_2$] can be completely substituted by olefins such as cyclo-octa-1,5-diene (cod) (Scheme 1). The reverse reaction, i.e. treatment of [Rh(β-diketonato)(cod)] with CO resulted in better yields of [Rh(β-diketonato)(CO)$_2$] than the conventional synthetic pathway by treating [Rh(Cl)(CO)$_2$]$_2$ with the β-diketone in certain cases.[2] Reactions of [Rh(β-diketonato)(CO)$_2$] involving triphenylphosphine (PPh_3) or triphenylarsine ($AsPh_3$) lead to substitution of only one of the carbonyl ligands.[1,3–6] Rhodium(I) complexes with bidentate β-diketonato ligands are well-known catalysts for hydroformylation of olefins.[7–9] We have recently shown that experimental second-order substitution rate constants of the [Rh(R'COCHCOR)(cod)] + phen → [Rh(phen)(cod)]$^+$ + (R'COCHCOR)$^-$ reaction relate to the density functional theory calculated energies of the highest occupied molecular orbital of thermodynamically stable reactant [Rh(R'COCHCOR)(cod)] (phen = 1,10-phenanthroline).[10] We were interested to see if a similar relationship exists if [Rh(R'COCHCOR)(cod)] is the product of a substitution reaction. An experimental study of the kinetics of the substitution reaction [Rh(R'COCHCOR)(CO)$_2$] + cod → [Rh(R'COCHCOR)(cod)] + 2(CO) (Scheme 1) showed that the order of the effect of the β-diketonato ligands (R'COCHCOR)$^-$ on the reactivity of the [Rh(β-diketonato)(CO)$_2$] complexes was $(CH_3COCHCOPh)^-$ < $(PhCOCHCOPh)^-$ < $(CF_3COCHCOCH_3)^-$ < $(CF_3COCHCOPh)^-$ < $(CF_3COCHCOCF_3)^-$, i.e. more electronegative substituents R or R' of the β-diketone led to a faster substitution rate.[11]

The aim of this study is to establish relationships and trends between density functional theory (DFT) calculated, empirical and experimental data in order to be able to predict the reactivity of β-diketonatodicarbonyl-rhodium(I)- systems from calculated descriptors.

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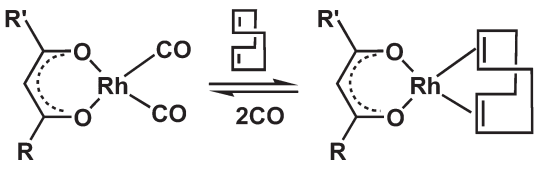
2. Methods

Density functional theory (DFT) calculations were carried out using the ADF (Amsterdam Density Functional) 2012 programme[12–14] with the GGA (Generalized Gradient Approximation) functional PW91 (Perdew-Wang 1991).[15] The TZ2P (Triple ζ polarized) basis set, with a fine mesh for numerical integration and tight convergence criteria, was used for



R'	R	
CH_3	CH_3	(1)
Ph	CH_3	(2)
Ph	Ph	(3)
CF_3	CH_3	(4)
CF_3	Ph	(5)
CF_3	CF_3	(6)

Scheme 1 Substitution of cod for CO in [Rh(β-diketonato)(CO)$_2$] leads to the formation of [Rh(β-diketonato)(cod))].

Table 1 Kinetic rate constants of the substitution of cod for CO in [Rh(R′COCHCOR)(CO)$_2$], empirical electronic parameters and calculated energies and charges of [Rh(R′COCHCOR)(CO)$_2$] complexes **1–6**. The complexes are arranged in the order of reactivity as measured by the substitution rate constant.

			Experimental	Electronic parameters				Calculated descriptors					
	R	R′	k_2/dm^3 mol^{-1} s^{-1} [a]	pK_a [b]	$(\chi_R + \chi_{R'}$/ (Gordy scale) [c]	$(\sigma_R + \sigma_R)$ [d]	ΣE_L [e] *vs.* SHE/V	E_{HOMO}/eV	$\Sigma Q_{Mulliken}$/au	$\Sigma Q_{Hirshfeld}$/au	$\Sigma Q_{Voronoi}$/au	ΣQ_{MDC}/au	ΣQ_{Bader}/au	ΣQ_{NPA}/au
1	CH_3	CH_3	–	8.95	4.68	–0.14	1.90	–5.441	0.458	0.150	0.755	0.516	0.549	0.344
2	C_6H_5	CH_3	0.10	8.7	4.55	–0.01	1.92	–5.476	0.471	0.154	0.762	0.530	0.547	0.350
3	C_6H_5	C_6H_5	0.36	9.35	4.42	0.12	1.94	–5.511	0.481	0.158	0.765	0.543	0.549	0.356
4	CF_3	CH_3	2.30	6.3	5.35	0.36	2.01	–5.843	0.501	0.200	0.796	0.558	0.590	0.386
5	CF_3	C_6H_5	4.10	6.3	5.22	0.49	2.03	–5.834	0.511	0.200	0.798	0.570	0.586	0.388
6	CF_3	CF_3	200	4.71	6.02	0.86	2.15	–6.247	0.544	0.251	0.839	0.599	0.627	0.426

