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Introduction of Modified Electronic Parameters – Searching for a Unified Ligand Properties Scale through the Electrophilicity Index Concept

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In order to quantify the contribution of mainly, but not only, diimine ligands to the electronic properties of the corresponding complexes, two novel indices, namely modified electronic parameters (*ModEP*) and electrophilicity, ω, are introduced and discussed in this report. First, we introduce the concept of *ModEP*, a novel scale relating to the electronic properties of diimine ligands. Mainly on the basis of well-characterized M(diimine)(dithiolato) complexes (M = Pt, Pd, or Ni), we derive the contribution of the diimine ligand to the reduction potentials of the complexes, and incorporating its contribution to the main charge-transfer band of the UV/Vis spectra, we obtain our *ModEP* values. The applicability of the introduced scale to several other classes of diimine compounds (W, Re, and Ru) is then tested. The performance of our scale in predicting the values of the reduction potentials and the position of the charge-transfer bands is very satisfactory. With this approach, some interesting aspects of ligand coordination were revealed. Next, we employ the recently introduced electrophilicity index ω, in order to correlate our *ModEP* scale with various other empirical scales that are already known and extensively used. This permits us to unify most known scales, which were primarily derived for different types of ligands (e.g. *ModEP* for diimines, Tolman's for phosphanes). The proposed method of ω calculation (at the semiempirical AM1 level) avoids any experimental limitation and can be employed even for ligands that are not yet experimentally available, whereas its correlation to the known scales would immediately provide the properties of the compound. This supports the idea that the electrophilicity index could become a powerful tool in coordination and organometallic chemistry.

Introduction

All the properties of inorganic and organometallic complexes and their potential applications, from the field of homogeneous catalysis to materials and from photochemistry to DNA binding and intercalation are determined by the combination of metal and ligand. However, for a given series of homologous compounds with the same metal, the role of the ligand in terms of both electronic and steric effects becomes dominant. For decades, coordination and organometallic chemists have been trying to find a way to predict the effect of a ligand change upon the properties of a complex,[1–7] trying to avoid the need for extensive synthetic work. This essential need for knowledge of ligand effects on a certain core or fragment is extended not only to different types of known ligands, but also to ones that have merely been considered for future work. In this sense, great effort has been put into the development of ligand parameters, on the basis of which properties of known compounds would be documented and properties of new ones could be predicted.

Of known importance is Tolman's electronic parameter (*TEP*) relating to phosphanes (PR_3).[1] It was derived on the basis of the A_1 ν(CO) stretching vibration of $(R_3P)Ni(CO)_3$ complexes. As it is justified by backbonding theory, the greater the donor power of the phosphane the lower the stretching mode becomes. *TEP* has found wide usage over the years, but the expansion of the model is limited by the requirement that a new ligand L along with the corresponding $NiL(CO)_3$ complex should be synthesized and spectroscopically investigated, and this is not always an easy task.

This limitation is overcome by Crabtree's calculated electronic parameters (*CEP*).[2] In this approach, the A_1 ν(CO) frequency is no longer experimentally derived, but it is calculated by means of density functional theory (DFT). The relative donor powers of a wide variety of cationic, neutral, and negatively charged ligands are reliably predicted; expanding the model, these parameters also correlate well with other empirically derived parameters. Even though the method avoids any experimental limitations, it incurs computational costs and provides no values for bidentate ligands, such as diimines.

Lever's electronic parameters (*LEP*)[3] are based on the electrochemical $E°$ value for various redox couples, notably Ru^{III}/Ru^{II}, in series of complexes containing the ligands of interest. *LEP* cover a much wider set of ligands than Tol-

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man's scale, including anionic, O- and N-donor ligands. On the other hand, it has the disadvantage that an electrochemical apparatus for measurements is necessary, which is not always available. Another disadvantage of *LEP* is that electrochemical irreversibility can degrade the quality of the data for certain ligands, and solvation and ion-pairing effects could interfere to some extent.

Hammett substitution constants σ have found wide usage both with organic and inorganic compounds.[5] These were defined by the ionization constants of the appropriately substituted benzoic acids. The most extensively employed are σ_p and σ_m, relating to *para*- and *meta*- substituent effects, respectively. Hammett constants in most of the cases have only qualitative value, providing synthetic chemists with trends, but not with accurate properties of compounds under preparation. Moreover, they are limited by their own nature. They provide the trends that would arise by the substitution of a ligand in certain positions, but they can not show which effects would arise from a different ligand. Thus, in the case of the 2,2′-bipyridine ligand, for example, Hammett substitution constants might work if the substituents are added in the 4 and 4′ positions, but they will fail to predict what will happen if bipyridine is replaced by 1,10-phenanthroline or an aliphatic ligand, such as diiminosuccinonitrile.

Recently, Arca et al.[6] gave a quantitative description of the effect induced by both the metal and the ligands to the value of $\lambda_{\max}$ in a series of dithiolene complexes of the M(R,R′timdt)$_2$ type and Poë et al.[7] presented an analysis of CO dissociative kinetics of Ru(CO)$_4$L (L = P-donor ligands).

Keeping all of the above in mind, herein we present our efforts to obtain a unified ligand properties scale. Our investigation for a quantitative analysis of ligand effects (QALE)[8–14] was carried out at two levels. In the first, we introduce the concept of modified electronic parameters (*ModEP*), a novel scale relating to the electronic properties of diimine ligands. Mainly on the basis of the well-characterized M(diimine)(dithiolato) complexes (M = Pt, Pd, or Ni), we derive the contribution of the diimines to the reduction potential of the complexes; in the next step, we incorporate their effect on the main charge-transfer band of the visible spectra of the complexes, and then we obtain our *ModEP* values. There are two reasons for choosing this class of complexes for our analysis. First of all, an extensive series of this type of compounds has been presented.[15–72] Furthermore, the interest toward mixed diimine–dithiolato complexes of d^8 metals is related to their unique properties, which include solution luminescence, solvatochromism, large molecular hyperpolarizabilities, and large excited-state oxidation potentials. Because of these properties, they are considered to be very promising candidates for nonlinear optical (NLO) materials, molecular photochemical devices (MPD), and photosensitizers for solar cells.

The electronic properties depend most likely on the existence in the same molecule of two different unsaturated chelating ligands, one of which is a good π*-donor (the dithiolato ligand) and the other a good π*-acceptor (the diimine). The possibility of applying mixed diimine–dithiolato complexes to any of the above-mentioned technologies mainly relies on the intense solvatochromic, visible absorption in the neutral state, $E_{\mathrm{MMLL'CT}}$, caused by the mixed-metal–ligand-to-ligand-charge-transfer (MMLL′CT)[26] transition between the HOMO and LUMO, where the former is a mixture of metal and dithiolato ligand orbital and the latter a π* orbital of the diimine. This assignment has been confirmed by TD-DFT calculations,[69–72] and both experimental[16–34] and theoretical results[69–72] indicate that its frequency can be tuned from near-Vis to NIR by changing the substituents both at the diimine and dithiolate moieties. These complexes face a reversible, diimine-based, reduction process, which is well characterized.

Up to now, despite the extensive study of M(diimine)(dithiolato) complexes, only some general trends of the nature of the substituent groups on the main substrate of the diimine or dithiolato ligand have been revealed, but none of this data is in quantitative form. Between the two ligands, the one that is less studied from the point of view of its effect on the properties of a molecule is certainly the diimine.

The applicability of the introduced scale is then tested on several other types of W, Re, and Ru diimine compounds. The performance of our scale in predicting the value of the reduction potentials and the position of the charge-transfer bands is very satisfactory.

In the next level of investigation, we employ the recently introduced electrophilicity index ω,[73] in order to correlate our *ModEP* scale with various other empirical scales that are already known and extensively used. This procedure gives us the chance to unify all these scales, which were derived by investigating different types of ligands (e.g. *ModEP* on diimines, Tolman's on phosphanes). This supports the idea that the electrophilicity index could become a powerful tool in coordination and organometallic chemistry.

Computational Details

All the experimental data presented are taken from already published reports. In the following discussion, the abbreviations used for compounds are as follows: tdt = toluene-3,4-dithiolato, bpy = 2,2′-bipyridine, php = 1,10-phenanthrolinopyrrole, tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline, 3,5,6,8-tetramethyl-1,10-phenanthroline, *i*Pr-pya = *N*-isopropylpyridine-2-carbaldimine, dmphen = 4,7-dimethyl-1,10-phenanthroline, Bu-pya = *N*-butylpyridine-2-carbaldimine, 6,6′-dmbpy = 6,6′-dimethyl-2,2′-bipyridine, dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, dmbpy = 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dmbpy = 5,5′-dimethyl-2,2′-bipyridine, 2,9-dmphen = 2,9-dimethyl-1,10-phenanthroline, 5,6-dmphen = 5,6-dimethyl-1,10-phenanthroline, 2,9-dm-4,7-dpphen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, mphen = 5-methyl-1,10-phenanthroline, dpphen = 4,7-diphenyl-1,10-phenanthroline, pphen = 4-phenyl-1,10-phenanthroline, phen = 1,10-phenanthroline, dpbpy = 4,4′-

diphenyl-2,2′-bipyridine, Cl-phen = 5-chloro-1,10-phenanthroline, Br-phen = 5-bromo-1,10-phenanthroline, Br_2-bpy = 4,4′-dibromo-2,2′-bipyridine, Cl_2-bpy = 4,4′-dichloro-2,2′-bipyridine, NO_2-phen = 5-nitro-1,10-phenanthroline, bipym = 2,2′-bipyrimidine, EHC-bpy = 4,4′-bis(2-ethylhexyloxycarbonyl)-2,2′-bipyridine, *t*Bu-DAB = *tert*-butyl-*N*,*N*′-bis(1,4-diazabutadiene), EC-bpy = 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine, dcphen = 4,7-dicarboxy-1,10-phenanthroline, dcbpy = 4,4′-dicarboxy-2,2′-bipyridine, BABA = biacetylbisaniline, dthdi = *N*,*N*′-ditolyl-3,4-hexanediimine, $(CF_3)_2$-bpy = 4,4′-ditrifluoromethyl-2,2′-bipyridine, $(NO_2)_2$-bpy = 4,4′-dinitro-2,2′-bipyridine, disn = diiminosuccinonitrile, bbqdi = *semi*-4-benzoylbenzoquinonediimine.

