

Computational Design of New N-Heterocyclic Silyl Pincer Fullerenes

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Abstract

A density functional study was performed to design a new N-heterocyclic silyl pincer fullerenes based on the reactions of diaminofullerene with chlorosilanes SiHRCl_2 . Reaction energies of the formation of pincer fullerene ligands increased through the substitution of flanking arms with CH_3 and phenyl groups. However, substituting hydrogen of SiH_2 with methyl slightly increased the corresponding reaction energies, replacing of hydrogen with phenyl groups decreased the reaction energies of the considered pincer fullerenes. While the calculated electrophilicity values of the pincer fullerenes are larger than the electrophilicity values obtained for the fullerene derivatives, the substitution of hydrogen atoms of central SiH_2 and PH_2 did not have a noticeable impact on the electrophilicity values of the pincer fullerenes. The only exception was $\text{SiHPh}(\text{NCH}_2\text{PH}_2)_2\text{C}_{60}$. Natural bonding orbital analysis showed that the delocalization of electrons from the lone pairs of flanking arms phosphorous atoms to the n^* orbital of transition metal atoms was a key factor for stabilizing the considered complexes. The strongest interaction was due to the delocalization of electrons from lone pairs of phosphorous atoms in the flanking arms to the LP^* of transition metals, which was followed by the delocalization of electrons of the $\text{Si-H } \sigma^*$ orbitals to the LP^* of transition metals.

1. Introduction:

There has been an extensive growth in the interest in the chemistry of complexes of transition metals of pincer ligands after Moulton and Shaw's outstanding report in 1976 about a wide range of pincer-ligated metal complexes [1]. Strong binding to the metal center is made by the tridentate coordination of pincer ligands and this outcomes in high stability of the pincer metal unit and decomposition on heating happens only at temperature higher than 100°C [2]. The robustness of pincer-type complexes together with hemilability of donor group positions are of highly significant for designing the catalysts that should be satisfactorily stable to resist the harsh reaction conditions [2–7]. On the other hand, the donor groups don't need to be strongly bonded to make sure that it might reversibly dissociate and form a coordination site needed for activating inert bonds. They can react with external ligands (e.g. isocyanides, H_2 , CO , CO_2 , dihalides, water, acids, oxidizing and reducing agents, or even Na metal) with the assistance of the thermal stability and tight binding of pincer complexes [8–10]. Simultaneously, they keep the pincer coordination of the ligand even at raised temperature. This explains how several pincer-type catalysts can be utilized as catalysts for extensively endothermic reactions like the dehydrogenation of organic substrates [7, 8]. There has been a great deal of attention to this among researchers after the main report by Jensen et al. [11] of an example of iridium pincer complex for alkane dehydrogenation. Therefore, the reasonable design and synthesis of pincer-type ligands, of which stereoelectronic properties are controllable using practical modification, have been long an objective in inorganic and organometallic chemistry [12].

In the pincer ligands, a central moiety supplies two electrons from the donor atom (like phosphorus, nitrogen, oxygen, and carbon) to the transition metal. The two atoms are donated through a covalent

bond that is also an “anchor.” Two neutral pendant arms are on either side of the central donor atom, which provide a lone pair of electrons from heteroatoms (e.g. nitrogen, oxygen, sulfur, or phosphorus). These aspects play a critical role in stabilizing the metal center and characterizing the “active sector” in the coordination of the complex, see Fig. 1. As seen, there is a straight impact on the steric hindrance about the metal in bulky R groups that can add chirality in the complex through chiral LR_n groups. However, the ring size relies upon the size of the linker arms (Y); consequently, it affects the reactivity of the complex and the bite angle. It is feasible to modulate the adjustments in the electronic properties of the pincer ligands utilizing the fine control given by the nature of the substituent on the central aromatic ring (Z). This minimumly affects the steric of the ligand. The nature of the central donor atom (X, typically C, N, O or P) may likewise have a significant electronic effect, particularly through the variety of the trans impact [11–13]. The probability of including other less conventional donor atoms as the equatorial donor is another field of study. Silicon, as a donor, have gotten a unique consideration as electropositive σ -silyl ligands can stabilize higher oxidation states and gratitude to their solid trans impact they can labialize trans ligands, while the both have likely uses in catalysis. Stobart et al. [14] were the first group to introduce the phosphine/silyl-based pincer ligands with flexible alkyl backbones and then extended to the NSiN [15, 16], PSiP [17, 18], and SSiS [19] pincer frameworks. Dixon et al. [20] depicted silicon-based pincer ligands and enforced the meridional geometry by adding an appropriately stiff backbone. They announced the synthesis of the primary instances of N-heterocyclic σ -silyl pincer ligands that is highlighted with a PSiP-LXL donor triad with reactions of $1,2-C_6H_4(NHCH_2PPh_2)_2$ with chlorosilanes $SiHRCl_2$ (R = Ph, Cl) along with trimethylamine, see Fig. 2. Regardless of the relevance between experimental and theoretical efforts about the pincer-ligated metal complexes, we tracked down no theoretical/experimental work about pincer ligands on the fullerene surface. Thinking about a similar procedure, diamino fullerene $C_{60}(NH_2)_2$ can be used as precursors and for designing of new pincer fullerene ligands [21–23]. The reactions of $1,2-C_6H_4(NHCH_2PPh_2)_2$ with chlorosilanes $SiHRCl_2$ (R = H, CH_3 and ,Ph) were taken into account in the design of $SiHR(NCH_2PPL_2)_2C_{60}$ R and L = H, CH_3 and phenyl, see Fig. 2. Nine pincer fullerene ligands $SiHR(NCH_2PL_2)_2C_{60}$, R and L = H, CH_3 and phenyl were taken into account, see Fig. 3. Then, the pincer-ligated metal complexes were developed by adding a transition metal (Fe, Co, Ni and Cu) to the pincer bites to examine their formation using their electronic properties and stability.

