

Electron-donor/acceptor properties of carbynes, carbenes, vinylidenes, allenylidenes and alkynyls as measured by electrochemical ligand parameters

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Abstract

The bases of the main redox potential parameterization approaches and their extensions are reviewed with the methods to estimate the corresponding electrochemical ligand and metal center parameters. They are applied, in most cases for the first time, to series of carbyne, vinylidene, allenylidene and alkynyl complexes, allowing the estimate of the Pickett's P_L and Lever's E_L ligand parameters for quite a significant number (ca. 135) of ligands of these types which can then be ordered according to their net π -electron acceptor minus σ -donor character and compared with other ligands. The dependence of such parameters on the electronic properties of various groups and their transmission along the carbon skeleton of those ligands are illustrated and limitations and scopes of the parameterization approaches are discussed.

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1. Introduction

Redox potentials of coordination compounds have been correlated along the years to many other properties namely the HOMO energy, the gas-phase ionization potential, the ligand field stabilization energy, the Hammett's σ and related constants, the energy of charge transfer bands, infra-red stretching frequencies, X-ray photoelectron spectroscopy binding energies, NMR parameters, ligand structural parameters and ligand unsaturation in macrocyclic ligand complexes, apart from solvent and supporting electrolyte effects [1–11]. These features are often dependant on the electronic/structural properties of the ligands and their coordination metal centers, suggesting that one could define suitable electrochemical parameters, based on the redox potential, for measuring such ligand and metal site properties.

The research has often been oriented towards the establishment of simple additive ligand effects on the redox potential. This has already been recognized [10] since long for the series of closely related 18-electron octahedral carbonyl/isocyanide complexes $[\text{Mn}(\text{CO})_{6-x}(\text{CNR})_x]^+$ ($x = 1-6$). They undergo a single-electron reversible oxidation at an oxidation potential that was shown [10] to correlate linearly with the HOMO energy, a higher value of the former corresponding to a greater stability of the latter, as expected for an electron removal from this orbital. Stepwise replacement of a carbonyl by an isocyanide leads to a corresponding sequential decrease of the oxidation potential in accord with the lower stabilizing effect, on the HOMO, of CNR in comparison with CO, thus reflecting the stronger π -electron acceptance ability of CO.

Consistent with this behavior, the linear relationship (1) between the oxidation potential and the degree of carbonyl substitution (x), the former decreasing with the increase of the latter, was proposed [11] for the first-row transition metal complexes $[\text{M}(\text{CO})_{6-x}\text{L}_x]^{y+}$

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$$E^\circ = A + x(dE^\circ/dx)_L + 1.48y, \quad (1)$$

where A is a constant that depends on the metal, the solvent and the reference electrode, and $(dE^\circ/dx)_L$, i.e., the shift of the oxidation potential per each CO replacement by L, is a measure of the effect of the L ligand.

These types of relationships played a key role for the further development of the main systematic approaches, described below, based on the Pickett's and Lever's models.

These models have already been applied to numerous ligands with electron donor and π -electron acceptor characters span over quite wide ranges, binding various types of metal centers, and a main purpose of the current work is to show that carbyne, carbene, vinylidene, allenylidene and alkynyl ligands can also be the object of such a type of study.

In contrast to the impressive development of the organometallic chemistry of such ligands, the parameterization of the redox potentials of their complexes has been attempted only rather scantily. The subject is reviewed in this work which also provides, for the first time in many instances, the estimate of the electrochemical parameters for those types of ligands from the reported values of the redox potentials of their complexes found in the literature and adequate for treatment. Nevertheless, the study does not intend to be comprehensive.

For that purpose, it was often necessary to convert the redox potentials to a common reference, the normal hydrogen electrode (NHE) to which the Lever's model parameters refer. This has been done as follows [12,13]. When the potentials were quoted relative to the saturated calomel electrode (SCE) or when the Ag/AgCl standard electrode was used, the redox potential data have been converted to the NHE by adding 0.245 or 0.222 V, respectively. The use of the ferrocium/ferrocene $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{+/0}$ redox couple as the reference has also been frequently reported, and the potentials have been converted in the other scales by considering that, for this redox couple, $E^\circ = 0.53, 0.55$ or 0.42 V vs. SCE (in 0.2 M $[\text{NBu}_4]/\text{CH}_2\text{Cl}_2$, THF or NCMe, respectively, as measured in the author's Laboratory) or 0.77(5), 0.79(5) or 0.66(5) V vs. NHE, correspondingly.

Nevertheless, comparisons of subtle effects on the redox potentials are better done when the latter have been measured under identical experimental conditions and within the same series of complexes.

2. The Pickett ligand P_L and the Lever ligand E_L parameters and associated metal center parameters

Linear relationships (given by Eq. (2) applied to a general ligand L and to CO) between the oxidation potentials of the members of a series of closed-shell octahedral-type complexes $[\text{M}_s\text{L}]$ (with a variable L ligand binding the 16-electron M_s metal site) and the oxidation potentials of the homologous complexes with the $\{\text{Cr}(\text{CO})_5\}$ site, i.e., $[\text{Cr}(\text{CO})_5\text{L}]$, have been observed experimentally by Pickett et al. [14]

$$E_{1/2}^{\text{ox}}[\text{M}_s\text{L}] - E_{1/2}^{\text{ox}}[\text{M}_s(\text{CO})] = \beta \cdot \left\{ E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5\text{L}] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6] \right\}. \quad (2)$$

The slope β , named the *polarizability of the metal site*, is a measure of the sensitivity of the redox orbital energy to a change in the ligand L, and $E_{1/2}^{\text{ox}}[\text{M}_s(\text{CO})]$, the oxidation potential of the carbonyl complex with the $\{\text{M}_s\}$ center, constitutes a measure of the *electron richness (E_s) of the metal site* (the higher this richness, the lower the oxidation potential of the complex (Eq. (3))). The shift of the oxidation potential resulting from the replacement of one carbonyl ligand in $[\text{Cr}(\text{CO})_6]$ by one L ligand, i.e., the difference $E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5\text{L}] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6]$, is defined as the electrochemical *ligand P_L parameter* (Eq. (4)) [14]. This parameter is identical to $(dE^\circ/dx)_L$ in Eq. (1), for $\text{M} = \text{Cr}$, and, since it is a difference of redox potentials, it does not depend on the reference electrode, in contrast to E_s . By definition, P_L is nul for the carbonyl ligand:

$$E_s\{\text{M}_s\} = E_{1/2}^{\text{ox}}[\text{M}_s(\text{CO})], \quad (3)$$

$$P_L(\text{L}) = E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5\text{L}] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6], \quad (4)$$

$$E_{1/2}^{\text{ox}}[\text{M}_s\text{L}] = E_s + \beta \cdot P_L. \quad (5)$$

The P_L parameter has been proposed [14] as a measure of the *net* electron-donor minus electron-acceptor ability of the ligand L: the higher this net ability, the less stabilized will be the HOMO at $[\text{Cr}(\text{CO})_5\text{L}]$ and thus the lower its oxidation potential, i.e., the lower the P_L value. It should be clarified that the oxidation potential of $[\text{Cr}(\text{CO})_5\text{L}]$ (as of any other species) does not depend only on its HOMO energy but on both the energetics (see below the relationship of E° with ΔG°) of this species and of its oxidized derivative $[\text{Cr}(\text{CO})_5\text{L}]^+$. Nevertheless, for a series of closely related complexes, such as normally these ones (with only one variable L ligand at the common pentacarbonylchromium center), a linear correlation of the oxidation potential with the HOMO energy can be expected (see above for a carbonyl/isocyanide series of manganese complexes [10]).

The P_L reflects the overall *combined* σ - and π -electronic properties of the coordination bond and general behaviors are indicated in Table 1. Strong π -electron acceptors, like nitrosyl NO^+ , carbynes, carbon monoxide, bent isocyanides and vinylidenes (see below) exhibit high P_L values (i.e., commonly less negative, above -0.3 V), whereas moderate π -acceptors, such as linear isocyanides, carbenes (see below) and phosphines have less high P_L values (typically from -0.3 to -0.6 V). Moderate σ -electron donors without a π -accepting character, such as ammonia and pyridine, show intermediate P_L values (-0.6 to -0.8 V) and anionic very strong σ -donors (eventually also π -donors, in a few cases), like halides, alkynyls, hydride, azide, hydrogen cyanamide (NCNH^-) and hydroxide, aryls, alkyls and NO^- , display the lowest values of P_L (below -1.1 V).

The P_L ligand parameter reflects the variation of the free-energy difference of the redox processes (consider the known expression $\Delta G^\circ = -nFE^\circ$, in which n is the number of electrons transferred and F is the Faraday constant) and

Table 1

General relationship between the electrochemical P_L or E_L ligand parameters and the electronic properties of the ligand (L)

L (example)	M–L bond	P_L/V^a	E_L/V vs. NHE ^a	
σ -donor and strong π -acceptor ($\equiv CR, =CNH_2^+$), CO, bent CNR, $=C=CR_2$, NO^+)	$M \begin{array}{c} \xrightarrow{\pi} L \\ \xleftarrow{\sigma} \end{array}$	Above -0.3	Above 0.5	High
σ -donor and moderate π -acceptor ($=CR_2$, linear CNR, NCR, PR_3)	$M \begin{array}{c} \xrightarrow{\pi} L \\ \xleftarrow{\sigma} \end{array}$	-0.3 to -0.6	0.5 – 0.3	Less high
σ -donor (NH_3 , pyridine, imidazole, indazole)	$M \begin{array}{c} \xrightarrow{\sigma} L \\ \xleftarrow{\pi} \end{array}$	-0.6 to -0.8	0.3 – 0	Intermediate
Very strong σ -donor and eventually also π -donor (halide, $C\equiv CR^-$, H^- , N_3^- , $NCNH^-$, OH^- , R^- , NO^-)	$M \begin{array}{c} \xrightarrow{\pi} L \\ \xleftarrow{\sigma} \end{array}$	Below -1.1	Below -0.2	Low

^a Common ranges.

has some analogies (consider also the known relationship $\Delta G^\circ = -RT \ln K$) with the Hammett σ_p constant [15,16] defined as $\log K_X - \log K_H$ [17], in which K_X and K_H are the acidic constants of the p -substituted benzoic acid $HOOCC_6H_4X$ and of benzoic acid itself, respectively.

Another ligand electrochemical parameter (E_L) has been proposed by Lever [18–22], based on the additive contribution of all the ligands to the redox potential of a complex with the $[M^{n+1/n}]$ redox couple, as expressed by Eq. (6) in volts vs. NHE. S_M (slope) and I_M (intercept) depend upon the metal and redox couple, the spin state and the stereochemistry, and E_L is an additive ligand parameter

$$E_{1/2}[M^{n+1/n}] = S_M \left(\sum E_L \right) + I_M/V \text{ vs. NHE.} \quad (6)$$

The E_L parameter for each ligand L was normally obtained through a statistical analysis of the reported redox potentials of the large number of known complexes with the $Ru^{III/II}$ redox couple and the possible ligands, as given by Eq. (7) (ideally, for the $Ru^{III/II}$ complexes, S_M should be unity and I_M nul). In other cases, E_L was estimated from Hammett relationships [23–26]

$$E_{1/2}[Ru^{III/II}] = \sum E_L(L). \quad (7)$$

In contrast to the P_L parameter, E_L is dependent on the reference electrode and commonly is referred to the NHE.

