Theoretical study of redox induced isomerizations, structure and bonding of nitrile, isocyanide and carbonyl complexes of rhenium

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Quantum chemical calculations at the B3LYP level of theory have been performed on the *trans*- and *cis*-isomers of nitrile, isocyanide and carbonyl phosphinic chloro-complexes and dinitrile complexes of rhenium (as well as on their mono- and dioxidized forms) *trans-/cis*-[ReClL(PH$_3$)$_4$]$^{n+}$ (L = NCCH$_3$, CNCH$_3$, CO; $n = 0$–2) and *trans-/cis*-[Re(NCCH$_3$)$_2$(PH$_3$)$_4$]$^{m+}$ ($m = 1$–3), taken as models of the corresponding real species *trans-/cis*-[ReClL(dppe)$_2$]$^{n+}$ (L = NCR, CNR, CO) and *trans-/cis*-[Re(NCR)$_2$(dppe)$_2$]$^{m+}$, allowing the interpretation of the influence of the electronic structure, of the electron π-acceptor/σ-donor character and the nature of the ligand L, and of the electron releasing/acceptor ability of the binding metal centre on the structural, spectral, chemical (towards protonation) and redox properties and on the relative stability of the geometrical isomers, thus providing also a rationale for electron-transfer induced geometrical isomerizations. For the non-oxidized forms, the *cis*-isomers are more stable than the respective *trans*-isomers for the complexes with the relatively weak π-acceptor acetonitrile ligand while for the stronger π-acceptor ligands, *i.e.* isocyanide and carbonyl, the latter isomers are more stable than the former. The oxidation results in the inversion of the relative stability as well as of the relative values of the ionization potentials for the *trans*- and *cis*-isomers. The nature of the coordination bond is also investigated using the natural bond orbital (NBO) method and the charge decomposition analysis (CDA).

Introduction

Theoretical methods of quantum chemistry provide convenient tools for the interpretation of the structural, spectral and electrochemical properties of complexes, and for understanding the nature of their coordination bonds and the driving forces of their chemical reactions, and can also play an important predictable role namely in the cases of unstable compounds or intermediates which are not easily accessible by experimental methods. In particular, theoretical studies of transition metal complexes with small unsaturated molecules such as carbonyl,[1–7] carbenes, vinylidenes or carbynes[1j,3,8–11] and π-bonded ligands[11a,b,12–15] have been carried out extensively during the last decade, resulting in numerous articles and series of reviews.[16] However, the detailed quantum chemical investigations of nitrile[3,17,18] and isocyanide[3,17b,19,20] transition metal complexes are still scarce.

Moreover, within the multiplicity of possible reactions of such complexes, structural changes induced by electron-transfer (ET), without requiring any further reagent, constitute a conceptually "simple" type. It has relevant biological significance and has been a matter of growing and current interest, being particularly amenable to electrochemical investigations which have already been reviewed.[21,22] Such a type of reactions also constitutes an open field for theoretical studies which, however, still remains virtually unexplored. In particular, for the most electrochemically studied octahedral-type complexes, although ET-promoted geometrical isomerizations, the relative isomeric stability and the redox behaviours of the isomers are known to depend on factors such as the electronic configuration of the metal and the electron donor/acceptor character of the ligands, systematic studies and general rationalizations are still lacking, the matter being also the subject of considerable debate in a number of cases involving, *e.g.* differing semiempirical predictions of the redox potentials,[1m] theoretical calculations[1l,23] and experimental observations.[24,25]

Hence, a theoretical study of series of complexes that are known to undergo such a type of reactions appears timely, and we have performed a DFT study on models of the series of nitrile, isocyanide and carbonyl rhenium phosphine complexes *trans-/cis*-[ReCl(L)(dppe)$_2$] (L = NCR, CNR or CO; dppe =

Ph$_2$PCH$_2$CH$_2$PPh$_2$) and *trans-/cis*-[Re(NCR)$_2$(dppe)$_2$]$^+$, whose electrochemical behaviours and ET-induced isomerizations have been investigated[26–31] in a systematic way, in our laboratory. We now report the results of this theoretical study, undertaken for the corresponding complex models and oxidized forms *trans-/cis*-[ReCl(L)(PH$_3$)$_4$]$^{n+}$ (L = NCCH$_3$, CNCH$_3$ or CO; $n = 0$–2) and *trans-/cis*-[Re(NCCH$_3$)$_2$(PH$_3$)$_4$]$^{m+}$ ($m = 1$–3), that includes the geometry optimization at the B3LYP level of theory, the analysis of the MO composition, the relative stability of the geometrical isomers, their structural and redox properties and the nature of the coordination bonds. It provides also an interpretation for the experimental success or failure to obtain some of the members of the series (or to convert them into others) and for the observed electrochemical behaviours, in particular the relative redox potentials and the ET-induced isomerizations.

Computational details

The full geometry optimization of model fragments has been carried out at the DFT level of theory using a quasi-relativistic effective core potentials (ECPs)[32] with help of the Gaussian-98[33] package. The calculations have been performed using Becke's three-parameter hybrid exchange functional[34] in combination with the gradient-corrected correlation functional of Lee, Yang and Parr[35] (B3LYP). The restricted approximations for the structures with closed electron shells and the unrestricted methods for the structures with open electron shells have been employed. For all the dioxidized structures, both singlet and triplet spin states have been calculated at the restricted and unrestricted B3LYP level, respectively. The Hessian matrix, the harmonic vibrational frequencies and the corresponding zero-point vibrational energies (ZPE) have been estimated analytically for all structures which correspond to minima on the potential surface (for all structures there are no imaginary frequencies). A quasi-relativistic Stuttgart pseudo-potential described 60 core electrons and the appropriate contracted basis set (8s7p6d)/[6s5p3d][36] for the rhenium atom were used. For other non-hydrogen atoms, the analogous pseudo-potentials and basis sets[37] were applied. The standard basis set
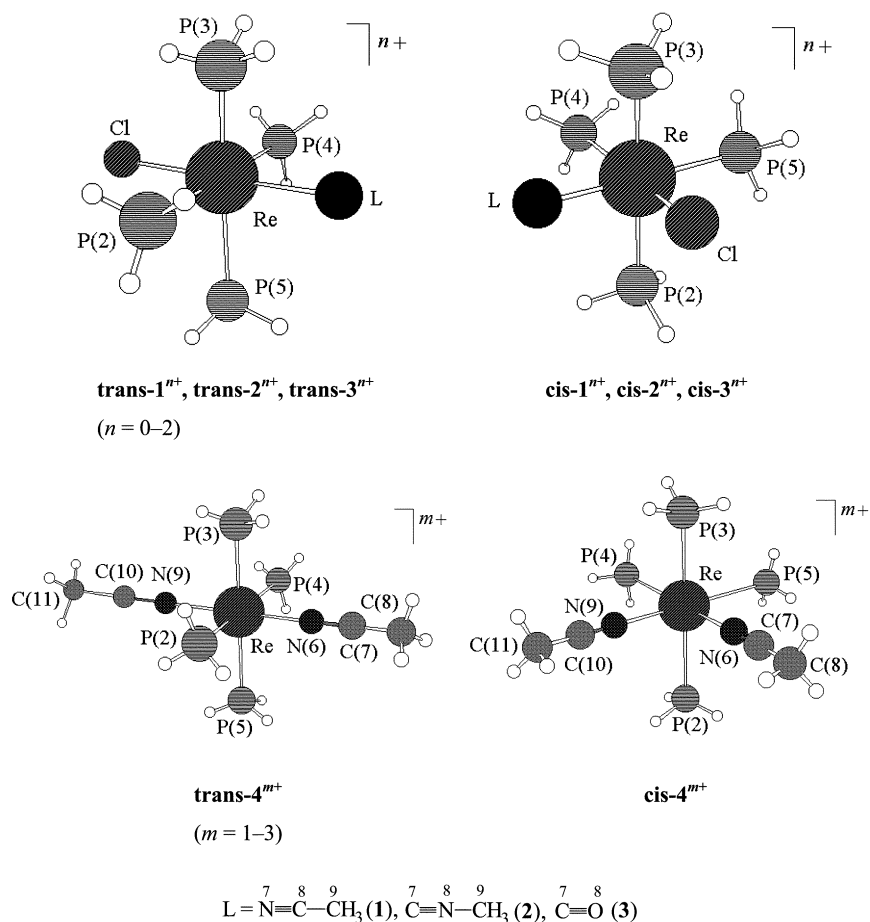
trans-1^{n+}**, trans-2**$^{n+}$**, trans-3**$^{n+}$
(n = 0–2)