2. Computational Aspects

Taking into account the immensity of investigated systems, optimization method is qualified bit by bit. The geometries of the fullerene pincer ligands $SiHR(NCH_2PPL_2)_2C_{60}$ R and L = H, CH_3 and phenyl (1–9, Fig. 3) were optimized at the beginning at the M06-2X/3-21G level of theory. Thereafter, the optimal geometries of the structures determined in past stages were calculated based on standard 6-311G(d, p) and 6-311G+(d, p) basis set. Frequency calculations were performed for the whole systems at the same level of theory, and the actual frequencies were supported as all of them were structures with little energy. The geometries of these pincer fullerene ligands together and the significant geometrical parameters are illustrated by Fig. 3. The pincer-ligated metal complexes were determined by adding transition metals and

then optimal geometries for all the structures were obtained at the same level of theory. The M06-2X functional is in a new generation of hybrid meta-generalized gradient approximation exchange-correlation functionals consisting an accurate treatment of the dispersion energy. The M06-2X functional [24] and 6-311G+(d, p) basis sets were utilized for optimization of geometry and single-point energy calculations. The basis set superposition error (BSSE) effects on the energies are also considered via a counterpoise [25] method. All DFT calculations are performed utilizing GAMESS suite of programs [26, 27]. Wave functions determined at the M06-2X/6-311 + G(d, p) level of theory were analyzed by the natural bond orbital (NBO) method [28, 29].

3. Results And Discussion

Twelve pentagons in six pyracylene units designed C_{60} fullerene cage with icosahedral (I_h) symmetry which led to a single type of carbon atom and two types of C-C bonds including the [6, 6] and [5, 6] ring fusion sites. The length of the bond at [6, 6] and [5, 6] ring fusions in the optimized structure of C_{60} were estimated about 1.392 and 1.455 Å respectively, at the M06-2X/6-311 + G(d, p) level. They are in a perfect agreement with the previously reported values (1.401 and 1.458 Å correspondingly) [48, 49, 50, 51]. Each amination reaction added the elements NRR and H across a [6, 6] π -bond on [60] fullerene. A number of regiochemistry are possible but experimental evidence recommends that aminations prefer either a 1,2- or a 1,4-addition. The addition reaction of C_{60} with amines is a widely studied topic [21–23]. Moreover, 1,2-addition of amine to the [6, 6]-bond of fullerene C_{60} led to formation of two newly C-N bonds with 1.469 Å at the M06-2X/6-311 + G(d, p) level of theory. The [6, 6] C-C bond lengths of 1,2-diamino fullerene were equal to 1.628 Å, which are lengthier than normal C-C bond lengths in fullerene (1.401 Å) [30, 31]. To design of nine pincer fullerene ligands in this study, 1,2-diamino fullerene were utilized as precursors. The geometries of these pincer fullerene ligands together and the significant geometrical parameters are illustrated in Fig. 3. Table S1 (supplementary material) shows the geometrical coordination of the considered structures, calculated at the M06-2X/6-311G+(d, p) level of theory. The geometrical characteristics of the optimized structures of the pincer fullerene ligands are discussed shortly to have better pictures of these derivatives. There is a change from 108° in the pristine C_{60} fullerene and 95.5° in the diamino fullerene to ~ 99.1–99.3° in the pincer fullerenes in the obtained calculated bond angle between each of the attached sites and the two first neighboring atoms of the pentagon changes. In addition, the hexagon-hexagon bond is pulled outward from the fullerene surface with the bond length decreasing from 1.628 Å (in the $C_{60}(NH_2)_2$) to 1.603–1.609 Å in pincer fullerenes. The selected bond distances (Å) i.e. C_{cage} -N 1.465–1.469, N – Si 1.760–1.767, Si – H 1.494–1.499, C – N 1.451–1.456, C – P 1.920–1.930 Å are consistent with the reported values for N-Heterocyclic σ -silyl pincer ligands [20]. As mentioned above, the IR vibrational frequencies were computed for the systems at the same level of theory. In addition, the actual frequencies showed that they were structures with minimized energy. The distinctive IR spectroscopic fingerprints yielded valuable insight into the future experimental detections. However, it is notable that at the beginning, theoretical frequencies are overestimated universally in comparison with the results even in the case of more accurate methods. Therefore, the preset study is not an attempt to predict the exact frequencies. This study is aimed at finding patterns in the data than can