Both the E_L and P_L ligand parameters reflect the net electron donor/acceptor character of a ligand and a linear relationship (Eq. (9)) has been experimentally observed [18] between them, for a considerable number of ligands. Hence, the two parameters (Table 1) are expected to follow parallel trends and one can derive any of them from the knowledge of the other one

$$P_L = 1.17E_L - 0.86. \quad (8)$$

However, this expression should be used cautiously since it appears to be invalid for ligands (like CO [18,27,28], carbynes [29] and isocyanides [18,27,30]) that are strong π -acceptors. In fact, for ligands with an extensive π -stabilizing influence on the HOMO, the need to introduce not only positive corrections to E_L but also corrective terms to the general expression (6) has been recognized. The latter equation then assumes, for carbonyl complexes, the form (9) [18,21] in which x is the number of CO π^* -orbitals that interact with the HOMO and c is an empirical correction. Further corrections ($c'x'$, etc.) should be added if the com-

plex has also other strong π -acceptor ligands e.g. isocyanides. These corrections can reach values up to 0.3 V [18,21,30]

$$E_{1/2}[M^{n+1/n}] = S_M \left(\sum E_L \right) + I_M + cx. \quad (9)$$

The P_L parameter for a particular ligand can be directly derived, by definition, from Eq. (4) only when the corresponding $[Cr(CO)_5L]$ is available. Otherwise, the use of Eq. (5) is more convenient, provided one knows the oxidation potential of an 18-electron complex $[M_sL]$ with that particular ligand L coordinated to a metal center $\{M_s\}$ with known E_s and β parameters.

The general expression (6) can be applied to estimate E_L of a particular ligand provided one knows: (i) the redox potential of a complex with this ligand bound to a $M^{n+1/n}$ metal redox couple with known I_M and S_M parameters and (ii) the E_L values of the other ligands.

If E_s and β are unknown for $\{M_s\}$, they can be obtained by application of the general Eq. (5) to as many as possible members (the minimum of two can lead to a high uncertainty) of the series $[M_sL]$ with known oxidation potentials and known P_L for the corresponding L ligands. A similar approach, *mutatis mutandis*, can be used for the estimate of I_M and S_M for a particular $M^{n+1/n}$ redox center, provided $\sum E_L$ is known for the available complexes.

Indirect methods can also be applied, namely by comparing the homologues of the $[M_sL]$ and the auxiliary series $[M'_sL]$ with E_s and β known for $\{M'_s\}$. These parameters are then obtained for $\{M_s\}$ from the intercept and the slope of Eq. (10) derived from the application of the general equation (5) to both series

$$\begin{aligned} E_{1/2}^{\text{ox}}[M_sL] - E_{1/2}^{\text{ox}}[M'_sL] \\ = (E_s\{M_s\} - E_s\{M'_s\}) + (\beta\{M_s\} - \beta\{M'_s\}) \cdot P_L(L). \end{aligned} \quad (10)$$

Other indirect methods for the estimate of E_s , β and/or P_L have been used for certain types of 18-electron complexes, such as $[M_sLL']$ [31–33] and $[M_sL_n]$ [5,13]

Values of the P_L and E_L parameters for selected ligands are shown in Table 2 [14,18,21,27,29–34,36,41–54], whereas E_s , β and S_M , I_M parameters are listed in Tables 3 [5,14,27,30,32–35,42,44–47,49,55,56] and 4 [18,19,33–37,54], respectively, for a variety of metal centers that include, apart from others, those used to estimate the above ligand parameters.

Table 2
 Values of the P_L and E_L parameters for selected ligands L^a

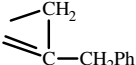

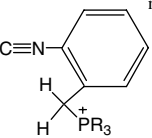
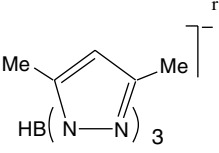
L	P_L/V	Ref.	E_L/V vs. NHE	Ref.
NO^+	+1.40 ^b	[14]	>1.5	[18,21]
<i>Carbynes</i> ^c	+0.24 to +0.21 ^b	[29]	ca. 1.2 ^{d,e}	[29]
$\equiv\text{C}-\text{CH}_2\text{CO}_2\text{R}$ (R = Me, Et)	+0.24			
$\equiv\text{C}-\text{CH}_2\text{Ph}$	+0.23			
$\equiv\text{C}-\text{CH}_2\text{C}_6\text{H}_4\text{Me-4}$	+0.22			
$\equiv\text{C}-\text{CH}_3$	+0.21			
$\equiv\text{C}-\text{CH}_2^t\text{Bu}$	+0.21			
η^2 -Vinyl ^c				
	+0.22	[41]	ca. 1.2 ^{d,e}	TW
<i>Aminocarbyne</i> ($\equiv\text{CNH}_2$) ^c	+0.09	[41]	ca. 1.1 ^{d,e}	TW
CO	0	[14]	0.99	[18]
<i>Isocyanides (bent)</i> ^f				
				
R = aryl	-0.07 to -0.14	[27,31,32,42]		
R = alkyl	-0.17 to -0.18	[27,31,32,42]		
<i>Metallo-dinitriles</i> ^k				
$\text{N}=\text{C}-\text{X}-\text{C}=\text{N}-\text{ML}_{n-1}$	-0.18 to -0.40 ^b	[43]	0.58–0.39 ^d	TW
<i>Nitriles</i> ($\text{N}=\text{CR}$)	-0.23 to -0.58	[14,34]	0.49–0.33	[18]
<i>Ferricinium isocyanides</i> ^{l,m}				
$\text{C}=\text{N}-\text{Fc}^+$	-0.22	[44,45]	0.55 ^d	TW
$\text{C}=\text{N}-\text{CH}_2\text{Fc}^+$	-0.28	[44,45]	0.50 ^d	TW
$\text{C}=\text{N}-\text{CH}(\text{Men})\text{Fc}^+$	-0.28	[44,45]	0.50 ^d	TW
$\text{C}=\text{N}-\text{BF}_3^e$	-0.24	[46]	0.20	[46]
<i>Metallo-cyanides</i> ($\text{C}=\text{N}-\text{ML}_{n-1}^-$) ^c	-0.25 to -0.61	[46,47]	0.50–0.21 ^d	TW
	-0.28 to -0.36	[30]	0.50–0.43 ^d	[30]
PR ₃ = PPh ₃	-0.28		0.50	
PPh ₂ (CH ₂ Ph)	-0.30		0.48	
PMe ₃	-0.36		0.43	
<i>Vinylidenes</i> ^g				
$=\text{C}=\text{CR}_2$	0 to -0.6	TW	0.8–0.2	TW
<i>Allenylden</i> ^h				
$=\text{C}=\text{C}=\text{CR}_2$	0 to -0.8	TW	0.8–0	TW
Me ₂ SO	-0.19 ⁱ	TW	0.57	[48]
η^2 -Allene ^j	-0.21	[41]	0.56 ^d	TW
η^2 -CH ₂ =C=CHPh				
<i>Isocyanides (linear)</i> ^o $\text{C}=\text{N}-\text{R}$	-0.33 to -0.44	[31,32,42,49]	0.56–0.32	[18]
<i>Carbenes</i> ^p	-0.4 to -1.7	TW	0.5 to -0.7	TW
<i>Phosphines</i>				
PPh ₃	-0.35	[14]	0.39	[18]
Ph ₂ PCH ₂ CH ₂ PPh ₂ (dppe)	-0.44 ⁱ	TW	0.36	[18]
Ph ₂ PCH ₂ PPh ₂ (dppm)	-0.45 ⁱ	TW	0.35 ^q	TW
Me ₂ PCH ₂ CH ₂ PPh ₂ (dmpe)	-0.53 ⁱ	TW	0.43	[18]
$\text{C}=\text{N}-\text{BPh}_3^k$	-0.51	[50]	0.28	[18]
Indazole	-0.56 ⁱ	TW	-0.05	[46]
<i>Cyanamides</i> ($\text{N}=\text{C}-\text{NR}_2$)	-0.57 to -0.85	[33,51–53]	0.25–0.01 ^d	TW
Pyridine	-0.59	[14]	0.25	[18]
Imidazole	-0.72 ⁱ	TW	0.12	[18]

Table 2 (continued)

L	P_L/V	Ref.	E_L/V vs. NHE	Ref.
NH ₃	-0.77	[14]	0.07	[18]
C≡N ⁻	-1.00 ^m	[14]	0.02	[18]
	-0.74 ^k	[46]	-0.26 ^k	[46]
Alkynyls ^s	-0.9 to -1.7	TW	-0.1 to -0.7	TW
	-1.13 ⁱ	TW	-0.23	[36]
Pyrazolate	-1.14 ⁱ	TW	-0.24	[18]
Cl ⁻	-1.19	[14]	-0.24	[18]
H ⁻	-1.22	[14]	-0.30	[18]
N ₃ ⁻	-1.26	[14]	-0.30	[18]
NCNH ^{-t}	-1.34	[53]	-0.41 ^d	TW
Aryls, alkyls, NO ⁻	-1.7 to -1.9 ⁱ	TW	-0.70 to -0.90	[21]

^a Ordered generally from higher to lower P_L values; TW, this work.

^b Estimated by using Pickett's equation (5).

^c Considered as either cationic 2e-donor or neutral 3e-donor ligands at *trans*-{ReCl(dppe)₂} or *trans*-{ReCl(dppe)₂}⁺, respectively.

^d Estimated from P_L using Eq. (8).

^e After an assumed correction of ca. 0.25 V, identical to that of CO.

^f Bent isocyanides at an electron-rich metal center such as *trans*-{ReCl(dppe)₂} or *trans*-{TcH(dppe)₂}.

^g For details see Table 6.

^h For details see Table 7.

ⁱ Estimated from E_L using Eq. (8).

^j At *trans*-{ReCl(dppe)₂}.

^k At *trans*-{FeH(dppe)₂}⁺.

^l Oxidized ferrocenyl isocyanide ligands, with $Fc^+ = Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4)^+$, Men = (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl.

^m At {Cr(CO)₅}.

ⁿ Phosphonium functionalized isocyanides at {M(CO)₅} (M = Cr, Mo, W).

^o At a metal centre with a low or medium electron-richness, e.g. {M(CO)₅} (M = Cr, Mo, W).

^p For details see Table 5.

^q See text.

^r Hydrotris(3,5-dimethylpyrazolyl)borate.

^s For details see Table 8.

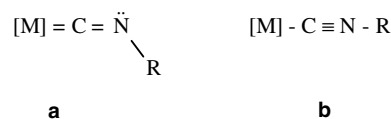
^t Hydrogen-cyanamide, at *trans*-{Re(CNR)(dppe)₂}⁺ (R = alkyl).

The Pickett model, initially proposed only to 18-electron six-coordinate octahedral-type complexes, has been extended to open-shell 17-electron [34] and square planar 16-electron [35] complexes, and further extensions to even lower numbers of valence electrons can be anticipated, when the redox potentials of suitable series of complexes will become available. The possibility of being extended to 18-electron half-sandwich η^7 -cycloheptatrienyl complexes has also been shown [55].

Extensions of the Lever model, typically applied only to six-coordinate complexes, to square planar four-coordinate and five-coordinate Rh^{I/II} complexes [35–37] have also been achieved, in particular by using, in the former case, a series of carbene, vinylidene, allenylidene and pentatetraenylidene complexes. It has also been applied to Ru clusters [38–40] and sandwich complexes [20,21,24], and to ligand-centered reduction processes [21].