The calculation of the ground-state electronic structure of a Pt(bpy)(tdt) complex has been performed by using density functional theory[73,74] methods with the GAUSSIAN 1998 software package.[75] The functional used throughout this study is the B3LYP, consisting of a hybrid exchange functional as defined by Becke's three-parameter equation[76] and the Lee–Yang–Parr correlation functional.[77] The ground-state geometry was obtained in the gas phase by full geometry optimization, under no symmetry constraint. The VeryTight option was used, which demands tighter convergence criteria than the default ones, while numerical integration was performed with the UltraFine option, which requests a pruned (99,590) grid. The optimum structures located as stationary points on the potential energy surfaces were verified by the absence of imaginary frequencies. The derived wavefunctions were found to be free from internal instabilities. The basis set used for all nonmetal atoms was the well-known valence triple-zeta 6-311+G*.[78,79] The quasi-relativistic Stuttgart–Dresden effective core potential of the type ECP60MWB was used for Pt, and complemented by the corresponding valence basis sets.[80] Percentage compositions of molecular orbitals from the three contributing fragments were calculated with the AOMix program.[81,82]

Ground-state electronic structure calculations of all other compounds including the net ligands have been performed by using the AM1[83] and PM3[84,85] semiempirical techniques, with MOPAC2000[86] as implemented in the CAChe software package.[87] Structures have been preoptimized under the MM3 force field.[88] The ground-state geometries were obtained in the gas phase by full geometry optimization, under no symmetry constraint. Structures of the 2,2′-bipyridine derivatives and nonaromatic bidentate ligands have been considered under their planar arrangement (the binding N–C–C–N dihedral angle was set to zero). These geometries correspond to the first-order saddle point (transition state) that links the two energy minima at the potential energy surface through rotation of the C1–C1′ bond. We preferred to use this structure, because the compounds have this structure at the time of complex formation. For the rest of the compounds under study, the optimum structures were verified by the absence of imaginary frequencies. Frontier orbital contour plots presented herein were prepared with the aid of MOLEKEL.[89]

Results and Discussion

Deriving the Model – Modified Electronic Parameters

Our methodology for obtaining a structure-to-properties relation (SPR) will be based on Lever's arguments[3] and the general theory of ligand properties additivity,[90–93] starting from electrochemical data. According to the additivity theory, redox potentials of the complexes can be regarded as an additive property made up of the contributions of both the metals and the coordinated ligands. The weight of these contributions is defined by the percentage of each component of the LUMO orbital of the complex, since the relation between $E°$ and LUMO energy is well documented.[67,68] Our approach has five levels and provides the following equation [Equation (1)].

$$ModEP = -0.0001343\ E_{\mathrm{MMLL'CT}} + 1.1671129\ (R^2 = 1) \qquad (1)$$

(1) As we have already mentioned, we set the basis of our reasoning on the M(diimine)(dithiolato) complexes and especially on those with Pt, not only for their plethora, but also because they are more important candidates for potential applications.[17] In these compounds, the LUMO orbital is localized mainly on the diimine core as has been indicated both experimentally and theoretically.[69–72] Moreover, we needed a model compound, and Pt(bpy)(tdt) contains all the necessary prerequisites for this. First of all, platinum is coordinated to two bidentate ligands; both of them are good σ-donors, having medium π*-donating (the dithiolato)/π*-accepting (the diimine) ability. Secondly, there is a series of eight Pt(diimine)(tdt) complexes that are well characterized, with defined electrochemical and spectroscopic behavior (vide infra).[24]

(2) The origin of our model is based on reduction potentials. Pt(bpy)(tdt) has a reversible reduction wave at –1.339 V in a DMF solution.[24] This value arises from the contribution of both the diimine and the Pt/tdt fragment. In order to determine the contribution of diimine to this, we performed ground-state electronic calculations for the complex under investigation at the DFT level of theory. The frontier orbital energies along with the contributions from the two ligands and the metal are given in Table 1, while the HOMO and LUMO are presented in Figure 1.

The HOMO, a b_1 orbital in the local sense, is composed mainly of sulfur $3p_z$ orbitals on the chelating ring, while the LUMO is calculated to be located almost on the diimine with a limited contribution from the metal and dithiolato ligand. The calculated contribution of 2,2′-bipyridine to the LUMO orbital is 87%. Thus, we dissect the first reduction potential into two parts and *credit by definition* a value of E_1 = –1.165 V to the diimine, according to its contribution to the whole potential (87% of $E(Pt^{0/–})$). The remaining E_2 = –0.174 V is attributed to the system Pt/tdt. Once these values are well defined, we can obtain the corresponding values for all diimine ligands that are bound to the Pt(tdt) fragment, bearing in mind that the experimental conditions for the derivation of the corresponding potentials must be the same.

Table 1. Contribution of different fragments to Pt(bpy)(tdt) valence orbitals. The HOMO and LUMO are shown in bold.

MO	*E* [eV]	Metal	Dithiolato	Diimine
Unoccupied				
95	–0.64	38.7	2.4	58.9
94	–1.02	44.9	47.4	7.7
93	–1.78	1.4	0.5	98.2
92	–2.02	1.4	0.5	98.1
91	**–2.90**	**5.4**	**7.4**	**87.2**
Occupied				
90	**–4.67**	**9.5**	**80.5**	**10.0**
89	–5.05	13.8	84.5	1.7
88	–6.37	68.5	23.9	7.6
87	–6.60	28.5	67.2	4.3
86	–6.74	33.7	60.5	5.8
85	–7.23	43.6	52.6	3.8

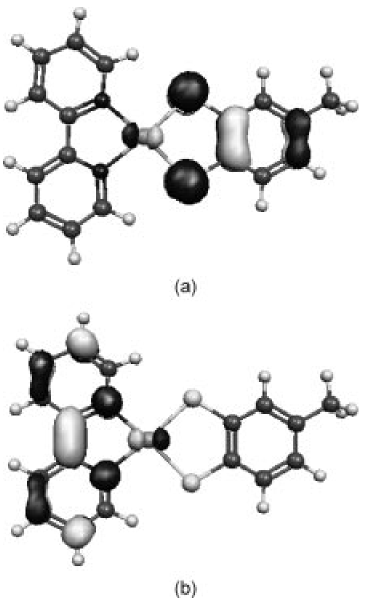

Figure 1. Contour plots of HOMO (a) and LUMO (b) orbitals of Pt(bpy)(tdt).

(3) Assuming that the E_2 value is kept constant along the series of eight Pt(diimine)(tdt) complexes,[24] we obtain the corresponding electronic parameters (*EP*) / contributions for the diimine ligands (taking the $E°$ values from Table 2) according to Equation (2).

$$EP = E_{\mathrm{red\ (of\ each\ complex)}} - 0.13E_{\mathrm{red/(dpy)Pt(tdt)}} \qquad (2)$$

Thus, we get *EP* = –1.321 V for tmphen, –1.224 V for dbbpy, –1.197 V for dmbpy, –1.165 V for bpy, –1.145 V for phen, –1.083 V for Cl-phen, –0.869 V for Cl_2-bpy, and –0.788 V for EC-bpy.

On the basis of the well-documented interconnection of LUMO, E_{red}, and $E_{\mathrm{MML'CT}}$, there should be a linear relation between the derived *EP* and the observed values of $E_{\mathrm{MMLL'CT}}$ for the main low-energy solvatochromic band of these compounds. As a matter of fact, this is true, and an excellent correlation coefficient of 0.98 is derived (Figure 2).

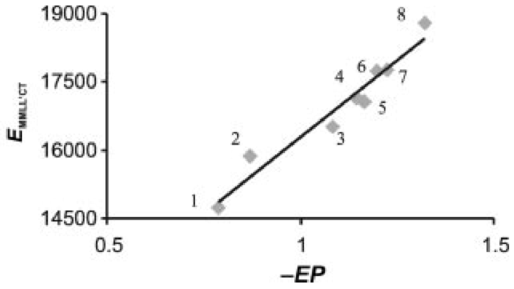

Figure 2. Graphic representation of the function $E_{\mathrm{MMLL'CT}} = f(-EP)$ for M(diimine)(tdt) complexes. Spectra of Pt(EC-bpy(tdt) (1), Pt(Cl_2-bpy)(tdt) (2), Pt(Cl-phen)(tdt) (3), Pt(bpy)(bdt) (4), Pt(phen)(tdt) (5), Pt(dmbpy)(tdt) (6), Pt(dbbpy)(tdt) (7), and Pt(tmphen)(tdt) (8) were recorded in CH_2Cl_2.

(4) Using the regression line derived from the original data, we recalculated *EP* values for any prespecified $E_{\mathrm{MMLL'CT}}$. This recalculation was done in order to predict the *EP* values of the ligands not included in our primary data, on the basis of their $E_{\mathrm{MMLL'CT}}$ values and also to reduce the error introduced by the assumption that the contribution of the Pt/tdt fragment to the reduction potential of the compound is the same.

So, *EP*s are reevaluated for these eight diimines, and the obtained values are called, for the needs of our discussion, modified electronic parameters (*ModEP*). Thus, *ModEP* becomes –1.359 V for tmphen, –1.220 V for dbbpy, –1.215 V for dmbpy, –1.126 V for bpy, –1.138 V for phen, –1.054 V for Cl-phen, –0.966 V for Cl_2-bpy, and –0.812 V for EC-bpy, according to Equation (1).

(5) Mainly on the basis of a large number of data for M(diimine)(dithiolato) compounds (Table 2) and the eight "starting" values derived in the previous paragraph, we have obtained the *ModEP* values for a satisfactory number of diimines (Table 3).

Explanation and Physical Basis

Up to now, we have indicated the formulation employed in order to obtain *ModEP* values. In this section, we shall try to explain the properties of the new scale and the necessary prerequisites that a complex should satisfy in order for the additivity concept to be valid. First of all, *ModEP* values are given in V, but as soon as they are calculated they no longer depend on any experimental condition. This fact is justified, because *ModEP* values correspond to differences in reduction potentials and shifts in the energy of a charge-transfer band, measured under the same experimental conditions. So, for a series of compounds with different diimines, *ModEP* should correlate well with a ligand-based reduction potential and with the corresponding charge-transfer band as long as the experimental conditions are the same, no matter what these are. Subsequently, the *ModEP* values were calculated in order to provide the link between the ligands and the properties of the corresponding complexes. In this sense, diimines with large *ModEP* values when coordinated to a metal lead to easier reduction of the

Table 2. Electrochemical and spectroscopic results for M(diimine)(dithiolato) complexes. Please consult the original literature for the precision and the experimental conditions. The solvent provided refers to λ_{max}, since compounds under study are highly negatively solvatochromic.