(a) Kinetic rate constants 25.0(1) °C in acetone form reference 11.
(b) Acid dissociation constant pK_a from refs. 43 and 44.
(c) The group electronegativity $(\chi_R + \chi_{R'})$ is calculated on the Gordy scale with χ_{CF3} = 3.01,[45] χ_{CH3} = 2.34,[46] χ_{Ph} = 2.21[45].
(d) The Hammett meta substituent constants $\sigma_R + \sigma_{R'}$ from references 19 and 20 with σ_{CF3} = 0.43, σ_{CH3} = –0.069 and σ_{Ph} = 0.06.
(e) Lever electrochemical ligand parameter E_L of β-diketonato from reference 21.

minimum energy searches. Throughout, all calculations have been performed with no symmetry constraints (C_1) and all structures have been calculated as spin-restricted singlet states. All calculations have been done in the gas phase. Optimized geometries obtained were used to perform an NBO analysis by the NBO 3.1 module.[16]

3. Results and Discussion

3.1. Kinetic Rate Constant and Electronic Parameters

The experimentally measured second-order rate constant k_2 for the substitution of cod for CO in [Rh(R′COCHCOR)(CO)$_2$] is tabulated in Table 1 (cod=1,5-cyclooctadiene).[11] Empirical parameters that are related to the electron donating property of the R and R′ groups on the β-diketonato ligand (R′COCHCOR)$^-$, the sum of the Gordy scale group electronegativities $(\chi_R + \chi_{R'})$,[17,18] the sum of the Hammett meta substituent σ constants, $(\sigma_R + \sigma_{R'})$,[19,20] and the sum of the Lever electronic parameter ΣE_L[21–24] for the [Rh(R′COCHCOR)(CO)$_2$] complexes are also given in Table 1. Figure 1 visualizes the linear relationships between ln k_2 and the electronic parameters.

$$\ln k_2 = 4.25\,(\chi_R + \chi_{R'}) - 20.9 \qquad (R^2 = 0.91)$$

$$\ln k_2 = 8.48\,(\sigma_R + \sigma_{R'}) - 2.24 \qquad (R^2 = 0.99)$$

$$\ln k_2 = 31.8\,\Sigma E_L - 63.0 \qquad (R^2 = 0.99)$$

A lower (more acidic) pK_a value of the free β-diketone generally resulted in a faster substitution rate (see data in Table 1), but did not give a good linear fit. The Hammett constants and Lever parameters originate from substitution rate constants and electrochemical potentials respectively. The Hammett constants σ_R are empirical constants that relate the logs of rate or equilibrium constants for reactions of the substituted (k_R, R = substituent) and the unsubstituted (k_H, no substituent) benzoic acid derivatives to the reaction rate ρ: log $(k_R/k_H) = (\sigma_R)\rho$. σ_R depends solely on the nature and position of the substituent R.[25] In as much as the substituents on the β-diketonato chelate ring are *meta* with respect to rhodium, the σ values used are those for *meta* position substitution.[26] Since the β-diketonato ligand in [Rh(R′COCHCOR)(cod)] has two *meta* substituents relative to rhodium, the σ value is taken as the sum of the values for the two groups present. The Lever parameter is a redox potential

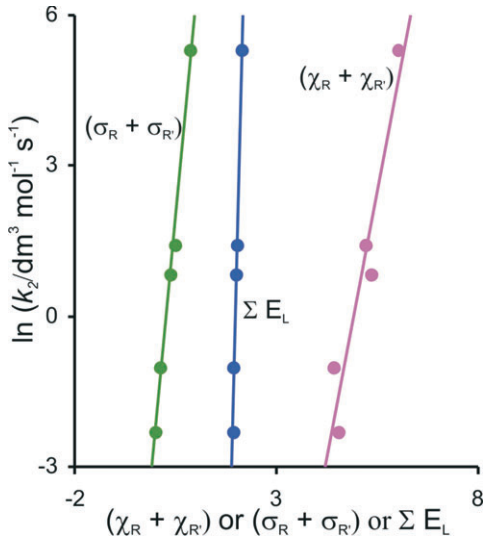


Figure 1 Linear dependence of the substitution rate constant k_2 on the empirical quantities $((\chi_R + \chi_{R'})$, $(\sigma_R + \sigma_{R'})$ and $\Sigma E_L)$ of complexes **2–6**. Data are in Table 1.