Although the ligand parameters P_L and E_L were initially considered to be independent of the binding metal center, it has later been recognized, in some situations, the influence

of the latter, namely for isocyanides [27,31,32,42] and cyanide [46] (Table 2), nitriles [34] and cyanamides [33,51–53]. Hence, at an electron-rich site such as *trans*-{ReCl(dppe)₂} ($E_s = 0.68$ V) with a high π -electron releasing character, the isocyanides are quite effective π -acceptors [57], present a bent geometry at N [58] (form **a** with a carbene character) and have P_L values ca. 0.26 V [31,32,42] higher than when ligating (linear geometry **b**) a metal center with a much lower electron-richness, namely {Cr(CO)₅} ($E_s = 1.50$ V).



The requirement for E_L corrections for strong π -electron acceptor ligands has already been mentioned above.

As discussed below, P_L and E_L for vinylidenes, allenylidenes and alkynyls may also be dependent on the type of binding metal site.

Table 3
Values of the electron-richness (E_S) and polarizability (β) parameters for selected 16-, 15- and 14-electron metal sites $\{M_S\}$

$\{M_S\}^a$	E_S/V vs. SCE	β	Ref.
<i>16-electron</i>			
<i>Square pyramidal</i>			
$\{Fe(CO)(depe)_2\}^{2+}$	2.3	–	[33]
$\{W(\equiv C-CH=\overline{C}(CH_2)_n\overline{C}H_2)(CO)_2(dppe)\}^+$			
n = 3	1.69	0.73	[49]
n = 6	1.63	0.61	[49]
$\{Cr(CO)_5\}$	1.50	1.00	[14]
$\{Mo(CO)_5\}$	1.50	0.86	[30]
$\{W(CO)_5\}$	1.50	0.90	[30]
$\{Re(CO)(dppe)_2\}^+$	1.42	0.62	[32]
$\{Re(N_2)(dppe)_2\}^+$	1.38	0.92	[5]
	1.20	0.74	[14]
$\{FeBr(depe)_2\}^+$	1.32	1.10	[34]
$\{Re(CNR)(dppe)_2\}^+$			
R = aryl, alkyl	1.19–1.15	0.75–0.92	[31,32]
$\{FeH(dppe)_2\}^+$	1.04	1.0	[14]
$\{Mn(CO)(dppm)_2\}^+$	0.86	0.75	[44]
$\{Re(CN)(dppe)_2\}$	0.78	3.7	[45]
$\{Re(NCS)(dppe)_2\}$	0.73	–	[46]
$\{Re(Cl)(dppe)_2\}$	0.68	3.4	[42]
$\{Re(NCO)(dppe)_2\}$	0.63	–	[46]
$\{Re(N_3)(dppe)_2\}$	0.55	–	[46]
<i>cis</i> - $\{Re(Cl)(dppe)_2\}$	0.41	1.88	[34]
$\{TcH(dppe)_2\}$	0.34	4.0	[27]
$\{Mo(CO)(dppe)_2\}$	–0.11	0.72	[14]
<i>mer</i> - $\{ReCl(N_2)[P(OMe)_3]_3\}$	–	1.0	[47]
<i>Half-sandwich^b</i>			
$\{Mo(\eta^7-C_7H_7)(dppe)_2\}^+$	1.16 ^c	1.04	[55], TW ^c
$\{Mo(\eta^7-C_7H_7)(^tBu-dab)\}^+$	1.14	0.68	[55]
$\{Mo(\eta^7-C_7H_7)(bipy)\}^+$	0.78	0.71	[55]
<i>15-electron</i>			
$\{Fe^{III}Br(depe)_2\}^{2+}$	1.98	1.30	[34]
<i>cis</i> - $\{Re^{II}(Cl)(dppe)_2\}^+$	1.42	1.30	[34]
<i>14-electron^d</i>			
$\{Rh(acac)(CO)\}^e$	1.64	1.96	[35]

^a The bis(diphosphine) centers have *trans* geometry, except when stated otherwise; TW, this work.

^b Cycloheptatrienyl complexes; ^tBu-dab=1,4-^tBu₂-1,3-diazabutadiene; bipy = 2,2'-bipyridine.

^c E_S as the intercept from the plot of E° (values taken from [56]) vs. P_L (more data points than those in [55]).

^d Square planar.

^e acac = MeC(O)CHC(O)Me[–].

One should also be prepared to accept that the proposed general S_M and I_M metal center parameters may require adjustments for particular cases. In view of the high generality of Lever's expression (6), applicable, in principle, to all six-coordinate complexes with a particular $M^{n+1/n}$ redox couple, it cannot distinguish particular series of complexes or isomeric forms. Hence, different S_M and I_M sets of values that fit better the experimental data have already been proposed for particular series of $Fe^{II/III}$ complexes such as *trans*- $[FeL_2(depe)_2]^{2+/3+}$ (L = CO, aryl and alkyl NCR, NCNH₂) [33] and *trans*- $[FeBr(L)(depe)_2]^{+/2+}$ (L = CO, NCR, Br[–]) [34] (Table

4). Correction isomeric terms have been applied [18,19] and curved E° vs. $\sum E_L$ relationships for a wide range of $\sum E_L$ values have also been considered [19,29,34].

Such limitations are much less pronounced with the Pickett's equation (5) which can reflect subtle electronic and structural variations once it concerns series of closely related complexes $[M_S L]$ with a single variable ligand L at a common particular metal center $\{M_S\}$. The disadvantage is the loss of the high generality associated to the Lever's model.

The electrochemical ligand parameters have been correlated with other properties of the complexes that are also

Table 4
Values of the S_M and I_M parameters for six- and four-coordinate complexes in organic medium^a

Redox couple	S_M	I_M/V vs. NHE	Ref.
<i>Six-coordinate</i>			
Nb ^{V/IV}	0.76	1.24	[18]
Nb ^{IV/III}	0.75	-0.12	[18]
Ta ^{V/IV}	0.79	0.66	[18]
	1.17	-0.86	[18]
Cr ^{III/II} (LS)	1.18	-1.72	[18]
Cr ^{III/II} (HS)	0.84	-1.18	[18]
Cr ^{I/0}	0.52	-1.75	[18]
Mo ^{I/0}	0.74	-2.25	[18]
Mo ^{II/I}	0.81	-1.76	[18]
Tc ^{IV/III}	1.00	0.65	[19]
Tc ^{III/II}	1.28	-0.89	[19]
Tc ^{II/I}	1.42	-2.09	[19]
Re ^{IV/III}	0.86	0.51	[19]
Re ^{III/II}	1.17	-0.88	[19]
Re ^{II/I} (upper)	0.76	-0.95	[19]
Re ^{II/I} (lower)	0.27	-1.43	[19]
Fe ^{IV/III} (particular) ^b	1.49	-0.18	[34]
Fe ^{III/II} (LS)	1.10	-0.43	[18]
Fe ^{III/II} (LS) (particular) ^c	1.07	-0.3	[33]
Fe ^{III/II} (LS) (particular) ^d	1.32	-0.57	[34]
Fe ^{III/II} (HS)	0.89	-0.25	[18]
Ru ^{IV/III}	1.03	1.68	[54]
Ru ^{III/II}	0.97	0.04	[18]
Os ^{III/II}	1.01	-0.40	[18]
<i>Four-coordinate^{e,f}</i>			
Rh ^{I/II}	1.68	-0.87	[35,36]

^a LS, low spin; HS, high spin.

^b Established for the series $trans-[FeBrL(depe)_2]^{2+/3+}$ (L = CO, aryl and alkyl N≡CR).

^c Established for the series $trans-[FeL_2(depe)_2]^{2+/3+}$ (L = CO, aryl and alkyl N≡CR, N≡C-NR₂).

^d Established for the series $trans-[FeBrL(depe)_2]^{+/2+}$ (L = CO, aryl and alkyl N≡CR, Br⁻).

^e Square planar.

^f The values $S_M = 1.83$ and $I_M = -1.22$ V vs. NHE have also been proposed [37] on the basis of a smaller number of data points.

dependent on their electronic and structural features [5,6,20,21] such as infra-red data [28,35,53,59–63], the Tolman's electronic parameter (TEP) [64] for phosphines and a computed electronic parameter (CEP) [26] based (as TEP) on the infrared $A_1 \nu(\text{CO})$ frequency in $[\text{NiL}(\text{CO})_3]$ (also dependent on the electronic effect of L), the Hammett's and related constants [23,24,26,42,60,65], the photoelectron binding energies or gas-phase vertical ionization potentials [66], the energy of a metal-to-ligand charge transfer [21] and chemical reactivity [14,43,62,63,67,68]. Ligand coordination criteria have also been proposed [14,15,42,48] on the basis of the electrochemical parameters.

Bursten [69–71] has proposed another redox potential additive model which includes an isomer dependent parameter that reflects the difference between the abilities of the ligands to stabilize the metal d_π orbital involved in the HOMO. This model is not so easy to apply as those discussed above and has still been little explored.

3. Carbynes, aminocarbene and η^2 -vinyl

The carbyne, η^2 -vinyl and aminocarbene complexes $trans-[ReCl(L)(dppe)_2]^+$ {L = C-CH₂R (R = alkyl, aryl, CO₂R) [29], η^2 -C(CH₂)CH₂Ph [41], CNH₂ [41]}, derived from protonation of the corresponding vinylidene [29], η^2 -allene [72,73] and isocyanide [57,74–76] compounds $trans-[ReCl(L')(dppe)_2]$ (L' = C=CHR, CH₂=C=CHPh, CNH), exhibit considerably higher oxidation potentials than the analogous carbonyl complex and therefore those ligands are expected to behave as more effective π -electron acceptors than CO.

From the knowledge (Table 3) of E_s and β of the $trans$ -{ReCl(dppe)₂} binding center and by using Eq. (5), the corresponding P_L values have been estimated (Table 2): carbynes (0.24–0.21 V) [29] \geq η^2 -vinyl (0.22 V) [41] > aminocarbene (0.09 V) [41]. They are higher than for CO ($P_L = 0$ V) and those ligands can be ordered as above according to their π -acceptance character. Carbynes and the η^2 -vinyl, both formal 3e-donor ligands, are the most effective π -acceptors, being surpassed only by NO⁺ ($P_L = 1.40$ V [14]), also a 3e-donor, whereas the aminocarbene, with an aminocarbene character, $[M]=C=NHR^+$ [75,76], as suggested by X-ray diffraction and IR, behaves as a significantly weaker π -acceptor, although still stronger than carbon monoxide.

Another evidence (based on electrochemical parameters) for the strong π -acceptance of a carbyne ligand is provided by the rather low electron-richness and polarizability (high E_s and low β values, i.e., 1.69–1.63 V and 0.73–0.61, respectively [49]) (Table 3) of the $\{W(\equiv C-CH=C(CH_2)_nCH_2)(CO)_2(dppe)_2\}^+$ (n = 3,6) sites {M_s} which comprise an alkenyl-carbyne ligand. The strong π -acceptance of this ligand results (i) in the stabilization of the HOMO of the complex (high E_s) and (ii) in its delocalization towards the carbyne (or CO) ligand, as indicated by MO calculations [49]. The latter effect attenuates the changes of the energy of the HOMO (low β) upon changing a ligand in the corresponding [M_sL] complexes.