Complex	Solvent	λ_{max} [nm]	$E_{MMLL'CT}$ [cm^{-1}]	E_{redI} [V]	E_{redII} [V]	E_{ox} [V]	Ref.
Pt(bpy)(tdt)[a]	CH_2Cl_2	586	17065	–1.339r	r[m]	+0.376qr	[24]
Pt(bpy)(bdt)[a]	$CHCl_3$	600	16667	–1.31r[b]	–1.99ir	+0.40/0.70[b,c]	[68]
				–1.775r[b,d]	–	+0.025[b,d]	[69]
Pt(bpy)(dpdt)[e]	CH_2Cl_2	614	16287	–	–	+0.26r	[35]
Pt(bpy)(bbdt)[e]	CH_2Cl_2	590	16949	–	–	+0.22r	[35]
Pt(phen)(mnt)[a]	$PhNO_2$	510	19608	–1.21r	–1.75r	+1.15ir[m]	[33]
Pt(phen)(i-mnt)[a]	$PhNO_2$	423	23641	–1.22r	–1.73r	+1.15ir	[33]
Pt(phen)(qdt)[a]	DMSO	458	21834	–1.06r	–	+0.95ir	[25,26]
Pt(phen)(tdt)[a]	CH_2Cl_2	583	17153	–1.319r	r	+0.376qr[m]	[22,24,41]
Pt(phen)(dpdt)[e]	CH_2Cl_2	620	16129	–	–	+0.30r	[35]
Pt(phen)(bbdt)[e]	CH_2Cl_2	627	15949	–	–	+0.24r	[35]
Pt(bipym)(mnt)[e]	DMSO	493	20284			+1.32ir	[44]
Pt(bipym)(dmit)[e]	DMSO	560	17857			+0.80ir	[44]
Pt(BABA)(mnt)[e]	CH_2Cl_2	620	16129	–0.70r	–1.50qr[f]	+0.8ir[f]	[43]
Pt(BABA)(tdt)[e]	CH_2Cl_2	682	14663	–0.94r	–1.66qr[f]	+0.64ir[f]	[43]
Pt(dmbpy)(ecda)[e]	$CHCl_3$	450	22222	–1.28r[g]	–1.77r	+0.83ir[g]	[34]
Pt(dmbpy)(mnt)[h]	CH_2Cl_2	492	20325	–1.21qr[g,h]		+0.81ir[g,h]	[29]
				–1.17qr[g]		+1.22qr[g]	[29]
				–1.29r[g,a]	–1.78r	+1.07ir[g,a]	[33]
Pt(dmbpy)(i-mnt)[a]	CH_2Cl_2	417	23981	–1.28r	–1.83r	+1.16ir	[33]
Pt(dmbpy)(tdt)[a]	CH_2Cl_2	563	17762	–1.371r	r	+0.390ir	[22,24,41]
Pt(dpbpy)(mnt)[a]	CH_2Cl_2	513	19493	–1.18r	–1.68r	+0.70	[33]
Pt(dpbpy)(i-mnt)[a]	CH_2Cl_2	448	22321	–1.11r	–1.71r	+0.72	[33]
Pt(dbbpy)(tbcda)[a]	CH_2Cl_2	437	22883	–1.302r	r	+0.963ir	[24]
Pt(dbbpy)(cpdt)[a]	CH_2Cl_2	434	23041	–1.274r	r	+0.957ir	[24]
Pt(dbbpy)(endt)[a]	CH_2Cl_2	480	20833	–1.484r	r	+0.431ir	[24]
Pt(dbbpy)(dmqdt)[a]	CH_2Cl_2	481	20790	–1.334r	r	+0.814ir	[24]
Pt(dbbpy)(mnt)[a]	CH_2Cl_2	497	20121	–1.266r	r	+0.944ir	[24]
Pt(dbbpy)(tdt)[a]	CH_2Cl_2	563	17762	–1.398r	r	+0.389ir	[24]
Pt(dbbpy)(S-4-py)$_2$[e]	CH_2Cl_2	452	22124	–1.73r	–	+0.66ir	[20]
Pt(Cl_2-bpy)(tdt)[a]	CH_2Cl_2	630	15873	–1.043r	r	+0.380ir	[24]
Pt(EC-bpy)(tdt)[a]	CH_2Cl_2	679	14728	–0.962r	r	+0.412ir	[24]
Pt(dcbpy)(ecda)[e]	EtOH/MeOH	440	22727	–1.1ir[i]	–	+0.95ir	[37,38]
Pt(dcbpy)(qdt)[e]	EtOH/MeOH	460	21739	–1.1ir[i]	–	+0.85ir	[37–39]
Pt(dcbpy)(tdt)[e]	EtOH/MeOH	580	17241	–1.2ir[i]	–	+0.45ir	[37–39]
Pt(dpphen)(ecda)[e]	$CHCl_3$	468	21368	–1.12r[g]	–1.68r	+0.83ir[g]	[34]
Pt(dpphen)(mnt)[j]	CH_2Cl_2	520	19231	–1.24qr[g,h]		+0.81ir[g,h]	[29]
				–1.17qr[g]		+1.22qr[g]	[29,33]
				–1.15r[a, g]	–1.72r	+0.72ir[a, g]	[33]
Pt(dpphen)(i-mnt)[a]	CH_2Cl_2	444	22523	–1.18r	–1.73r	+0.75ir	[33]
Pt(tmphen)(tdt)[a]	CH_2Cl_2	532	18797	–1.495r	r	+0347ir	[24]
Pt(Cl-phen)(tdt)[a]	CH_2Cl_2	605	16529	–1.257r	r	+0.359qr	[24]
Pt(dcphen)(ecda)[e]	EtOH/MeOH	436	22936	–1.2ir[i]	–	+0.98ir	[37–39]
Pt(dcphen)(qdt)[e]	EtOH/MeOH	480	20833	–1.0ir[i]	–	+0.90ir	[37–40]
Pt(dcphen)(tdt)[e]	EtOH/MeOH	568	17606	–1.2ir[i]	–	+0.49ir	[37–39]
Pt(dcphen)(bdt)[e]	EtOH/MeOH	565	17699	–1.1ir[i]	–	+0.52ir	[37–39]
Pt(Et-pya)(dmit)	DMSO	580	17241				[51]
Pt(*i*Pr-pya)(dmit)	DMSO	570	17544				[51]
Pt(Bu-pya)($C_8H_4S_8$)	CH_2Cl_2	808	12376				[42,49]
Pt(C_{10}-pya)(dmit)[j]	CH_2Cl_2	660	15152			+0.36[k]	[53]
Pt(C_{10}-pya)($C_8H_4S_8$)[j]	CH_2Cl_2	770	12987			+0.26[k]	[53]
Pd(bpy)(bdt)[e]	$CHCl_3$	510	19608	–1.846r	–	+0.165ir	[67]
Pd(BABA)(tdt)[e]	CH_2Cl_2	688	14535	–0.98r	–1.66qr[f]	+0.58ir[f,l]	[62]
						+1.20ir[f]	[62]
Pd(BABA)(mnt)[e]	CH_2Cl_2	600	16667	–0.78r	–1.50qr[f]	+1.18ir[f]	[62]
Ni(bpy)(bdt)	$CHCl_3$	557	17953	–1.828r	–	+0.084ir	[67]
Ni(BABA)(tdt)[e]	CH_2Cl_2	696	14368	–1.00r	–1.66qr[f]	+0.48ir[f,l]	[62]
						+1.20ir[f]	[62]
Ni(dpphen)(tbcda)	CH_2Cl_2	465	21505				[22]
Ni(dpphen)(tfd)	$CHCl_3$	543	18416				[43,50]
Ni(dthdi)(mnt)	$CHCl_3$	651	15361				[41,50]
Ni(dthdi)(tfd)	$CHCl_3$	671	14903				[41,50]
Ni(disn)(tfd)	$CHCl_3$	703	14225				[41,50]
Ni(EHC-bpy)(mnt)	$CHCl_3$	583	17153				[41,50]
Ni(EHC-bpy)(tfd)	$CHCl_3$	602	16611				[41,50]
Ni(bbqdi)(tfd)	$CHCl_3$	745	13423				[41,50]
Ni(NO_2-bpy)(tfd)	$CHCl_3$	742	13477				[41,50]

[a] Observed potential vs. NHE. [b] The observed differences are quite substantial. [c] Two oxidations 1/2e$^-$. [d] Observed potential vs. Fc$^+$/Fc (0.400 V vs. NHE). [e] Observed potential vs. SCE, Hg/Hg_2Cl_2 (KCl sat.) and $E^{25\,°C}$ = 0.2444 V. [f] Value for $E_{p/2}$. [g] There is a difference in the assignment of the wave. [h] Observed potential vs. SSCE, Hg/Hg_2Cl_2 (NaCl sat.). [i] Value for E_p. [j] Observed potential vs. Ag/AgCl (a_{Cl^-} = 1 M) and $E^{25\,°C}$ = 0.22234 V. [k] Value for E_0'. [l] The wave corresponds to a two-electron procedure. [m] The symbols r, ir, and qr stand for reversible, irreversible, and quasi reversible waves, respectively.

Table 3. Modified electronic parameters (*ModEP*) for the most frequently used diimines in synthesis.

Diimine	*ModEP* [V]
php	–1.408
tmphen	–1.359
3,5,6,8-tmphen	–1.297
*i*Pr-pya	–1.284
dmphen	–1.270
Bu-pya	–1.270
6,6′-dmbpy	–1.241
dbbpy	–1.220
dmbpy	–1.215
5,5′-dmbpy	–1.203
2,9-dmphen	–1.199
5,6-dmphen	–1.194
2,9-dm-4,7-dpphen	–1.188
mphen	–1.172
dpphen	–1.150
pphen	–1.143
phen	–1.138
dpbpy	–1.132
bpy	–1.126
Cl-phen	–1.054
Br-phen	–1.044
Br_2-bpy	–0.980
Cl_2-bpy	–0.966
NO_2-phen	–0.963
bipym	–0.956
EHC-bpy	–0.926
EC-bpy	–0.812
dcphen	–0.799
dcbpy	–0.787
*t*Bu-DAB	–0.785
BABA	–0.729
dthdi	–0.703
$(CF_3)_2$-bpy	–0.681
$(NO_2)_2$-bpy	–0.582
disn	–0.514
bbqdi	–0.508

resultant complexes in a way that can be accurately predicted. Moreover, they stabilize the LUMO of the complexes. In other words, they cause a red shift of the main charge-transfer band, and its λ_{max} is accurately predicted by correlations of the $E_{MMLL'CT} = f(ModEP)$ type.