cis-1^{n+}**, cis-2**$^{n+}$**, cis-3**$^{n+}$

trans-4^{m+}
(m = 1–3)

cis-4^{m+}

$$L = \overset{7}{N} \equiv \overset{8}{C} - \overset{9}{C}H_3 \; (\mathbf{1}), \; \overset{7}{C} \equiv \overset{8}{N} - \overset{9}{C}H_3 \; (\mathbf{2}), \; \overset{7}{C} \equiv \overset{8}{O} \; (\mathbf{3})$$

Fig. 1 Model complexes *trans-/cis*-[ReCl(L)(PH$_3$)$_4$]$^{n+}$ (L = NCCH$_3$ **1**, CNCH$_3$ **2** or CO **3**; n = 0–2) and *trans-/cis*-[Re(NCCH$_3$)$_2$(PH$_3$)$_4$]$^{m+}$ (**4**, m = 1–3).

of Gauss functions 6-31G[38] was selected for the hydrogen atoms.

The hypothetical complexes *trans-/cis*-[ReCl(L)(PH$_3$)$_4$]$^{n+}$ (L = NCCH$_3$ **1**, CNCH$_3$ **2** or CO **3**; n = 0–2) and *trans-/cis*-[Re(NCCH$_3$)$_2$(PH$_3$)$_4$]$^{m+}$ (**4**, m = 1–3) were chosen, for our calculations, as model compounds of the real ones, *trans-/cis*-[ReCl(L)(dppe)$_2$]$^{n+}$ and *trans-/cis*-[Re(NCCH$_3$)$_2$(dppe)$_2$]$^{m+}$. Symmetry operations were not applied for all structures.

The bonding nature in the complexes has been studied with the help of the natural bond orbital (NBO) partitioning scheme.[39] The analysis of the relative contribution of the ligand-to-metal donation and metal-to-ligand back-donation terms has been performed for the closed-shell structures by the CDA method of Dapprich and Frenking[40] with the help of the CDA 2.1 program.[41]

For comparative purposes, the calculations were also performed at HF//HF and MP2//HF levels of theory. The results obtained are coherent with those of the DFT calculations and are not discussed.

Results and discussion

Structure of the complexes

The calculations demonstrate that, for all the dioxidized (d^4) species, the triplet state appears to be more stable than the singlet one by 8.7–21.6 kcal mol^{-1}, and only the former is further discussed. The coordinational polyhedra of all the model complexes [ReCl(L)(PH$_3$)$_4$]$^{n+}$ (L = NCCH$_3$ **1**, CNCH$_3$ **2** or CO **3**) and [Re(NCCH$_3$)$_2$(PH$_3$)$_4$]$^{m+}$ **4** (Fig. 1) correspond to octahedra, the maximum deviation of the *trans*-ligand–Re–ligand angles from 180° not exceeding 10°. For both the *trans*-**2** and *cis*-**2** complexes, a bent isocyanide ligand structure (CNC angle of 148.7 and 157.0°, respectively) was found, while the linear

ligand geometry is predicted for the other compounds. This agrees with experimental X-ray data that indicate a bent ligand geometry for *trans*-[ReCl(CNCH$_3$)(dppe)$_2$] (CNC angle of 139.4(10)°)[42] and the linear one for *trans*-[ReCl(NCCH$_3$)-(dppe)$_2$],[43] *cis*-[ReCl(NCC$_6$H$_4$OMe-4)(dppe)$_2$]$^+$ (ref. 44) and *trans*- or *cis*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$]$^+$.[24,45]

The higher stability of a bent CNR structure (**a**), relatively to the linear one (**b**), was predicted theoretically previously,[19a,46] when the isocyanide ligates an electron-rich metal centre (such as the Re^I of this study) with a strong π-electron releasing ability. The π-back bonding component should then play a significant role and the metal–carbon bond acquires some double bond character, with a resulting bending at the N atom and localization therein of an electron lone pair (structure **a**). Upon oxidation, the π-electron releasing character of the metal centre falls and, for the oxidized complexes of Re^{II} and Re^{III}, the linear structure **b** becomes the more stable one, as indicated by the theoretical calculations.

$$M = C = \overset{..}{N} \diagdown_R \qquad M - C \equiv N - R$$
$$\;\;\;\;\;\;\; \mathbf{a} \; \mathbf{b}$$

The calculated Re–Cl, Re–P and Re–L (for *trans*-**1** and *trans*-**2**) bond lengths are higher, by 0.011–0.095 Å, than the corresponding experimental data for the above similar complexes with dppe ligands (Table 1).[31,42–45] For *cis*-**1**, *trans*-**3** and *trans*-**4+**, the Re–L bond is shorter by 0.010–0.067 Å than that in the real complexes. The calculated bond lengths within the ligands L are in a good agreement (often within the 3σ dispersion) with the experimental values, except the C≡O distance in the *trans*-isomer of the carbonyl complex (1.203 Å) in view of the unusually short experimental value for *trans*-[ReCl-(CO)(dppe)$_2$] (1.003(7) Å[31]) when compared with other rhenium

Table 1 Selected bond lengths (Å) of the calculated structures. Experimental values for some of the complexes are also given (in square brackets) for comparison