help us determining different forms of pincer fullerenes. Figure 4 shows the simulated IR vibrational spectra of the $\text{SiH}_2\text{-(NCH}_2\text{PH}_2)_2\text{C}_{60}$, and the prominent peaks are quite clear. Thus, it is better to discuss the spectra region by region. In the different vibrational frequencies theoretically found for $\text{SiH}_2\text{(NCH}_2\text{PH}_2)_2\text{C}_{60}$, two lowest-energy modes of 505.6 and 612.0 cm^{-1} correspond to out-of-plane bending of C-C bonds and breathing mode of fullerene cage. On the other hand, the following vibrations frequencies at 830.8 and 1011.6 cm^{-1} are due to the out of plane wagging and in-plane scissoring of HSiH angles, respectively. The vibrational frequency at 2285 cm^{-1} with highest intensity is assigned to the symmetric stretching of the SiH bonds coupled with the symmetric stretching of the PiH bonds. The $\text{SiH}_2\text{(NCH}_2\text{PH}_2)_2\text{C}_{60}$ exhibits symmetric and asymmetric stretching of CH bonds at 3034 and 3113 cm^{-1} respectively. Similar data were obtained for the pincer fullerene ligands, which are in agreement with those values obtained for N-Heterocyclic σ -silyl pincer ligands.

In order to investigate the formation of the pincer fullerene ligands $\text{SiHR(NCH}_2\text{PL}_2)_2\text{C}_{60}$, R and L = H, CH_3 and phenyl, the reactions of $\text{C}_{60}\text{(NHCH}_2\text{PPh}_2)_2$ with chlorosilanes SiHRCl_2 (R = H, CH_3 and phenyl) were taken into account (Fig. 2), and the reaction energies, E_r were obtained in the standard way as follows:

$$E_r = E_{\text{SiHR(NCH}_2\text{PL}_2)_2\text{C}_{60}} + E_{[\text{Cl}_2]} - E_{[\text{C}_{60}\text{(NHCH}_2\text{PPh}_2)_2]} - E_{[\text{SiHRCl}_2]} \quad (1)$$

where $E_{\text{SiHR(NCH}_2\text{PL}_2)_2\text{C}_{60}}$ and $E_{[\text{C}_{60}\text{(NHCH}_2\text{PPh}_2)_2]}$ are total energies of the pincer fullerenes and $\text{C}_{60}\text{(NHCH}_2\text{PPh}_2)_2$ and $E_{[\text{Cl}_2]}$ and $E_{[\text{SiHRCl}_2]}$ refer to energies of Cl_2 and chlorosilanes, respectively. As listed in Table 1, the calculated E_r values of the formation of the considered pincer fullerenes is in 46.8–61.6 kcal/mol range, which are lower than the E_r values obtained for the $\text{SiHR(NCH}_2\text{PPh}_2)_2\text{C}_6\text{H}_4$ at the same theory level. In comparison between the calculated reaction energies of pincer fullerenes, some important results were found. As noted, to analyze the influence of the nature of the flanking arms and central silicon atom on fullerene pincer ligands, the substitution of flanking arms and central silicon atom with CH_3 and phenyl groups was changed. Clearly, substituting flanking arms with CH_3 and phenyl groups increased the reaction energies of the pincer fullerene ligands formation. While substituting of hydrogen of SiH_2 with methyl led to a slight increase of the reaction energies, replacing of hydrogen with phenyl groups decreased the reaction energies of the considered pincer fullerenes.

