REVIEW ARTICLE

Special Issue on 150 years of the Periodic Table

Designing M-bond (X-M···Y, M = transition metal): σ-hole and radial density distribution

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Abstract. Following the ubiquitous H-bond, there is a growing interest in weak non-covalent interactions involving other elements, *viz.,* the Z-bonds (X-Z···Y, Z = halogens, chalcogens, etc.). Although almost all the main group elements can act as Z bond donors, the search for a similar role for transition metals in X-M···Y, (M = transition metal) interaction, called the Metal-bond, is still in its infancy. This article summarizes our attempts to understand the participation of transition metal elements as electron acceptors in a weak interaction with electron-rich species Y. Cambridge Structural Database analysis revealed that except Group 11 and 12 transition metal complexes (Type-II), electron-saturated (18 electron) metal complexes having partly filled d orbitals (Group 3–10; Type-I) hesitate to form Metal-bonds. This is attributed to the partial σ-hole screening by core electron density and diminished stabilization from charge polarization in Type I complexes. We also show that Type-I complexes could be forced to form Metal-bonds by employing extreme ligand conditions, thereby opening new areas of research where Metal-bonds can act as emerging non-covalent interaction in designing supramolecular architectures.

Keywords. Weak interactions; H-Bond; M-Bond; sigma-hole; MESP; radial density distribution.

1. Introduction

While we celebrate the year of the periodic table of elements, it is worthwhile to examine any phenomenon in chemistry and take it through the chemistry of the entire series of elements. In this article, we examine the prevalence of weak intermolecular interactions among different sets of elements of the periodic table. The simplest of these, the hydrogen bond, is also the most ubiquitous in Nature, (X-H···Y).[1–6] The last several decades witnessed the flourishing weak intermolecular interactions beyond hydrogen bonding, and there are now examples to include almost all of the main-group elements in the Periodic Table. Halogen bonding,[7,8] chalcogen bonding,[9,10] pnicogen bonding,[11,12] tetral bonding,[13,14] triel bonding,[15,16] beryllium bonding,[17,18] lithium bonding,[19,20] and aerogen bonding,[21,22] are new additions to this field.

One of the pre-requisites for most of the X-Z molecules to take part in X-Z···Y interaction (Z-bonding such as halogen, chalcogen, tetral bonding, etc.)[23,24] is the presence of a σ-hole on the Z-atom.[25–27] The σ-hole is defined as the region of the positive electrostatic potential on the Z-atom along the extension of the X-Z σ-bond. The rationale of a majority of Z-bonds is the electrostatic attraction between the σ-hole on the Z-bond donor and the electron density on the Y-group.[28] This led Politzer *et al.,* to coin the term '*σ-hole bonding*' to unify all those Z-bonds formed *via* σ-hole interaction.[29] Apart from this, charge transfer from the Y to the antibonding molecular orbital on the X-Z is another important factor that controls the nature and stability of Z-bonds.[23,28,30]

In the year of the periodic table of elements, we seek the possibility of extending the week bond to transition metals and search for the existence of transition metal bonds as in X-M···Y interaction (M = Transition Metal; Metal-bond). Is it possible for an electron saturated (18-electron) transition metal complex to participate in Metal-bond formation? In view of the unanticipated examples of electronegative fluorine[31,32] and noble gas atoms[21,33,34] participating

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in Z-bond formation, it is natural to expect an electropositive transition metal in its ligated environment to act as a Metal-bond donor. Here, the designation, Metal-bond, is strictly applied only to *electron saturated 18-electron transition metal complexes that act as an electron acceptor*, and neglect complexes with 16 or less number of electrons, for obvious reasons.

There are several reports in the literature that deal with non-covalent interactions in transition metal systems. The recently proposed regium bonds involving the interaction of σ-hole on a metal cluster with nucleophilic species such as NH_3 and HCN^{35} or with aromatic surfaces[36,37] is one such example. The presence of σ-holes on the edges and corners of gold nanoparticles are recently correlated with its catalytic effects.[38] In the same line, σ-lump[39] interactions in noble metal nanoparticles and coinage metal dimers are also proposed.[40] Other types of non-covalent interactions involving transition metal complexes are hemichelation and double hemichelation,[41–43] donor-acceptor interactions,[44,45] stabilizing heterodox bonding,[46–48] etc. However, our detailed analysis of each of them revealed that none of them falls under the definition of the Metal-bond.[24] This led us to formulate the title question of the paper.

