Tailoring transition metal complexes for non linear optics applications
A theoretical investigation of the electronic structure of M(CO)$_x$Cl$_y$L complexes (M = Cr, W, Re, Ru, Os, Rh, Ir; L = Pyz, PyzBF$_3$, BPE, BPEBF$_3$)

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Dedicated to Prof. Renato Ugo on the occasion of his 65th birthday

Abstract

Density functional theory (DFT) investigations of title organometallic compounds led to identification of electronic features which determine the magnitude and the orientation of the dipole moment. The analysis of our theoretical results shows that the presence of a strong acidic BF$_3$ group, or more generally, the substitution of ligands in the M(CO)$_x$Cl$_y$L complexes can affect the orientation of the dipole moments, out of the direction of the first charge transfer (CT) excitation and, as a consequence, the magnitude of the vector part of the second order hyperpolarizabilities.
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1. Introduction

The interest for organometallic and coordination compounds as materials with non linear optical (NLO) properties is related to the possibility of obtaining a class of molecules even broader than the class of organic compounds [1–12]. However, the rules for a rational design of NLO organometallic systems are not yet fully understood, and, in particular, the electronic role of the transition metal (TM) atom is still unclear.

The numerous TM compounds already investigated as potential NLO materials, are characterised by π-delocalised ligands such as stilbazoles, pyridines, bipyridines, and terpyridines [10–18]. Recently we reported the synthesis, electronic properties and second order NLO response of asymmetric heteronuclear push–pull bimetallic complexes with pyrazine (Pyz)

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and *trans*-1,2-bis(4-pyridyl)ethylene (BPE) as polarizable linkers between the $W(CO)_5$ fragment and *cis*-$Re(CO)_4Cl$ or BF_3 [19]. These complexes are the organometallic counterparts of classical push–pull NLO aromatic systems [20–23]: the $M(CO)_xCl_y$ fragment may act either as electron withdrawing group (accepting electronic charge from the aromatic ligand) or as donor group, via π back-donation to the empty molecular orbitals (MOs) of the aromatic ring. The strong acceptor BF_3 group can enhance the extent of the charge shift.

When BPE is present, the magnitude of the second order NLO response is comparable to that of classical push–pull stilbenic compounds, whereas, when Pyz is the linker, the response can be even higher but strongly dependent on the electronic features of the inorganic moiety.

A clear view of the electronic origin of NLO effects in TM compounds can be obtained by means of density functional theory (DFT) computational methodologies. In this context, we studied two groups of TM complexes. The first group (A) includes the $M(CO)_5L_{1,2}$ complexes, where M is Cr or W, $L_1 =$ Pyz and $L_2 =$ BPE. Both ligands have two nitrogen atoms: one is coordinated to the metal centre and the other is either free (L_1, L_2) or involved in acid–base adduct with BF_3 (L_1', L_2'). The group A includes eight species, all with the metal atom in a d^6 configuration and zero oxidation state. The second group (B) includes various species of type $M(CO)_xCl_yL$ ($x = 2$–4, $L = L_1 =$ Pyz) with M belonging to groups 7–9 and characterised by d^6 or d^8 configuration and oxidation states $+1$ or $+2$: $Re(CO)_4ClL_1$, $M(CO)_3Cl_2L_1$ ($M =$ Ru, Os), $M(CO)_2ClL_1$ ($M =$ Rh, Ir).

Our study aims at determining the best molecular geometry of the complexes, their charge distribution and dipole moment which is an important factor in determining second order NLO properties.

2. Computational methods

DFT calculations were carried out using the hybrid B3LYP exchange-correlation functional [24–27] and effective atomic core potentials of Hay and Wadt [28] for the metal centres and Cl atoms which are described by a double-zeta valence set. All other atoms are described at double-zeta basis and all-electron level [29].

Minima of the energy hypersurface have been located by means of energy gradient techniques [30]. Electron population analysis have been performed according to the natural bond orbital (NBO) theory [31–36].

3. Results and discussion

3.1. Molecular geometries of group A complexes

The geometries of the compounds of the group A are schematically shown in Fig. 1. For all the W complexes, the aromatic ring of Pyz or BPE lies in the plane defined by the metal centre and equatorial carbonyl ligands, in the Cr compounds the plane of the aromatic ligand forms a $45°$ angle with the pairs of equatorial CO ligands. The two different orientations of the ligands L (L_1, L_2, L_1', L_2') are due to repulsive interactions between the aromatic protons and the carbonyl C atoms, which are stronger in the Cr complexes than in the W complexes (the Cr–N distances are shorter than the W–N ones).

In the 16 electrons (16e) square pyramidal species $W(CO)_5$, the M–C distances of the axial and four equatorial carbonyl ligands are equal to 1.943 and 2.042 Å, respectively. In the presence of the aromatic ligands L_1 or L_2, the M–C distance elongates by more than 0.05 Å in the axial CO but is almost unaffected in the equatorial COs. The computed M–N distances are significantly affected by the BF_3 group: for both Cr and W, the M–N distance is about 0.03 Å shorter in $M(CO)_5L_1'$ than in $M(CO)_5L_1$ complexes. On the contrary, the presence of BF_3 has a very small effect on M–N distances in the case of the $M(CO)_5L_2'$ derivative. The shortening of M–N distance in $M(CO)_5PyzBF_3$, caused by BF_3 is accompanied by an increase of the M–C distance *trans* to M–N bond of about 0.01 Å, for both Cr and W compounds. The effects of the BF_3 group on molecular geometry is localised along the molecular axis, a fact confirmed by the analysis of the charge distribution, as discussed in the following.