Table 1

The total energies (E_t in hartree), reacton energies (E_r in kcal/mol), electrophilicities (ω in eV) and natural charge Q/e ($e = 1.6 \times 10^{-19}$ C), for for the N-Heterocyclic Silyl Pincer Fullerenes $\text{RSiH}(\text{NCH}_2\text{PL}_2)_2\text{C}_{60}$ at the M06-2X/6-311 + G(d, p) level of theory.

		Et	Er	ω	Q/e(Si)	Q/e(P)
1	$\text{SiH}_2(\text{NCH}_2\text{PH}_2)_2\text{C}_{60}$	-3430.441947	49.8	4.12	1.367	0.234
2	$\text{SiH}_2(\text{NCH}_2\text{P}(\text{CH}_3)_2)_2\text{C}_{60}$	-3586.817778	60.8	4.17	1.373	0.77
3	$\text{SiH}_2(\text{NCH}_2(\text{PpH})_2)_2\text{C}_{60}$	-4349.193209	59.9	4.11	1.375	0.806
4	$\text{SiHCH}_3(\text{NCH}_2\text{PH}_2)_2\text{C}_{60}$	-3469.548665	50.6	4.14	1.65	0.229
5	$\text{SiHCH}_3(\text{NCH}_2\text{P}(\text{CH}_3)_2)_2\text{C}_{60}$	-3625.924495	61.6	4.16	1.661	0.766
6	$\text{SiHCH}_3(\text{NCH}_2(\text{PpH})_2)_2\text{C}_{60}$	-4388.2994	61.0	4.12	1.659	0.797
7	$\text{SiHPh}(\text{NCH}_2\text{PH}_2)_2\text{C}_{60}$	-3660.144867	46.8	4.13	1.654	0.236
8	$\text{SiHPh}(\text{NCH}_2\text{P}(\text{CH}_3)_2)_2\text{C}_{60}$	-3816.519828	58.4	4.22	1.653	0.779
9	$\text{SiHPh}(\text{NCH}_2(\text{PpH})_2)_2\text{C}_{60}$	-4578.897951	55.8	4.23	1.664	0.815

To examine the electronic properties of the considered pincer ligands, electrophilicity was calculated, which can be used as a base to examine the electrophilic competency of the system under consideration through using the electronic chemical potential (μ) to measure tendency of the system to obtain an extra electron from next electron-rich species. At the same time, it uses hardness (η) to describe the system resistance to electron exchange with the environment. Parr et al. defined a general index for the electrophilicity strength [32]. The definition is based on the quantitative chemical concepts in DFT such as the electronic chemical potential (μ) and hardness (η) [33, 34]. Employing a quadratic and finite difference approximation, Parr et al. [32] interpreted that μ and η may be equal to $\mu = -(IP + EA)/2$ and $\eta = IP - EA$ [73]. The values of $IP = E(\text{M}^+) - E(\text{M})$ and the $EA = E(\text{M}) - E(\text{M}^-)$ were obtained based on vertical ionization potentials and electron affinities. Finally, the electrophilicity index was defined as $\omega = \mu^2/2\eta$ [33]. Therefore, electrophilicity ω values were obtained for the pincer ligands based the mentioned formula and listed in Table 1. As listed Table 1, the obtained electrophilicity values of the pincer fullerenes are in 4.11–4.23 eV range, which are larger than the electrophilicity values obtained for the fullerene derivatives with heterocyclic ring systems. It is notable that the substitution of hydrogen atoms of central SiH_2 and PH_2 do not have noticeable impact on the electrophilicity values of the pincer fullerenes, except for $\text{SiHPh}(\text{NCH}_2\text{PH}_2)_2\text{C}_{60}$ in which substituting flanking arms with CH_3 and phenyl increases the electrophilicity of the considered pincer fullerenes.