Recently, we reported a Cambridge Structural Database (CSD) analysis combined with computational studies looking for the possible existence of Metal-bonded complexes.[30] Our CSD search involving over 300000 structures indeed resulted in locating a large number of seemingly Metal-bonded complexes. However, a careful analysis of the nature of the σ-hole, as well as the direction of electron flow during the weak bond formation, showed that most of the species extracted from the database do not belong to the Metal-bond category.[30] Our studies helped us to classify transition metal complexes as Type I (Group 3-10) and Type II (Group 11-12) based on their ability to participate in σ-hole driven interaction called as Metal-bonds (X-M···Y).[30] Though Type I complexes could not form Metal-bonds, the possible existence of Metal-bond in Type-II complexes is known for long,[49–52] even though they were not designated as Metal-bonded complexes. Our analysis further validated the striking similarity between the Z-bonds in the main-group and Type-II metal complexes. We witnessed a contrast in the behavior of Type-I metal complexes with that of Type-II and all others in the main-group. Here, we review these results to understand the electronic structure reasons for the reluctance of Type-I complexes to participate in Metal-bond formation and suggest possible remedies to make them compatible with Metal-bonding.

2. Computational details

Geometry optimization, vibrational frequency calculation, and electron density analysis were performed using the Gaussian09 quantum chemistry package at the M06/Def2-QZVP level of theory.[53] The Cambridge Structural Database (CSD) searches were carried out using the ConQuest package available from the CCDC. The radial density distribution (RDF) plots were generated using the scalar relativistic DFT calculations at ZORA-PBE/TZ2P level.[54] The ETS-NOCV[55] scheme implemented in the ADF-2014 package at the M06-D3/QZ4P level was employed to generate the deformation density maps.[54]

3. Results and Discussion

Most of the non-covalent X-Z···Y interactions derive their stabilization from the electrostatic attraction between the σ-hole on the Z and electron density on the Y. Thus, as a first step, we have decided to understand the origin of σ-hole[56] in the main group compounds and its possibility in electron saturated transition metal complexes.

A positive potential region on the molecular electrostatic potential (MESP) map of a molecule plotted at 0.001 a.u isosurface is defined as the σ-hole.[57] The 0.001 a.u isosurface is generally considered as the van der Waals surface of the molecule.[58] Since the total electron density around a molecule is the summation of electron density distribution from individual molecular orbitals, it is fair to approximate that the MESP at the van der Waals surface is inherently decided by the nature of the valance molecular orbitals. Thus, one could generate σ-holes at the van der Waals surface of a molecule by carefully engineering the frontier molecular orbitals.