	trans-**1**[a]	*trans*-**1+**	*trans*-**1++**
Re–Cl	2.626 [2.531(2)]	2.490	2.370
Re–P	2.430 [2.374(2)–2.420(2)]	2.491–2.492	2.556
Re–N	1.989 [1.978(5)]	2.033	2.080
C–N	1.181 [1.141(9)]	1.173	1.168
C–C	1.460 [1.480(11)]	1.458	1.453
	cis-**1**	*cis*-**1+**[b]	*cis*-**1++**
Re–Cl	2.611	2.482 [2.471(13)]	2.365
Re–P(2), Re–P(3)	2.428, 2.430	2.466, 2.468 [2.426(13), 2.446(13)]	2.554, 2.555
Re–P(4)	2.372	2.487 [2.396(13)]	2.608
Re–P(5)	2.446	2.525 [2.450(13)]	2.551
Re–N	2.020	2.056 [2.076(13)]	2.089
C–N	1.172	1.167 [1.147(15)]	1.166
C–C	1.459	1.457 [1.416(17)]	1.455
	trans-**2**[c]	*trans*-**2+**	*trans*-**2++**
Re–Cl	2.641 [2.607(5)]	2.495	2.367
Re–P	2.438, 2.439 [2.40 av]	2.495–2.496	2.556
Re–C	1.930 [1.861(12)]	2.000	2.097
C(7)–N(8)	1.204 [1.210(15)]	1.186	1.170
N(8)–C(9)	1.420 [1.417(17)]	1.434	1.447
	cis-**2**	*cis*-**2+**	*cis*-**2++**
Re–Cl	2.617	2.480	2.359
Re–P(2), Re–P(3)	2.435, 2.436	2.514, 2.516	2.560, 2.563
Re–P(4)	2.384	2.492	2.612
Re–P(5)	2.512	2.541	2.601
Re–C	1.955	1.992	2.056
C(7)–N(8)	1.202	1.183	1.171
N(8)–C(9)	1.433	1.435	1.446
	trans-**3**[d]	*trans*-**3+**	*trans*-**3++**
Re–Cl	2.622 [2.542(2)]	2.496	2.376
Re–P	2.453 [2.387(2)–2.443(2)]	2.516–2.522	2.569–2.588
Re–C	1.877 [1.944(8)]	1.928	2.013
C–O	1.203 [1.003(7)]	1.180	1.158
	cis-**3**	*cis*-**3+**	*cis*-**3++**
Re–Cl	2.597	2.460	2.349
Re–P(2), Re–P(3)	2.450	2.533, 2.535	2.579
Re–P(4)	2.401	2.516	2.615
Re–P(5)	2.554	2.584	2.610
Re–C	1.902	1.916	2.000
C–O	1.194	1.179	1.157
	trans-**4+**[e]	*trans*-**4++**	*trans*-**4+++**
Re–P	2.453 [2.392(3), 2.409(2)]	2.516	2.587
Re–N	2.053 [2.063(7)]	2.071	2.067
C–N	1.172 [1.102(13)]	1.169	1.171
C–C	1.460 [1.417(14)]	1.456	1.448
	cis-**4+**[f]	*cis*-**4++**	*cis*-**4+++**
Re–P(2), Re–P(3)	2.455 [2.375(6), 2.384(6)]	2.540, 2.548	2.586
Re–P(4), Re–P(5)	2.451 [2.367(6), 2.368(5)]	2.507, 2.508	2.595
Re–N	2.051 [2.05(2), 2.08(2)]	2.081	2.082
C–N	1.171 [1.11(2), 1.14(2)]	1.168	1.170
C–C	1.460 [1.44(1), 1.50(1)]	1.458	1.451
Free ligands	NCCH$_3$	CNCH$_3$	CO
C≡N/C≡O	1.167	1.182	1.152

[a] *trans*-[ReCl(NCCH$_3$)(dppe)$_2$].   [b] *cis*-[ReCl(NCC$_6$H$_4$OMe-4)(dppe)$_2$][BF$_4$].   [c] *trans*-[ReCl(CNCH$_3$)(dppe)$_2$].   [d] *trans*-[ReCl(CO)(dppe)$_2$]. [e] *trans*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$]$^+$. [f] *cis*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$]$^+$.

Table 2 Calculated total energies E_{tot} (Hartree), relative energies, E_{rel} (kcal mol^{-1}) and zero-point energies, ZPEs (kcal mol^{-1})

	E_{tot}	E_{rel}[a]	ZPE		E_{tot}	E_{rel}[a]	ZPE
trans-**1**	−149.685668	0.0	96.26	*trans*-**3**	−148.371305	0.0	72.86
cis-**1**	−149.687592	−1.21 (−1.08)	96.39	*cis*-**3**	−148.355374	+10.00 (+9.64)	72.50
trans-**1+**	−149.492234	0.0	97.59	*trans*-**3+**	−148.125026	0.0	73.25
cis-**1+**	−149.489308	+1.84 (+1.77)	97.52	*cis*-**3+**	−148.125472	−0.28 (−0.36)	73.17
trans-**1++**	−149.139798	0.0	97.83	*trans*-**3++**	−147.716000	0.0	73.05
cis-**1++**	−149.132952	+4.30 (+4.41)	97.94	*cis*-**3++**	−147.721740	−3.60 (−3.59)	73.06
trans-**2**	−149.697143	0.0	97.09	*trans*-**4+**	−157.542131	0.0	126.26
cis-**2**	−149.687765	+5.88 (+5.62)	96.83	*cis*-**4+**	−157.542198	−0.04 (+0.33)	126.63
trans-**2+**	−149.484943	0.0	98.06	*trans*-**4++**	−157.216887	0.0	126.90
cis-**2+**	−149.479928	+3.15 (+2.84)	97.75	*cis*-**4++**	−157.208524	+5.25 (+5.46)	127.11
trans-**2++**	−149.116839	0.0	98.23	*trans*-**4+++**	−156.726320	0.0	125.87
cis-**2++**	−149.116258	+0.36 (+0.35)	98.22	*cis*-**4+++**	−156.719340	+4.38 (+4.83)	126.32

[a] ZPE corrected values of E_{rel} (kcal mol^{-1}) in parentheses; $E_{rel} = E_{tot}(cis) - E_{tot}(trans)$.

complexes with an halide in a *trans* position to the CO ligand (for example, ref. 47).

The multiple bond lengths C≡N/O increase upon coordination for all the non-oxidized complexes. Such an elongation (Δl) rises from the acetonitrile to the carbonyl species in accord with an enhancement of the π-electron acceptor properties along the row NCCH$_3$–CNCH$_3$–CO. There is also a clear tendency for Δl to decrease from the non- to the di-oxidized species, consistent with the drop of the π-electron releasing ability of the metal centre upon oxidation, what is confirmed by the MO composition and NBO analysis discussed below.

The variations of the Re–L bond lengths normally correlate inversely with those of the CN or CO multiple bond lengths, reflecting, in particular, alterations in the electronic release from the metal d-orbitals to the ligand antibonding π*(L) orbitals which lead to opposite effects on the strengths of the C≡N/O and Re–L bonds. Such relations generally agree with experimental data.[43,47g,48–50]

Relative stability of the *trans*- and *cis*-isomers and electron-transfer induced isomerization

The electrochemical studies of *trans*-/*cis*-[ReCl(L)(dppe)$_2$] (L = NCR or CO) and *trans*-/*cis*-[ReL$_2$(dppe)$_2$]$^+$ (L = NCR), reported earlier by one of us,[26,27,31,51] allowed to compare the relative thermodynamic stability of some of the *trans*- and *cis*-isomers and to investigate its variation upon oxidation. The theoretical study aims to provide a rationalization of the relative isomeric behaviours and to predict the relative stability of the geometrical isomers, also for unstable complexes whose investigation by experimental methods would not be possible.

The absolute (E_{tot}) and relative [$E_{rel} = E_{tot}(cis) - E_{tot}(trans)$] values of the total energies and zero-point energies are summarized in Table 2 and used for the plots of Fig. 2(A). The comparison of the total energies of the *trans*- and *cis*-isomers of the *acetonitrile* complexes indicates that (*i*) the non-oxidized complex *cis*-**1** is more stable than the *trans*-**1** species and (*ii*) the oxidation leads to the inversion of the relative isomeric stability. Indeed, the relative energy of the *cis*- *vs.* *trans*-complexes becomes positive upon oxidation and the oxidized *trans*-isomer appears to be more stable than the *cis*-one. For the *diacetonitrile* complexes, *trans*-**4+** presents a similar stability to that of *cis*-**4+**, and the oxidation to the mono-oxidized level also results in the increase of the relative stability of the *trans*-isomer, although further oxidation does not result in a further enhancement of this effect.