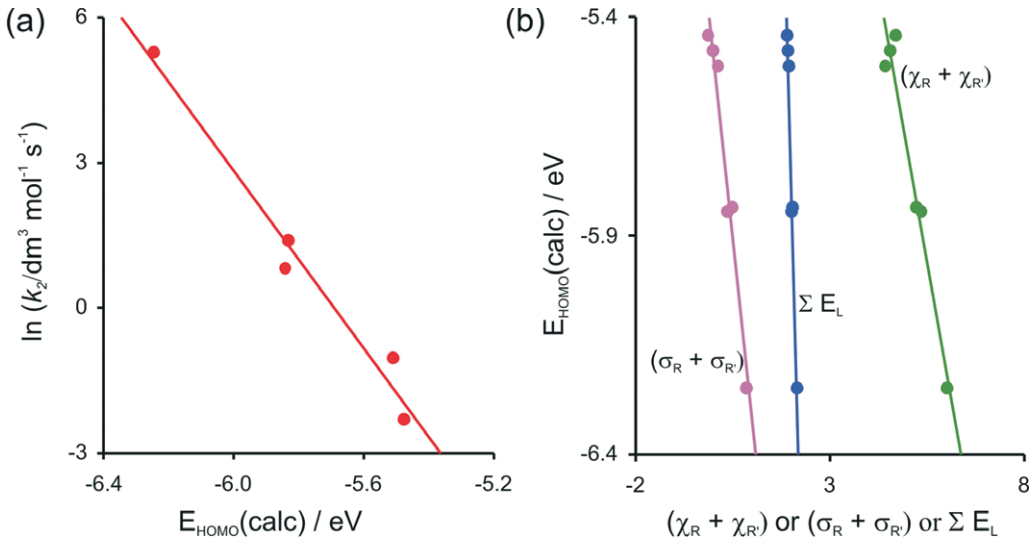


Figure 2 (**a**) Linear dependence of the substitution rate constant k_2 on the calculated HOMO energy of complexes **2**–**6**. (**b**) Linear dependence of the calculated HOMO energy of complexes **1**–**6** on the empirical quantities (($\chi_R + \chi_{R'}$), ($\sigma_R + \sigma_{R'}$) and ΣE_L). Data are in Table 1.

Table 2 Linear correlation coefficients R^2 obtained for various plots between calculated, empirical and experimental data related to [Rh(R'COCHCOR)(CO)$_2$] complexes **1**–**6**.

	E_{HOMO}	$\Sigma Q_{Mulliken}$/au	$\Sigma Q_{Hirshfeld}$/au	$\Sigma Q_{Voronoi}$/au	ΣQ_{MDC}/au	ΣQ_{Bader}/au	ΣQ_{NPA}/au	Average R^2
ln k_2	0.97	0.99	0.97	0.98	0.99	0.95	0.98	**0.98**
($\chi_R + \chi_{R'}$)	0.95	0.84	0.95	0.94	0.79	0.98	0.93	**0.91**
($\sigma_R + \sigma_{R'}$)	0.96	1.00	0.96	0.97	1.00	0.93	0.98	**0.97**
ΣE_L	0.99	0.98	0.99	0.99	0.97	0.96	0.97	**0.98**
E_{HOMO}	–	0.96	1.00	1.00	0.93	0.99	1.00	**0.98**
Average R^2	**0.97**	**0.95**	**0.97**	**0.98**	**0.94**	**0.96**	**0.97**	–

parameterization approach,[21] involving an empirical relationship between the oxidation potential (in volts *vs*. SHE) of the redox couple M(q)/M(q+1) of a complex and the Lever electrochemical parameters determined by the ligands and the metal centre, E_{redox} (*vs*. SHE) = $S_M \Sigma E_L + I_M$. ΣE_L is the sum of the values of the Lever ligand E_L parameters for all the ligands (additive effects) in the complex and S_M and I_M represent the slope and intercept (dependent on the metal, redox couple, spin state and stereochemistry). We observe that both the Hammett constants and the Lever parameters give excellent descriptions of reactivity patterns of the [Rh(R'COCHCOR)(CO)$_2$] complexes containing different R and R' substituents as experimentally measured by the substitution rate constant k_2.