The pincer-ligated metal complexes were prepared by adding a transition metal (Fe, Co, Ni and Cu) to the pincer bites. Through this, their formation based on structure, electronic properties, stability was predicted. Two five-member metallocyclic rings were formed by the complexation of a metal to three adjacent coplanar sites of pincer fullerene ligands. Figure 5 illustrates the geometries and the important

geometrical parameters of these complexes. The criteria of stability of different pincer-ligated metal complexes namely the difference between the total energy of pincer-ligated metal complexes, the constituent, and individual transition metals, and pincer fullerene ligands were used to calculate binding energies (E_b). Using the counterpoise (CP) method [25], the binding energies were corrected for basis set superposition error (BSSE). Clearly, binding energies range from -84.24 to -88.59 eV. It is notable that the metal-silicon bonds are shorter than expected for single covalent bonds. For example, Co-Si and Co-P bond lengths in Co-SiHPh(NCH₂PH₂)₂C₆₀ (2.271 and 2.201 Å) is smaller than the corresponding single Co-Si and Co-P bond lengths (2.43 and 2.19 Å). When the hybrid orbitals of the ligands and the hybrid orbitals of the metal atoms in the metal complexes are overlapped, delocalization of electrons happens. Therefore, we perform NBO analysis to have a deeper insight into the nature of electronic conjugation among the bonds in the pincer-ligated metal complexes. The NBO analysis is a useful tool to determine these delocalizations of the electrons. The NBOs have close relationship with the picture of localized bonds and lone pairs as basic units of molecular structure. It is possible therefore, to interpret ab initio wave-functions based on the classical Lewis structure concepts through transforming these functions to NBO form [28]. The present study is mostly about the results of second-order perturbation theory analysis of Fock matrix in NBO of the complexes. With regard to each donor NBO(i) and acceptor NBO(j), the stabilization energy $E^{(2)}$ pertinent to delocalization is obtained as follows [28, 29].

$$E^{(2)} = q_i \frac{\langle i|\hat{F}|j\rangle^2}{\epsilon_j - \epsilon_i}$$

where q_i represents the donor orbital occupancy, ϵ_i and ϵ_j represent the orbital energies, and $\langle i|\hat{F}|j\rangle$ stands for the off-diagonal NBO Fock matrix element. With higher values of the $E^{(2)}$, the interaction between the donors and acceptors is intensified [10]. The strongest interactions of n^* orbitals of transition metal atoms with lone pairs of phosphorous atoms and the Si-H σ^* orbitals of central silicon atoms are listed Table 2. As seen, the strongest interaction of all happens because of the delocalization of electrons from lone pairs of phosphorous atoms (donor) in the flanking arms to the LP* of transition metals (acceptor) followed by the Si-H σ^* orbitals of central silicon atoms (donor) to the LP* of transition metals (acceptor). For example the delocalization of electrons from the lone pairs of flanking arms phosphorous atoms to the n^* orbitals of Fe atom resulted in the interaction of LP P with LP* Fe stabilizing the complex by about 48.41 kcal/mol. On the other hand, the delocalization of electrons from the Si-H σ^* orbitals of central silicon atoms to the LP* orbitals of Fe atom stabilizes the complex by only 13.37 kcal/mol. Therefore, it seems that the delocalization of electrons from the lone pairs of flanking arms phosphorous atoms to the n^* orbitals of Fe atoms is a more important factor for stabilizing the complexes in comparison to the orbitals of central silicon atoms.

Table 2
Binding energies (E_b in kcal/mol), M-Si and M-P bond lengths in A together with the second-order perturbation theory analysis of Fock matrix within NBO of the pincer-ligated metal complexes.

	E_b	M-Si	M-P	$E^{(2)*}$	$E^{(2)**}$
Fe-SiHPh(NCH ₂ PH ₂) ₂ C ₆₀	-85.47	2.267	2.184	12.99	48.41
Co-SiHPh(NCH ₂ PH ₂) ₂ C ₆₀	-88.59	2.271	2.201	13.37	50.65
Ni-SiHPh(NCH ₂ PH ₂) ₂ C ₆₀	-87.31	2.259	2.211	13.28	50.05
Cu-SiHPh(NCH ₂ PH ₂) ₂ C ₆₀	-84.24	2.244	2.209	13.1	48.25
* BD SiH (donor) → LP* Fe (acceptor) in kcal/mol					
** LP P (donor) → LP* Fe (acceptor) in kcal /mol					

4. Conclusion

A density functional study was carried out to design of new n-heterocyclic silyl pincer fullerenes. The reactions of C₆₀(NH₂)₂ with chlorosilanes SiHRCl₂ (R = H, CH₃, and Ph) were taken into account to design the nine pincer fullerene ligands SiHR(NCH₂PL₂)₂C₆₀, R and L = H, CH₃, and Ph and the pincer-ligated metal complexes achieved by adding a transition metal to the pincers. According to the findings, following points are notable. Substituting flanking arms with CH₃ and phenyl groups increases the reaction energies of the formation of the pincer fullerene ligands. While substituting the hydrogen of SiH₂ with methyl leads to a slight increase of the reaction energies, replacing of hydrogen with phenyl groups decreases the reaction energies of the considered pincer fullerenes. In addition, the calculated electrophilicity values of the pincer fullerenes range are larger than the electrophilicity values obtained for the fullerene derivatives. Therefore, the substitution of hydrogen atoms of central SiH₂ and PH₂ do not have noticeable impact on the electrophilicity values of the pincer fullerenes, except for SiHPh(NCH₂PH₂)₂C₆₀. Natural bonding orbital analysis (NBO) showed that the interaction of the phosphorous lone pairs in the flanking arms with the n^* orbitals of transition metal atoms was stronger than the interaction of Si-H σ^* orbitals of central silicon atoms with the LP* of transition metals.