The theoretical results are in overall agreement with the observed[26,28] electrochemical behaviour of the related nitrile and dinitrile complexes *cis*-[ReCl(NCC$_6$H$_4$Me-4)(dppe)$_2$] and *cis*-[Re(NCR)$_2$(dppe)$_2$][BF$_4$] (R = alkyl) [Fig. 3(A, B)] which undergo anodically induced *cis*-to-*trans* isomerization, the isomeric equilibrium shifting towards the *trans*-isomer upon oxidation (the equilibrium constants of the former species
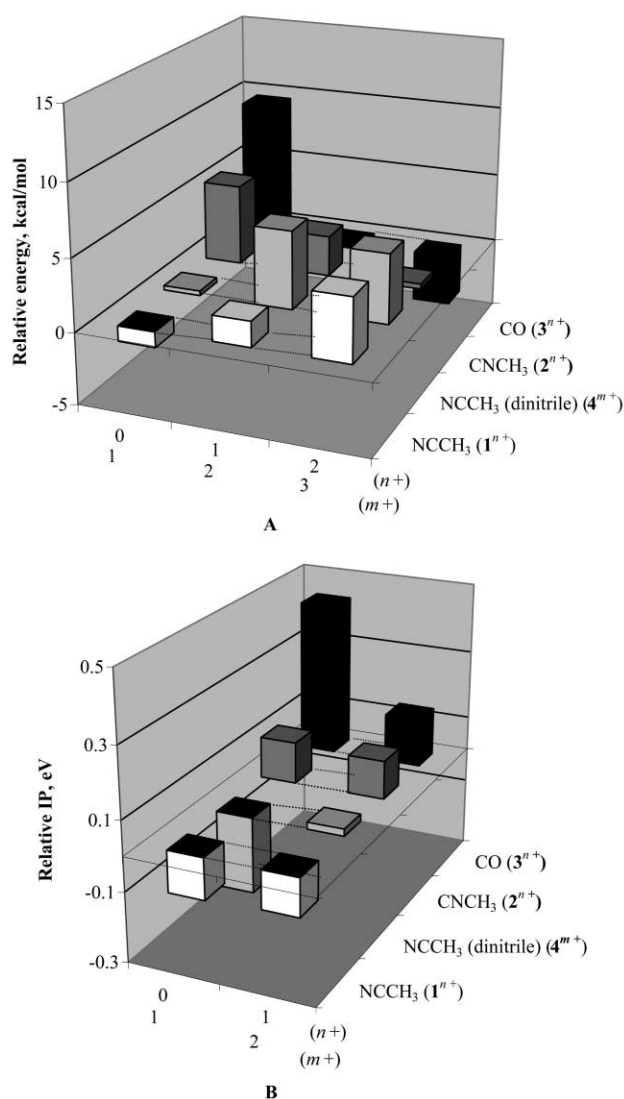

Fig. 2 Relative energy [$E_{rel} = E_{tot}(cis) - E_{tot}(trans)$] (A) and relative ionization potential [$IP_{rel} = IP(trans) - IP(cis)$] (B) for the isomeric series of complexes **1**$^{n+}$, **2**$^{n+}$, **3**$^{n+}$ ($n = 0–2$) and **4**$^{m+}$ ($m = 1–3$).
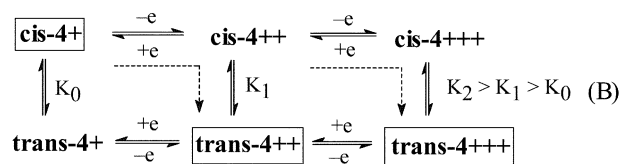
corresponding to the increasing oxidation state levels, measured in THF at 0 °C, are $K_0 = 6.9\cdot10^{-4} < K_1 = 1.5 < K_2 = 5.6$). Meanwhile, no *cis*-to-*trans* isomerization was observed for the Re^I complexes, in accord with the stability of the former.

In contrast to the nitrile species, for the neutral *carbonyl* complexes [ReCl(CO)(PH$_3$)$_4$] **3** the *trans*-isomer is more stable than the *cis*-one and this is in full agreement with the observed conversion (in solution or even in the solid state) of the *cis*- into the *trans*-isomer of [ReCl(CO)(dppe)$_2$], whereas the reverse transformation was not detected. Moreover, and also in
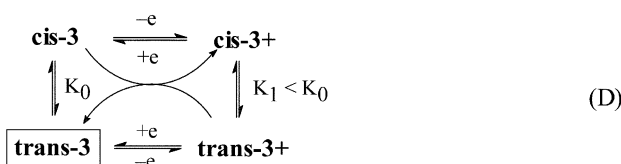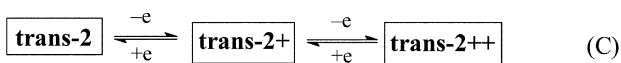
(A)

cis-1 ⇌(−e/+e) cis-1+ ⇌(−e/+e) cis-1++

K_0 | K_1 | $K_2 > K_1 > K_0$

trans-1 ⇌(+e/−e) trans-1+ ⇌(+e/−e) trans-1++
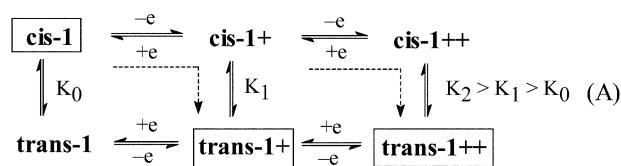
$E(\mathbf{cis\text{-}1/cis\text{-}1+}) > E(\mathbf{trans\text{-}1/trans\text{-}1+})$,

$E(\mathbf{cis\text{-}1+/cis\text{-}1++}) > E(\mathbf{trans\text{-}1+/trans\text{-}1++})$

(B)

cis-4+ ⇌(−e/+e) cis-4++ ⇌(−e/+e) cis-4+++

K_0 | K_1 | $K_2 > K_1 > K_0$

trans-4+ ⇌(+e/−e) trans-4++ ⇌(+e/−e) trans-4+++

$E(\mathbf{cis\text{-}4+/cis\text{-}4++}) > E(\mathbf{trans\text{-}4+/trans\text{-}4++})$,

$E(\mathbf{cis\text{-}4++/cis\text{-}4+++}) > E(\mathbf{trans\text{-}4++/trans\text{-}4+++})$

(C)

trans-2 ⇌(−e/+e) trans-2+ ⇌(−e/+e) trans-2++

(D)

cis-3 ⇌(−e/+e) cis-3+

K_0 | $K_1 < K_0$

trans-3 ⇌(+e/−e) trans-3+

$E(\mathbf{cis\text{-}3/cis\text{-}3+}) < E(\mathbf{trans\text{-}3/trans\text{-}3+})$

Fig. 3 Anodic behaviours and redox induced isomerizations for the complexes cis-/trans-[ReCl(NCR)(dppe)$_2$] (cis-**1**/trans-**1** model, R = aryl)[26a] (A), cis-/trans-[Re(NCR)$_2$(dppe)$_2$]$^+$ (cis-**4+**/trans-**4+** model, R = alkyl)[26b] (B), trans-[ReCl(CNR)(dppe)$_2$] (trans-**2** model, R = alkyl or aryl) (unknown cis-complexes)[29] (C) and cis-/trans-[ReCl(CO)(dppe)$_2$] (cis-**3**/trans-**3** model)[31] (D). The most stable isomer of each isomeric pair is boxed.

opposition with the above nitrile complexes, oxidation of the carbonyl species results in a *decrease* of the relative stability of the trans-isomer which becomes clearly less stable than the cis-isomer at the dioxidized level (**3++** complexes), in accord with the electrochemical data[31] which showed a dramatic decrease of the isomeric equilibrium constant upon oxidation, i.e. $K_1/K_0 = (1.5 \pm 0.7)\cdot 10^{-6}$ [Fig. 3(D)].