The existence of σ-hole[56] in H-Cl and F-Cl was demonstrated using the molecular orbital (MO) theory approach. It is known from our conventional wisdom that Cl atom of HCl molecule possesses large electron density at the extension of H-Cl σ-bond that results in large negative potential over the Cl atom, Figure 1a. This, in turn, results in the generation of a σ-hole at the H-atom of H-Cl molecule. The negative potential on the Cl-atom of H-Cl can be converted into a positive potential (σ-hole) by replacing H-atom with more electronegative F-atom. An interaction diagram connecting the valance atomic orbitals of F- and Cl- to form the molecular orbitals of F-Cl is presented in Figure 1b. It can be viewed from the MO diagram that the highest occupied molecular orbitals (HOMOs) are
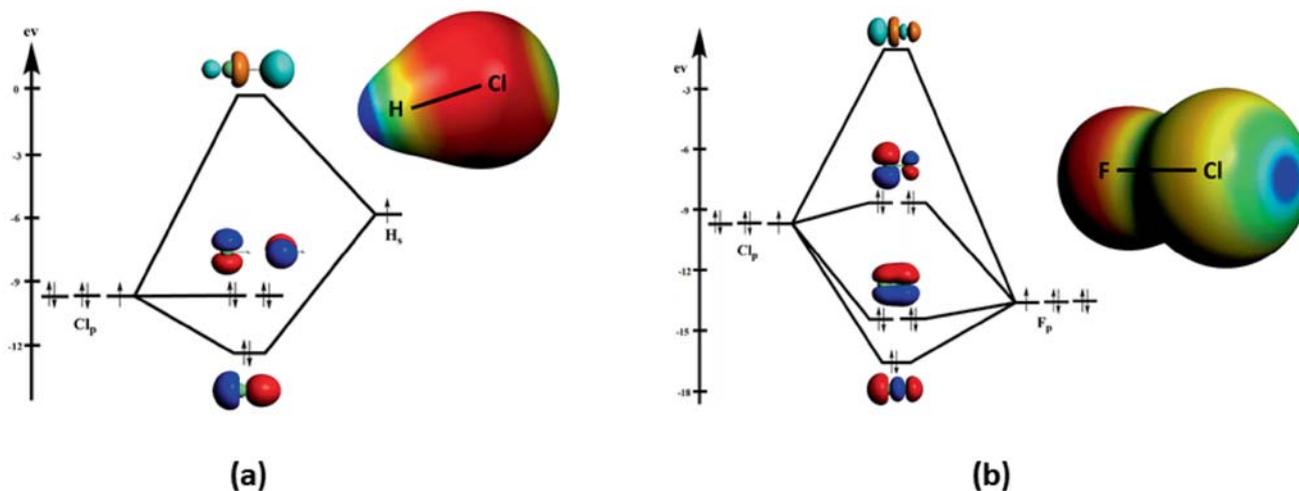
Figure 1. Orbital interaction diagram and molecular electrostatic potential (MESP) map of (a) H-Cl and (b) F-Cl molecules. Only one of the doubly degenerate π-MOs is shown in the F-Cl interaction diagram. The blue and red regions in the MESP map represent the maximum positive and negative electrostatic potential regions respectively.

the π-type MOs mostly located over the peripheral region of Cl atom and the lowest unoccupied molecular orbital (LUMO) is a σ-type MO centered over the Cl. Thus, one could expect that Cl atom in F-Cl would show a ring of negative electrostatic potential at the π-framework, and an absence of electron density at the exterior part of Cl atom in the σ-bonding direction. The expected effects can be observed in the electrostatic potential map of F-Cl molecule given in Figure 1b, where a region of positive potential, the σ-hole, can be seen at the exterior end of Cl atom (blue region) surrounded by a crown of negative potential (yellow region). It naturally derives from the MO diagram that the magnitude of σ-hole can be controlled by fine-tuning the electronegativity difference between the interacting atoms.

A similar analysis can be extended to the transition metal complexes also. Compared to main group compounds, transition metal complexes possess slightly different bonding pattern due to the presence of metal-based d-orbitals. The bonding molecular orbitals are formed by the combination of metal $(n + 1)$s, $(n + 1)$p and nd-orbitals with the ligand group orbitals (LGO), where the lower occupied MOs are mostly concentrated over the ligands and the higher occupied MOs are mostly over the metal. Herein, we focus on the electronic structure of electron-saturated square pyramidal complexes that can retain the sixth coordination site vacant for the incoming nucleophile's attack. The HOMO of a square pyramidal 18-electron complex is an anti-bonding combination of LGO with the metal d_{z^2} orbital pointing towards the vacant sixth coordination site. The anti-bonding nature of HOMO makes the metal center

electron-rich and encourages it to act as an electron donor. The restricted square pyramidal (C_{4v}) geometry of $Fe(CO)_5$ can be used as a prototype to analyze the influence of frontier molecular orbitals on the nature of electrostatic potential at the metal center. The high electron density concentration at the sixth vacant coordination site of $Fe(CO)_5$ is evident from the nature of the HOMO, that results in large electron localization at the metal center and leads to a negative potential at the MESP map, Figure 2. Because of this reason, electron saturated transition metal complexes act as Z-bond acceptors (takes the role of Y)[59] rather than a Metal-bond donor.