Declarations

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Conflict of Interest Self-Declaration Form for All Authors

Criteria	Applicability
Funding	Not applicable
Conflicts of interest/Competing interests	There is no conflict of interest in the manuscript.
Availability of data and material	All data are provided in supplementary material.
Code availability	Not applicable
Authors' contributions	Not applicable
Additional declarations for articles in life science journals that report the results of studies involving humans and/or animals	Not applicable
Ethics approval	All authors approved Ethics.
Consent to participate	All the authors approve consent for participate of this submission.
Consent for publication	All the authors approve consent for publication of this submission.

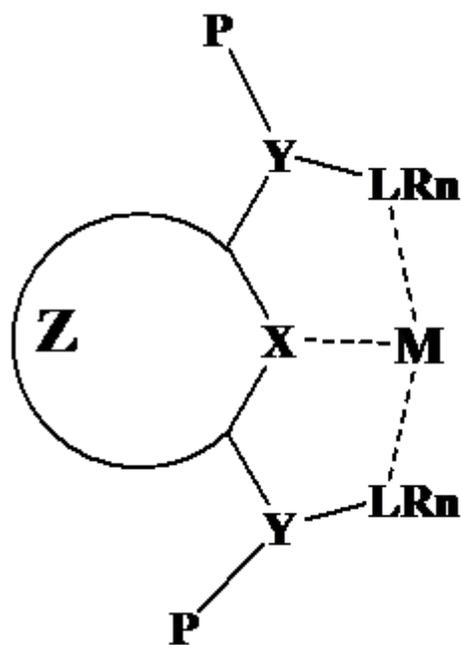
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Figures



M: Transition Metal—early, late and f-block.

Z: Determines electron density of central donor.

X: electronic control.

Y, P: Determine ring size and bite angle.

L: Steric control by modification of R and
Introduction of chirality
electronic control by modification of L

Figure 1

Schematic diagram of a pincer ligand.