For the *isocyanide complexes* [ReCl(CNCH$_3$)(PH$_3$)$_4$] **2**, the theoretical calculations predict that the trans-**2** isomer is more stable than the cis-**2** one (by 5.62 kcal mol^{-1}) and the higher stability of the former isomer still remains on oxidation in spite of the *decrease* of its relative stability as for the carbonyl complexes. These results are consistent with the fact that the cis-isomers of the isocyanide complexes were not obtained experimentally even upon oxidation [Fig. 3(C)].[29,52] The relative isomeric stability of the neutral and dioxidized isocyanide complexes **2** and **2++** is intermediate between those of the corresponding acetonitrile **1**, **1++** and carbonyl **3**, **3++** complexes, following the intermediate π-acceptor ability of the isocyanide ligand in comparison with NCCH$_3$ and CO.

Ionization potentials

The calculated ionization potential (IP) values for the complexes are listed in Table 3 and relative values [IP$_{rel}$ = IP(trans) − IP(cis)] were used for the plots of Fig. 2(B). The comparable

Table 3 Calculated ionization potentials IP (eV) of the non-oxidized and mono-oxidized complexes

Complexes	IP
trans-**1**	5.26 (5.32)
cis-**1**	5.40 (5.44)
trans-**1+**	9.59 (9.60)
cis-**1+**	9.70 (9.71)
trans-**2**	5.77 (5.82)
cis-**2**	5.66 (5.70)
trans-**2+**	10.02 (10.02)
cis-**2+**	9.90 (9.91)
trans-**3**	6.70 (6.72)
cis-**3**	6.26 (6.28)
trans-**3+**	11.13 (11.12)
cis-**3+**	10.99 (10.98)
trans-**4+**	8.85 (8.88)
cis-**4+**	9.08 (9.10)
trans-**4++**	13.35 (13.30)
cis-**4++**	13.31 (13.28)

[a] ZPE corrected values of IP (eV) in parentheses.

complexes [ReCl(L)(PH$_3$)$_4$]$^{n+}$ exhibit similar dependences of their calculated IP and measured oxidation potential on the ligand L, both parameters increasing in the order of the π-electron withdrawing ability of this ligand (NCCH$_3$ < CNCH$_3$ < CO). The IPs of the acetonitrile complexes cis-**1** and cis-**4+** are higher than the corresponding ones for trans-**1** and trans-**4+**. These results correlate with the experimental oxidation potential values for the trans-/cis-[ReCl-(NCC$_6$H$_4$Me-4)(dppe)$_2$] ($E°(trans^{0/+}) = -0.31$, $E°(cis^{0/+}) = -0.13$ V vs. SCE[26a]) and trans-/cis-[Re(NCCH$_3$)$_2$(dppe)$_2$][BF$_4$] ($E°(cis^{+/2+}) = 0.22$, $E°(cis^{+/2+}) = 0.36$ V vs. SCE[26a]) complexes.

The isocyanide and carbonyl complexes [ReCl(L)(PH$_3$)$_4$]$^{n+}$ (**2**$^{n+}$ L = CNCH$_3$, **3**$^{n+}$ L = CO; n = 0 or 1) follow a distinct behaviour, i.e. the ionization potentials of the trans-isomers are higher than those of the corresponding cis-ones, consistent with the experimental data for the trans-/cis-[ReCl(CO)(dppe)$_2$] complexes with $E°(trans^{0/+}) = 0.68$ and $E°(cis^{0/+}) = 0.41$ V vs. SCE.[31] The difference IP(trans) − IP(cis) is lower for the isocyanide complexes than for the carbonyl ones.

The relative IP of the trans-structures in comparison with the cis-ones increases in the order L = NCCH$_3$ < CNCH$_3$ < CO, following the same trend of the relative geometrical stability, as clearly shown by comparing Fig. 2(B) and (A). Hence, the relative IP and the relative geometrical stability appear to correlate along the series of the complexes studied. Moreover, although there is not necessarily a direct correlation between the calculated IP for isolated molecules and the experimental oxidation potential measured for their solutions, the comparison of their trends can be of interpretative and predictive value.

Molecular orbitals

Further understanding of the nature of the coordination bonds in the studied complexes can be provided by the analysis of the valence molecular orbital composition in terms of frontier orbital theory.[53]

The three HOMOs of the {ReCl(PH$_3$)$_4$} or {Re(PH$_3$)$_4$}$^+$ fragments are localized on the metal atom. For the former case, two of these HOMOs – degenerated for the trans-isomers or having similar energy for the cis-ones – include also p(Cl) orbitals which give antibonding combination with d(Re) AOs.

As a result of the interaction of the metal fragment with L to give the complex, the two HOMOs with favourable symmetry include the π and π* MOs of L. For the nitrile complexes, the contributions of the π(NC) and π*(NC) MOs in the HOMOs are similar and small, suggesting a weak π-acceptor ability of NCCH$_3$. In fact, such HOMOs (Fig. 4) can be represented as a linear combination of the d(Re) (or π*$_{Re-Cl}$), π(NC) and π*(NC) orbitals:
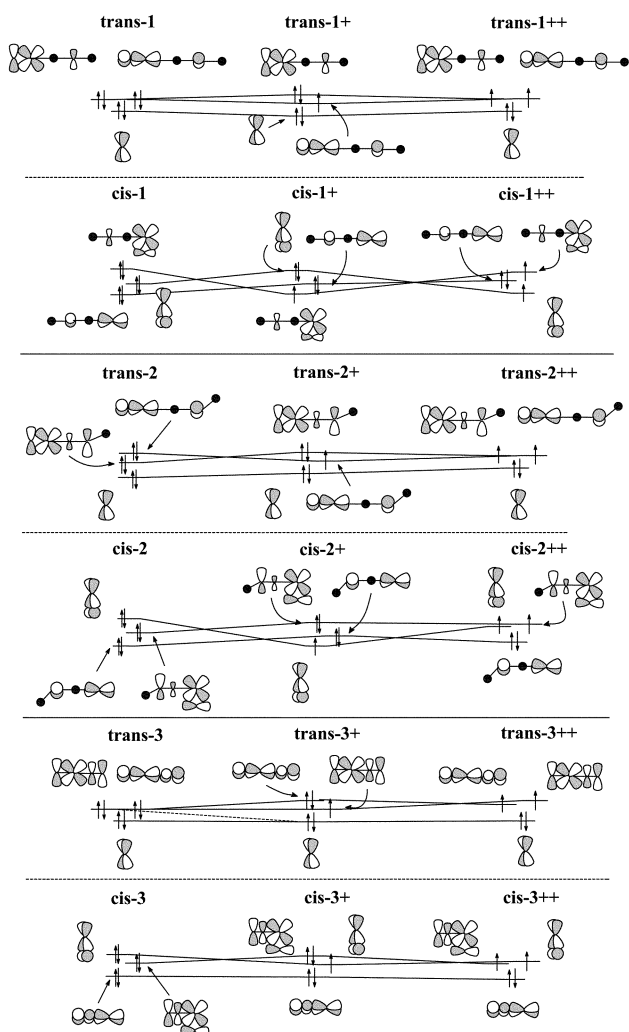
Fig. 4 Correlation MO diagrams for the chloro-complexes *trans-/cis-*
[ReCl(L)(PH$_3$)$_4$]$^{n+}$ [L = NCCH$_3$ **1**, CNCH$_3$ **2**, CO **3**; *n* = 0, 1, 2]. The Cl
atoms are placed along the *y*-axis for the *cis*-isomers or the *x*-axis for
the *trans*-isomers, and the L ligands are oriented along the *x*-axis for all
isomers.
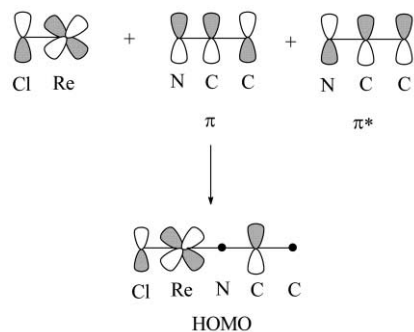
As a result of this combination, the total contribution of
the p(N) AOs becomes close to zero while the involvement
of the β–C atom orbitals increases providing the well known
effect of orbital polarization.[1q]