4. Carbenes

The estimated ligand parameters for carbenes are shown in Table 5. Most of them have been obtained in this work from the quoted oxidation potential of their complexes commonly with the {M(CO)₅} (M = Cr, Mo, W) metal center [5,30,35–37,77–81], but, in the case of the cyclic oxocarbene $\bar{C}CH_2CH_2CH_2\bar{O}$, the available complex has the half-sandwich cycloheptatrienyl {Mo(η^7 -C₇H₇)(dppe)}⁺ center [55,56]. P_L has been calculated by using either its definition expression (Eq. (4)) for the {Cr(CO)₅} site, or Eq. (5) for the other metal centers. The required E_s and β values for these binding centers are given in Table 3. The corresponding E_L value was then calculated from Eq. (8) that relates this parameter with P_L .

However, for diphenylcarbene, CPh₂, the available oxidation potential concerns a square planar Rh^I complex [37] and E_L was obtained from Lever's equation (6) by using the

Table 5
Values of the P_L and E_L ligand parameter for carbene ligands^a

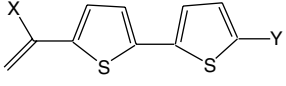





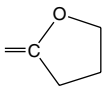


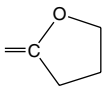


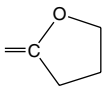






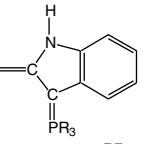
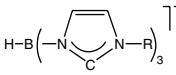
	P_L / V^b	Ref.	E_L / V vs. NHE ^c	Ref.												
Diphenylcarbene $=CPh_2^d$	-0.40 ^e	TW	0.39 0.51	TW ^f [37] ^g												
Bithiophene-carbenes 	-0.38 to -0.62	[76]	0.41 to 0.21	TW												
<table border="1" data-bbox="159 553 542 712"> <thead> <tr> <th>X</th> <th>Y</th> </tr> </thead> <tbody> <tr> <td>OEt</td> <td>C(OEt)=Cr(CO)₅</td> </tr> <tr> <td></td> <td>H</td> </tr> <tr> <td>OEt</td> <td>H</td> </tr> </tbody> </table>	X	Y	OEt	C(OEt)=Cr(CO) ₅		H	OEt	H	-0.38 -0.56 -0.62		0.41 0.26 0.21					
X	Y															
OEt	C(OEt)=Cr(CO) ₅															
	H															
OEt	H															
Oxocarbenes $=C(OR)Y$ R = alkyl, Ph Y = 2-furyl, 2-thienyl, aryl, 2-thiazolyl	-0.51 to -0.64	TW ^{h,i,j}	0.30 to 0.19	TW												
<table border="1" data-bbox="159 872 542 1266"> <thead> <tr> <th>R</th> <th>Y</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td></td> </tr> <tr> <td>Me, Et, Ph</td> <td>4-methylthiazol-2-yl , 4-C₆H₄^k X = O (2-furyl) =S (2-thienyl)</td> </tr> <tr> <td>Et</td> <td>Ph</td> </tr> <tr> <td>Me</td> <td>C₆H₄OMe-4^k</td> </tr> <tr> <td></td> <td></td> </tr> </tbody> </table>	R	Y	Me		Me, Et, Ph	4-methylthiazol-2-yl  , 4-C ₆ H ₄ ^k X = O (2-furyl) =S (2-thienyl)	Et	Ph	Me	C ₆ H ₄ OMe-4 ^k			-0.51 -0.57 to -0.58 -0.60 -0.64 -0.54	h i i i j	0.30 0.25 to 0.24 -0.22 0.19 0.27	
R	Y															
Me																
Me, Et, Ph	4-methylthiazol-2-yl  , 4-C ₆ H ₄ ^k X = O (2-furyl) =S (2-thienyl)															
Et	Ph															
Me	C ₆ H ₄ OMe-4 ^k															
																
Hydroxocarbene $=C(OH)Ph$ $=C(OH \cdots X^-)Ph$ X	-0.64 to -1.00	TW ^l	0.19 to -0.12	TW												
<table border="1" data-bbox="159 1425 542 1521"> <tbody> <tr> <td>H₂SO₄</td> <td>-0.64</td> <td>0.19</td> </tr> <tr> <td>ClO₄</td> <td>-0.70</td> <td>0.14</td> </tr> <tr> <td>CF₃COO</td> <td>-1.00</td> <td>-0.12</td> </tr> </tbody> </table>	H ₂ SO ₄	-0.64	0.19	ClO ₄	-0.70	0.14	CF ₃ COO	-1.00	-0.12							
H ₂ SO ₄	-0.64	0.19														
ClO ₄	-0.70	0.14														
CF ₃ COO	-1.00	-0.12														
Thiocarbenes $=C(SR)Y$ R = alkyl, Ph Y = 2-furyl	-0.66 to -0.68	TW ⁱ	0.17 to 0.15	TW												
Ferrocenyl-oxocarbenes ^m $=C(OR)ferrocenyl$ R = alkyl	-0.70 to -0.91 (-0.77) ⁿ	TW ⁱ	0.14 to -0.04 (0.08) ⁿ	TW												
Aminocarbenes $=C(NRR')Y$ NRR' = NH ₂ , NHCy, NMe ₂ , NEt ₂ , aziridin-1-yl, azetidin-1-yl, pyrrolidin-1-yl, piperidin-1-yl Y = alkyl, Ph, 2-furyl, 2-thienyl	-0.69 to -0.80	TW, [5] ⁱ	0.15 to 0.05	TW												

Table 5 (continued)

		P_L / V^b	Ref.	E_L / V vs. NHE ^c	Ref.
NRR^a	Y				
	Ph	-0.69		0.15	
	Ph	-0.72		0.12	
	Ph	-0.74		0.10	
	Ph	-0.75		0.09	
NMe ₂	Ph	-0.75		0.09	
NEt ₂	Me	-0.76		0.09	
NH ₂	2-furyl,2-thienyl	-0.76		0.09	
NHCy	Et	-0.76		0.09	
NMe ₂	Me	-0.78		0.07	
	2-furyl	-0.79		0.06	
	2-thienyl	-0.80		0.05	
NHMe	Me	-0.80		0.05	
Phosphoylide-aminocarbenes					
		-0.79 to -0.87	[30]	0.06 to -0.01	[30]
PR ₃ =	PPh ₃	-0.79		0.06	
	PPh ₂ (CH ₂ Ph)	-0.82		0.03	
	PMe ₃	-0.87		-0.01	
Tris(imidazolin-2-ylidene)borate^p					
	R = Me, Et	-0.88 ^c -0.93 ^c	TW TW	-0.02 ^q -0.06 ^r	TW TW
Ferrocenyl-aminocarbenes^m					
=C(pyrrolidin-1-yl)Y		-0.99 to -1.11 (-1.05) ⁿ	TW ⁱ	-0.11 to -0.21 (-0.16) ⁿ	TW
Anionic oxycarbenes					
{=C(O ⁻)Y}NMe ₄ ⁺		-1.05 to -1.71	TW ^{h,i}	-0.16 to -0.73	TW
Y					
4-methylthiazol-2-yl		-1.05	h	-0.16	
2-furyl		-1.44	i	-0.50	
CH ₂ SiMe ₃		-1.54	i	-0.58	
ferrocenyl ^m		-1.71	i	-0.73	

^a Ordered generally from higher to lower values; TW, this work.

^b Estimated from Eqs. (4) or (5) at {Cr(CO)₅} or {M(CO)₅} (M = W, Mo) sites (reversible oxidation waves), respectively, unless stated otherwise.

^c Estimated from P_L by using Eq. (8), unless stated otherwise.

^d At a four-coordinated square planar Rh^I center.

^e Estimated from E_L by using Eq. (8).

^f Estimated from the oxidation potential of a square planar Rh^I complex quoted in [37] and using Lever's equation (6) with the S_M and I_M values given in [35,36] calculated with a higher number of data points (see Table 4).

^g Proposed on the basis of S_M and I_M values obtained from a restricted number of data points (see Table 4).

^h Estimated from the data quoted in [78] (E_p^{ox} for a quasi-reversible wave).

ⁱ Estimated from the data quoted in [79].

^j Estimated from the data quoted in [56], concerning the carbene complex with the {Mo(η^7 -C₇H₇)(dppe)}⁺ metal center.

^k Quasi-reversible oxidation wave.

^l Estimated from the data quoted in [80] (E_p^{ox} for irreversible wave); value dependent on the H-bonding with the solvent or the conjugate base X⁻ of the acid used in the preparation of [(CO)₅Cr=C(OH)Ph] upon protonation (by HX) of the benzoyl complex precursor [(CO)₅Cr-C(O)Ph]⁻.

^m Since the oxidation of the complexes conceivably involves both the {M(CO)₅} (M = Cr, W) and ferrocenyl-iron centers, the P_L (and E_L) values should merely be considered as formal ones (see text).

ⁿ Average of the values at {Cr(CO)₅} and {W(CO)₅}.

^o Their protonated forms (possibly at the β -carbon of the carbene ring) have the following higher P_L and E_L values (in V and in V vs. NHE, respectively): -0.51 (P_L) and 0.30 (E_L) (PR₃ = PPh₃, PPh₂(CH₂Ph)), -0.60 (P_L) and 0.22 (E_L) (PR₃ = PMe₃) [30].

^p Triscarbene (TRIS^R), the C-isomer of tris(pyrazolyl)borate, at [Fe(TRIS^R)₂]⁺ [81].

^q Estimated from the original $E^\circ(\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}})$ reversible reduction given in [81] by using Lever's equation (6) and assuming a low spin system.

^r As in footnote 'p', but assuming a high-spin system.

S_M and I_M values calculated [35,36] for a higher number of data points than those initially proposed [37]. The corresponding P_L value was then estimated from Eq. (8).

Carbenes (P_L and E_L below -0.4 and 0.5 V vs. NHE, respectively) behave as weaker net electron π -acceptors minus σ -donors than carbynes, η^2 -vinyl, aminocarbyne, CO and bent isocyanides (all of them with P_L values higher than -0.2 V, see above) (Table 2).

The net electron acceptance is rather sensitive to the nature of the groups attached to the carbene carbon as indicated by the quite wide ranges of the estimated P_L and E_L values (over 1.3 and 1.1 V respectively) (Table 5), in the following order: diphenylcarbene ($P_L = -0.40$ V, $E_L = 0.39$ V vs. NHE) > bithiophene-carbenes ($P_L = -0.38$ to -0.62 V, $E_L = 0.41$ – 0.21 V vs. NHE) \geq oxocarbenes C(OR)Y ($P_L = -0.51$ to -0.64 V, $E_L = 0.30$ – 0.19 V vs. NHE) > thiocarbenes C(SR)Y ($P_L = -0.66$ to -0.68 V, $E_L = 0.17$ – 0.15 V vs. NHE) > aminocarbenes C(NRR')Y ($P_L = -0.69$ to -0.80 V, $E_L = 0.15$ – 0.05 V vs. NHE) \geq phosphoylide-aminocarbenes ($P_L = -0.79$ to -0.87 , $E_L = 0.06$ to -0.01 V vs. NHE) > anionic oxocarbenes C(O⁻)Y ($P_L = -1.05$ to -1.71 V, $E_L = -0.16$ to -0.73 V vs. NHE).

The strongest π -electron acceptors, i.e., diphenylcarbene and bithiophene-carbenes, display an extended conjugated π -system, and the above order parallels that of the expected increasing electron donor strength (to the carbene carbon) of the group with the heteroatom: OR < SR < NRR' < O⁻ \cdots NMe₄⁺.