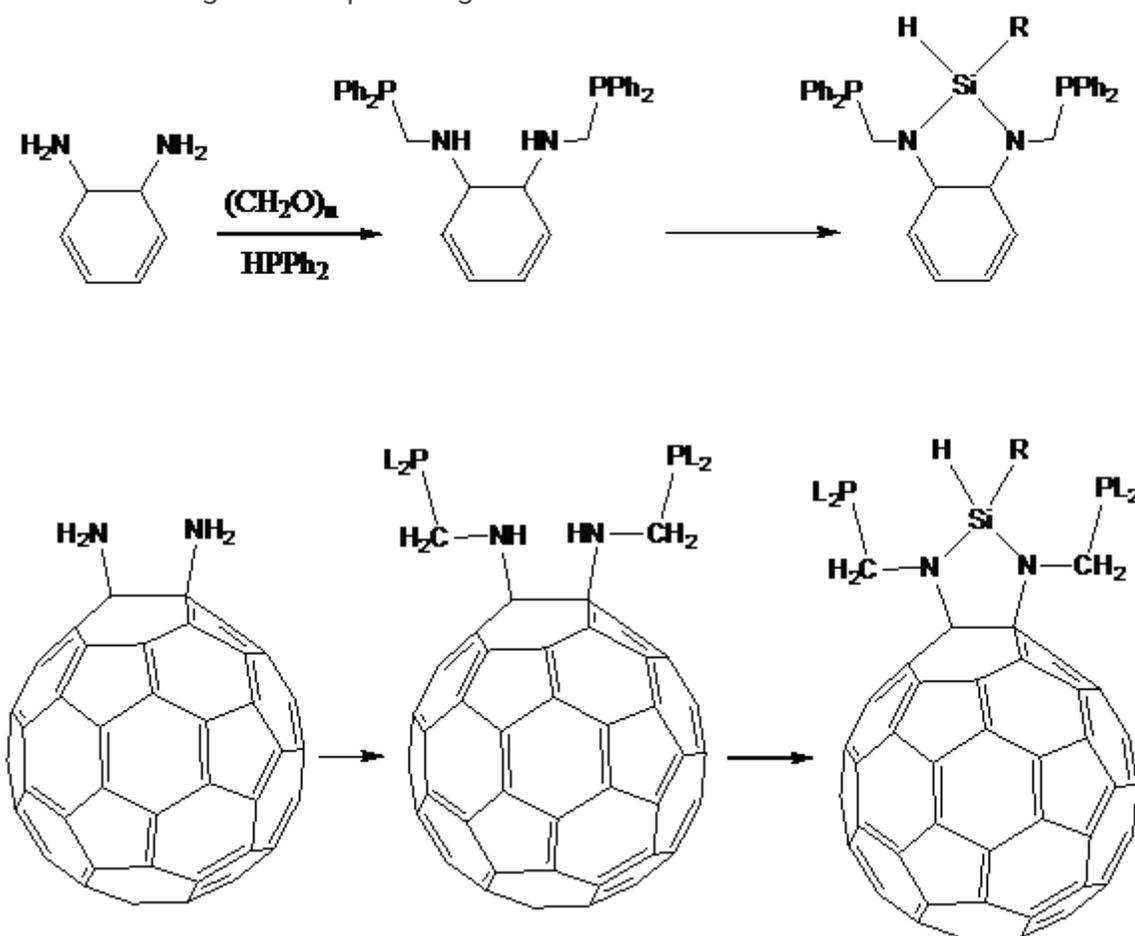


Figure 2

reactions of $C_{60}H_4(NHCH_2PPh_2)_2$ -1,2 [4] with chlorosilanes $RHSiCl_2$ in the presence of trimethylamine and formation of N-heterocyclic σ -silyl pincer ligands. A similar strategy, for the reactions of $C_{60}(NHCH_2PPh_2)_2$ with chlorosilanes $HRSiCl_2$ ($R = H, CH_3$ and Ph) to design the new pincer fullerene ligands $HRSi-(NCH_2PPL)_2C_{60}$ (R and $L = H, CH_3$ and phenyl)