3.2. Kinetic Rate Constant, Electronic Parameters and DFT Calculated Energies

The reactivity of the rhodium complexes is in many respects due to the nature of ligand surroundings[27] and determined largely by the relative frontier orbital energies.[28–30] The Frontier Molecular Orbital Theory (FMO Theory) simplifies reactivity to interactions between the HOMO of one species and the LUMO of the other[31] The reactivity of the [Rh(R'COCHCOR)(CO)$_2$] complex is therefore related to the energy of its HOMO. The high correlation found between the DFT calculated energy of the HOMO (highest occupied molecular orbital) of the [Rh(R'COCHCOR)(CO)$_2$] complexes **2**–**6**, E_{HOMO} and the substitution rate constant (Figure 2 (a)) shows that the substitution reaction is frontier controlled:

$$\ln k_2 = -9.16\, E_{HOMO} - 52.1 \qquad (R^2 = 0.97)$$

The d-occupation of the [Rh(R'COCHCOR)(CO)$_2$] complexes **1**–**6** is $d_{xz}^2\, d_{yz}^2\, d_{xy}^2\, d_{z2}^2\, d_{x2\text{-}y2}^0$ with the HOMO mainly d_{z2} on rhodium, see Fig. 3. The calculated HOMO energy is largely influenced by the electronic effect of the substituent groups R and R' on rhodium. Figure 2 (b) displays the relationships between the various empirical parameters describing the electron-donating/withdrawing power of the R and R' groups and the energy of the HOMO of complexes **1**–**6**:

$$E_{HOMO} = -0.502\,(\chi_R + \chi_{R'}) - 3.20 \qquad (R^2 = 0.95)$$

$$E_{HOMO} = -0.835\,(\sigma_R + \sigma_{R'}) - 5.49 \qquad (R^2 = 0.96)$$

$$E_{HOMO} = -3.34\,\Sigma E_L + 0.928 \qquad (R^2 = 0.99)$$

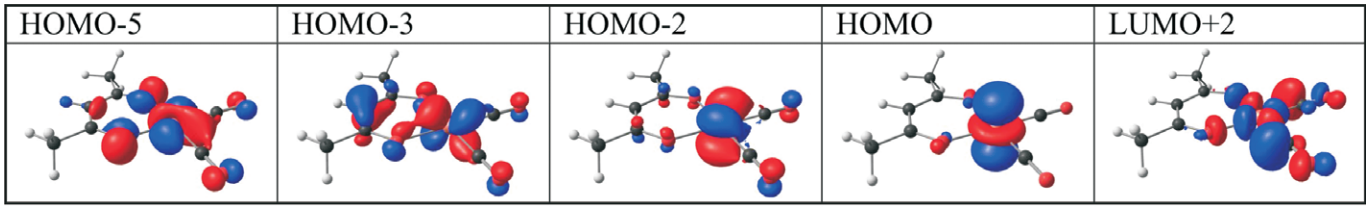


Figure 3 Kohn-Sham metal d-based frontrier orbitals of **1** from PW91/STO-TZ2P calculations. Colour code: H (white), C (grey), O (red) and Rh (orange).