Thus, any strategy to decrease this accumulated electron density at the metal center would be desirable to generate a σ-hole at the metal (just like the HCl vs. FCl case). This can be achieved by a proper
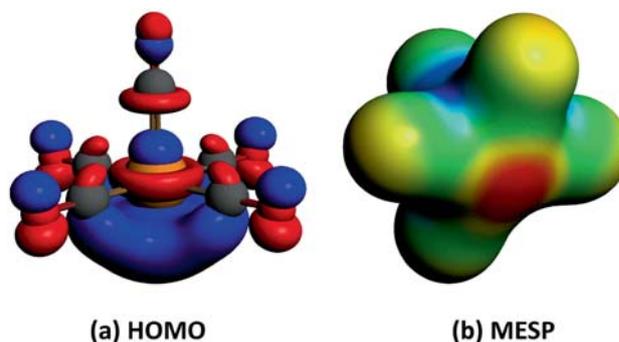

Figure 2. (a) The highest occupied molecular orbital (HOMO) and (b) the molecular electrostatic potential (MESP) map of square pyramidal $Fe(CO)_5$ complex. The blue and red regions in the MESP map represent the maximum positive and negative electrostatic potential regions, respectively.

combination of electron-withdrawing ligands at the metal center. However, to the best of our understanding, such a complex does not exist in the whole of the CSD database.[30] This realization prompted us to speculate that there exists a more fundamental electronic structural reason for the Type-I metals to show resistance towards the σ-hole formation. To make our argument clearer, here we consider the MESP map of three species in Figure 3; F-Cl as a main group example, $(PF_3)_4RhI$ as a Type-I complex, and $(PF_3)_3$-AgI as a Type-II complex. Here, the positive contours (blue color) represent the spread of the σ-hole at the Z-atom. A visual inspection of the +0.04 au contour for the three cases shown in Figure 3 helps to understand the contrasting behavior of the σ-hole for the above-mentioned complexes. For the main group and Type-II complexes, the σ-hole is more spread into the exterior of the Z-atom, whereas that for the Type-I complex it is more shielded and placed near the metal core hindering an incoming Y group from feeling its presence. This screening of σ-hole, therefore, is the major distinguishing factor in the behavior of Type-I complexes with that of the main group and Type-II complexes. The next very obvious question is, what is the fundamental electronic structure reason that hinders Type-I metals to have a spatially diffused σ-hole?

An in-depth analysis of the electronic structure of the Type-I metals resolved the dilemma. The valence region of Type-I metals (groups 3–10) consists of partially filled nd- and (n + 1)s- orbitals. However, for Type-II metals, the valence space is occupied by (n + 1)s orbital only, and the fully filled nd-orbitals (nd^{10}) occupy the core region. A plot of the radial density distribution of 3s, 3p, 3d, and 4s orbitals for Co (Type-I) and Cu (Type-II) are shown in Figure 4 (valence orbitals are shaded). Cobalt possesses 3d and 4s orbitals in the valence region, whereas for Copper, 4s orbital is in the valence space and fully filled 3d orbital is in the core region.