The contribution of the π*(L) orbital – total and relative to
that of the π(CN) MO – increases from nitrile to isocyanide and
further to carbonyl complexes, demonstrating the π-back don-
ation effect and following the enhancement of the π-acceptor
character of L. This trend correlates with the decrease of the
energy gap between the HOMOs of the metal fragment and the
π*(L) MO of the ligand as well as with the growing stabilization
of the HOMOs from L = NCCH$_3$ to CO.

The analysis of the MO composition of the mono-oxidized
complexes indicates that one electron is removed from the

HOMO upon oxidation, *i.e.*, for all *trans*-isomers as well as
*cis-***1** and *cis-***4+**, from the orbital involving d(Re), π(L), π*(L)
and, for some of the complexes, p(Cl) AOs (Fig. 4). Thus, this
MO becomes a singly-occupied orbital (SOMO). For *cis-***2** and
*cis-***3**, the electron is removed from the π*(Re–Cl) orbital. In this
case, two metal–ligand MOs remain doubly-occupied, but the
contribution of the π*(L) is lower than that for the non-
oxidized species. It is interesting to mention that the SOMO is
the second or third HOMO of the mono-oxidized complexes as
a result of the rearrangement of the MOs upon oxidation.

In the second oxidation, the electron is also removed from the
HOMO (not from the SOMO), and the triplet structures with
two singly-occupied MOs appear to be more stable than the
singlet structures. For the *trans*-isomers of the doubly-oxidized
complexes, both SOMOs include d(Re) and p(Cl) AOs, π and
π* MOs of L, while the third, doubly-occupied MO of the
complexes, is the orthogonal d(Re) orbital (the third orbital of
the t$_{2g}$ set). For the *cis*-isomers, one SOMO also includes the
orbitals of Re, Cl and L whereas the second one is localized
only on the Re and Cl atoms. Thus, the second oxidation leads
to further reduction of the π*(L) contribution in the HOMOs
because the second electron is removed from the metal–ligand
MOs of the mono-oxidized complexes (except *cis-***1+**). There is
also an overall decrease of the occupancy of HOMOs which,
within the ligand L framework, are mostly localized at the
β-atom. Such features correspond to the expected decrease,
upon oxidation, of the metal π-electron release and of the acti-
vation of L towards electrophiles, what correlates with the
chemical behaviour, structural features and results of the NBO
analysis.

In fact, the neutral Re^{I} nitrile and isocyanide complexes
[ReCl(L)(dppe)$_2$] (L = NCR[54] or CNR[46,52,55,56]) undergo ready
β-protonation at L to give the corresponding azavinylidene
(or methyleneamide) [ReCl(N=CHR)(dppe)$_2$]$^+$ [eqn. (1)] and
aminocarbyne [ReCl(C=NHR)(dppe)$_2$]$^+$ complexes. However,
the reaction does *not* occur for the oxidized forms.

$$[ReCl(N\equiv CR)(dppe)_2] + H^+ \longrightarrow [ReCl(N=CHR)(dppe)_2]^+ \quad (1)$$
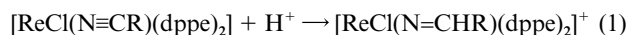
The C≡O and C≡N stretching frequencies associated to the L
ligand are also expected to reflect the strength of π-back-
donation which should result into a lowering of such frequen-
cies upon L coordination, although the σ-bond component and
electrostatic interactions can also provide significant effects.[16f]
For the complexes of the present work, the calculated non-
scaled vibrational frequencies v(CE) (E = N or O) are given in
Table 4, whereas the coordination shift $\Delta v = v$(CE)$_{comp}$ −
v(CE)$_{free}$ is plotted (with inverted sign) in Fig. 5. The latter is
negative (−Δv positive) and its absolute magnitude increases
from L = NCCH$_3$ to CNCH$_3$ and further to CO for the non-
oxidized complexes, in agreement with the experimental
trend[26a,29,31] and with the rise of the π-acceptor ability of L.
Oxidation leads to a decrease of −Δv for the chloro-complexes
[the v(CE) frequency can even become higher than in the free
ligand], consistent with the weakening of the π-electron releas-
ing character of the metal centre. The −Δv parameter is also
higher for the oxidized carbonyl than for the oxidized iso-
cyanide complexes. However, for the dinitrile complexes, with a
cationic metal center, there is not a clear trend for the change of
Δv upon oxidation, and this frequency should be mostly deter-
mined by other factors, in particular the electrostatic inter-
action. Moreover, for the complexes **1** and **4+**, the v(C≡N)
vibration is strongly mixed with the stretching v(PH) and bend-
ing δ(CH$_3$) vibrations, and the stretching of the CN group is
within several normal vibrational modes.

NBO and CDA analyses

Additional information about binding in the complexes can be
obtained by NBO and CDA analyses (Tables 5 and 6). For the

Table 4 Calculated frequencies for the $\nu(C\equiv N)$ or $\nu(C\equiv O)$ modes (cm^{-1}) of the complexes and free ligands. Experimental values for the corresponding dppe complexes are given in parentheses