In order to appreciate the reliability of our computational approach, our computed M–CO and MC–O distances may be compared with experimental values. For instance, in the case of $Cr(CO)_5$ and $Cr(CO)_5L$ complexes the DFT computed equatorial Cr–C and C–O distances are in error by about 0.03 Å [39]. In
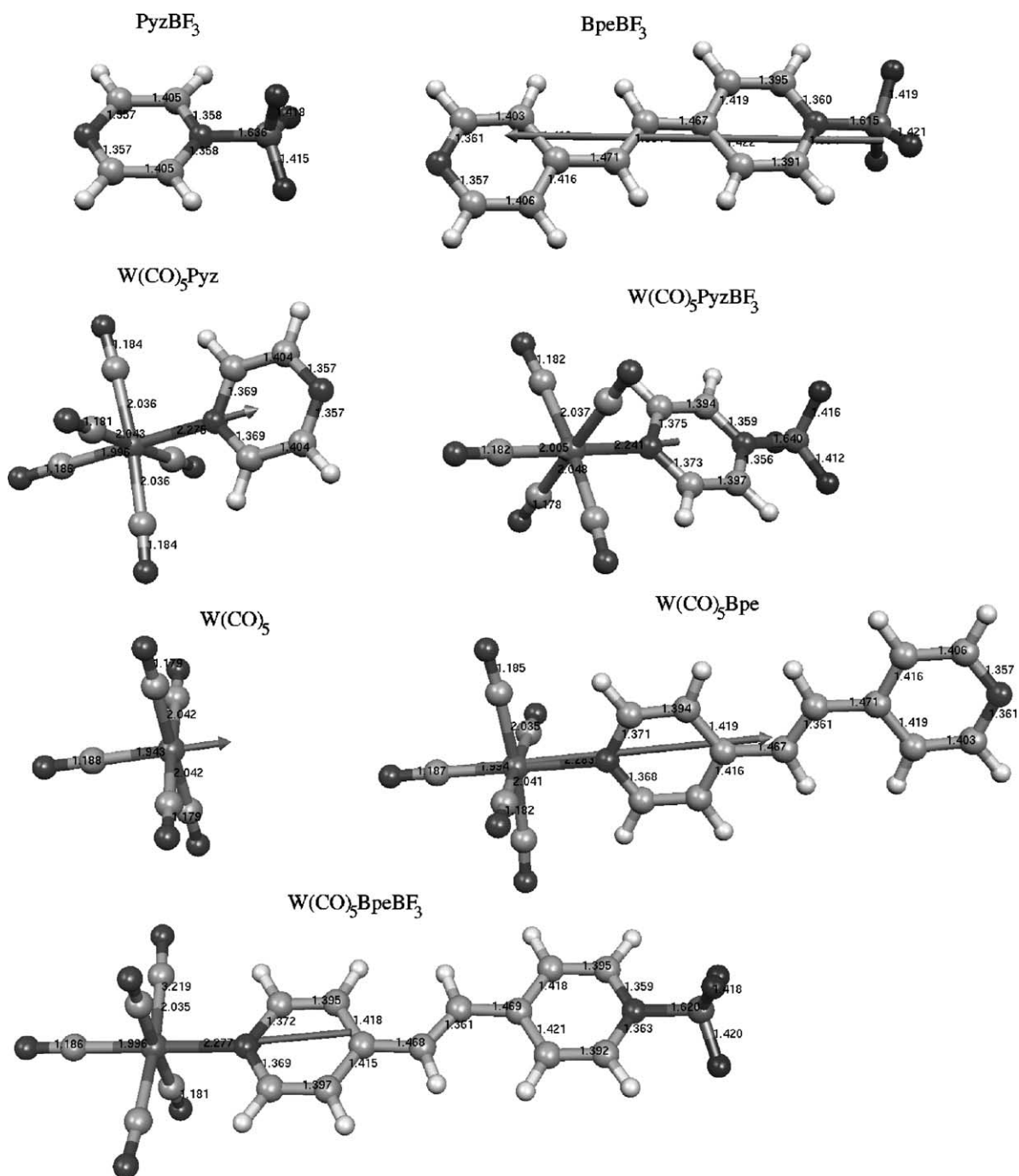
Fig. 1. Molecular structures with selected geometry parameters (bond distances in Angstrom) of compounds of group A.
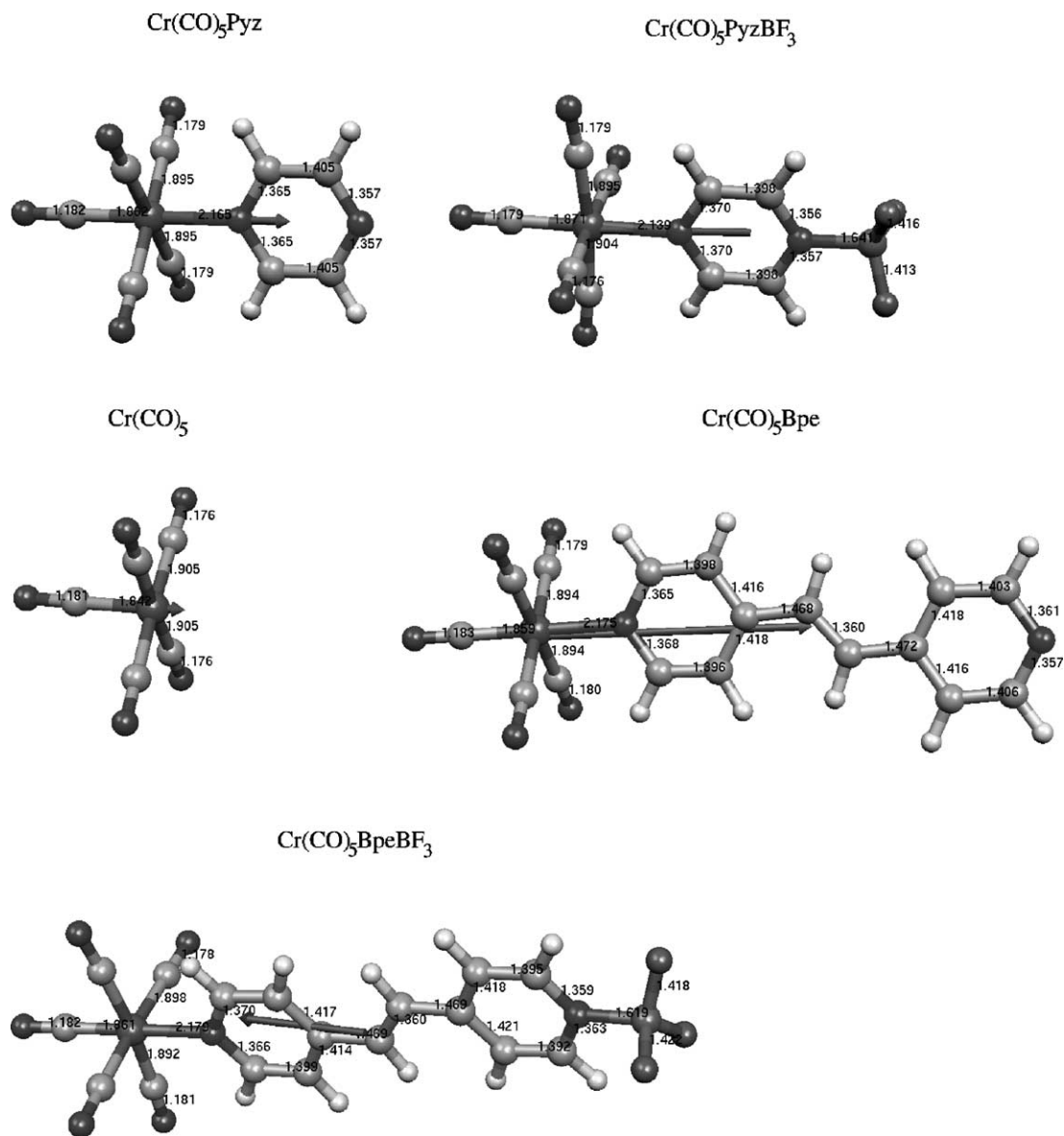
Cr(CO)₅Pyz