Visual inspection of the radial density distribution of cobalt (Type-I) reveals that the spatial distribution of the valence 3d-orbitals is in fact inside the core 3s and 3p orbitals. This is due to the absence of any primogenic repulsion to 3d-orbitals from the inner core orbitals of same angular distribution.[60–64] It results in a spatially congested 3d orbital (0.36 Å) that remain inside the core levels (0.36 Å),[65] Figure 4. Interested readers can consult reference[62] for more details about primogenic repulsion and its consequences to the electronic structure of molecules. The immediate consequence of this effect is the increased Pauli repulsion experienced by the incoming ligands towards any electron donation to the 3d-orbital. The presence of core orbitals in the valence region also shields the possible existence of any σ-hole at the metal center. Thus, the spatially congested σ-hole at the metal center, and increased Pauli repulsion from core orbitals hinders an incoming electron-rich Y-group to approach the metal, and thereby reluctance to form Metal-bond. However, in the case of copper (Type-II), fully filled 3d orbital is in the core region and the valence space is occupied by spatially diffused 4s orbital that can receive electron density from the incoming Y-group without any hindrance from the core orbitals. Thus, Type-II metal complexes with proper ligand combination behave just like the main group Z-bond donors.
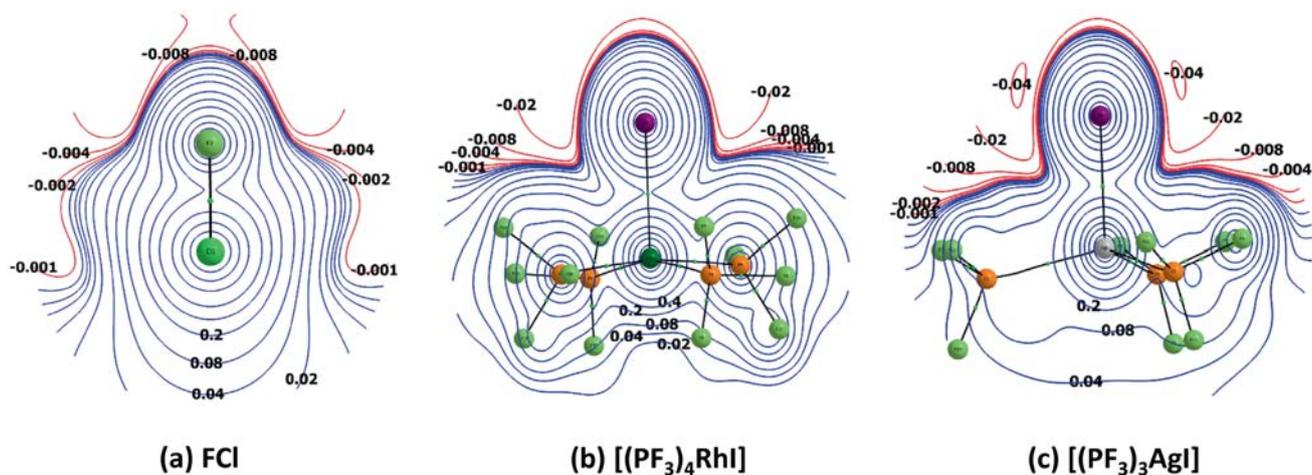

Figure 3. MESP contours of (a) FCl, (b) $[(PF_3)_4RhI]$, and (c) $[(PF_3)_3AgI]$ molecules. Blue and red contours represent positive and negative MESP regions respectively. Adapted with permission from reference[30]. Copyright (2017) American Chemical Society.
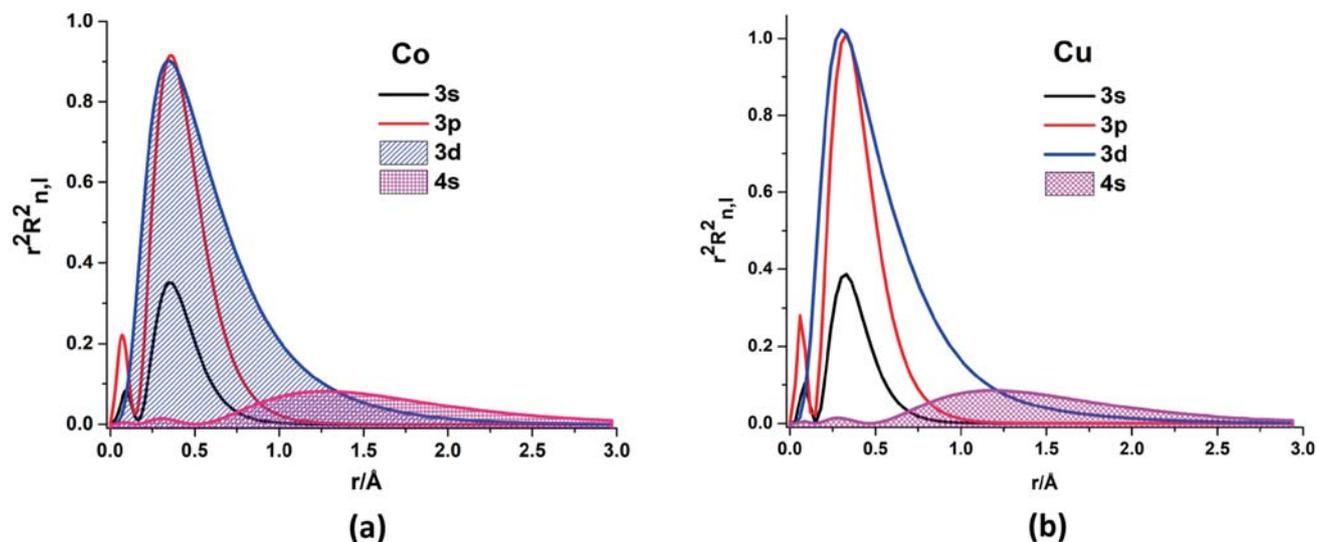
Figure 4. Radial density distribution $r^2R(r)^2$ of 3s, 3p, 3d, and 4s orbitals of (a) Cobalt and (b) Copper from scalar relativistic DFT calculations using ZORA-PBE/TZ2P level of theory. r = radial distance from the nucleus in angstrom unit. Shaded orbitals belong to the valence region and others to the core region.