NCCH$_3$		*trans*-**1**	*trans*-**1+**	*trans*-**1++**
2315.8		2228.0, 2200.3 (2050)	2229.5 (2130)	2258.9
		cis-**1**	*cis*-**1+**	*cis*-**1++**
		2273.9, 2264.4, 2244.2, (2175)	2278.2	2296.9
		trans-**4+**	*trans*-**4++**	*trans*-**4+++**
		2290.8, 2258.5, 2254.5 (2140)	2267.3, 2262.2	2243.7, 2234.1
		cis-**4+**	*cis*-**4++**	*cis*-**4+++**
		2260.2, 2250.2 (2230–2185)	2286.9, 2278.3	2264.3, 2250.4
CNCH$_3$		*trans*-**2**	*trans*-**2+**	*trans*-**2++**
2188.0		1982.7	2128.0	2214.1
		cis-**2**	*cis*-**2+**	*cis*-**2++**
		2065.3	2180.2	2232.1
CO		*trans*-**3**	*trans*-**3+**	*trans*-**3++**
2026.1		1779.5 (1800)	1862.8	1960.6
		cis-**3**	*cis*-**3+**	*cis*-**3++**
		1813.0 (1840)	1894.0	1990.2
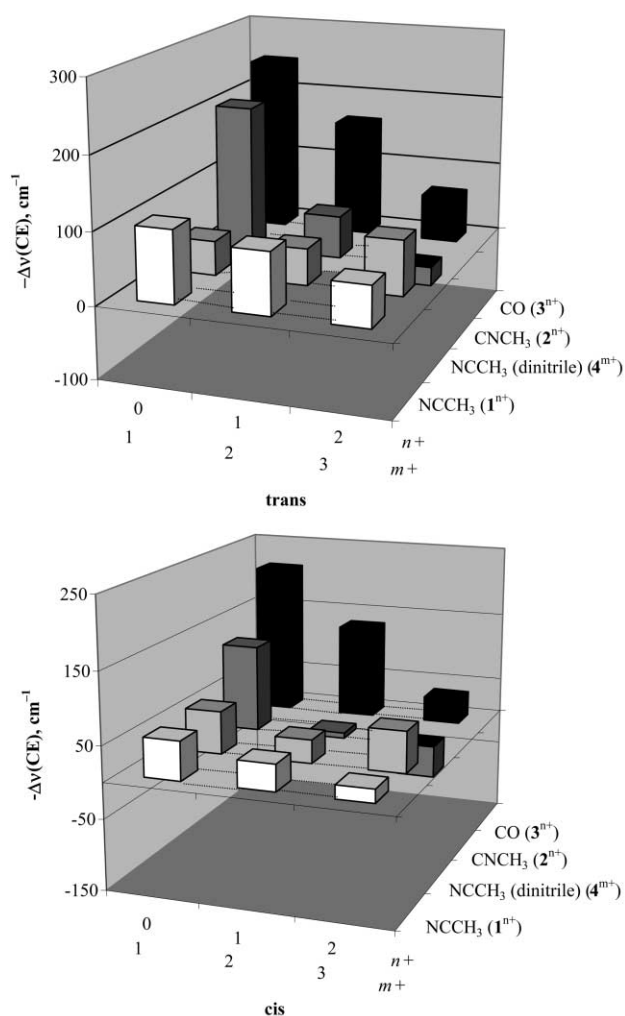
Fig. 5 Coordination $\nu(CE)$ (E = N or O) shift (with inverted sign) for the NCCH$_3$, CNCH$_3$ or CO ligands: $-\Delta\nu(CE) = -[\nu(CE)_{complex} - \nu(CE)_{free}]$.

nitrile compounds, the NBO analysis gives the Re–N bond orbital only for *trans*-**1** while for *cis*-**1**, and for all the oxidized nitrile species, this orbital was not detected indicating a conceivable predominant Coulomb-type Re–ligand interaction. The Re–N bond is polarized towards the nitrogen atom *ca.* 80% at N) which is sp-hybridized, whereas the d and s orbitals of the metal (mainly the former) are also involved in the bond formation. For all the isocyanide species, the Re–C bond which is polarized towards the C atom, was found, and the metal atom has sd-hybridization. All the σ- and π-CN bonding orbitals are clearly polarized towards the nitrogen end, especially for the isocyanide complexes.

For the carbonyl *trans*-**3** compound, three natural bond orbitals for the Re–C bond and one orbital for the CO bond were detected. One Re–C bond orbital is polarized towards the carbon atom (*ca.* 66% at C) and the s and d orbitals of Re take part in the bonding, similarly to the cases of the nitrile and isocyanide complexes. Two other Re–C bond orbitals are strongly polarized toward the metal atom (*ca.* 80% at Re) and only d-orbitals of Re are included into the bonding. Thus, the two latter natural bond orbitals correspond mostly to the d-lone pairs of Re. This situation is probably a consequence of some overestimate of the strength of the Re–ligand interaction in this complex for correlated levels. Indeed, the calculated Re–C and C≡O bond lengths are shorter and longer, respectively, than the experimental values for similar carbonyl complexes (see above). The CO bond orbital is polarized towards the oxygen end. For all other carbonyl complexes, one Re–C and three CO natural bond orbitals were found, the former being also polarized towards the carbon atom. One σ and two π CO bond orbitals are polarized to the O end providing the sp hybridization for the carbon.

The results of the CDA analysis are presented in Table 6. First of all, it is necessary to mention that the nonclassical residual term Δ which describes the mixing of unoccupied orbitals of the two {L} and {ReCl(PH$_3$)$_4$} fragments is very close to zero for all the structures, suggesting that they are typical donor–acceptor complexes and can be considered in terms of the Dewar–Chatt–Duncanson model.[57] Comparison of the ratio of the back-donation (*b*) and donation (*d*) terms for the different structures indicates that the carbonyl ligand is the best net electron acceptor and the nitrile ligand is the weakest one in the complexes studied since the *ratio* of the *b* and *d* terms increases along the row NCCH$_3$ < CNCH$_3$ < CO, following the same trend as the electrochemical P_L[51,58,59] and E_L[51,60,61] ligand parameters, a measure of the net π-electron acceptor minus σ-donor character of a ligand. Although the absolute values of the *d* and *b* terms have a limited meaning[11a,16f,40] it is worthwhile to mention that the donation term has the highest value for the isocyanide ligand and the smallest one for the nitrile ligand while the back-donation term decreases distinctly from L = CO to NCCH$_3$.

Final remarks

The above theoretical studies have been applied successfully to the interpretation of electronic, structural, redox and chemical properties and behaviours of a variety of octahedral-type 18-, 17- and 16-electron complexes comprising a tetraphosphine-rhenium centre coordinating two other ligands whose electron donor/acceptor properties are spread along wide ranges [one strong σ- and π-donor (Cl) and one strong (CO), medium (CNCH$_3$) or weak (NCCH$_3$) π-acceptor; or two weak (NCCH$_3$) π-acceptors], in situations that cannot be adequately treated by

Table 5 Results of NBO analysis of the chloro-complexes (q − NBO partial charge)[a]

Bond orbital		trans-**1**	cis-**1**	trans-**1+**	cis-**1+**	trans-**1++**	cis-**1++**
Re–N	occ.	1.96					
	%Re	20.17; sd$^{75.44}$					
	%N	79.83; sp$^{46.92}$					
N≡C (σ)	occ.	1.99	1.98	0.99	0.99	0.99	0.99
	%N	61.86; sp$^{52.97}$	61.04; sp$^{47.37}$	61.30; sp$^{41.29}$	60.66; sp$^{56.85}$	61.32; sp$^{40.41}$	61.52; sp$^{59.88}$
	%C	38.14; sp$^{55.33}$	38.96; sp$^{60.76}$	38.70; sp$^{58.19}$	39.34; sp$^{68.67}$	38.68; sp$^{57.63}$	38.48; sp$^{71.36}$
N≡C (π)	occ.	1.98	1.98	0.99	0.99	0.99	0.99
	%N	57.63; p^{100}	58.20; p$^{99.91}$	57.65; p$^{98.51}$	59.35; sp$^{83.26}$	58.96; p$^{99.98}$	61.19; sp$^{80.51}$
	%C	42.37; p^{100}	41.80; p$^{99.94}$	42.35; p$^{98.92}$	40.65; sp$^{88.23}$	41.04; p$^{99.98}$	38.81; sp$^{86.12}$
N≡C (π)	occ.	1.98	1.98	0.99	0.99	0.99	0.99
	%N	57.64; p^{100}	58.57; p$^{92.45}$	58.09; p$^{99.84}$	58.13; p^{100}	58.96; p$^{99.99}$	61.08; p^{100}
	%C	42.36; p^{100}	41.43; p$^{95.57}$	41.91; p$^{99.89}$	41.17; p^{100}	41.04; p$^{99.99}$	38.92; p^{100}
q(Re)		−0.77	−0.80	−0.33	−0.35	0.06	0.10
q(N)		−0.34	−0.33	−0.41	−0.40	−0.48	−0.47
q(C(8))		0.31	0.38	0.46	0.49	0.58	0.56
q(C(9))		−0.76	−0.76	−0.77	−0.78	−0.79	−0.79
q(Cl)		−0.60	−0.59	−0.43	−0.41	−0.18	−0.17