Cr(CO)₅PyzBF₃

Cr(CO)₅

Cr(CO)₅Bpe

Cr(CO)₅BpeBF₃

Fig. 1. (*Continued*).

addition our results on M(CO)₅ fragments are in perfect agreement with those reported in [40], obtained with very flexible numerical basis. The same accuracy characterises also our results concerning W(CO)₅Pyz when they are compared with X-ray data obtained for W(CO)₅L, where L is a substituted pyridine [41].

3.2. Dipole moments and atomic charges of group A complexes

The dipole moments of the compounds of group A are graphically shown in Fig. 1, the corresponding numerical components are reported in Table 1. The orientation of M(CO)₅L complexes is determined by

Table 1
Dipole moments (in Debye) of the compounds of group A

	μ_x	μ_y	μ_z	$|\boldsymbol{\mu}|$
$PyzBF_3$	−6.521	0.001	−0.223	6.525
$BPEBF_3$	−8.988	0.738	−0.339	9.024
$W(CO)_5$	2.857	0.000	0.000	2.857
$W(CO)_5Pyz$	5.260	0.001	0.001	5.260
$W(CO)_5PyzBF_3$	−3.327	0.223	−0.006	3.335
$W(CO)_5BPE$	7.328	−0.411	−0.004	7.410
$W(CO)_5BPEBF_3$	−2.323	0.186	−0.401	2.365
$Cr(CO)_5$	2.279	0.000	0.000	2.279
$Cr(CO)_5Pyz$	4.425	0.000	0.000	4.425
$Cr(CO)_5PyzBF_3$	−3.593	0.012	−0.306	3.606
$Cr(CO)_5BPE$	6.260	−0.378	−0.009	6.260
$Cr(CO)_5BPEBF_3$	−3.190	0.171	−0.393	3.220

Table 2
Charges of selected fragments of the compounds of group A

	M	$M(CO)_5$	Pyz	BPE	BF_3
$PyzBF_3$	–	–	0.299	–	−0.299
$BPEBF_3$	–	–	–	0.320	−0.320
$W(CO)_5$	−0.334	0.000	–	–	–
$W(CO)_5Pyz$	−0.535	−0.157	0.157	–	–
$W(CO)_5PyzBF_3$	−0.520	−0.059	0.349	–	−0.290
$W(CO)_5BPE$	−0.528	−0.184	–	0.184	–
$W(CO)_5BPEBF_3$	−0.528	−0.161	–	0.475	−0.314
$Cr(CO)_5$	−0.947	0.000	–	–	–
$Cr(CO)_5Pyz$	−1.263	−0.220	0.220	–	–
$Cr(CO)_5PyzBF_3$	−1.237	−0.149	0.438	–	−0.289
$Cr(CO)_5BPE$	−1.259	−0.241	–	0.241	–
$Cr(CO)_5BPEBF_3$	−1.241	−0.173	–	0.488	−0.315

the principal axes of inertia; the $M(CO)_5$ and BF_3 fragments are in the negative and positive regions of the molecular axis x (hereafter referred as x_- and x_+, respectively).