Hydroxocarbene, C(OH)R, can be considered a particular case of an oxocarbene. However, its effective net electron donor character is quite sensitive to the experimental conditions, as observed for C(OH)Ph, in view of the tendency to hydrogen bond, namely with the solvent and with the conjugated base (X⁻) of the acid used in its preparation (protonation by HX of the benzoyl precursor) to form the adduct C(OH \cdots X⁻)Ph.

Hence, the P_L value of the hydroxocarbene can vary from -0.64 V, still within the typical range for oxocarbenes, to -1.00 V due to H-bonding with CF₃COO⁻, as estimated from the oxidation potential values quoted [80] for the [Cr(CO)₅C(OH \cdots X⁻)Ph] species. Nevertheless, the net electron-donor character of the H-bonded hydroxocarbene is still lower than those of the parent benzoyl (COPh⁻) ligand ($P_L = -1.10$ V) and of the anionic oxocarbenes C(O⁻)Y (see below).

A P_L dependence on H-bonding formation has also been recognized [82] for the cyano ligand at a Re^I diphosphinic center.

Phosphoylide-aminocarbenes ($P_L = -0.79$ to -0.87 V [30]) are stronger net electron donors than usual aminocarbenes on account of the electron donation of the ylide to the carbene carbon.

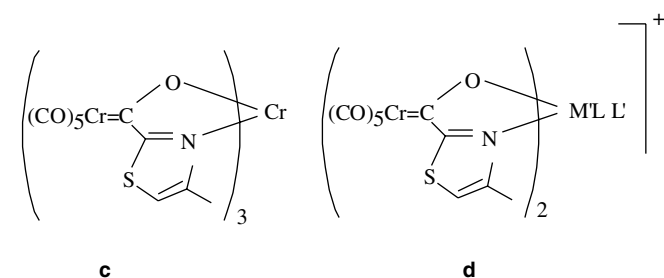
The ferrocenyl-carbene complexes, with the {M(CO)₅} site (M = Cr, W), systematically exhibit lower oxidation potentials than the related carbene complexes with an alkyl or aryl group instead of ferrocenyl. This behavior, which has been observed for ferrocenyl-oxocarbenes, ferrocenyl-

aminocarbenes and anionic ferrocenyl-oxocarbenes, suggests that the ferrocenyl-carbenes are stronger electron-donors than the corresponding alkyl or aryl carbenes, on account of an effective π -electron-donor ability of the ferrocenyl group to the carbene (the ability of ferrocenyl to enter into conjugation with a neighboring center by π -electron donation of the former is known since long [7,83]). However, the estimated P_L (and E_L) values given in Table 5 should be taken cautiously since the HOMO of the [M(ferrocenyl-carbene)(CO)₅] complexes conceivably encompasses both the redox M⁰ and Fe^{II} centers [79] and is not simply localized at the former.

Within each type of carbene ligand, group electronic effects can still be noticed, but in many cases are not pronounced.

The strongest net electron donor carbenes are the anionic ones, C(O⁻)Y ($P_L \leq -1.1$ V), which can behave as more effective donors than other anionic ligands such as halides (P_L ca. -1.2 V [14]), a number of alkynyls (see below) or even OH⁻ ($P_L = -1.55$ V [14]).

The anionic carbene ligands can also ligate a further metal through the carbene oxygen atom [84] and in particular the metaloxycarbene [(CO)₅CrC(O⁻)Y] (Y = 4-methylthiazol-2-yl) can behave as a bidentate N,O-ligand (via also the imine N of the thiazolyl group) to Cr^{III}, Co^{III} and Ni^{III} centers in complexes **c** and **d** (M' = Co, L = 4-methylthiazole, L' = THF. M' = Ni, L = L' = 4-methylthiazole) [78]. In the case of **d** the metal M' was initially in the +2 oxidation state and the complexes were neutral but, since it is oxidized at a lower potential than the Cr⁰ centers, it is already at the +3 oxidation state (cationic complex) at the oxidation potential of the latter. The effect of this further coordination on the anionic carbene ligand is similar to that of alkylation, since the new metaloxycarbene ligand exhibits an estimated P_L value (-0.48 V in **c** or -0.50 V in **d**, based on E_p^{ox} of the quasi-reversible oxidation of the Cr⁰ center) that is identical to that (-0.51 V) obtained for the neutral C(OMe)(4-methylthiazol-2-yl) carbene ligand.



The P_L values of the anionic carbenes are expected to depend, at least slightly, on the counter-ion due to ion-pairing, but such a dependence does not appear to have been investigated, the quoted potentials [78,79] corresponding to complexes with the NMe₄⁺ counter-ion, i.e., C(O⁻ \cdots NMe₄⁺)Y.

Tris(imidazolin-2-ylidene)borate (TRIS^R, R = Me, Et), the C-isomer of tris(pyrazolyl)borate, also behaves as quite

Table 6
Values of the P_L and E_L ligand parameters for vinylidene ligands^a

	P_L/V	Ref.	E_L/V vs. NHE	Ref.
At <i>trans</i> -{ReCl(dppe) ₂ }				
=C=CHCO ₂ R (R = Me, Et)	-0.13 ^b	[29]	0.62 ^c	[29]
=C=CH ₂	-0.21 ^b	[29]	0.56 ^c	[29]
=C=CHPh	-0.25 ^b	[29]	0.52 ^c	[29]
=C=CHC ₆ H ₄ Me-4	-0.26 ^b	[29]	0.51 ^c	[29]
=C=CH ^t Bu	-0.27 ^b	[29]	0.50 ^c	[29]
At <i>trans</i> -{RuCl(LL) ₂ } ⁺ (LL = dppm ^d)				
=C=CHCHPh ₂ ^e	-0.04 ^f	TW	0.70 ^{g,h}	TW
=C=CHC ₆ H ₄ NO ₂ -4	-0.13 ^f	TW	0.62 ^{g,i,j}	TW
	-0.16 ^{e,f}	TW	0.59 ^{e,g,i}	TW
=C=CHC ₆ F ₄ OMe-4	-0.18 ^f	TW	0.58 ^{g,j}	TW
=C=CHC ₆ H ₄ CHO-4	-0.20 ^f	TW	0.56 ^{g,i}	TW
	-0.28 ^{e,f}	TW	0.50 ^{e,g,i}	TW
=C=CHC ₆ H ₄ $\overline{\text{CHO(CH}_2)_3\text{O}}$ -4	-0.23 ^f	TW	0.54 ^{g,k}	TW
=C=CHC ₆ H ₄ C \equiv CC ₆ H ₄ NO ₂ -4,4'	-0.30 ^f	TW	0.48 ^{g,i}	TW
=C=CHPh	-0.35 ^f	TW	0.44 ^{g,i,j}	TW
	-0.42 ^{e,f}	TW	0.38 ^{e,g,i}	TW
=C=CHC ₆ H ₄ CH=CHPh-4	-0.35 ^f	TW	0.44 ^{g,l}	TW
=C=CHC ₆ H ₄ CHO-3	-0.39 ^f	TW	0.40 ^{g,k}	TW
=C=CHC ₆ H ₄ C \equiv CPh-4	-0.39 ^f	TW	0.40 ^{g,i}	TW
=C=CHC ₆ H ₄ CH=CHC ₆ H ₄ NO ₂ -4,4'	-0.52 ^f	TW	0.29 ^{g,i}	TW
	-0.58 ^{e,f}	TW	0.24 ^{e,g,i}	TW
=C=CHC ₆ H ₄ CHO-2	-0.53 ^f	TW	0.28 ^{g,k}	TW
At <i>trans</i> -{RuCl(Me ₂ bipy)(PPh ₃) ₂ } ⁺				
=C=CHPh	-0.35 ^f	TW	0.44 ^{g,m}	TW
	-0.22 ^f	TW	0.55 ^{g,n}	[85]
=C=CHC ₆ H ₄ Me-4	-0.44 ^f	TW	0.36 ^{g,m}	TW
	-0.31 ^f	TW	0.47 ^{g,n}	[85]
At <i>trans</i> -{RhCl(^t PPR ₃) ₂ }				
=C=CPh ₂	0.0 ^f	TW	0.73 ^{g,o}	TW
			0.83 ^{g,p}	[37]
At {Mo(η^7 -C ₇ H ₇)(dppe)} ⁺				
=C=C(Me) ^t Bu	-0.11 ^{b,q}	TW	0.64 ^c	TW

^a Ordered from higher to lower values within each metal center series; TW, this work.

^b Estimated from Pickett's equation (5).

^c Estimated from P_L using Eq. (8).

^d LL = dppm, except when stated otherwise.

^e LL = dppe.

^f Estimated from E_L using Eq. (8).

^g Estimated from Lever's equation (6).

^h Original E° value from [86].

ⁱ Original E^{ox} value from [87] (irreversible wave).

^j Original E^{ox} value from [88] (irreversible wave).

^k Original E^{ox} value from [89] (irreversible wave).

^l Original E^{ox} value from [90] (irreversible wave).

^m Original E° value from [85].

ⁿ Obtained [85] upon a proposed correction of +0.36 V to the measured E° value (vs. SCE) based on the assumption that the measured E° of the dichloro complex [RuCl₂(Me₂bipy)(PPh₃)₂] should be identical to that predicted by using Lever's equation (6).

^o Estimated from the original E° quoted in [37] and by using S_M and I_M values from [35,36] calculated with a higher number of data points (see Table 4).

^p Proposed [37] on the basis of S_M and I_M values obtained from a restricted number of data points (see Table 4).

^q Original E° value from [56].

an effective electron-donor. This is consistent with the negative charge and with X-ray data for the hexacarbene [Fe(TRIS^R)₂]⁺ [81] that indicate the absence of any metal-carbene ligand multiple bond character, i.e., of π -electron release from the metal to the carbene. The Fe^{III/II} redox potential of [Fe(TRIS^R)₂]⁺ [81] was the basis of the estimate of the η^3 -TRIS^R E_L value (-0.02 or -0.06 V vs.

NHE for each coordinating arm, if the complexes are low or high spin, respectively, what has not been indicated). In any case the electron-donor character of TRIS^R does not appear to reach that of tris(pyrazolyl)borate since an E_L value of -0.23 V vs. NHE has been proposed [36] for hydrotris(3,5-dimethylpyrazolyl)borate, identical to that of pyrazolate.

5. Vinylidenes

The electrochemical ligand parameters for vinylidenes (Table 6) have been estimated in two ways: (i) when ligating the *trans*-{ReCl(dppe)₂} center [29], a Rh^I T-shaped center [35–37] or the half-sandwich {Mo(η⁷-C₇H₇)(dppe)}⁺ site [56] (all with known *E*_s and β parameters), *P*_L was directly obtained by using Pickett's equation (5), and *E*_L was derived thereof from relation (8); (ii) when ligating *trans*-{RuCl(LL)₂}⁺ (LL = dppe [86,87], dpmm [88–90] or {RuCl(Me₂bipy)(PPh₃)₂}⁺ [85]) with unknown *E*_s and β values, *E*_L was directly estimated by using Lever's equation (6), and *P*_L was then obtained from expression (8). Method (ii) requires the knowledge of *E*_L for all the ligands of the metal center and that used, along this work, for dpmm (*E*_L = 0.35 V vs. NHE) is now proposed on the basis of various arguments (see Appendix A).