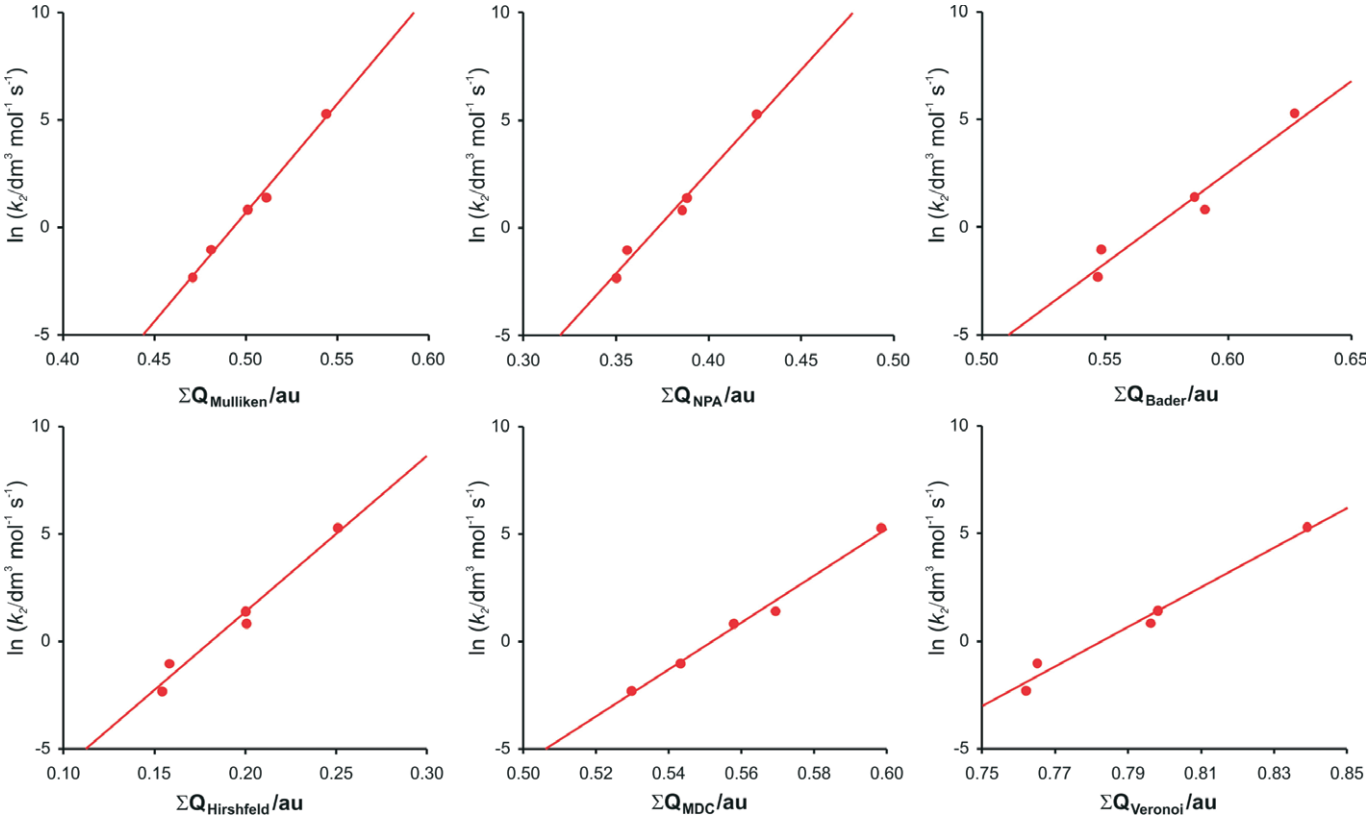


Figure 4 Linear dependence of the experimental ln(k_2) on the indicated calculated charges on the Rh(CO)$_2$ fragment of complexes **2**–**6**.

The above relationships all show that more electron withdrawing R and R′ substituent groups lead to a more negative E_{HOMO}, i.e. a more stable HOMO.

Experimental rate constants k_2 relate to the activation energy E_a by the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

where, R = gas constant, T = temperature and A = pre-exponential factor. We have previously shown that the relationship between the DFT calculated activation energy and the experimentally measured kinetic parameter ln k_2 of the oxidative addition reaction [Rh(β-diketonato)(P(OPh)$_3$)$_2$] + CH_3I is less accurate than the relationship between E_{HOMO} and ln k_2.[32] Therefore we do not consider relationships involving transition states in this study.

3.3. Kinetic Rate Constant, Electronic Parameters and DFT Calculated Charges

A detailed quantum chemical examination of electron state variations of an active metal-containing centre *versus* different ligand characteristics may lead to a better understanding of the relationship between the activity and catalyst structure, as well as to ways of predicting catalytic activity. The wavefunction population analysis methods assign a partial charge to each atom. Although the absolute magnitudes of the atomic charges yielded by population analysis have little physical meaning,[33] the relative magnitude of the numbers can be interpreted and can yield useful information.[34,35] The Mulliken population analysis[36] is one of the oldest, simplest and most common population analysis methods. The calculated Mulliken charge on the Rh(CO)$_2$ fragment in the reactant [Rh(R′COCHCOR)(CO)$_2$] complexes **1**–**6** relates to the experimental and empirical parameters tabulated in Table 1 (average R^2 = 0.95, see Figs 4 and 5):