The nature of the ligands clearly affects the dipole moment of the TM complexes. The 16e species $W(CO)_5$ has $|\boldsymbol{\mu}| = 2.857\,D$ with $\boldsymbol{\mu}$ directed along x_+, that is a direction opposite to the direction W–$(CO)_{axial}$. Both ligands Pyz and BPE in their free form have null dipole moment by symmetry, but they are able to induce an important increase of $|\boldsymbol{\mu}|$ in their complexes: $|\boldsymbol{\mu}| = 5.260$ and $7.410\,D$ in $W(CO)_5Pyz$ and in $W(CO)_5BPE$, respectively.

As it will be discussed later, the $W(CO)_5$ fragment competes with BF_3 as an accepting group. This induces the L_1' and L_2' ligands to be less polarised than L_1 and L_2; correspondingly the magnitude of $\boldsymbol{\mu}$ reduces from 5.260 to 3.335 D for the substitution $L_1 \rightarrow L_1'$ and from 7.410 to 2.365 D for the substitution $L_2 \rightarrow L_2'$. However, the withdrawing power of BF_3 is much stronger than that of $W(CO)_5$, to the point that the direction of $\boldsymbol{\mu}$ is reversed in $W(CO)_5L_1'$ and $W(CO)_5L_2'$ with respect to $W(CO)_5L_1$ and $W(CO)_5L_2$ complexes.

All the electronic features so far commented for W complexes are fully confirmed by the analysis of the electron distribution in Cr complexes. $|\boldsymbol{\mu}|$ for $Cr(CO)_5$ is smaller (2.279 D) than for $W(CO)_5$ (2.857 D), a trend observed also for the complexes $Cr(CO)_5Pyz$ (4.425 D versus 5.260 D) and $Cr(CO)_5BPE$ (6.260 D versus 7.328 D) compounds. The dipole moment of the three Cr complexes is always directed along x_+,

but it is again reversed in L_1' and L_2' due to the effect of BF_3.

To get a further information on the electron distribution within the complexes we studied also the charges of isolated fragments $M(CO)_5$ (M = W, Cr), Pyz, BPE and BF_3.

The charge accumulated on $W(CO)_5$ is larger in $W(CO)_5Pyz$ than in the corresponding BF_3-adduct (see Table 2). This indicated that $PyzBF_3$ has a reduced donor property with respect to Pyz. Note that net charges on the metal atom in $W(CO)_5Pyz$ and $W(CO)_5PyzBF_3$ are almost identical and therefore the charge reorganisation is almost completely internal to the carbonyl ligands. In the case of $BPEBF_3$ ligand, the BF_3 group is too far from $W(CO)_5$ to induce a significant effect (see Table 2). For the Cr complexes, the negative charge on $Cr(CO)_5$ is systematically larger than that on $W(CO)_5$ in the corresponding W complexes (see Table 2). A significant reduction of the negative charge on the $Cr(CO)_5$ group is caused by the presence of BF_3 in the $PyzBF_3$ derivative and, to a similar extent, also in the $BPEBF_3$ one.

The details of the electronic structure of the Cr and W compounds can be analysed in terms of the occupation of selected MOs determined according to the natural bond orbitals theory. Our approach is based on an ad hoc definition of localised electronic sites (atomic-like orbitals on metals atoms, lone pairs and π^* MOs on ligands). The formation of the complex may be represented as a charge transfer (CT) between localised sites; their occupancies are reported in Table 3 for group A complexes. The first comment

Table 3
NBO population of selected orbitals in group A complexes

	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}	$\pi^*_{trans\text{-}CO}$ [a]	$\pi^*_{cis\text{-}CO}$ [a]	$Lp_{trans\text{-}C}$ [b]	$Lp_{cis\text{-}C}$ [b]	Lp_N [c]
PyzBF$_3$	–	–	–	–	–	–	–	–	–	1.932
BPEBF$_3$	–	–	–	–	–	–	–	–	–	1.929
W(CO)$_5$	1.406	1.406	1.356	0.802	1.000	0.262	0.183	1.423	1.559	–
W(CO)$_5$Pyz	1.384	1.369	1.372	0.932	1.045	0.228	0.220	1.452	1.541	1.743
W(CO)$_5$PyzBF$_3$	1.397	1.332	1.383	0.930	1.045	0.212	0.194	1.457	1.542	1.744
W(CO)$_5$BPE	1.378	1.371	1.368	0.935	1.046	0.234	0.201	1.453	1.541	1.734
W(CO)$_5$BPEBF$_3$	1.382	1.365	1.370	0.933	1.045	0.229	0.201	1.453	1.541	1.736
Cr(CO)$_5$	1.647	1.649	1.572	1.111	0.828	0.178	0.113	1.413	1.492	–
Cr(CO)$_5$Pyz	1.590	1.556	1.513	0.997	1.156	0.186	0.155	1.400	1.468	1.704
Cr(CO)$_5$PyzBF$_3$	1.582	1.535	1.524	0.995	1.152	0.176	0.131	1.397	1.468	1.711
Cr(CO)$_5$BPE	1.584	1.560	1.504	1.000	1.159	0.191	0.156	1.400	1.467	1.692
Cr(CO)$_5$BPEBF$_3$	1.564	1.566	1.509	0.997	1.157	0.188	0.139	1.396	1.468	1.700

[a] Arithmetic mean of the populations of the π^* orbitals of the CO *trans* ($\pi^*_{trans\text{-}CO}$) and *cis* ($\pi^*_{cis\text{-}CO}$) to the aromatic ligand.