As we go down the group, primogenic repulsion from inner d-orbitals pushes the valence d-orbitals out of the core region and tends to generate σ-hole. However, in contrast to the main group elements, the electronegativity of the metals increases down the group (due to relativistic effect) along with a decrease in the polarizability, which ultimately results in weakening of the σ-hole.[66] Thus, a balance in all these destabilizing effects could possibly be found in the 4d-series, and perhaps the best candidate for metal bonding in Type-I complexes, if at all possible.

Although difficult to achieve, extreme ligand conditions can be employed on an 18-electron square pyramidal complex of the Type-I to generate a σ-hole at the metal center. Here, we present one such computationally optimized Type-I complex, $CoCl(CN)_2(NO)_2$, having a σ-hole at the metal center. It is then allowed to interact with an electron donor molecule, CO_2, to form Metal-bonded complexes having binding energy of 2.8 kcal/mol. This brings us back to our CSD search for Metal-bonded complexes. Figure 5 shows a comparison between the deformation density map of a Type-I Co-complex (CSD identifier = QUCBIA), and a Type-II Ag complex (CSD identifier = YOBRAJ) with our designed $CoCl(CN)_2(NO)_2$ complex. Here, the direction of electron flow is from red → blue. It is evident from Figure 5 that the metal center in Type-I complex acts as an electron donor (red) and the adduct CH_2Cl_2 acts as the acceptor (blue). Thus, the Type-I system shown here does not belong to the Metal-bond category but instead is a halogen bonded complex. This is not the

case for the Type-II complex, wherein the metal accepts electron density from the chloride donor fulfilling the criteria to be called a Metal-bond. This was the contrast that we have been discussing all along. Finally, a clear inspection of the deformation density map of our designed complex of Type-I category implies that the metal now acts as the electron acceptor from the oxygen atom of the CO_2 resulting in the generation of a Metal-bond. Although we were able to design a Metal-bonded complex, it should always be kept in mind that the inherent tendency of these Type-I complexes is to donate electrons rather than to accept. Thus, the experimental realization of Type-I Metal-bonded complexes would always be a daunting task.