Bond orbital		trans-**2**	cis-**2**	trans-**2+**	cis-**2+**	trans-**2++**	cis-**2++**
Re–C	occ.	1.94	1.93	0.97	0.97	0.98	0.98
	%Re	32.36; sd$^{72.87}$	33.39; sd$^{67.69}$	30.80; sd$^{71.27}$	32.48; sd$^{68.26}$	29.54; sd$^{70.79}$	32.20; sd$^{67.83}$
	%C	67.64; sp$^{37.64}$	66.61; sp$^{38.18}$	69.20; sp$^{38.32}$	67.52; sp$^{38.61}$	70.46; sp$^{39.29}$	67.80; sp$^{39.93}$
C≡N (σ)	occ.	1.99	1.99	1.00	1.00	1.00	1.00
	%C	35.47; sp$^{62.16}$	35.51; sp$^{62.60}$	35.11; sp$^{61.57}$	35.30; sp$^{61.45}$	34.80; sp$^{60.69}$	35.13; sp$^{60.15}$
	%N	64.53; sp$^{46.47}$	64.49; sp$^{46.28}$	64.89; sp$^{46.95}$	64.70; sp$^{46.81}$	65.20; sp$^{47.58}$	64.87; sp$^{47.57}$
C≡N (π)	occ.	1.98	1.98	0.99	0.99	0.99	0.99
	%C	28.89; p^{100}	29.51; p$^{99.71}$	28.72; p^{100}	31.09; p$^{99.88}$	30.34; p^{100}	32.15; p$^{99.98}$
	%N	71.11; p$^{99.99}$	70.49; p$^{99.83}$	71.28; p^{100}	68.91; p^{100}	69.66; p^{100}	67.85; p$^{99.97}$
C≡N (π)	occ.	1.98	1.98	0.99	0.99	0.99	0.95
	%C	28.92; p^{100}	28.64; p$^{99.34}$	29.25; p^{100}	31.44; p$^{99.99}$	30.34; p^{100}	32.34; p^{100}
	%N	71.08; p^{100}	71.36; p$^{99.61}$	70.75; p^{100}	68.56; p^{100}	69.66; p^{100}	67.66; p^{100}
q(Re)		−0.89	−0.89	−0.46	−0.42	−0.09	−0.02
q(C(7))		0.33	0.38	0.29	0.34	0.27	0.30
q(N)		−0.53	−0.51	−0.40	−0.43	−0.31	−0.33
q(C(9))		−0.44	−0.45	−0.46	−0.46	−0.47	−0.46
q(Cl)		−0.62	−0.58	−0.44	−0.38	−0.18	−0.15

Bond orbital		trans-**3**	cis-**3**	trans-**3+**	cis-**3+**	trans-**3++**	cis-**3++**
Re–C	occ.	1.96	1.94	0.98	0.98	0.98	0.98
	%Re	34.29; sd$^{72.96}$	34.82; sd$^{67.02}$	31.78; sd$^{68.58}$	34.33; sd$^{67.83}$	29.82; sd$^{68.37}$	32.32; sd$^{66.83}$
	%C	65.71; sp$^{34.14}$	65.18; sp$^{34.25}$	68.22; sp$^{34.73}$	65.67; sp$^{35.13}$	70.18; sp$^{35.20}$	67.68; sp$^{35.82}$
Re–C	occ.	1.92					
	%Re	80.20; sd$^{97.24}$					
	%C	19.80; p^{100}					
Re–C	occ.	1.94					
	%Re	80.57; d$^{99.95}$					
	%C	19.43; p^{100}					
C≡O (σ)	occ.	2.00	2.00	1.00	1.00	1.00	1.00
	%C	31.55; sp$^{64.71}$	31.13; sp$^{65.50}$	31.26; sp$^{34.33}$	31.33; sp$^{64.14}$	30.90; sp$^{64.02}$	30.97; sp$^{63.80}$
	%O	68.45; sp$^{56.81}$	68.87; sp$^{56.97}$	68.74; sp$^{56.09}$	68.67; sp$^{55.89}$	69.10; sp$^{55.68}$	69.03; sp$^{55.73}$
C≡O (π)	occ.		2.00	1.00	1.00	1.00	1.00
	%C		23.79; p$^{99.96}$	24.31; p$^{99.99}$	25.52; p$^{99.99}$	25.58; p^{100}	26.50; p$^{99.73}$
	%O		76.21; p$^{99.95}$	75.69; p$^{99.96}$	74.48; p$^{99.99}$	74.42; p^{100}	73.50; p$^{99.82}$
C≡O (π)	occ.		2.00	1.00	1.00	1.00	1.00
	%C		24.31; p$^{99.36}$	24.62; p^{100}	25.83; p^{100}	25.51; p$^{99.96}$	26.45; p$^{99.99}$
	%O		75.69; p$^{99.22}$	75.38; p^{100}	74.17; p^{100}	74.49; p$^{99.84}$	73.55; p$^{99.99}$
q(Re)		−0.85	−0.85	−0.39	−0.37	−0.08	−0.06
q(C)		0.48	0.54	0.47	0.53	0.50	0.54
q(O)		−0.57	−0.53	−0.44	−0.45	−0.32	−0.33
q(Cl)		−0.61	−0.55	−0.44	−0.34	−0.16	−0.08

[a] The hybridization of the atoms is indicated with the percent contribution of the metal-centred d or (and) p orbitals as a superscript. For the open-shell structures, only α-orbitals are given.

simplified models namely those based on the expected ligand field splitting of the metal-centred filled d_π orbitals[21] or on some semiempirical rationalizations of the redox potentials.[1m] The complexity of the combined multiple effects leads to behaviours that reflect a delicate balance of factors whose interpretation requires more elaborate calculation methods, such as those applied in this study. The success of the approach to all the above cases that have been experimentally investigated suggests a high predictive value that encourages its application to other situations including those that have not yet been the object of an empirical study (extension to a wider variety of ligands, e.g. two strong π-electron donors or two strong π-electron acceptors, change of the metal and of the number of phosphine co-ligands, etc.).

Table 6 Results of the CDA analysis of the closed-shell complexes (*d* – donation, *b* – back-donation, *r* – repulsive part, *Δ* – residual part)

Structure	*d*	*b*	*b/d*	*r*	*Δ*
trans-**1**	0.355	0.202	56.9%	−0.406	−0.003
cis-**1**	0.350	0.152	43.4%	−0.370	−0.007
trans-**2**	0.643	0.376	58.5%	−0.481	−0.009
cis-**2**	0.686	0.320	46.6%	−0.429	0.001
trans-**3**	0.459	0.408	88.9%	−0.537	−0.004
cis-**3**	0.537	0.377	70.2%	−0.473	0.001

Acknowledgements

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