[b] Population of the lone pair of the carbonyl C atom *trans* ($Lp_{trans\text{-}C}$) and *cis* ($Lp_{cis\text{-}C}$) to the aromatic ligand.

[c] Population of the lone pair of the coordinating N atom.

concerns the occupation of the $d_{x^2-y^2}$ and d_{z^2} orbitals (acceptors) which is systematically higher in Cr(CO)$_5$L than in W(CO)$_5$L complexes. This shows that Cr is a σ-acid stronger than W. This is obviously confirmed by the population of the lone pairs on the N atom of Pyz or BPE and on the C atoms of CO which are always lower in Cr(CO)$_5$L than in W(CO)$_5$L.

The π back-donation to the empty MOs of the ligands involves the d_{xy}, d_{xz} and d_{yz} donor orbitals of the metal. The corresponding orbital occupancy in W(CO)$_5$L is significantly lower than in Cr(CO)$_5$L, thus, showing that W is a better π-donor than Cr. Correspondingly, the computed occupations of the π* orbitals of the carbonyl ligands are higher in W than in Cr derivatives (see Table 3). Finally, the effect of the BF$_3$ group is to induce a significantly more pronounced π back-donation toward the aromatic ligands (see Table 3).

3.3. Molecular geometries of group B complexes

The group B is formed by complexes of general formula M(CO)$_x$Cl$_y$Pyz in which the metal centres are atoms of groups 7 (Re), 8 (Ru, Os) and 9 (Rh, Ir). In the case of Re, Os and Ir species, we have also considered the isomers with a Cl$^-$ ligand in *trans* to the aromatic ligand, which will be labelled as *trans*-M(CO)$_x$Cl$_y$Pyz. The geometries

of the compounds of the group B are schematically shown in Fig. 2. For all the compounds, but *trans*-Re(CO)$_4$ClPyz the aromatic ring of Pyz is rotated by about 45° with respect to the plane defined by the metal centre and two equatorial carbonyl ligands. Such a conformation is caused by the presence of Cl$^-$ ligands on the equatorial plane. Indeed, the complex *trans*-Re(CO)$_4$ClPyz assumes an eclipsed conformation.

Let us consider first the 5d-metal complexes W(CO)$_5$Pyz, Re(CO)$_4$ClPyz and Os(CO)$_3$Cl$_2$Pyz, all in a d^6 configuration but with increasing oxidation state (0, +1 and +2), and Ir(CO)$_2$ClPyz with a d^8 configuration and oxidation state +1.

The M–N bond lengths of these compounds decrease significantly by increasing the oxidation state of the metal (W–N = 2.275 Å, Re–N = 2.241 Å, Os–N = 2.155 Å) or with the effective nuclear charge of the metal (Ir–N = 2.111 Å). A similar trend is also observed for the M–C bond length *trans* to the aromatic ligand, which, in the same series is equal to 1.996, 1.942, 1.928 and 1.872 Å. These values are almost unchanged in corresponding complexes of 4d metals (see Fig. 2). The M–N bond lengths of the compounds with the Cl$^-$ ligand in *trans* to the aromatic ring are systematically shorter than those of the compounds with a *trans* CO by 0.073, 0.011 and 0.065 Å, in *trans*-Re(CO)$_4$ClPyz, *trans*-Os(CO)$_3$Cl$_2$Pyz and *trans*-Ir(CO)$_2$ClPyz, respectively.