Furthermore, *ModEP* values are indicative of the σ- and π- bonding ability of the diimines, covering a range of 1000 mV. In addition to this, when comparing diimines of the same core, such as 1,10-phenanthroline derivatives (e.g. dpphen and phen), *ModEP* values could be used as indices of only π-effects, provided that in these ligands the σ-donating ability is almost the same.

On the basis of the aforementioned discussion, we can set up the necessary arguments in order for the additivity concept to be valid and the expected accuracy of a prediction to be high. Thus, (i) reduction potentials under consideration must be reversible or at least quasi-reversible, (ii) the reduction process must be described by the scheme ML(diimine$^-$), (iii) the reduction must occur to the same unoccupied orbital (from an energetic and symmetry point of view). In the complexes under study, this is the diimine-based LUMO. Further, (iv) the charge-transfer band must be attributed to the same orbital, for example, in the case of M(diimine)(dithiolato) compounds, the main UV/Vis band arises from a singlet state well described by the HOMO → LUMO notion,[69–72] and (v) the effect of the solvent must be taken into account: comparison between either spectroscopic or electrochemical results is only possible if the same solvent is used. The reason for this is quite obvious. M(diimine)(dithiolato) complexes are greatly solvatochromic as a result of their polar ground state, and the nonpolar (or even polar in the opposite direction) excited state and this solvatochromism affects also their redox behavior.

Before testing the applicability of *ModEP*, we investigated its correlation to Hammett constants, since the latter meet a general acceptance and have found wide application. These were defined by the ionization constants of the appropriately substituted benzoic acids. In the case under study and in order to find out whether there are any correlations, we had to make a concession that had to do with the applicability of Hammett constants. Hammett constants can find application only in cases of ligands that have the same core, differing in terms of the substituting groups in exact positions, e.g. 4,4′-X,X-2,2′-bipyridines. In order to partly overcome this problem, we employed σ_t values, as defined by Equation (3), where σ_p, σ_m, and σ_o, represent *para*-, *meta*-, and *ortho*- substituent effects, respectively.

$$\sigma_t = \Sigma\sigma_p + \Sigma\sigma_m + \Sigma\sigma_o \qquad (3)$$

It is obvious that the *ModEP* scale surpasses Hammett constants in the sense that the former contains at the same time aromatic (e.g. 1,10-phenanthroline), "semi-aromatic" (e.g. *N*-butyl-pyridine-2-carbaldimine), and aliphatic (e.g. diiminosuccinonitrile) entries, while the latter gives the relation among ligands that are derivatives of the same parent compound. The Hammett constants employed are presented in Table 4 (vide infra). For 13 bipyridine derivatives, we obtain the relation in Equation (4) (Figure 3).

$$\sigma_t = 2.74\ ModEP + 3.10 \qquad (4)$$

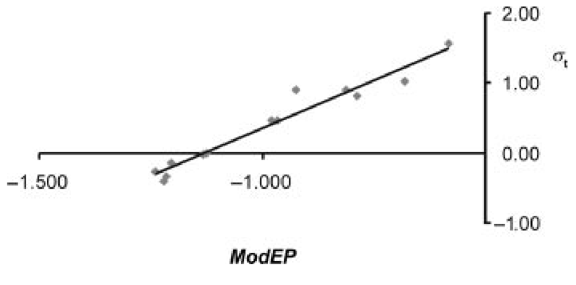

Figure 3. Graphic representation of the relation $\sigma_t = f(ModEP)$ for 13 2,2′-bipyridine derivatives (R^2 = 0.96).

The fit is excellent (r = 0.96). Moreover, in Figure 4, the corresponding correlation for 14 1,10-phenanthroline derivatives is depicted. A linear relation is also evident (r = 0.93) here [Equation (5)].

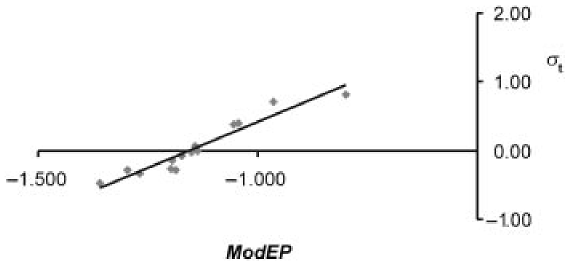

Figure 4. Graphic representation of the relation $\sigma_t = f(ModEP)$ for 14 1,10-phenanthroline derivatives ($R^2 = 0.93$).

$$\sigma_t = 2.68\ ModEP + 3.09 \tag{5}$$

Comparing Equations (4) and (5), we conclude that the same substituent groups on both aromatic ligands, namely phen and bpy, have a similar effect. Moreover, assuming that σ- donation is identical along the same series, this supports our belief that *ModEP* values are indicative of π- effects.

For an extensive series of M(diimine)(dithiolato) compounds, keeping the M(dithiolato) fragment constant and correlating *ModEP* with the experimentally derived reduction potentials and the charge-transfer energies, we conclude that our scale works fine with the compounds under consideration. The maximum error in the ligand-based reduction potential is 43 mV (the experimental error in most cases is around 10 mV) and a few nm in the case of the UV/Vis spectra. As a result, we are able to predict the properties of compounds that are not yet prepared. As an example, we employ again the series of Pt(diimine)(tdt) compounds mentioned earlier and three 1,10-phenanthroline derivatives, namely NO_2-phen (*ModEP* = –0.963 V), pphen (*ModEP* = –1.143 V), and 5,6-dmphen (*ModEP* = –1.194 V). Equation (6) gives the relation $E_{red} = f(ModEP)$ and Equation (7), the relation $E_{MMLL'CT} = f(ModEP)$.

$$E_{red} = 1.049\ ModEP - 0.107 \tag{6}$$

$$E_{MMLL'CT} = -7742\ ModEP + 8685 \tag{7}$$

NO_2-phen is anticipated to have a reduction potential of –1.117 V and a CT band at 631 nm, whereas the corresponding values for pphen and 5,6-dmphen should be –1.306 V and 582 nm, and –1.360 V and 569 nm, respectively. The standard deviation in all cases is around 39 mV and less than 1 nm (the low value for the latter comes also from the modification employed).

From all the experimental data available, we conclude that the *ModEP* scale finds application in M(diimine)(dithiolato) complexes. On the other hand this class of compounds was used in order for this scale to be extracted. So, the potential use of the *ModEP* scale must be tested on other classes of compounds. In the next two sections, several examples will be presented along with a discussion on the way in which the *ModEP* scale could be enriched and what its chemical meaning really is.

Potential Applications

Trying to investigate the potential applications of the *ModEP* scale, we tested its response in several classes of compounds. In all cases, the rules i–v formulated in the previous section were observed to hold. The cases where the overall correlation was very good were employed to enrich the *ModEP* scale.

M(diimine)(CO)$_4$ (M = W, Mo, Cr)

The first class of compounds on which we tested our model was $M(diimine)(CO)_4$. These compounds are known for their negative solvatochromism and luminescence in solution and find potential applications in material science.[94–101] They have a solvatochromic band that is attributed to a MLCT transition. On the basis of data from ref.[94–101] we obtain the correlation shown in Figure 5.

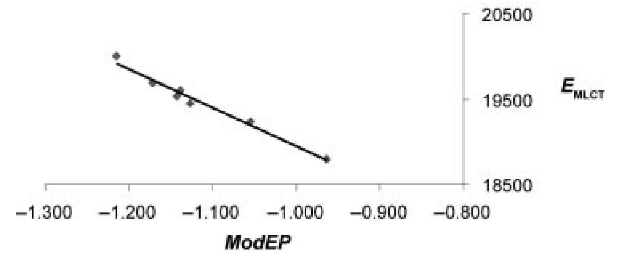

Figure 5. Graphic representation of the relation $E_{MLCT} = f(ModEP)$ for a series of $W(diimine)(CO)_4$ complexes ($R^2 = 0.98$). Transition energies were collected in benzene.

The relation $E_{MLCT} = f(ModEP)$ is linear and is described by Equation (8).

$$E_{MLCT} = -4502\ ModEP + 14449 \tag{8}$$

The maximum error anticipated for this range of transition energies is only 2 nm. Analogous relations hold also in the case of Mo and Cr, shown in Equations (9) ($R^2 = 0.97$) and (10) ($R^2 = 0.92$), respectively. Transition energies were collected in benzene.

$$E_{MLCT} = -5111\ ModEP + 14536 \tag{9}$$

$$E_{MLCT} = -4832\ ModEP + 13561 \tag{10}$$

The maximum errors in these cases are slightly larger, 3 and 5 nm, respectively, but they are certainly at a more than acceptable level. This fact supports the use of the *ModEP* scale for prediction purposes. For example, the charge-transfer band for the complex $W(5,6\text{-dmphen})(CO)_4$, which, to the best of our knowledge, has not been prepared yet, is anticipated to be 504 ± 1 nm in benzene, on the basis of the *ModEP* value of the ligand (–1.194 V).

fac-[Re(CO)$_3$(CNx)(diimine)]$^+$

Rhenium(I) tricarbonyl complexes containing bidentate heterocyclic ligands have been a source of interest for several years, largely because of their potential use in solar energy conversion.[95,102] These compounds display intense luminescence in the visible region of the spectrum and have long emission lifetimes. Recently, Rillema et al. prepared a series of *fac*-[Re(CO)$_3$(CNx)(diimine)]$^+$ complexes.[103–106] These complexes have a diimine-based reversible reduction process. We tested the *ModEP* scale, searching for a correlation of the type $E_{\text{red}} = f(ModEP)$. In Figure 6, this correlation is schematically depicted, and Equation (11) gives the corresponding linear regression. The maximum deviation from linearity in this case is 42 mV.

$$E_{\text{red}} = 1.027\ ModEP - 0.035 \tag{11}$$

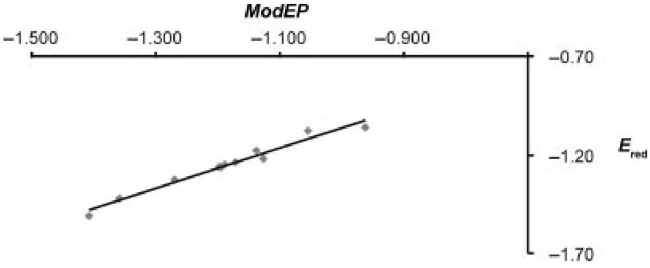

Figure 6. Graphic representation of the relation $E_{\text{red}} = f(ModEP)$ for a series of *fac*-[Re(CO)$_3$(CNx)(diimine)]$^+$ complexes ($R^2 = 0.98$). Potentials are reported vs. SSCE in CH$_3$CN at room temperature, taken from ref.[103–106]