Although a number of the estimated ligand parameters for vinylidenes should be taken cautiously (namely those based on the potentials quoted [87–90] for irreversible oxidation waves of vinylidene complexes with the *trans*-{RuCl(LL)₂}⁺ centers), they generally are consistent with the others based on the potentials of reversible oxidation processes and therefore the set allows some conclusions to be drawn, such as the following ones.

The *P*_L and *E*_L values fall in the ranges from 0 to –0.6 and 0.8–0.2 V vs. NHE, respectively, thus showing that vinylidenes normally behave as stronger net π-electron acceptors minus σ-donors than carbenes which usually exhibit lower *P*_L and *E*_L values (Table 5).

The diphenylvinylidene C=CPh₂ is the most effective π-acceptor, exhibiting a *P*_L value (0.0 V) identical to that of CO. Within the C=CHR vinylidenes, the order of net electron-acceptance, as expected, tends to follow that of the R group, e.g., C₆H₄NO₂-4 > CO₂R > C₆F₄OMe-4, C₆H₄CHO-4 > Ph > C₆H₄Me-4 > tBu. A conjugated phenyl substituent of the yne or ene type appears to lead to an increase of the net electron donor character of the vinylidene. The effect of the substituent (NO₂) tends to decrease with the chain lengthening and is lower for the *meta* or *ortho* positions than for the *para* (CHO).

A possible dependence of the ligand parameters on the binding metal center appears to be recognized for C=CHPh with e.g., the *P*_L value (–0.25 V) at the electron-rich *trans*-{ReCl(dppe)₂} center being higher than that (–0.35 V) at the other less electron-rich sites, suggesting a stronger π-acceptance at the former site.

6. Allenyldenens

The *E*_L parameter for the allenylidene ligands has been estimated in this study by using Lever's equation (6) and *P*_L has then been obtained from the relation (8) between these parameters. However, in the case of the *trans*-{FeBr(depe)₂}⁺ binding center [91], *P*_L could be obtained directly from Pickett's equation (5) and the derived *E*_L values (according to Eq. (8)) were identical to those estimated

by using Lever's equation (6), thus corroborating the agreement of both methods and the validity, for allenyldenens, of the relationship (8) between *P*_L and *E*_L. The estimated values are given in Table 7.

A first overall observation is that they appear to depend on the nature of the binding metal center, increasing in the order *trans*-{FeBr(depe)₂}⁺ < *trans*-{RuCl(LL)₂}⁺ (LL = dppe, depe, dpmm) < *trans*-{OsCl(dpmm)₂}⁺, as shown typically for C=C=CPh₂ (e.g., *P*_L values of –0.32 [89], –0.15 to –0.19, or 0.0 V, respectively). This can reflect a similar order of the net π-electron releasing minus σ-donor accepting ability of the Fe^{II}, Ru^{II} and Os^{II} centers.

A dependence on the binding metal center has been also recognized for isocyanides [27,31,32,42] and related unsaturated ligands such as cyanide [46], nitriles [34], cyanamides [33,51–53] and possibly vinylidenes, as discussed above, and has been interpreted mainly on the basis of π-effects.

Allynyldenens appear to be, as isocyanides, considerable π-electron acceptors and their *P*_L values at *trans*-{FeBr(depe)₂}⁺ (–0.32 to –0.38 V [91]) are close to those of linear isocyanides (–0.33 to –0.44 V [18,31,32,42,49], Table 2). However, they generally behave as weaker net electron-acceptors than vinylidenes, e.g., C=C=CPh₂ exhibiting *P*_L and *E*_L values that are lower than those of C=C=CPh₂ (Table 6).

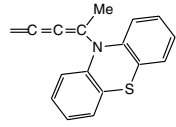
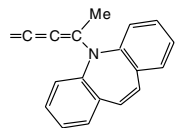
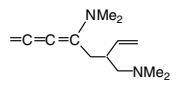
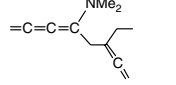
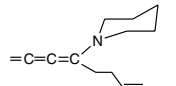
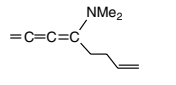
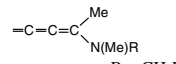
Most of the electrochemical studies of allenylidene complexes have been performed with the *trans*-{RuCl(dpmm)₂}⁺ center [92–96] (in a few cases with the analogous dppe [86,94] or depe [94] sites) which has allowed to establish the following order of net electron acceptance: arylallynyldenens =C=C=CRR' (*P*_L = –0.15 to –0.31 V, *E*_L = 0.61–0.47 V vs. NHE) > selenoallynyldenens =C=C=C(Ser) (alkyl) (*P*_L = –0.22 to –0.26 V, *E*_L = 0.55–0.51 V vs. NHE) > thioallynyldenens =C=C=C(SR)(alkyl) (*P*_L = –0.26 to –0.31 V, *E*_L = 0.51–0.47 V vs. NHE) > aminoallynyldenens (*P*_L = –0.39 to –0.84 V, *E*_L = 0.41–0.0 V vs. NHE), pyrrolyl or indolyl substituted allenylidenens (*P*_L = –0.53 to –0.65 V, *E*_L = 0.28–0.18 V vs. NHE). This order reflects the electronic effects of the groups at the C_γ which are transmitted to the binding metal center through the allenylidene unsaturated carbon chain.

On account of the ability of the amino group for electron release by resonance, the aminoallynyldenens can reach a net electron donor character (*P*_L and *E*_L down to –0.84 and 0.02 V vs. NHE, respectively, for C=C=C(NEt₂)Me) comparable to that of isopropylamine or ammonia (*E*_L = 0.05 or 0.07 V vs. NHE [18], respectively).

On the other extreme of the aminoallynylidene series lie the phenothiazine and aminostilbene derivatives with the highest ligand parameters (*P*_L = –0.39 or –0.41 V, and *E*_L = 0.41 or 0.39 V vs. NHE, respectively). This can be accounted for [95] by the lower basicity of the N atom of the unsaturated heterocycles, rather than by the involvement in the oxidation of the expected electroactive heterocycles.

As a general behavior, an increase of the electron-donor ability of the X group at C_γ, in an allenylidene C=C=C(X)R ligand, results in the relative growth of weight of an alkynyl-

Table 7
Values of the P_L an E_L ligand parameters for allenylidene ligands^a

	P_L	Ref.	E_L / V vs. NHE	Ref.
At <i>trans</i>-{FeBr(depe)₂}⁺				
=C=C=CPh ₂	-0.32 ^b	[92]	0.45 ^{c,d}	[91]
=C=C=C(Me)Ph	-0.35 ^b	[92]	0.42 ^{c,d}	[91]
=C=C=C Et ₂	-0.38 ^b	[92]	0.40 ^{c,d}	[91]
At <i>trans</i>-{RuCl(LL)₂}⁺ (LL = dppm^e)				
<i>Arylallenylidenes</i>				
=C=C=C(C ₆ H ₄ Cl-4) ₂	-0.15 ^f	TW	0.61 ^{c,g}	TW
=C=C=CPh ₂	-0.15 ^f	TW	0.61 ^{c,h}	TW
	-0.19 ^f	TW	0.57 ^{c,g}	TW
	-0.18 ^{i,f}	TW	0.58 ^{c,i,j}	TW
=C=C=C(Me)Ph	-0.18 ^f	TW	0.58 ^{c,h}	TW
=C=C=C(C ₆ H ₄ Me-4) ₂	-0.31 ^f	TW	0.47 ^{c,g}	TW
<i>Selenoallenylidenes</i>				
=C=C=C(SeR)(alkyl)	-0.22 to -0.26 ^f	TW	0.55 to 0.51 ^{c,h}	TW
<i>Thioallenylidenes</i>				
=C=C=C(SR)(alkyl)	-0.26 to -0.31 ^f	TW	0.51 to 0.47 ^{c,h}	TW
<i>Aminoallenylidenes</i>				
	-0.39 to -0.84 ^f	TW	0.41 to 0.0 ^{c,k,l}	TW
	-0.39		-0.41 ^l	
	-0.41		-0.39 ^l	
	-0.55		0.26 ^k	
	-0.62		0.20 ^k	
	-0.65		0.18 ^k	
	-0.66		0.17 ^k	
	-0.58 ⁱ		0.24 ^{ik}	
	-0.54		0.27 ^k	
				
R = CH ₂ Ph	-0.65		0.18 ^l	
Bu ^l	-0.66		0.17 ^l	
9-anthracenylCH ₂	-0.71		0.13 ^l	

(continued on next page)

Table 7 (continued)

	P_L	Ref.	E_L / V vs. NHE	Ref.
	-0.84		0.02 ^l	
<i>Pyrrolyl or indolyl allenylidenes</i>	-0.53 to -0.65 ^f	TW	0.28 to 0.18 ^{c,m}	TW
	-0.53		0.28	
	-0.54		0.27	
	-0.56		0.26	
	-0.59		0.23	
	-0.65		0.18	
<i>At trans-{OsCl(dppm)}₂⁺</i>				
$=C=C=C(C_6H_4Cl-4)_2$	0.08 ^f	TW	0.80 ^{c,g}	TW
$=C=C=CPh_2$	0.01 ^f	TW	0.74 ^{c,g}	TW
$=C=C=C(C_6H_4Me-4)_2$	-0.08 ^f	TW	0.67 ^{c,g}	TW
<i>At trans-{RhCl(PPRⁱ)₂}</i>				
$=C=C=CPh_2$	-0.18 ^f	TW	0.58 ^{c,n} 0.71 ^{c,o}	TW [37]

^a Ordered from higher to lower values within each metal center series; TW, this work.

^b Estimated by using Pickett's equation (5).

^c Estimated by using Lever's equation (6).

^d A comparable value is obtained from P_L by using Eq. (8).

^e LL = dppm, except when stated otherwise.

^f Estimated from E_L by using Eq. (8).

^g Original E° from [92].

^h Original E° from [93].

ⁱ LL = dppe.

^j Original E° from [86].

^k Original E° from [94].

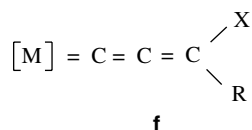
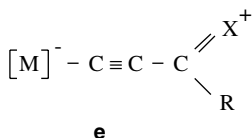
^l Original E° from [95].

^m Original E° from [96].

ⁿ Estimated from the original E° quoted in [37] and by using S_M and I_M values from [35,36] calculated with a higher number of data points (see Table 4).

^o Proposed [37] on the basis of S_M and I_M values obtained from a restricted number of data points (see Table 4).

type resonance form such as **e** with a concomitant decrease of that of a genuine cumulenonic form e.g., **f**. The former (with a considerable contribution, e.g., for X = amino group) has an alkynyl character, consistent (see below) with the stronger electron-donor capacity.



7. Alkynyls

The ligand parameters for alkynyls ligating the *trans*-{FeBr(depe)₂}⁺, *trans*-{RuCl(LL)₂}⁺ (LL = dppm, dppe), {RuCl(Me₂bipy)(PPh₃)₂}⁺ and *trans*-{OsCl(LL)₂}⁺ centers have been estimated in the ways indicated above for the vinylidene and allenylidene ligands, and are collected in Table 8. For the Fe^{II} center, it was possible to apply [91] separately both Pickett's and Lever's equations (5) and (6), thus obtaining independently P_L and E_L , respectively, which follow the relationship (8), showing the agreement

of the two approaches, as observed in the allenylidene cases.