3.4. Dipole moments and atomic charges of group B complexes

Fig. 2 shows graphically the dipole moments of the compounds of the group B, whereas numeric values of the components are reported in Table 4. The $M(CO)_xCl_yPyz$ complexes are oriented along the principal axes of inertia; the $M(CO)_xCl_y$ and Pyz fragments are in x_- and x_+ regions, respectively. The Cl^- ions *cis* to the Pyz ligand are in the y_- region.
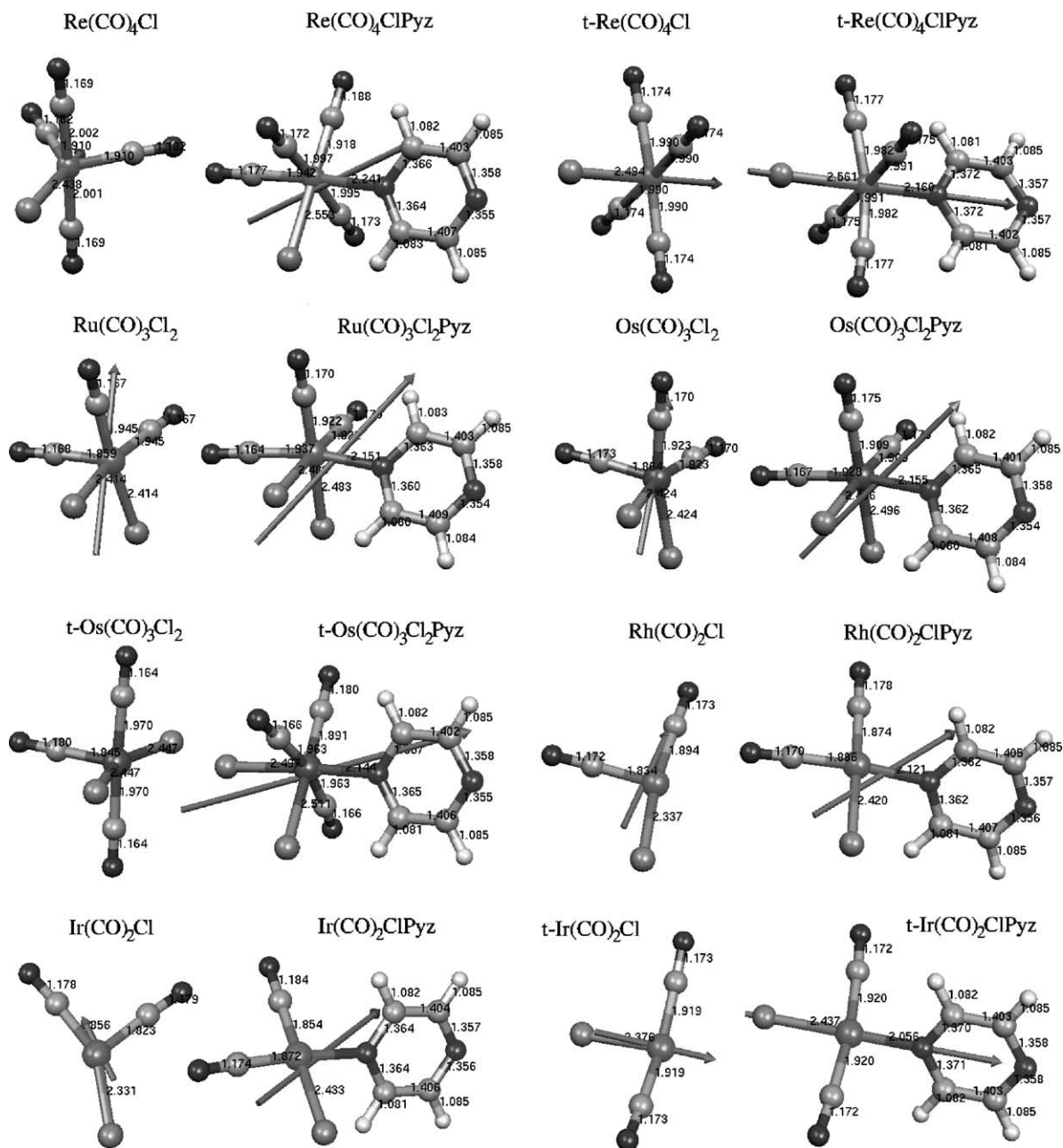

Fig. 2. Molecular structures with selected geometry parameters (bond distances in Angstrom) of compounds of group B.

Table 4
Dipole moments (in Debye) of the compounds of group B

	μ_x	μ_y	μ_z	$|\boldsymbol{\mu}|$
Re(CO)$_4$Cl	0.000	1.397	0.000	1.397
Re(CO)$_4$ClPyz	4.478	2.319	−0.924	5.127
trans-Re(CO)$_4$Cl	4.558	0.000	0.000	4.558
trans-Re(CO)$_4$ClPyz	7.867	0.000	0.000	7.867
Ru(CO)$_3$Cl$_2$	−0.383	5.210	0.000	5.225
Ru(CO)$_3$Cl$_2$Pyz	3.131	4.992	0.001	5.893
Os(CO)$_3$Cl$_2$	−1.539	4.126	0.000	4.404
Os(CO)$_3$Cl$_2$Pyz	3.488	4.489	0.005	5.684
trans-Os(CO)$_3$Cl$_2$	−0.180	0.004	−0.001	0.180
trans-Os(CO)$_3$Cl$_2$Pyz	7.692	2.586	−1.764	8.304
Rh(CO)$_2$Cl	−0.275	3.032	0.009	3.045
Rh(CO)$_2$ClPyz	3.720	3.115	0.416	4.869
Ir(CO)$_2$Cl	−1.763	0.150	−0.003	1.770
Ir(CO)$_2$ClPyz	−4.356	2.440	0.360	5.006
trans-Ir(CO)$_2$Cl	3.152	0.000	−0.661	3.220
trans-Ir(CO)$_2$ClPyz	6.966	−0.002	−0.019	6.966

As clearly shown in Fig. 2, the dipole moments of this group of compounds are strongly affected by the presence of Cl$^-$ ligands, both for magnitude and direction. As shown in Table 4, very different orientations and lengths of the dipole can be obtained, just varying the oxidation state of the metal and, as a consequence, the number of coordinated Cl$^-$ ions. In addition, the complexes with the Cl$^-$ in *trans* to the aromatic ligand are always characterised by a large $|\mu|$, exactly parallel to the molecular axis x in *trans*-Re(CO)$_4$ClPyz

and *trans*-Ir(CO)$_2$ClPyz or oriented along the direction (x_+, y_+) in *trans*-Os(CO)$_3$Cl$_2$Pyz.

Therefore, only in the case of M(I) complexes μ can be fully oriented along the molecular axis, while for M(II) species the dipole is necessarily away from the molecular axis and its projection along x is shorter. In some specific case, the resulting μ is almost parallel to y_+ and orthogonal to the molecular axis. Such a reorientation of μ caused by Cl$^-$ ligands has a great effect on the NLO properties, as discussed in the next section.