$$\ln k_2 = 101\ \Sigma Q_{Mulliken}(Rh(CO)_2) - 49.9 \quad (R^2 = 0.99)$$

$$\Sigma Q_{Mulliken}(Rh(CO)_2) = 0.0470\ (\chi_R + \chi_{R'}) + 0.257 \quad (R^2 = 0.84)$$

$$\Sigma Q_{Mulliken}(Rh(CO)_2) = 0.0851\ (\sigma_R + \sigma_{R'}) + 0.470 \quad (R^2 = 1.00)$$

$$\Sigma Q_{Mulliken}(Rh(CO)_2) = 0.333\ \Sigma E_L - 0.170 \quad (R^2 = 0.98)$$

The natural population analysis (NPA), another wavefunction population analysis method, yields natural charges. The natural charge on rhodium generally increased (became less negative) in going from complex **1** to **6** (fastest substitution rate, most reactive). The charge alteration of the rhodium-dicarbonyl fragment correlates with the different experimental and empirical parameters (see Figs 4 and 5, data are in Table 1):

$$\ln k_2 = 94.7\ \Sigma Q_{NPA}(Rh(CO)_2) - 35.2 \quad (R^2 = 0.98)$$

$$\Sigma Q_{NPA}(Rh(CO)_2) = 0.0493\ (\chi_R + \chi_{R'}) + 0.127 \quad (R^2 = 0.93)$$

$$\Sigma Q_{NPA}(Rh(CO)_2) = 0.0841\ (\sigma_R + \sigma_{R'}) + 0.351 \quad (R^2 = 0.98)$$

$$\Sigma Q_{NPA}(Rh(CO)_2) = 0.334\ \Sigma E_L + 0.290 \quad (R^2 = 0.99)$$

From the relationships obtained above, we note that the calculated charges are valuable indicators of chemical behaviour. Other computational methods[37] of atomic charge determination include the partitioning of electron density distributions (e.g. Bader charges obtained from an atoms in molecules analysis[38] and Hirshfeld[39] charges) and charges derived from density-dependent properties (e.g. MDC, Multipole derived atomic charges[40]). See Figs 4 and 5 for a visualization of the good relationships obtained between the calculated charges and experimental and empirical parameters (data are in Table 1):

$$\ln k_2 = 84.7\ \Sigma Q_{Bader}(Rh(CO)_2) - 48.3 \quad (R^2 = 0.95)$$

$$\Sigma Q_{Bader}(Rh(CO)_2) = 0.0527\ (\chi_R + \chi_{R'}) + 0.309 \quad (R^2 = 0.98)$$

$$\Sigma Q_{Bader}(Rh(CO)_2) = 0.0848\ (\sigma_R + \sigma_{R'}) + 0.551 \quad (R^2 = 0.93)$$