At the $\{\text{WH}_2(\text{dppe})_2\}^+$ center, the $\text{C}\equiv\text{CPh}$ ligand is suggested [5,98] to have P_L and E_L values identical to those of the hydride ligand on account of the identical oxidation potential values for $[\text{WH}_2(\text{C}\equiv\text{CPh})_2(\text{dppe})_2]$ and $[\text{WH}_4(\text{dppe})_2]$.

Although the influence of the metal center cannot be ascertained since cases of a common alkynyl at different sites are rare, it is noteworthy to mention that, for the available comparable cases ($\text{C}\equiv\text{CPh}$ and phenyl-substituted ones), E_L and P_L are significantly higher at $\text{trans}\text{-}\{\text{OsCl}(\text{LL})_2\}^+$ ($\text{LL} = \text{dpmm}, \text{dppe}$) than at $\text{trans}\text{-}\{\text{RuCl}(\text{LL})_2\}^+$, suggesting that the Os^{II} centers are weaker net electron-acceptors than the Ru^{II} sites, in accord with the observed (see above) for the related allenylidene complexes.

Alkynyls are quite strong net electron donors, with P_L and E_L values normally below -1.0 V (down to -1.7 V) and -0.1 V vs. NHE (down to -0.7 V vs. NHE), respectively, in similar ranges to those observed for anionic carbenes (Table 5).

The alkynyls are naturally anionic ligands but those with cationic groups like a phosphonium, as in $\text{C}\equiv\text{C-CPh}_2(\text{PMe}_3^+)$, or an ammonium, as in the 2-ammoniobutenyls $\text{C}\equiv\text{C-C(=CH}_2\text{)(NR}_3^+)$, are overall neutral and also the weakest net electron-donors of the series (P_L from -0.9 to -1.1 V, E_L from -0.1 to -0.3 V vs. NHE). They are followed by the alkynyls with electron-acceptor substituents in the benzenic ring (such as NO_2 , CHO , CN , F or azo $-\text{N}=\text{N}-$) (P_L from -1.1 to -1.3 V, E_L from -0.24 to -0.37 V vs. NHE). As observed for vinylidenes, a conjugated phenyl substituent of the yne or ene type appears to promote the net electron donor character of the alkynyl. The effect of the substituent (NO_2) tends to decrease with the chain lengthening and is lower for the *meta* than for the *para* position (CHO). Nevertheless, substituent effects can also be transmitted along quite extended conjugated systems what is of significance e.g., for the design of species with NLO properties [87–90,100,101].

A good number of data have been collected for butenyls $\text{C}\equiv\text{C-C(=CH}_2\text{)X}^-$ and show that the electronic properties are quite sensitive to the group (X) at the C_γ , indicating that the conjugated 3C-framework of such ligands is able to transmit an X effect to the metal. Hence, the order of net electron release to the metal is as follows: $\text{X} = \text{NR}_3^+ < \text{PR}_3^+ < \text{aromatic} < \text{alkyl}$. In addition, within the 2-ammoniobutenyls ($\text{X} = \text{NR}_3^+$), the more basic amines (NR_3) promote [94,99] the electron donation of the butenyl ligand.

The aminoalkynyls $\text{C}\equiv\text{C-CPh}_2(\text{NR}_2)$ ($\text{R}_2 = \text{H/Me}, \text{Me}_2$), in spite of the two phenyl groups, are within the strongest electron-donors (P_L ca. -1.35 V, E_L ca. -0.5 V vs. NHE [91]) on account of the electron donation, by resonance, of the amino group. The most effective electron-donors are the alkyl-alkynyls $\text{C}\equiv\text{C-R}$ ($P_L = -1.5$ to -1.7 V, $E_L = -0.51$ to -0.74 V vs. NHE)

and the substituted aromatic alkynyls with yne substituents in particular metal derivatives of 1,3,5-triethynylbenzene such as $\text{C}\equiv\text{CC}_6\text{H}_3(\text{C}\equiv\text{CH})\{\text{C}\equiv\text{C-RuCl}(\text{dpmm})_2\}$ ($P_L = -1.5$ V, $E_L = -0.54$ V vs. NHE). However, oxidation to Ru^{III} at this and at the related metalla-alkynyl $\text{C}\equiv\text{CC}_6\text{H}_3(\text{C}\equiv\text{C-Fc})\{\text{C}\equiv\text{C-RuCl}(\text{ppm})_2\}$ has a pronounced effect (increase of E_L by 0.20 or 0.24 V, respectively), the derived oxidized alkynyls $\text{C}\equiv\text{CC}_6\text{H}_3(\text{C}\equiv\text{CX})\{\text{C}\equiv\text{C-Ru}^{\text{III}}\text{Cl}(\text{dpmm})_2\}^+$ ($\text{X} = \text{H}, \text{Fc}$) exhibiting P_L and E_L values that approach those of $\text{C}\equiv\text{CC}_6\text{H}_4\text{CHO-4}$ and $\text{C}\equiv\text{CC}_6\text{H}_4\text{NO}_2\text{-4}$ with the strong electron-acceptor formyl or nitro groups. A similar effect occurs upon Os^{II} oxidation of $\text{C}\equiv\text{CC}_6\text{H}_3(\text{C}\equiv\text{CX})\{\text{C}\equiv\text{C-OsCl}(\text{dpmm})_2\}$ and it shows that there is an electronic communication between the Ru or Os center (via a diethynylbenzene framework) and the metal to which the metalla-alkynyl is coordinated.

Another aspect to be considered is the nature of the redox center. Both Lever's and Pickett's models assume the oxidation is centered at the metal, but dramatic changes in the oxidation potential can result when the redox center shifts to a ligand. Hence, at the luminescent Re^{I} bipyridine alkynyl complexes $[\text{Re}(\text{C}\equiv\text{CR})(\text{bpy})(\text{CO})_3]$ [104] and $[\text{Re}(\text{C}\equiv\text{CR})(\text{Me}_2\text{by})(\text{CO})_3]$ [105] ($\text{R} = \text{Ph}$, substituted phenyl, thiophene, bithiophene, pyridyl-W(CO)₅, dienyl), the HOMO has been shown [104,105] to be mainly localized at the alkynyl ligand rather than at the metal, being the antibonding combination of $\pi(\text{Re})$ with $\pi(\text{C}\equiv\text{CR})$ orbitals. Therefore, it is not surprising that the estimated E_L values (in the -0.33 to -0.84 V vs. NHE range) appear anomalous, e.g., -0.62 V vs. NHE for $\text{C}\equiv\text{CPh}^-$ which is a rather low value in accord with a destabilized HOMO. The irreversible character of the oxidation waves for these bipyridine alkynyl complexes can provide a further reason for the anomalies.

8. Final remarks

The establishment of redox potential-structure relationships, in Coordination and Organometallic Chemistries, of the types we have discussed, allow the development of electrochemical approaches to quantify the net electron donor/acceptor character of ligands and electronic features of their binding metal centers. A variety of ligands has already been studied in this way, but those of the present study, i.e., carbynes, carbenes, vinylidenes, allenylidenes and alkynyls had only been scarcely investigated under such an approach. It is expected that this work shows that these relevant types of ligands in Organometallic Chemistry are also subject to that type of electrochemical study (as illustrated, often for the first time, for ca. 135 ligands) which should complement the rich chemistry already developed.

In quite general terms and for similar organic groups and substituents, these ligands, in terms of their P_L and E_L values, can be ordered according to their *net* π -electron acceptance minus σ -donor character as follows: carbynes >

Table 8
Values of the P_L and E_L ligand parameters for alkynyl ligands^a

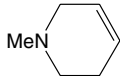
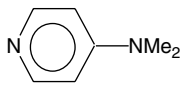
	P_L	Ref.	E_L/V vs. NHE	Ref.
At <i>trans</i> -{FeBr(depe) ₂ } ^{+b}				
–C≡C–CPh ₂ (PMe ₃) ^c	–1.08 ^d	[91]	–0.28 ^{e,f}	[91]
–C≡C–CPh ₂ (C≡N)	–1.18 ^d	[91]	–0.27 ^{e,f}	[91]
–C≡C–C(=CH ₂)Ph	–1.25 ^d	[91,97]	–0.33 ^{e,f}	[91,97]
–C≡C–CHPh ₂	–1.32 ^d	[91]	–0.38 ^{e,f}	[5,91,97]
–C≡C–C(=CHMe)Et	–1.34 ^d	[91]	–0.40 ^{e,f}	[91]
–C≡C–CPh ₂ (NHMe)	–1.34 ^d	[91]	–0.47 ^{e,f}	[91]
–C≡C–CPh ₂ (NMe ₂)	–1.35 ^d	[91]	–0.49 ^{e,f}	[91]
At <i>trans</i> -{RuCl(LL) ₂ } ^{+ (LL = dppm)^g}				
<i>2-ammoniobutenyls</i>				
–C≡C–C(=CH ₂)(NR ₃) ⁺	–0.9 to –1.1 ^h	TW	–0.1 to –0.2 ^e	TW
NR ₃ ⁺				
Me ₂ NCH ₂ C≡CEt	–0.93		–0.06 ⁱ	
Me ₃ NCH ₂ Ph	–0.94		–0.07 ^j	
NEt ₃	–0.95		–0.08 ⁱ	
EtN(C ₂ H ₄) ₂ O	–0.95		–0.08 ^j	
	–0.95		–0.08 ⁱ	
Me ₂ NCH ₂ C ₆ H ₄ OMe-3	–0.96		–0.09 ^j	
NPr ₃	–1.02		–0.14 ^j	
Quinuclidine	–1.02		–0.14 ^j	
	–1.08		–0.19 ^j	
–C≡CC ₆ H ₄ NO ₂ -4	–1.14 ^h	TW	–0.24 ^{e,k}	TW
	–1.16 ^{h,l}	TW	–0.26 ^{e,k,l}	TW
–C≡CC ₆ H ₄ CHO-4	–1.21 ^h	TW	–0.30 ^{e,k}	TW
	–1.23 ^{h,l}	TW	–0.32 ^{e,k,l}	TW
–C≡CC ₆ F ₄ OMe-4	–1.26 ^h	TW	–0.34 ^{e,m}	TW
–C≡CC ₆ H ₄ N=NC ₆ H ₄ NO ₂ -4,4'	–1.26 ^h	TW	–0.35 ^{e,n}	TW
–C≡CC ₆ H ₄ CHO-3	–1.29 ^h	TW	–0.37 ^{e,o}	TW
–C≡CC ₆ H ₄ C≡CPh-4	–1.34 ^h	TW	–0.41 ^{e,k}	TW
	–1.29 ^h	TW	–0.37 ^{e,l,p,q}	TW
–C≡CC ₆ H ₃ (C≡CH) ₂ -1,3,5	–1.31 ^h	TW	–0.39 ^{e,r}	TW
–C≡CC ₆ H ₃ (C≡CFc) ₂ -1,3,5	–1.31 ^h	TW	–0.39 ^{e,r}	TW
–C≡CC ₆ H ₄ C≡CC ₆ H ₄ NO ₂ -4,4'	–1.33 ^h	TW	–0.40 ^{e,k}	TW
–C≡CC ₆ H ₄ CH=CHC ₆ H ₄ NO ₂ -4,4'	–1.34 ^h	TW	–0.41 ^{e,k}	TW
	–1.40 ^{h,l}	TW	–0.46 ^{e,k,l}	TW
–C≡CPh	–1.34 ^h	TW	–0.41 ^e	TW
	–1.40 ^{h,l}	TW	–0.46 ^{e,k,l}	TW
–C≡C–CHPh ₂	–1.35 ^{h,l}	TW	–0.42 ^{e,l,s}	TW
–C≡CC ₆ H ₄ C≡CC ₆ H ₄ C≡CC ₆ H ₄ NO ₂ -4,4',4''	–1.36 ^h	TW	–0.43 ^{e,k}	TW
–C≡CC ₆ H ₄ CHO(CH ₂) ₃ O-4	–1.40 ^h	TW	–0.46 ^{e,o}	TW
–C≡CC ₆ H ₄ CH=CHPh	–1.46 ^h	TW	–0.51 ^{e,t}	TW
	–1.44 ^{h,l}	TW	–0.50 ^{e,l,t}	TW
–C≡CC ₆ H ₃ (C≡CFc){C≡C–RuCl(dppm) ₂ } ⁿ -1,3,5				
<i>n</i> = 0 (Ru ^{II})	–1.45 ^h	TW	–0.50 ^{e,r}	TW
<i>n</i> = +1 (Ru ^{III})	–1.17 ^h	TW	–0.26 ^{e,r}	TW
–C≡CMe	–1.46 ^{h,l}	TW	–0.51 ^{e,l,s}	TW
–C≡CPr ⁱ	–1.46 ^{h,l}	TW	–0.51 ^{e,l,s}	TW
–C≡CC ₆ H ₃ (C≡CH){C≡C–RuCl(dppm) ₂ } ⁿ -1,3,5				
<i>n</i> = 0 (Ru ^{II})	–1.49 ^h	TW	–0.54 ^{e,r}	TW
<i>n</i> = +1 (Ru ^{III})	–1.25 ^h	TW	–0.34 ^{e,r}	TW
At {RuCl(Me ₂ bipy)(PPh ₃) ₂ } ⁺				
–C≡CPh	–1.59 ^h	TW	–0.62 ^{e,u}	TW