[{(diimine)Re(CO)$_3$}$_3$(μ-L)]$^+$

The good correlation of $E_{\text{red}} = f(ModEP)$ obtained in the previous case, was tested also in a more demanding case. Sun and Lees prepared recently a series of trinuclear diimine Re$^{\text{I}}$ tricarbonyl complexes bridged by 1,3,5-tris-(4-ethenylpyridyl)benzene (L1) and 1,3,5-tris(4-ethynylpyridyl)benzene (L2).[107] These compounds have one or two reduction potentials, the first one representing the addition of one electron to the diimine ligands. Equations () and () give the corresponding correlations for the L1 and L2 bridges, respectively, and Figure 7 provides a graphic representation for the latter.

$$E_{\text{red}} = 2.638\ ModEP + 1.546 \tag{12}$$

$$E_{\text{red}} = 3.002\ ModEP + 1.902 \tag{13}$$

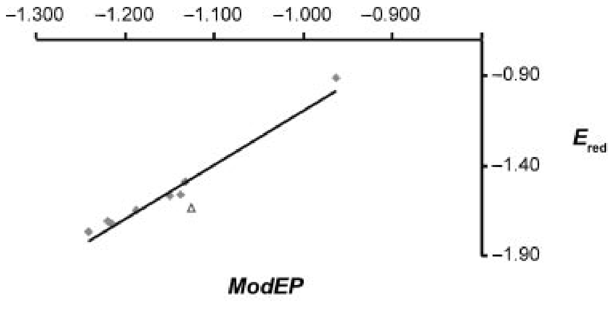

Figure 7. Graphic representation of the relation $E_{\text{red}} = f(ModEP)$ for a series of [{(diimine)Re(CO)$_3$}$_3$(μ-L2)]$^+$ complexes ($R^2 = 0.92$). The triangular point corresponds to bpy. Data taken from ref.[107]

For both cases very good correlations have been obtained. On the other hand, reduction potentials of the bpy complexes seem to deviate from linearity, but we can not provide a satisfactory explanation for that. Moreover, the slope of the linear relation is three times larger than the corresponding slope in *fac*-[Re(CO)$_3$(CNx)(dmbpy)]$^+$, which was previously described.

Cu$^{\text{II}}$ Uroporphyrin I Complexes

In 1983, Shelnutt reported Raman shifts of copper uroporphyrin I induced by complex formation with phenanthroline derivatives.[108] We correlated these Raman shifts with our *ModEP* scale. A linear relation was obtained (Figure 8). Bulky derivatives have been excluded from the correlation. Shelnut observed an analogous relation to the Hammett constants and assigned this inconsistency to the fact that sterically hindered ligands can not lie flat on the porphyrin ring.

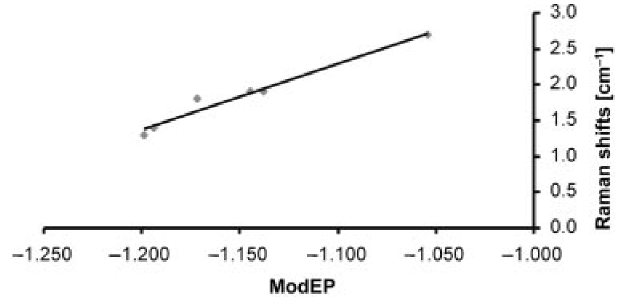

Figure 8. Graphic representation of the relation $\Delta\nu = f(ModEP)$ for the 1637 cm^{-1} line for a series of 1,10-phenanthroline derivatives ($R^2 = 0.96$). Data taken from ref.[108] The experimental error is less than 1.0 cm^{-1}.

The Case of [Ru(diimine)$_3$]$^{2+}$

[Ru(diimine)$_3$]$^{2+}$ complexes have proved to be one of the most important classes of photosensitizers ever synthesized.[109–113] Here, we shall investigate the applicability of the *ModEP* scale to these complexes and the way their properties could be predicted. First of all, this class of compounds is completely different in nature from those previously described. In their UV/Vis spectra, they have at least one MLCT band of a clear d → π^* (diimine) type. This means that both the HOMO (a$_1$ and e with D$_3$ symmetry) and the LUMO (a$_2$ and e with D$_3$ symmetry) depend on the nature of the ligand. Thus, a correlation between E_{MLCT} and *ModEP* or reduction potential is not expected. Moreover, more than one reversible reduction process is detected, but only one oxidation potential is present. The latter refers to the couple Ru$^{\text{II}}$/Ru$^{\text{III}}$ and can be assumed to involve the nonbonding or slightly π^*-antibonding t$_{2g}$ (a$_1$ and e) metal-centered orbital.[3,82,109–115] Firstly, we tested the *ModEP* scale on the oxidation process, for which a large amount of data is available.[110] Although this process deviates from the rules previously established, it is evident that E_{ox} is greatly dependent on the ligand. Thus, stronger σ-donors cause a lower oxidation potential of the Ru$^{\text{II}}$ complex, whereas more efficient π^*-acceptors have the opposite effect.[110] Lever employed E_{ox} also in order to derive his *LEP* parameters (vide infra). A graphic representation of the correlation $E_{ox} = f(ModEP)$ is provided in Figure 9. A regression coefficient of 0.92 is derived for this relation.

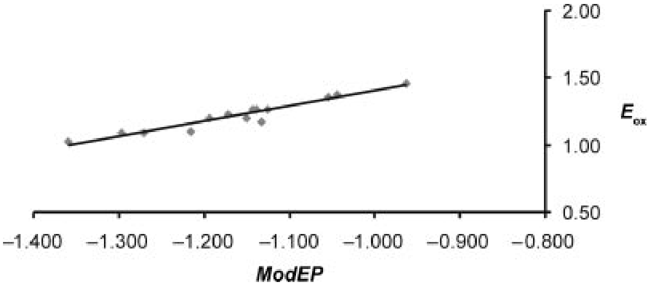

Figure 9. Graphic representation of the relation $E_{ox} = f(ModEP)$ for a series of $[Ru(diimine)_3]^{2+}$ complexes ($R^2 = 0.92$). Data taken from ref.[116]

A linear relation is obtained by employing data from ref.[116] Analogous results are extracted by employing data from ref.[110] [Equation (14)].

$E_{red} = 1.133\ ModEP + 2.535$ (14)

Trying to find a net ligand process that could be correlated to the *ModEP* scale, we ended up with the excited-state oxidation potentials. E_{ox}* refers to an abstraction of an electron from the LUMO, and this process must certainly be dependent on the ligand, surpassing delocalization problems. An almost perfect correlation is observed (Figure 10).

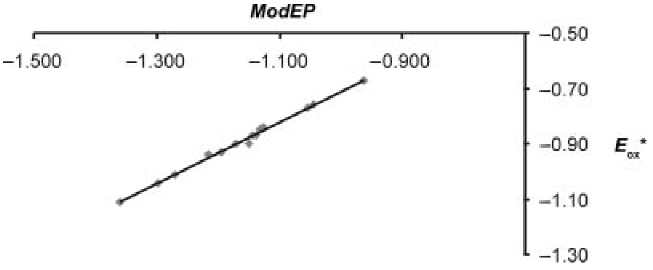

Figure 10. Graphic representation of the relation $E_{ox}^* = f(ModEP)$ for a series of $[Ru(diimine)_3]^{2+}$ complexes ($R^2 = 0.99$). Data taken from ref.[116]

The corresponding linear regression is given by Equation (15).

$E_{ox}^* = 1.109\ ModEP + 0.397$ (15)

Equation (15) is of great importance since the excited-state oxidation potential of these complexes determines their ability to act as photosensitizers, and according to the best of our knowledge, it is presented for the first time.

The same trend is observed for M(diimine)(dithiolato) complexes, as given by Equation (16) ($r = 0.92$).

$E_{ox}^* = 0.790\ ModEP - 0.561$ (16)

Interaction of $[Ru(NH_3)_4(diimine)]^{2+}$ with CT DNA

In 2004, Mahesvari and Palaniandavar[112,113] reported the interaction of a series of mixed ligand complexes of the type $[Ru(NH_3)_4(diimine)]^{2+}$ with calf thymus DNA. Our *ModEP* scale correlates well with the oxidation and formal peak potentials of the complexes both with and without DNA. Moreover, a good correlation is obtained in the case of the reduction potentials of the complexes, but not with reduction potentials in the presence of DNA, a fact that is an indication that the nature of the reduction in the DNA-bound form is not the same. These correlations are provided in Equations (17), (18), (19), (20), and (21).

$E_{ox} = 0.576\ ModEP + 1.044$ ($R^2 = 0.94$) (17)

$E_{red} = 0.452\ ModEP + 0.761$ ($R^2 = 0.94$) (18)

$E_{1/2} = 0.514\ ModEP + 0.883$ ($R^2 = 0.99$) (19)

$E_{ox} = 0.700\ ModEP + 1.135$ ($R^2 = 0.95$) (in the presence of CT DNA) (20)

$E_{1/2} = 0.515\ ModEP + 0.853$ ($R^2 = 0.97$) (in the presence of CT DNA) (21)

The ligand 2,9-dmphen has been excluded from the regression analysis because of its deviation from linearity. This is in accord with its relatively high values for the ratio i_{pa}/i_{pc} (1.39 in the case of DNA interaction) and ΔE_p (192 mV for the complex), which are strong indications of irreversible processes.

The Role of the Coordinating Ligand – Expanding the Model

In the previous sections, we set up the basis of the *ModEP* scale and tested its applicability to several demanding cases. Moreover, we showed that *ModEP* finds potential application in the description of every ligand-based/determined process.