$$\Sigma Q_{Bader}(Rh(CO)_2) = 0.341\ \Sigma E_L + 0.104 \quad (R^2 = 0.96)$$

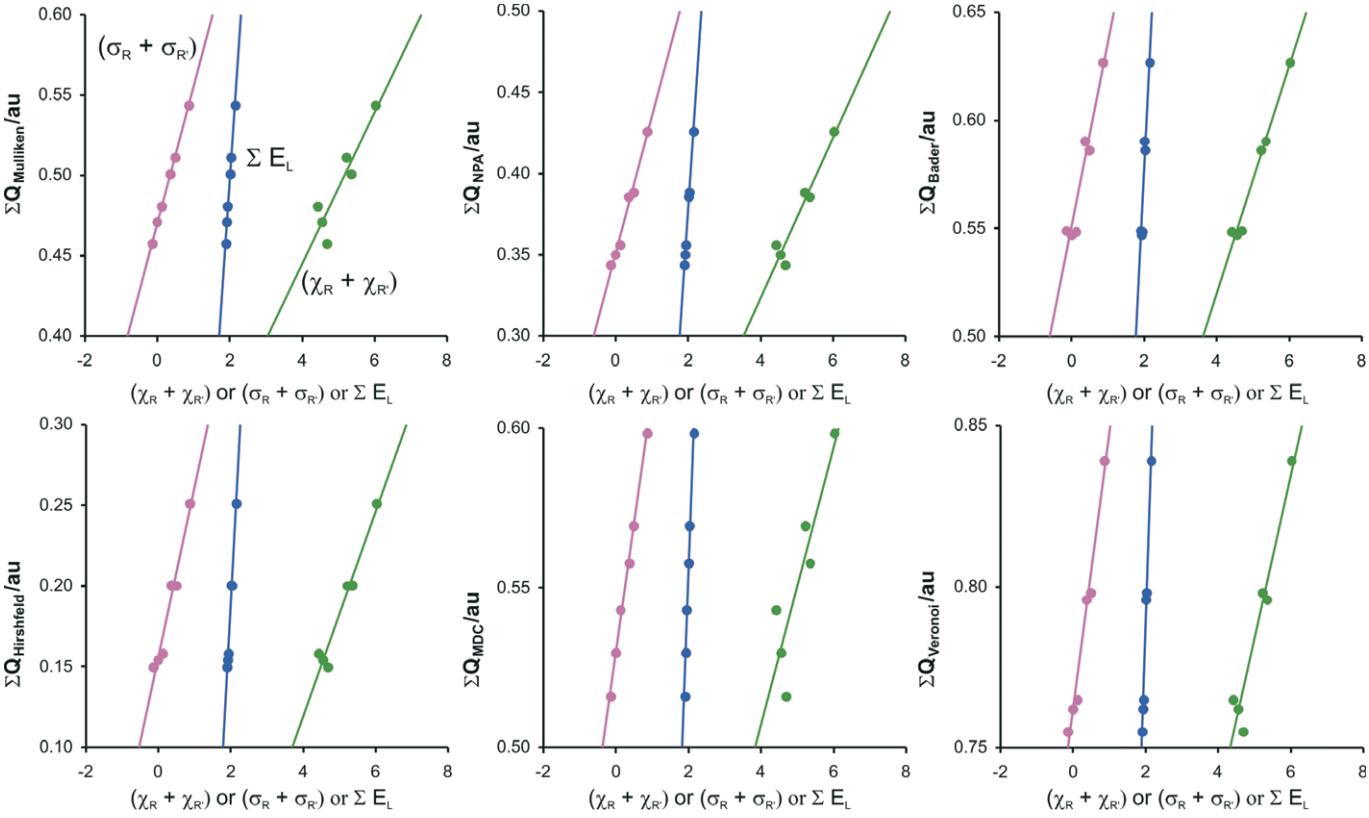


Figure 5 Linear dependence of the indicated calculated charges on the $Rh(CO)_2$ fragment of complexes **1**–**6** on the empirical quantities $(\sigma_R + \sigma_{R'})$ (magenta, left in each graph), ΣE_L (blue, middle in each graph) and $(\chi_R + \chi_{R'})$ (green, right in each graph).

$$\ln k_2 = 72.6\ \Sigma Q_{Hirshfeld}(Rh(CO)_2) - 13.1 \quad (R^2 = 0.97)$$
$$\Sigma Q_{Hirshfeld}(Rh(CO)_2) = 0.0633\ (\chi_R + \chi_{R'}) + 0.134 \quad (R^2 = 0.95)$$
$$\Sigma Q_{Hirshfeld}(Rh(CO)_2) = 0.105\ (\sigma_R + \sigma_{R'}) + 0.156 \quad (R^2 = 0.96)$$
$$\Sigma Q_{Hirshfeld}(Rh(CO)_2) = 0.421\ \Sigma E_L + 0.653 \quad (R^2 = 0.99)$$

$$\ln k_2 = 109\ \Sigma Q_{MDC}(Rh(CO)_2) - 60.3 \quad (R^2 = 0.99)$$
$$\Sigma Q_{MDC}(Rh(CO)_2) = 0.0434\ (\chi_R + \chi_{R'}) + 0.334 \quad (R^2 = 0.79)$$
$$\Sigma Q_{MDC}(Rh(CO)_2) = 0.0805\ (\sigma_R + \sigma_{R'}) + 0.530 \quad (R^2 = 1.00)$$
$$\Sigma Q_{MDC}(Rh(CO)_2) = 0.313\ \Sigma E_L + 0.0714 \quad (R^2 = 0.97)$$

Voronoi deformation density (VDD) is a method based on the partitioning of space into non-overlapping atomic areas modelled as Voronoi cells and then computing the deformation density within those cells.[41] The relationship between the calculated Voronoi charges and the experimental substitution rate and empirical electronic parameters is illustrated in Figs 4 and 5 (data are in Table 1):

$$\ln k_2 = 91.9\ \Sigma Q_{Voronoi}(Rh(CO)_2) - 72.0 \quad (R^2 = 0.98)$$
$$\Sigma Q_{Voronoi}(Rh(CO)_2) = 0.0505\ (\chi_R + \chi_{R'}) + 0.531 \quad (R^2 = 0.94)$$
$$\Sigma Q_{Voronoi}(Rh(CO)_2) = 0.08545\ (\sigma_R + \sigma_{R'}) + 0.762 \quad (R^2 = 0.97)$$
$$\Sigma Q_{Voronoi}(Rh(CO)_2) = 0.341\ \Sigma E_L + 0.107 \quad (R^2 = 0.99)$$