Table 8 (continued)

	P_L	Ref.	E_L/V vs. NHE	Ref.
–C≡CC ₆ H ₄ Me-4	–1.42 ^h	TW	–0.48 ^{e,v}	[85]
	–1.62 ^h	TW	–0.65 ^{e,u}	TW
	–1.46 ^h	TW	–0.51 ^{e,v}	[85]
–C≡CBu ^t	–1.73 ^h	TW	–0.74 ^{e,u}	TW
	–1.56 ^h	TW	–0.60 ^{e,v}	[85]
At <i>trans</i> -{OsCl(LL) ₂ } ⁺ (LL = dpmm) ^b				
–C≡CC ₆ H ₃ (C≡CH) ₂ -1,3,5	–1.09 ^h	TW	–0.20 ^{e,r}	TW
–C≡CC ₆ H ₃ (C≡CFc) ₂ -1,3,5	–1.09 ^h	TW	–0.20 ^{e,r}	TW
–C≡CC ₆ H ₄ C≡CPh-4	–1.11 ^{h,i}	TW	–0.21 ^{e,l,w}	TW
–C≡CPh	–1.14 ^{h,i}	TW	–0.24 ^{e,l,w}	TW
–C≡CC ₆ H ₃ (C≡CFc){C≡C–OsCl(dpmm) ₂ } ⁿ -1, 3, 5				
<i>n</i> = 0 (Os ^{II})	–1.22 ^h	TW	–0.31 ^{e,r}	TW
<i>n</i> = +1 (Os ^{III})	–1.00 ^h	TW	–0.12 ^{e,r}	TW
–C≡CC ₆ H ₃ (C≡CH){C≡C–OsCl(dpmm) ₂ } ⁿ -1, 3, 5				
<i>n</i> = 0 (Os ^{II})	–1.26 ^h	TW	–0.34 ^{e,r}	TW
<i>n</i> = +1 (Os ^{III})	–1.05 ^h	TW	–0.16 ^{e,r}	TW
At {WH ₂ (dppe) ₂ } ⁺				
–C≡CPh	–1.22 ^p	[5,98]	–0.30 ^{w,x}	[5,98]

^a Ordered from higher to lower values within each metal center series; TW, this work.

^b Unless stated otherwise.

^c At *trans*-{Fe(NCMe)(depe)₂}²⁺.

^d Estimated from Pickett's equation (5).

^e Estimated from Lever's equation (6).

^f A comparable value is obtained from P_L using Eq. (8).

^g LL = dpmm unless stated otherwise.

^h Estimated from E_L by using Eq. (8).

ⁱ Original E° value from [94].

^j Original E° value from [99].

^k Original E° value from [87].

^l LL = dppe.

^m Original E° value from [88].

ⁿ Original E° value from [100].

^o Original E° value from [99].

^p Original E° value from [101].

^q Average value (identical to that of –C≡CPh) for the *trans*-{RuCl(dppe)₂}⁺ and *trans*-{Ru(C≡CPh)(dppe)₂}⁺ centers.

^r Original E° value from [102] upon conversion (+0.135 V) to our conditions with $E^\circ(\text{FcH}^{0/+})$ (CH₂Cl₂) = 0.525 V vs. SCE rather than 0.39 V vs. SCE.

^s Original E° value from [86].

^t Original E° value from [90].

^u Original E° value from [85].

^v Obtained [85] upon a proposed correction of +0.36 V to the measured E° value (vs. SCE) based on the assumption that the measured E° of the dichloro complex [RuCl₂(Me₂ bipy)(PPh₃)₂] should be identical to that predicted by using Lever's equation (6).

^w Original E° value from [103].

^x P_L and E_L values considered identical to those of hydride on account of the identical E° values shown by [WH₂(C≡CPh)₂(dppe)₂] and [WH₄(dppe)₂].

aminocarbene > CO > vinylidenes > allenylidenes > carbenes > alkynyls.

The ordering of the members within each type of these ligands, as determined by substituent effects, has also been discussed above.

The electrochemical approach is based on the dependence of the redox potential on ligand and metal site effects which usually are considered to be independent and added according to additive models. However, the additivity hypothesis can present limitations, in particular when synergisms (among the ligands and/or between them and the metal) occur, the ligand effects depend on the binding metal centers or the metal effects depend on the ligands. The maximum additivity is considered in the Lever's model which also exhibits the highest generality, but is often not sensitive to subtle structure/composition changes. The mini-

imum additivity is followed by the Pickett's model (only one L ligand is separated from the metal center {M_s} which comprises all the other ligands) which thus has a lower generality but can answer in a better way to those changes including isomeric ones.

The possibility of dependence of the ligand parameters on the binding metal centers has been recognized in this work for some of the ligands under study and therefore the estimated P_L and E_L values have been grouped, within the Tables, according to the type of metal site. Further studies, when more data will be available, should allow to clarify this point.

Another aspect concerns the accuracy of the proposed P_L and E_L values. Often they have been derived from a single complex and therefore a statistical analysis is not possible. If one assumes a maximum error of ±0.02 V for the

values of the redox potential, than P_L , as estimated from its definition equation (4), should display an associated maximum error of ± 0.04 V. This error can increase if P_L is estimated from Eq. (5). A lower accuracy is expected for the estimate of E_L from the general equation (6): if one assumes a maximum error of ± 0.02 V (although it can be higher) for each of the other eight electrochemical parameters values, including those of the five co-ligands, a typical maximum error of ± 0.14 V can be expected for the estimated E_L value. The use of more complexes (when available) for each of the ligands under study in order to get a more accurate P_L or E_L average value is thus highly recommended.

The nature and composition of the redox orbital also deserve a closer attention, in particular by using theoretical calculation methods, since different sets of parameters values are expected when that orbital is not mainly centered at the metal.

Initially, both models were only applied to octahedral-type (usually closed shell 18-electron) complexes but extensions to other structures and different electron-counts have already been achieved for particular cases and are expected to be further developed. In particular, half-sandwich complexes are highly attractive in view of the available high number of such complexes with carbenes and related ligands, and their interesting chemistry.

We have discussed the estimate of the ligand parameters from the redox potential of some of their complexes, but conversely once those parameters are known they can be applied to predict the redox potential of other complexes with those ligands, and this predictive value of such parameters should not be discarded.

Hopefully, relationships between the above electrochemical parameters and other properties (e.g., spectroscopic and reactivity) of the carbenes and related ligands will be recognized in the future.

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Appendix A. Proposal of a new E_L value for dppm

In spite of the usual similarity [87,90,94] of the oxidation potentials of the homologous complexes with $trans\text{-}\{RuCl(LL)_2\}^+$ ($LL = dppm, dppe$), the estimated E_L values for vinylidenes, allenylidenes or alkynyls at the dppm site, by using Lever's equation (6) and the quoted [18] E_L values for the diphosphines and chloride ligands, appeared remarkably lower than those at other diphosphine centers, such as $trans\text{-}\{RuCl(dppe)_2\}^+$, $trans\text{-}\{FeBr(depe)_2\}^+$ or $trans\text{-}\{ReCl(dppe)_2\}$.

This is suggestive of using a too high value for the E_L parameter for dppm (0.43 V vs. NHE [18]), when applying Lever's equation (6), what is corroborated by the quite considerably higher estimated oxidation potential (1.16 V vs. NHE) of the dichloro complex $trans\text{-}[ReCl_2(dppm)_2]$, by considering the above E_L value, in comparison with the observed potential (0.83 V vs. NHE) [87].

Further support comes from a comparison of the E_L values for the related arsines which shows that $Ph_2AsCH_2AsPh_2$ has a lower E_L value (0.35 V vs. NHE) than $Ph_2AsCH_2CH_2AsPh_2$ (0.44 V vs. NHE) [18], in contrast with the higher quoted value for $Ph_2PCH_2PPh_2$ (0.43 V vs. NHE) relatively to that of $Ph_2PCH_2CH_2PPh_2$ (0.36 V vs. NHE).

Therefore, we propose a corrected E_L value for dppm of 0.35 V vs. NHE obtained as shown below by comparing the reversible oxidation potentials (Table S1) of the homolugous Ru^{II} complexes $trans\text{-}[RuCl(LL)_2]^+$ [$LL = dppm, dppe$; $L = Cl^-$ [87], $C\equiv CPh^-$ [87], $C\equiv CC_6H_4CHO-4$ [87], $C\equiv CC_6H_4NO_2-4$ [87], $C\equiv CC_6H_4CH=CHPh$ [90], $C=C=C(NMe_2)(CH_2CH_2CH=CH_2)$ [94]]. The dppm complexes exhibit an oxidation potential that, on the average, is by 0.04 V lower than that of the homologous dppe ones. Applying Lever's equation (6) to this relation affords Eq. (A) from which, upon simplification, one gets (B), i.e., $E_L(dppm) = 0.35$ V vs. NHE once $E_L(dppe) = 0.36$ V vs. NHE and $S_M = 0.97$ [18]

$$S_M[4E_L(dppm) + E_L(Cl^-) + E_L(L)] + I_M = S_M[4E_L(dppe) + E_L(Cl^-) + E_L(L)] + I_M - 0.04, \quad (A)$$

$$S_ME_L(dppm) = S_ME_L(dppe) - 0.01. \quad (B)$$

By considering the corrected $E_L(dppe) = 0.35$ V vs. NHE, we have obtained E_L values for vinylidene, allenylidene and alkynyl ligands that normally are comparable with those estimated for other metal centers without dppm.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.07.111](https://doi.org/10.1016/j.jorganchem.2005.07.111).

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