From all the examples mentioned above, covering a range of diimine compounds from material to biochemical science, we conclude that the role of the ligand in a complex can be predicted in a quantitative manner. In addition, the previously extracted correlations imply that the ligands act in a completely analogous way regardless of the metal fragment to which they are coordinated; this refers to all classes of ligands. Let's demonstrate a provocative example. From the previous discussion and the way *ModEP* is derived, we should expect that the energy of the *MMLL′CT* band in the M(diimine)(dithiolato) complexes correlates well with $[Ru(diimine)_3]^{2+}$ excited-state oxidation potentials. This argument has proved correct ($r = 0.998$). This idea is the result of a simple mathematical/numerical regression, but it also possesses an inherent chemical meaning. It denotes that ligands act in a fully predictable way upon coordination to a metal, and this is because of their electronic characteristics. Under this prism, the coordination of a metal to a ligand determines a general property of a complex (e.g. luminescence) and causes the stabilization of ligands towards, for example, reduction, but it is the nature of the ligands that determines the extent of these properties. In other words, if we synthesize one or two compounds of a new family, we can predict with high accuracy their electronic properties with an extensive series of ligands, without the need to synthesize them individually.

In view of the above discussion, we conclude that a unified scale of ligand properties is what must become our main objective. In the Introduction, we mentioned some of the most widely accepted ligand scales. The major drawback of all of them is that they are oriented to certain types of ligands, e.g. diimines, phosphanes, and dithiolates. If we select one as the most appropriate, e.g. *CEP* or *TEP*, we must develop synthetic or computational routes in order to derive parameters for other types of ligands. In a different approach, for a large-scale comparison of data for different classes of compounds having different types of ligands, we could enrich the *ModEP* scale. However, both approaches are time consuming and constrained by experimental errors or different experimental conditions.

Herein, we suggest a different approach that can be employed for every type of ligand used or is under consideration for future work. This approach will be based on the electrophilicity index ω.

Electrophilicity Index ω – Application to Diimine Ligands

On the basis of an idea given by Maynard et.al.,[117] in 1999, Parr and co-workers defined the electrophilicity index, ω, as a measure of the electrophilicity of a ligand[73] [Equation (22)].

$$\omega \equiv \mu^2/2\eta \qquad (22)$$

where μ = chemical potential, defined by $\mu = [\partial E/\partial N]_v$ (and $\mu = -\chi$, χ = electronegativity) and η = chemical hardness defined by $\eta = [\partial^2 E/\partial N^2]_v$.

Following Parr's arguments, Equation (23) is presented, where ω corresponds to the energy produced from the maximal flow of electrons between the donor and acceptor, where I is the compound's ionization potential and A is its electron affinity.

$$\omega = \frac{(I+A)^2}{8(I-A)} \qquad (23)$$

Moreover, maximal electron flow is given by Equation (24).

$$\Delta N_{\max} = \frac{I+A}{2(I-A)} \qquad (24)$$

Both ω and electron affinity measure the capability of an agent to accept electrons. Nevertheless, the latter is by definition related strictly to a one-electron process, whereas the electrophilicity index measures the total energy lowering of a ligand due to maximal electron flow ($\Delta E = -\mu^2/2\eta$, $\Delta E < 0$, charge transfer being a spontaneous process), a value that could be different from unity.[73] The model was completed by Contreras et al., who introduced solvent effects,[118–121] and the importance of the electrophilicity index is well documented by Chattaraj et al.[122]

First of all, we tried to investigate the applicability of the electrophilicity index, ω, to large molecules and, more precisely, in the detection of the behavior of the complexed diimines. To the best of our knowledge, this approach is employed for the first time.

We employed Koopmans' theorem, as given by the following relations [Equations (25) and (26)].

$$I \cong -E_{\mathrm{HOMO}} \qquad (25)$$

$$A \cong -E_{\mathrm{LUMO}} \qquad (26)$$

Equation (26) is not really part of the theorem. Nevertheless, it is usually used in the literature as a good approximation. In a first approach to the problem, the semiempirical AM1 model was employed (the PM3 model gave similar results). Although neither method matches the high precision of ab initio calculations, their main advantage is low computational cost and wide acceptance in the description of organic molecules. Some first calculations of diimine properties at the HF and MP2 level of theory gave similar results, but their application was not possible as soon as the structures became more complex.

In Table 4, the parameters for the diimines under study calculated at the AM1 level are presented. It is obvious that electron-accepting groups increase the electrophilicity and maximal electron flow of the diimine, whereas good σ-donors contribute to their reduction.

Both ω and *ModEP* give a measure of the maximal electron flow that a ligand can accept, and on the basis of this fact we anticipate the function *ModEP* = $f(\omega)$ to be linear. Figure 11 shows the linear correlation between *ModEP* and the computed ω; a good correlation coefficient is found ($R^2 = 0.92$), and Equation (27) is obtained.

$$ModEP = 1.151\ \omega - 3.085 \qquad (27)$$

Thus, both *ModEP* and ω can find application as quantitative indices of a ligand's electronic behavior. The great advantage of ω is that it can be easily calculated for a broad range of ligand types. Thus, by definition it must correlate satisfactorily with the electronic descriptors of all other ligands, either experimentally derived (*TEP* and *LEP*) or computed (*CEP*).

Employing data points from ref.[2] (Table 5), we derived the linear relations that are obtained for 17 molecules that are often used in synthesis as ligands. These relations are given by Equations (28), (29), (30), and (31). The majority of the entries are for phosphane ligands, because *TEP* and *CEP* have been derived for these types of compounds. The last column in Table 5 corresponds to *ModEP* values computed from Equation (27) for the given molecules.

Table 4. Ionization potentials, electron affinities, electrophilicity index, and maximal electron flow calculated with the AM1 model, along with Hammett's constants and modified electronic parameters for the diimines under study. Energy values are provided in eV.

Diimine	*I*	*A*	*ω*	ΔN_{max}	σ_t	*ModEP*
php	10.691	0.491	1.532	0.548	–	–1.408
tmphen	10.716	0.521	1.548	0.551	–0.48	–1.359
3,5,6,8-tmphen	11.106	0.601	1.631	0.557	–0.28	–1.297
*i*Pr-pya	11.245	0.271	1.511	0.525	–	–1.284
dmphen	11.044	0.658	1.648	0.563		–1.270
Bu-pya	11.256	0.293	1.521	0.527	–	–1.270
6,6′-dmbpy	11.180	0.481	1.589	0.545	–0.26	–1.241
dbbpy	11.126	0.449	1.569	0.542	–0.40	–1.220
dmbpy	11.202	0.508	1.603	0.548	–0.34	–1.215
5,5′-dmbpy	11.260	0.566	1.635	0.553	–0.14	–1.203
2,9-dmphen	11.040	0.662	1.649	0.564	–0.26	–1.199
5,6-dmphen	11.173	0.692	1.679	0.566	–0.14	–1.194
2,9-dm-4,7-dpphen	10.918	0.648	1.628	0.563	–0.28	–1.188
5-mphen	11.175	0.706	1.685	0.567	–0.07	–1.172
dpphen	11.027	0.695	1.662	0.567	–0.02	–1.150
pphen	11.091	0.707	1.676	0.568	0.06	–1.143
phen	11.158	0.719	1.689	0.569	0.00	–1.138
dpbpy	11.120	0.560	1.615	0.553	–0.02	–1.132
bpy	11.271	0.585	1.644	0.555	0.00	–1.126
Cl-phen	11.480	0.945	1.832	0.590	0.37	–1.054
Br-phen	11.489	0.998	1.858	0.595	0.39	–1.044
Br_2-bpy	11.741	0.989	1.884	0.592	0.46	–0.980
Cl_2-bpy	11.743	0.952	1.867	0.588	0.46	–0.966
NO_2-phen	11.331	1.136	1.906	0.611	0.71	–0.963
bipym	11.524	0.942	1.836	0.589	–	–0.956
EHC-bpy	11.699	1.059	1.912	0.600	0.90	–0.926
EC-bpy	11.700	1.070	1.918	0.601	0.90	–0.812
dcphen	11.508	1.503	2.115	0.650	0.82	–0.799
dcbpy	11.822	1.203	1.997	0.613	0.82	–0.787
*t*Bu-DAB	12.296	0.889	1.905	0.578	–0.40	–0.785
BABA	12.900	0.998	2.029	0.584	–0.36	–0.729
dthdi	12.889	0.957	2.008	0.580	–0.40	–0.703
$(CF_3)_2$-bpy	12.076	1.388	2.120	0.630	1.02	–0.681
$(NO_2)_2$-bpy	10.411	1.853	2.197	0.717	1.56	–0.582
disn	13.620	1.099	2.163	0.588	1.32	–0.514
bbqdi	11.873	1.399	2.102	0.634	–	–0.508

The majority of the ligands in Table 5 are strong or weak π-donors. Hence, *ModEP* values are more negative than the corresponding values for the diimines.

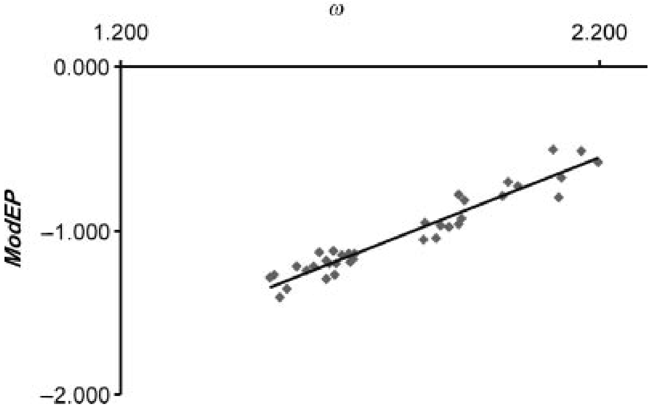

Figure 11. Graphic representation of the function *ModEP* = *f*(*ω*) for all compounds under study.

$$LEP_{(V)} = 0.9261\,\omega + 0.7124,\ R^2 = 0.90 \tag{28}$$

$$TEP_{(cm^{-1})} = 73.662\,\omega + 1989.2,\ R^2 = 0.95 \tag{29}$$

$$CEP_{(cm^{-1})} = 76.833\,\omega + 2074.3,\ R^2 = 0.94 \tag{30}$$

$$CEP^{*}_{(cm^{-1})} = 72.722\,\omega + 2077.1,\ R^2 = 0.93 \tag{31}$$

These relations enable us to express any experimental or computed parameter as a function of any other through the intermediacy of the easily computed *ω*. In this way, existing empirical parameters like *ModEP* or *LEP* that express contrary properties of the ligands can be combined and enrich each other. This fact demonstrates that our attempt was successful and at the same time establishes the electrophilicity index as one of the most promising tools in the effort of synthesizing both inorganic and organometallic complexes with predefined properties. The combination of the above parameters would enrich not only the *ModEP* scale but also any other scale.