The net charges of the molecular fragments (M, Cl$_{(1,2)}$, CO$_{(2,3,4)}$, M(CO)$_x$Cl$_y$ and Pyz) and the NBO population of selected orbitals of complexes belonging to the group B are shown in Tables 5 and 6, respectively. In the series of 5d-metal complexes, with the exception of Ir(CO)$_2$ClPyz, the accepting power of the metal centre increases with its oxidation state as shown, for instance, by the populations of the lone pair on the N coordinating atom, equal to 1.743 in W(CO)$_5$Pyz, 1.706 in Re(CO)$_4$ClPyz and 1.669 in Os(CO)$_3$Cl$_2$Pyz. The corresponding value for the d^8 Ir(I) (1.707) is similar to that of Re(I) complex. This shows that the trend of the σ-accepting ability of the metal is dominated by the oxidation number. The occupations of lone pair of the coordinating N atom are parallel to those of the accepting metal orbitals d$_{x^2-y^2}$ and d$_{z^2}$ (see Table 6).

Table 5
Charges of selected fragments of the compounds of group B

	M	Cl$_{(1,2)}$	CO$_{(2,3,4)}$	M(CO)$_x$Cl$_y$	Pyz
Re(CO)$_4$Cl	−0.163	−0.380	0.543	0.000	–
Re(CO)$_4$ClPyz	−0.329	−0.439	0.614	−0.205	0.205
trans-Re(CO)$_4$Cl	−0.220	−0.344	0.564	0.000	–
trans-Re(CO)$_4$ClPyz	−0.348	−0.432	0.580	−0.200	0.200
Ru(CO)$_3$Cl$_2$	0.051	−0.729	0.678	0.000	–
Ru(CO)$_3$Cl$_2$Pyz	−0.080	−0.882	0.714	−0.248	0.248
Os(CO)$_3$Cl$_2$	0.231	−0.728	0.497	0.000	0.000
Os(CO)$_3$Cl$_2$Pyz	0.105	−0.897	0.556	−0.236	0.236
trans-Os(CO)$_3$Cl$_2$	0.193	−0.748	0.555	0.000	0.000
trans-Os(CO)$_3$Cl$_2$Pyz	0.083	−0.847	0.518	−0.246	0.246
Rh(CO)$_2$Cl	0.190	−0.444	0.254	0.000	–
Rh(CO)$_2$ClPyz	0.079	−0.516	0.249	−0.188	0.188
Ir(CO)$_2$Cl	0.206	−0.414	0.208	0.000	–
Ir(CO)$_2$ClPyz	0.122	−0.502	0.187	−0.193	0.193
trans-Ir(CO)$_2$Cl	0.139	−0.262	0.123	0.000	–
trans-Ir(CO)$_2$ClPyz	0.109	−0.444	0.186	−0.149	0.149

Table 6
NBO population of selected orbitals of the compounds of group B

	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}	$\pi^*_{trans\text{-}CO}$[a]	$\pi^*_{cis\text{-}CO}$[a]	$Lp_{trans\text{-}C}$[b]	$Lp_{cis\text{-}C}$[b]	Lp_N[c]
Re(CO)$_4$Cl	1.542	1.569	1.578	0.910	1.092	0.245	0.144	1.400	–	–
Re(CO)$_4$ClPyz	1.584	1.552	1.567	1.036	1.128	0.194	0.150	1.406	1.506	1.706
trans-Re(CO)$_4$Cl	1.666	1.666	1.514	0.832	1.127	–	0.160	–	1.530	–
trans-Re(CO)$_4$ClPyz	1.648	1.595	1.530	0.950	1.173	–	0.175	–	1.508	1.658
Ru(CO)$_3$Cl$_2$	1.760	1.775	1.810	1.038	1.153	0.165	–	1.362	–	–
Ru(CO)$_3$Cl$_2$Pyz	1.782	1.787	1.793	1.108	1.170	0.125	–	1.440	–	1.663
Os(CO)$_3$Cl$_2$	1.676	1.688	1.722	1.023	1.142	0.202	–	1.349	–	–
Os(CO)$_3$Cl$_2$Pyz	1.700	1.704	1.706	1.107	1.162	0.142	–	1.411	–	1.669
trans-Os(CO)$_3$Cl$_2$	1.736	1.667	1.775	0.975	1.127	0.249	0.132	1.329	1.518	–
trans-Os(CO)$_3$Cl$_2$Pyz	1.779	1.741	1.671	1.035	1.185	–	0.136	–	1.514	1.647
Rh(CO)$_2$Cl	1.769	1.834	1.789	1.040	1.988	0.179	–	1.438	–	–
Rh(CO)$_2$ClPyz	1.775	1.835	1.788	1.088	1.982	0.151	–	1.494	–	1.619
Ir(CO)$_2$Cl	1.039	1.781	1.708	1.676	1.992	0.191	–	1.428	–	–
Ir(CO)$_2$ClPyz	1.701	1.773	1.717	1.110	1.984	0.170	–	1.440	–	1.707
trans-Ir(CO)$_2$Cl	1.775	1.982	1.678	0.968	1.929	–	0.162	–	1.583	–
trans-Ir(CO)$_2$ClPyz	1.729	1.923	1.680	1.056	1.980	–	0.162	–	1.558	1.650

[a] Arithmetic mean of the populations of the π^* orbitals of the CO trans ($\pi^*_{trans\text{-}CO}$) and cis ($\pi^*_{cis\text{-}CO}$) to the aromatic ligand.
[b] Population of the lone pair of the carbonyl C atom trans ($Lp_{trans\text{-}C}$) and cis ($Lp_{cis\text{-}C}$) to the aromatic ligand.
[c] Population of the lone pair of the coordinating N atom.