4. Conclusions

The inability of electron saturated transition metal complexes (Type I) of Groups 3–10 to participate in Metal-bond formation is explained based on molecular orbital theory and molecular electrostatic potential. One could engineer the desired potential on any molecule by the proper combination of substituents/ ligands. However, there are no experiments to support this. An analysis of the electronic structure of the transition metal atoms showed that the cause of this problem is in the radial density distribution of the valence and core orbitals of the metal. For the Type-I metals, the valence nd- orbitals are located very close to the fully filled core orbitals, and hence experience
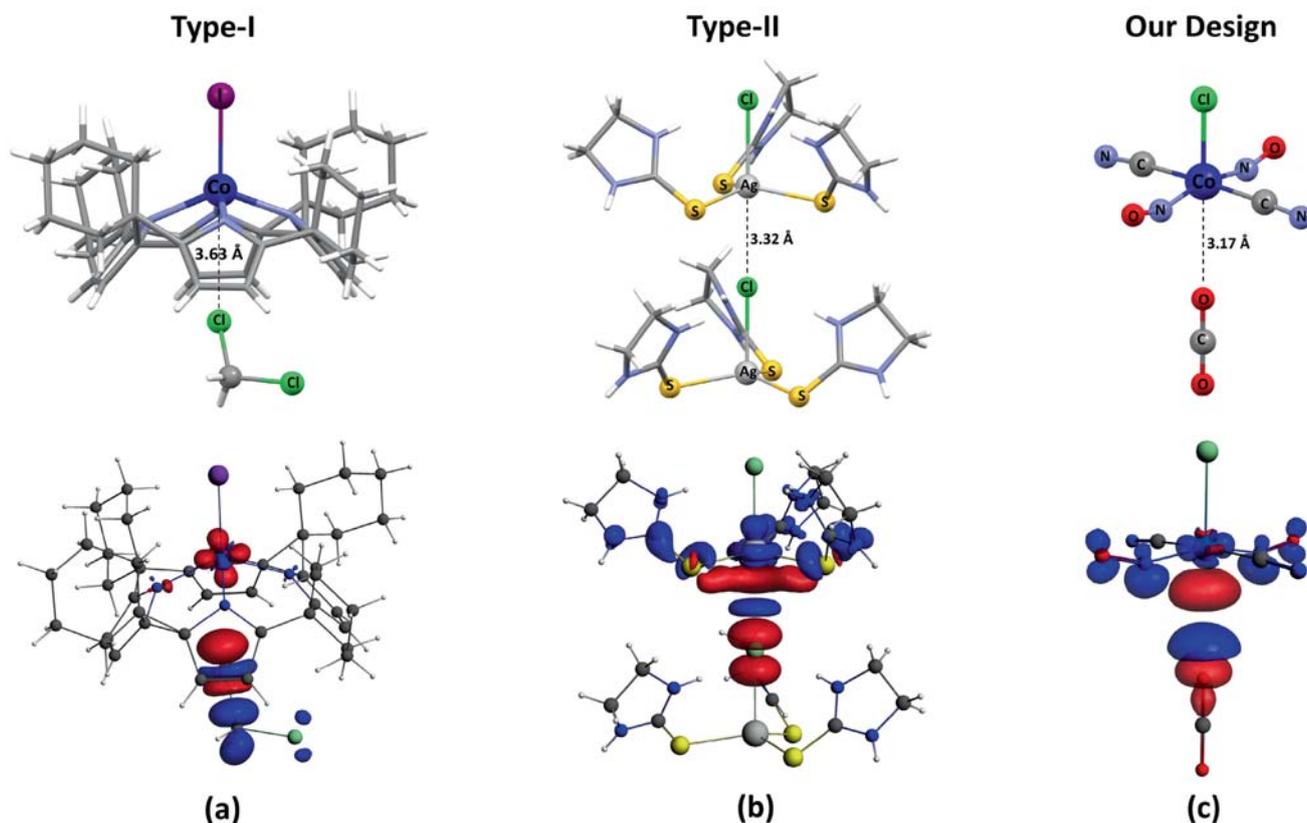
Figure 5. Geometries of the representative example for (a) Type-I (QUCBIA), (b) Type-II (YOBRAJ), and (c) our designed Type-I complex (c) along with their corresponding deformation density map. The direction of electron flow is red → blue.

extensive Pauli repulsion. This makes it extremely hard for an incoming donor molecule (Y) to access the shielded σ-hole on the metal. It eventually results in the reluctance of electron saturated transition metal complexes to participate in Metal-bond formation. The Pauli pressure slightly reduces as we go down the group, however, an increase in electronegativity due to relativistic effects complicates the situation further. Thus, the absence of Metal-bonded systems in the Cambridge Structural Database can be justified.

Based on our current understanding, a generalization can be made across the periodic table for Z-bond donors; the main group and Type-II metal complexes behave similarly and participate in weak Z-bond formation, whereas, Type-I complexes possess an inherent reluctance to form X-M···Y interaction. However, our findings show that extreme ligand conditions can be employed to generate a σ-hole on metal center in Type I complexes, thus the possibility of participating in Metal-bond. The exciting field of Z-bonds is ever-growing, and new members are being added to this family on a yearly basis. The Z-bonds of s- and p-block could be considered as matured, and scientists are now looking for their far stretched applications in various fields. However, Metal-bond is still in its infancy. We believe that the coming years will witness the true potential of Metal-bonds to control and manipulate the structure, bonding, and spectroscopic properties of transition metal complexes in the condensed phase.

Acknowledgements

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