Table 5. Electrophilicity index *ω* and *ModEP* for the ligands studied. Values for *TEP* [cm^{-1}][1], *LEP* [V][3], *CEP* [cm^{-1}][2], and *CEP**[2] were taken from the corresponding references, while values in italics have been calculated from the corresponding linear regressions of the functions *TEP* = *f*(*CEP*) and *LEP* = *f*(*CEP*) as described in ref.[2]

L	*I*	*A*	*ω*	*ΔN max*	*CEP*	*LEP*	*TEP*	*CEP**	*ModEP*
Ph^-	5.126	–5.991	0.008	–0.039	2085.8	–0.62	2000.5	2085.5	–3.075
MeS^-	2.572	–8.132	0.361	–0.260	2097.1	–0.48	2011.3	2097.0	–2.670
CN^-	3.150	–10.096	0.455	–0.262	2115.0	0.02	2028.5	2115.8	–2.561
MeO^-	3.573	–10.894	0.463	–0.253	2099.0	–0.46	2013.2	2098.9	–2.552
HS^-	2.258	–8.654	0.469	–0.293	2102.5	–0.42	2016.5	2102.5	–2.546
$P(NMe_2)_3$	11.953	–1.618	0.984	0.381	2151.0	0.19	2061.9	2150.5	–1.953
$SbMe_3$	13.413	–2.240	0.997	0.357	2155.9	0.25	2067.6	2155.7	–1.938
PMe_3	12.861	–1.874	1.024	0.373	2152.4	0.33	2064.1	2152.0	–1.907
NMe_3	15.707	–3.192	1.036	0.331	2155.9	0.25	2067.6	2155.9	–1.893
$P(OMe)_3$	13.311	–1.758	1.107	0.383	2171.3	0.42	2079.5	2170.9	–1.811
$PHMe_2$	13.438	–1.669	1.146	0.390	2158.1	0.28	2069.6	2157.9	–1.766
$AsMe_3$	13.790	–1.404	1.262	0.408	2155.2	0.24	2067.0	2154.9	–1.633
PH_2Me	14.017	–1.481	1.268	0.404	2164.3	0.35	2075.3	2164.2	–1.626
PHF_2	13.624	–1.155	1.315	0.422	2190.0	0.67	2100.8	2189.9	–1.572
PH_2F	13.927	–1.225	1.331	0.419	2179.6	0.54	2090.9	2179.6	–1.553
PH_3	14.387	–1.320	1.359	0.416	2170.8	0.43	2083.2	2170.9	–1.521
CO	16.302	–0.942	1.710	0.445	2210.6	0.99	2120.0	2193.2	–1.117

The main advantage of the electrophilicity index ω over the only other computed parameter, namely *CEP*, is on one hand the very low computational cost and on the other the fact that the information provided is not only for the ligand as a unit but also for the given complex.

Conclusions

In this paper, we report the derivation of a new empirical scale, namely the modified electronic parameters, and provide the necessary criteria for its use. The basis for our analysis was the electrochemical and spectroscopic data for M(diimine)(dithiolato) complexes, which are known for their peculiar electronic structure and are possible candidates for use in the NLO materials industry and as photosensitizers. Modified electronic parameters provide, by definition, the contribution of the ligand to the reduction potential of the corresponding complexes and can be employed in order to predict those properties of the complexes that are ligand-based. *ModEP* values for homologous compounds correlate with Hammett's σ_t constants. This correlation implies the same behavior in response to a change in the π-bonding properties of aromatic ligands as a result of changing their substituents.

ModEP was tested in several classes of compounds. Its high applicability denotes that ligands act in a fully predictable way upon coordination to a metal and this is due to their electronic characteristics. In other words, when a given series of ligands is coordinated to a metal fragment, it causes a fully predictable change in the ligand-based properties of the complex.

Trying to extrapolate our approach to other types of ligands, we introduced the relatively new concept of the electrophilicity index ω and proved its efficiency as a measure of the capability of a molecule to accept electrons. Thus, ω can become an important index for describing the behavior of the complexes, an approach that is referred to for the first time in this manuscript.

The general correlation between ω and all other electronic parameters such as *ModEP*, *LEP*, *TEP*, *CEP*, and Hammet's σ_t provides us with a useful tool to enrich each one of the aforementioned scales in a quantitative manner. On the basis of this fact, we conclude that, in our effort to find a unified ligand scale, the electrophilicity index, ω, should play a central role.

More contributions to these results will enrich and fully establish our study.

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[1] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
[2] L. Perrin, E. Clot, O. Eisenstein, J. Loch, R. H. Crabtree, *Inorg. Chem.* **2001**, *40*, 5806–5811.
[3] a) A. B. P. Lever, *Inorg. Chem.* **1990**, *29*, 1271–1285; b) A. B. P. Lever, *Inorg. Chem.* **1991**, *30*, 1980–1985.
[4] R. S. Drago, S. Joerg, *J. Am. Chem. Soc.* **1996**, *118*, 2654–2663.
[5] K. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195.
[6] M. C. Aragoni, M. Arca, T. Cassano, C. Denotti, F. A. Devillanova, R. Frau, F. Isaia, F. Lejl, V. Lipolis, L. Nitti, P. Romaniello, R. Tomassi, G. Verani, *Eur. J. Inorg. Chem.* **2003**, 1939–1947.
[7] C. Chen, L. Koshevoy, I. O. Babij, A. J. Poë, *Dalton Trans.* **2004**, 833–838.
[8] K. D. Cooney, T. R. Cundari, N. W. Hoffman, K. A. Pittard, M. D. Temple, Y. Zhao, *J. Am. Chem. Soc.* **2003**, *125*, 4318–4324.
[9] M. R. Wilson, A. Prock, W. P. Giering, A. L. Fernandez, C. M. Haar, S. P. Nolan, B. M. Foxman, *Organometallics* **2002**, *21*, 2758–2763.
[10] M. Nakano, H. Fujita, M. Takahata, K. Yamaguchi, *J. Am. Chem. Soc.* **2002**, *124*, 9648–9655.
[11] S. Tobisch, T. Ziegler, *J. Am. Chem. Soc.* **2002**, *124*, 13290–13301.
[12] R. S. Drago, A. P. Dadmun, *J. Am. Chem. Soc.* **1993**, *115*, 8592–8602.
[13] R. S. Drago, *Inorg. Chem.* **1995**, *34*, 3543–3548.
[14] L. Gonsalvi, H. Adams, G. J. Sunley, E. Ditzel, A. Haynes, *J. Am. Chem. Soc.* **2002**, *124*, 13597–13612.
[15] T. R. Miller, I. G. Dance, *J. Am. Chem. Soc.* **1973**, *95*, 6970–6979.
[16] S. Huertas, M. Hissler, J. E. McGarrah, R. Eisenberg, R. J. Lachicotte, *Inorg. Chem.* **2001**, *40*, 1183–1188.
[17] M. Hissler, I. E. McGarrah, W. B. Connick, D. K. Geiger, S. D. Cummings, R. Eisenberg, *Coord. Chem. Rev.* **2000**, *208*, 115–137.
[18] W. B. Connick, D. Geiger, R. Eisenberg, *Inorg. Chem.* **1999**, *38*, 3264–3265.
[19] M. A. Mansour, R. J. Lachicotte, H. J. Gysling, R. Eisenberg, *Inorg. Chem.* **1998**, *37*, 4625–4632.
[20] W. Paw, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **1998**, *37*, 4139–4141.
[21] W. Paw, S. D. Cummings, M. A. Mansour, W. B. Connick, D. K. Geiger, R. Eisenberg, *Coord. Chem. Rev.* **1998**, *171*, 125–150.
[22] S. D. Cummings, L.-T. Cheng, R. Eisenberg, *Chem. Mater.* **1997**, *9*, 440–450.
[23] W. Paw, R. Eisenberg, *Inorg. Chem.* **1997**, *36*, 2287–2393.
[24] S. D. Cummings, R. Eisenberg, *J. Am. Chem. Soc.* **1996**, *118*, 1949–1960.
[25] S. D. Cummings, R. Eisenberg, *Inorg. Chem.* **1995**, *34*, 3396–3403.
[26] S. D. Cummings, R. Eisenberg, *Inorg. Chem.* **1995**, *34*, 2007–2014.
[27] J. M. Bevilacqua, R. Eisenberg, *Inorg. Chem.* **1994**, *33*, 1886–1890.
[28] J. M. Bevilacqua, R. Eisenberg, *Inorg. Chem.* **1994**, *33*, 2913–2923.
[29] J. A. Zuleta, J. M. Bevilacqua, D. M. Proserpio, P. D. Harvey, R. Eisenberg, *Inorg. Chem.* **1992**, *31*, 2396–2404.
[30] J. A. Zuleta, J. M. Bevilacqua, J. M. Rehm, R. Eisenberg, *Inorg. Chem.* **1992**, *31*, 1332–1337.
[31] J. A. Zuleta, J. M. Bevilacqua, R. Eisenberg, *Coord. Chem. Rev.* **1992**, *111*, 237–248.
[32] J. A. Zuleta, M. S. Burberry, R. Eisenberg, *Coord. Chem. Rev.* **1991**, *111*, 237–248.
[33] J. A. Zuleta, M. S. Burberry, R. Eisenberg, *Coord. Chem. Rev.* **1990**, *97*, 47–64.
[34] J. A. Zuleta, C. A. Chesta, R. Eisenberg, *J. Am. Chem. Soc.* **1989**, *111*, 89168917.
[35] K. Kubo, M. Nakano, H. Tamura, G.-E. Matsubayashi, *Inorg. Chim. Acta* **2002**, *336*, 120–124.
[36] G. Matsubayashi, M. Nakano, H. Tamura, *Coord. Chem. Rev.* **2002**, *226*, 143–151.