The occupations of orbitals involved in the back-bonding have trend opposite to that commented above: the occupation numbers of d_{xz} is equal to 1.369 in W(CO)$_5$Pyz, 1.552, in Re(CO)$_4$ClPyz, 1.704 in Os(CO)$_3$Cl$_2$Pyz and 1.773 in Ir(CO)$_2$ClPyz. In the complexes with a Cl$^-$ ligand trans to the N-ligand, the population of the lone pair on N atom is systematically lower than in the cis isomers, indicating a larger σ charge transfer from the aromatic ligand to the metal centre (see Table 6).

The acceptor ability of the two metals in Ru(CO)$_3$Cl$_2$Pyz and Os(CO)$_3$Cl$_2$Pyz is quite similar, but Os behaves as a π-donor significantly better than Ru. The comparison of Rh and Ir metal centres in M(CO)$_2$ClPyz complexes shows that Rh is a more effective σ-acceptor than Ir with respect to the nitrogen lone pair of Pyz, but a less effective σ-acceptor with respect to the carbon lone pair of the CO trans to Pyz (see Table 6).

4. Conclusions

Our theoretical investigation shows that basic features of electron distribution in coordination compounds can be modulated by simple substitutions of ligands or by the presence of a strongly accepting group like BF$_3$. The DFT general description of the electronic structure is in full agreement with the chemical expectations based on acid–base theory of coordination. Our results are interesting, in particular, in the framework of the theory of the NLO properties, as it will be briefly discussed in the following, with a particular emphasis on second and third order responses. As well know, the dipole moment of a molecule subjected to an external (static) electric field is:

$$\boldsymbol{\mu} = \boldsymbol{\mu}^0 + \boldsymbol{\alpha} \cdot \boldsymbol{F} + \tfrac{1}{2}\boldsymbol{\beta} : \boldsymbol{F}^2 + \tfrac{1}{6}\boldsymbol{\gamma} \vdots \boldsymbol{F}^3 + \cdots,$$

where $\boldsymbol{\alpha}, \boldsymbol{\beta}, \boldsymbol{\gamma}, \ldots$ are tensors of second, third, fourth … order, $\boldsymbol{F}$ the external, static electric field and the usual notation for contraction of tensor has been adopted. Similar expansions hold also for frequency dependent fields $\boldsymbol{F}(\omega)$.

$\beta_{\mathbf{VEC}}$ is defined as the sum of the projections of the vector part of the tensor $\boldsymbol{\beta}$ along the components of the unit vector $\bar{\boldsymbol{\mu}} = \boldsymbol{\mu}/|\boldsymbol{\mu}|$: $\beta_{VEC} = \boldsymbol{\beta}^* \cdot \bar{\boldsymbol{\mu}}$, where $\boldsymbol{\beta}^*$ has components $\beta_p = \beta_{ppp} + (1/3)\sum_{q \neq p}(\beta_{pqq} + \beta_{qpq} + \beta_{qqp})$, $p, q = x, y, z$. As well known, β_{VEC} is also a (usually) dominant contribution to γ_{EFISH}, according

to the equation:

$$\gamma_{\text{EFISH}} = \frac{|\boldsymbol{\mu}| \cdot \beta_{\text{VEC}}(-2\omega; \omega, \omega)}{5kT} + \bar{\gamma}(-2\omega; \omega, \omega, 0)$$

where $\bar{\gamma} = (1/5)[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$ and a single line excitation of energy $h\omega$ is considered.

According to the approximation proposed by Oudar [37], based on the hypothesis that only the first excited state is important,[1] the sum over states (SOS) equation for β_{ppp}, reduces to the form:

$$\beta_{ppp} = \frac{3e^2}{2} \frac{\omega_{0e} f_{0e} \Delta\mu_{e0}}{(\omega_{0e}^2 - 4\omega^2)(\omega_{0e}^2 - \omega^2)}$$

where f_{0e}, ω_{0e} are the oscillator strength and the angular frequency for the ground state-excite state $|e\rangle \leftarrow |0\rangle$ excitation and $\Delta\mu_{e0}$ is the variation of the static dipole between $|e\rangle$ and $|0\rangle$ states.

For the group of complexes here considered, the hypothesis can be made that $|e\rangle \leftarrow |0\rangle$ is the metal–ligand charge transfer mainly involving d-type orbitals of the metal and π^* orbitals of the aromatic ligand, which are the low lying empty MOs. Such a CT is expected to be dominated by the x component of the transition dipole, parallel to the molecular axis. All other components do contribute to a much smaller extent or are important only for higher energy transitions. Correspondingly, β_{VEC} assumes large values if also the leading component of $\boldsymbol{\mu}$ is $\mu_p \equiv \mu_x$. Finally, to large value of β_{VEC} corresponds a large value of the T-dependent term of γ_{EFISH}. The connection between our DFT results and possibly interesting NLO properties is now quite clear. In M(CO)$_x$Cl$_y$L complexes, the direction and the orientation of $\boldsymbol{\mu}$ can be varied as a function of oxidation state of the metal and of the presence of a strong electron accepting group BF$_3$. All the complexes of the group A can be considered as suitable for high values of β_{VEC}, larger than those of the group B derivatives, just because in the group A conditions for parallelism of $\bar{\boldsymbol{\mu}}$ and $\boldsymbol{\beta}^*$ is fully satisfied.

The conclusions concerning the relative magnitude of β_{VEC} along the series of considered complexes, here derived from a qualitative discussion, seems to be confirmed by preliminary results of DFT evaluation

of first and second order hyperpolarizabilities [38]. In addition, our qualitative discussion is in a full agreement with all the observations based on experimental determinations of NLO properties [19] of some compounds considered in the present study.

Acknowledgements

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