In all the above relationships that involved calculated partial charges, the sum of the charges on the $Rh(CO)_2$ fragment gave relationships with a better fit than the charge on Rh alone. The thermodynamic *trans* influence of the two $O_{\beta\text{-diketonato}}$ atoms of the chelate ring *trans* to the carbonyl groups of [Rh(R'COCHCOR)$(CO)_2$] may contribute to this phenomenon. The *trans* influence of the $O_{\beta\text{-diketonato}}$ is due to the electron withdrawing power of the R group nearest to it. The Rh-CO bonding (CO-to-M σ bond) and back-bonding (M-to-CO π bond) may also contribute to this phenomenon. Shor similarly found that for [Rh(R'COCHCOR)$(CO)_2$] complexes the NPA charge alteration of the metal-dicarbonyl fragment (and not on Rh alone) in [Rh(R'COCHCOR)$(CO)_2$] correlated with CO bond lengths and vibration frequencies of carbonyl group.

The above relationships show the same trend; stronger electron attracting R and R' substituent groups decrease the electron density on $Rh(CO)_2$ in going from complex **1** to **6**, making the complex a stronger Lewis acid. The five-coordinate transition state[42] of the substitution reaction [Rh(R'COCHCOR)$(CO)_2$] + cod is therefore more stabilized as R and R' become more electron attracting. This leads to an increase of the reactivity of the complex towards substitution reactions.

The relationships obtained from DFT charges make the estimate of k_2 for any [Rh(R'COCHCOR)$(CO)_2$] complex possible with an accuracy of >97 %.

4. Conclusions

The aim of this study was to establish relationships and trends between calculated, empirical and experimental data in order to predict the reactivity as experimentally measured by the chemical substitution rate (k_2) of cod for CO in [Rh(R'COCHCOR)$(CO)_2$]. From the DFT optimized structures of [Rh(R'COCHCOR)$(CO)_2$] complexes **1**–**6** we found that both the HOMO energy and the charges on $Rh(CO)_2$ are valuable indicators of chemical behaviour. Results show that k_2 can be predicted with a high degree of accuracy by the following equations:

$$\ln k_2 = 4.25\ (\chi_R + \chi_{R'}) - 20.9 \quad (R^2 = 0.91)$$
$$= 8.48\ (\sigma_R + \sigma_{R'}) - 2.24 \quad (R^2 = 0.99)$$
$$= 31.8\ \Sigma E_L - 63.0 \quad (R^2 = 0.99)$$

$= -9.16\ E_{HOMO} - 52.1$ ($R^2 = 0.97$)

$= 101\ \Sigma Q_{Mulliken}(Rh(CO)_2) - 49.9$ ($R^2 = 0.99$)

$= 94.7\ \Sigma Q_{NPA}(Rh(CO)_2) - 35.2$ ($R^2 = 0.98$)

$= 84.7\ \Sigma Q_{Bader}(Rh(CO)_2) - 48.3$ ($R^2 = 0.95$)

$= 72.6\ \Sigma Q_{Hirshfeld}(Rh(CO)_2) - 13.1$ ($R^2 = 0.97$)

$= 109\ \Sigma Q_{MDC}(Rh(CO)_2) - 60.3$ ($R^2 = 0.99$)

$= 91.9\ \Sigma Q_{Voronoi}(Rh(CO)_2) - 72.0$ ($R^2 = 0.98$)

A lower (more negative) E_{HOMO}, i.e. a more stable HOMO, therefore systematically resulted in a faster substitution rate. The complex is therefore more reactive, due to the stabilization of the five-coordinate transition state of the substitution reaction. The electronic influence of R and R′ groups in [Rh(R′COCHCOR)$(CO)_2$] complexes is reflected in the stability of the HOMO of the complex. Higher group electronegativities ($\chi_R + \chi_{R'}$), higher Hammett meta substituent constants ($\sigma_R + \sigma_{R'}$), higher Lever electronic parameters ΣE_L and lower pK_a values of the free β-diketone result in a more stable HOMO with a lower (more negative) energy. Relationships between calculated and experimental parameters allow for the design of ligands that can enhance the substitution rate.

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