[37] A. Islam, H. Sugihara, K. Hara, L. P. Singh, R. Katoh, M. Yanakida, Y. Takahashi, S. Murata, H. Arakawa, *Inorg. Chem.* **2001**, *40*, 5371–5380.
[38] A. Islam, H. Sugihara, K. Hara, L. P. Singh, R. Katoh, M. Yanakida, Y. Takahashi, S. Murata, H. Arakawa, *J. Photochem. Photobiol. A: Chem.* **2001**, *145*, 135–141.
[39] A. Islam, H. Sugihara, K. Hara, L. P. Singh, R. Katoh, M. Yanakida, Y. Takahashi, S. Murata, H. Arakawa, *New J. Chem.* **2000**, *24*, 343–345.
[40] K. Natsuaki, M. Nakano, G.-E. Matsubayashi, R. Arakawa, *Inorg. Chim. Acta* **2000**, *299*, 112–117.
[41] C.-T. Chen, S.-Y. Liao, K.-J. Lin, C.-H. Chen, T.-Y. J. Lin, *Inorg. Chem.* **1999**, *38*, 2734–2741.
[42] C.-T. Chen, S.-Y. Liao, K.-J. Lin, L.-L. Lai, *Adv. Mater.* **1998**, *10*, 334–338.
[43] C.-T. Chen, T.-Y. J. Lin, C.-H. Chen, K.-J. Lin, *J. Chin. Chem. Soc.* **2000**, *47*, 197–201.
[44] G.-E. Matsubayashi, Y. Yamaguchi, T. Tanaka, *J. Chem. Soc. Dalton Trans.* **1988**, 2215–2219.
[45] B. W. Smucker, J. M. Hudson, M. A. Omary, K. R. Dunbar, *Inorg. Chem.* **2003**, *42*, 4714–4723.
[46] J. A. Weinstein, A. J. Blake, E. S. Davies, A. L. Davis, M. W. George, D. C. Grills, I. V. Lileev, A. M. Maksimov, P. Matousek, M. Y. Mel′nikov, A. W. Parker, V. E. Platonov, M. Towrie, C. Wilson, N. N. Zheligovskaya, *Inorg. Chem.* **2003**, *42*, 7077–7085.
[47] Y.-D. Chen, Y.-H. Qin, L.-Y. Zhang, L.-X. Shi, Z.-N. Chen, *Inorg. Chem.* **2004**, *43*, 1197–1205.
[48] Y.-D. Chen, L.-Y. Zhang, L.-X. Shi, Z.-N. Chen, *Inorg. Chem.* **2004**, *43*, 7493–7501.
[49] Z. Hao, Z. Tang, Q. Shi, *Inorg. Chim. Acta* **1999**, *284*, 112–115.
[50] C.-T. Chen, S.-Y. Liao, K.-J. Lin, T.-Y. J. Lin, L.-L. Lai, C.-H. Chen, *Nonlinear Optics* **1999**, *22*, 35.
[51] G.-E. Matsubayashi, M. Hirao, T. Tanaka, *Inorg. Chim. Acta* **1988**, *144*, 217–221.
[52] K. Kubo, M. Nakano, H. Tamura, G.-E. Matsubayashi, *Inorg. Chim. Acta* **2000**, *311*, 6–14.
[53] A. Nakahama, M. Nakano, G.-E. Matsubayashi, *Inorg. Chim. Acta* **1999**, *284*, 55–60.
[54] a) V. E. Kaasjager, E. Bouwman, S. Gorter, J. Reedijk, C. A. Grapperhaus, J. H. Reibenspies, J. J. Smee, M. Y. Darensbourg, A. Derecskei-Kovacs, L. M. Thomson, *Inorg. Chem.* **2002**, *41*, 1837–1844.
[55] K. H. Puthraya, T. S. Srivastava, *Tetrahedron* **1985**, *4*, 1579–1584.
[56] Y. Zhang, K. D. Ley, K. S. Schanze, *Inorg. Chem.* **1996**, *35*, 7102–7110.
[57] K. Base, M. T. Tierney, A. Fort, J. Muller, M. W. Grinstaff, *Inorg. Chem.* **1999**, *38*, 287–289.
[58] K. Base, M. W. Grinstaff, *Inorg. Chem.* **1998**, *37*, 1432–1433.
[59] J. Si, Q. Yang, Y. Wang, P. Ye, S. Wang, J. Qin, D. Lin, *Optics Commun.* **1996**, *132*, 311–315.
[60] R. Vicente, J. Ribas, P. Cassoux, C. Sourisseau, *Synth. Met.* **1986**, *15*, 79–89.
[61] A. Vogler, H. Kunkely, *Comments. Inorg. Chem.* **1990**, *9*, 201–220.
[62] A. Vogler, H. Kunkely, J. Hlavatsch, A. Merz, *Inorg. Chem.* **1984**, *23*, 506–509.
[63] A. Vogler, H. Kunkely, *J. Am. Chem. Soc.* **1981**, *103*, 1559–1560.
[64] C. Makedonas, C. Mitsopoulou, *J. Inorg. Biochem.* **2001**, *86*, 326.
[65] C. Makedonas, C. Mitsopoulou, *ICCC35*, Heidelberg, July **2002**.
[66] C. Makedonas, C. Mitsopoulou, *FIGIPS*7, Lisbon, June **2003**.
[67] T. M. Cocker, R. E. Bachman, *Inorg. Chem.* **2001**, *40*, 1550–1556.
[68] W. B. Connick, H. B. Gray, *J. Am. Chem. Soc.* **1997**, *119*, 11620–11627.
[69] C. Makedonas, C.-A. Mitsopoulou, F. J. Lahoz, A. I. Balana, *Inorg. Chem.* **2003**, *42*, 8853–8865.
[70] C. Makedonas, C.-A. Mitsopoulou, *Spectrochim. Acta A* **2006**, *64*, 918–930.
[71] C. Makedonas, C.-A. Mitsopoulou, *Eur. J. Inorg. Chem.* **2006**, 590–598.
[72] C. Makedonas, C.-A. Mitsopoulou, *Eur. J. Inorg. Chem.* **2006**, 2460–2468.
[73] R. G. Parr, L. V. Szentpály, S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 1922–1924.
[74] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, **1989**.
[75] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A Pople, *Gaussian 98, Revision A.9*, Gaussian Inc., Pittsburgh, PA, **1998**.
[76] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[77] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
[78] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648.
[79] R. Krishnan, J. S. Binkley, R. Seeyer, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.
[80] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.
[81] S. I. Gorelsky, *AOMix*, *Program for Molecular Orbital Analysis, Revision 5.95*, http://www.sg-chem.net/aomix/, York University, Toronto, Canada, **1997**.
[82] S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* **2001**, *635*, 187–196.
[83] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
[84] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209–220.
[85] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 221–264.
[86] *MOPAC2000*, version 1.21, Fujitsu Limited, **2000**.
[87] *CAChe Worksystem 4.4*, Fujitsu Limited, **2000**.
[88] N. L. Allinger, *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134.
[89] P. Flükiger, H. P. Lüthi, S. Portman, J. Weber, *MOLEKEL*, version 4.3, Swiss Center for Scientific Computing, Manno, Switzerland, **2000–2002**.
[90] C. J. Pickett, D. Pletchr, *J. Organomet. Chem.* **1975**, *102*, 327–333.
[91] J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett, D. R. Stanley, *J. Chem. Soc. Dalton Trans.* **1980**, 2032–2038.
[92] B. E. Bursten, M. R. Green, *Progr. Inorg. Chem.* **1988**, *36*, 474–485.
[93] J. Chatt, *Coord. Chem. Rev.* **1982**, *43*, 337–347.
[94] D. J. Stufkens, *Coord. Chem. Rev.* **1990**, *104*, 39–112.
[95] A. J. Lees, *Coord. Chem. Rev.* **1998**, *177*, 3–35.
[96] A. Vlček Jr, *Coord. Chem. Rev.* **2002**, *230*, 225–242.
[97] D. M. Manuta, A. J. Lees, *Inorg. Chem.* **1986**, *25*, 1354–1359.
[98] D. M. Manuta, A. J. Lees, *Inorg. Chem.* **1986**, *25*, 3212–3218.
[99] S. Záliš, I. R. Farrel, A. Vlček Jr, *J. Am. Chem. Soc.* **2003**, *125*, 4580–4592.
[100] I. R. Farrel, F. Hartl, S. Záliš, T. Mahabiersing, A. Vlček Jr, *J. Chem. Soc., Dalton Trans.* **2000**, 4323–4331.
[101] I. R. Farrel, J. van Slageren, S. Záliš, A. Vlček Jr, *Inorg. Chim. Acta* **2001**, *315*, 44–52.
[102] T. J. Meyer, *Pure Appl. Chem.* **1986**, *58*, 1193–1206.

[103] J. M. Villegas, S. R. Stoyanov, W. Huang, D. P. Rillema, *Inorg. Chem.* **2005**, *44*, 2297–2309.

[104] J. M. Villegas, S. R. Stoyanov, W. Huang, D. P. Rillema, *Dalton Trans.* **2005**, 1042–1051.

[105] S. R. Stoyanov, J. M. Villegas, A. J. Cruz, L. L. Lockyear, J. H. Reibenspies, D. P. Rillema, *J. Chem. Theory Comput.* **2005**, *1*, 95–106.

[106] J. M. Villegas, S. R. Stoyanov, J. H. Reibenspies, D. P. Rillema, *Organometallics* **2005**, *24*, 395–404.

[107] S.-S. Sun, A. J. Lees, *Organometallics* **2002**, *21*, 39–49.

[108] J. A. Shelnutt, *J. Phys. Chem.* **1983**, *87*, 605–616.

[109] K. Kalyanasundaram, M. Grätzel, *Coord. Chem. Rev.* **1998**, *177*, 347–414.

[110] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277.

[111] K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159–244.

[112] P. U. Maheswari, M. Palaniandavar, *Inorg. Chim. Acta* **2004**, *357*, 901.

[113] P. U. Maheswari, M. Palaniandavar, *J. Inorg. Biochem.* **2004**, *98*, 219.

[114] A. B. P. Lever, S. I. Gorelsky, *Coord. Chem. Rev.* **2000**, *208*, 153–167.

[115] S. I. Gorelsky, A. B. P. Lever, *Can. J. Anal. Sci. Spect.* **2003**, *48*, 93–105.

[116] C.-T. Lin, W. Böttcher, M. Chou, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **1976**, *98*, 6536–6544.

[117] A. T. Maynard, M. Huang, W. G. Rice, D. G. Covel, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 11578–11583.

[118] P. Pérez, A. Toro-Labbé, R. Contreras, *J. Am. Chem. Soc.* **2001**, *123*, 5527–5531.

[119] P. K. Fuentealba, P. Chattaraj, B. Gómez, R. Contreras, *J. Am. Chem. Soc.* **2000**, *122*, 348–351.

[120] P. K. Chattaraj, B. Sarkar, U. Maiti, *J. Phys. Chem. A* **2003**, *107*, 4973–4975.

[121] E. Chamorro, P. K. Fuentealba, P. Chattaraj, *J. Phys. Chem. A* **2003**, *107*, 7068–7072.

[122] P. K. Chattaraj, U. Sarkar, D. R. Roy, *Chem. Rev.* **2006**, *106*, 2065–2091.

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