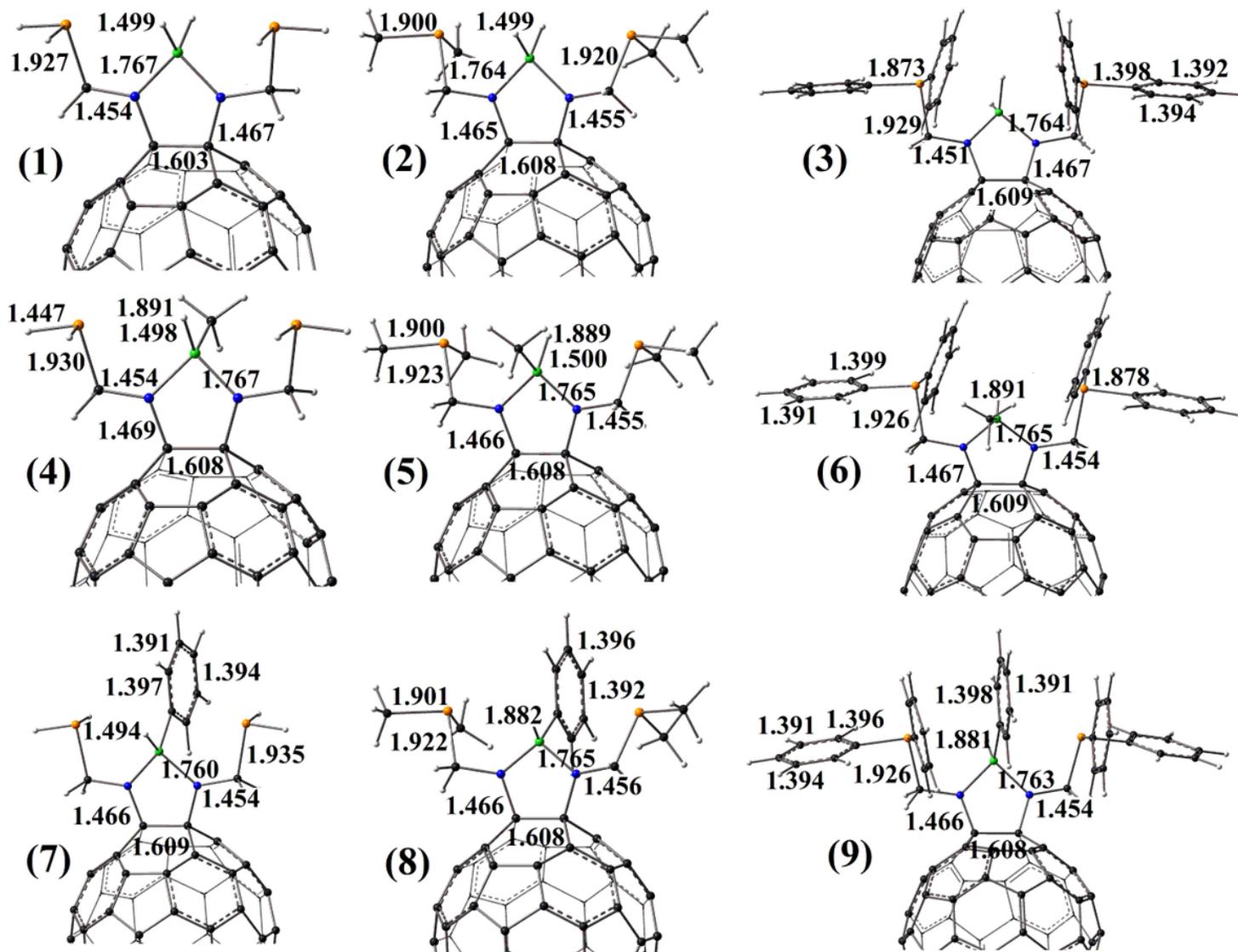


Figure 3

The optimized geometries of the pincer fullerenes $RSiH-(NCH_2PL)_2C_{60}$, R and $L = H, CH_3$ and phenyl. The geometrical parameters are shown in Å.

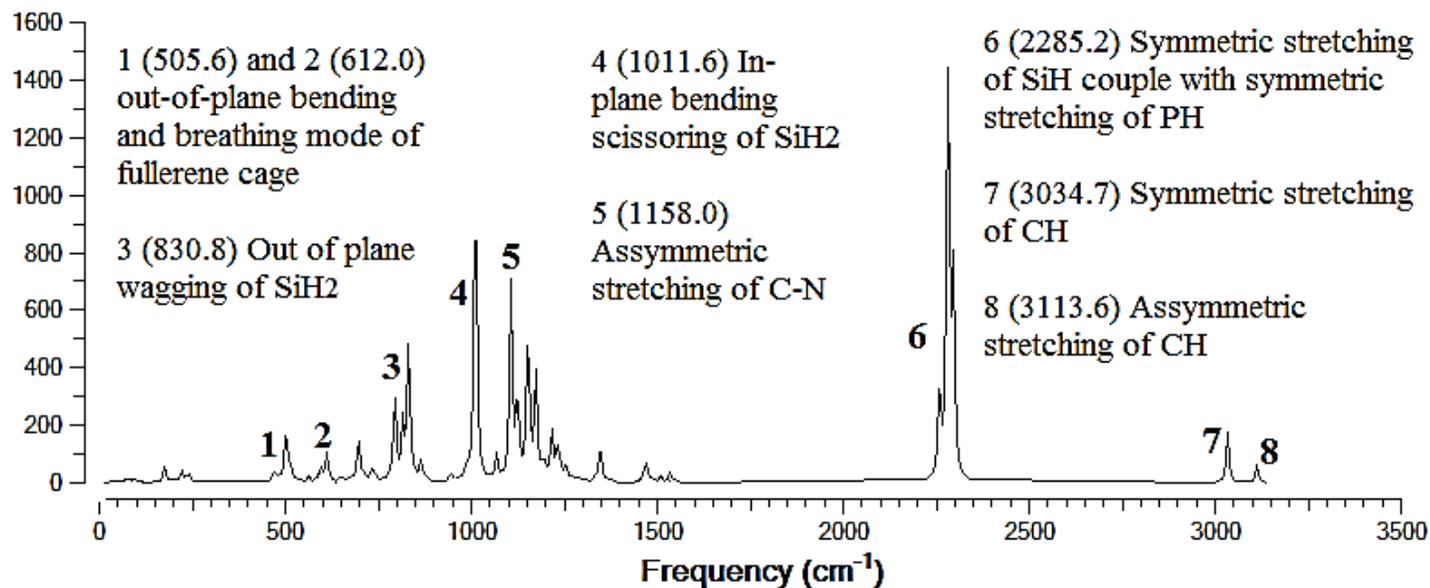


Figure 4

Simulated IR spectra of SiH₂-(NCH₂PH₂)₂C₆₀ together with the assignment of some important modes.

Image not available with this version

Figure 5

Figure 5

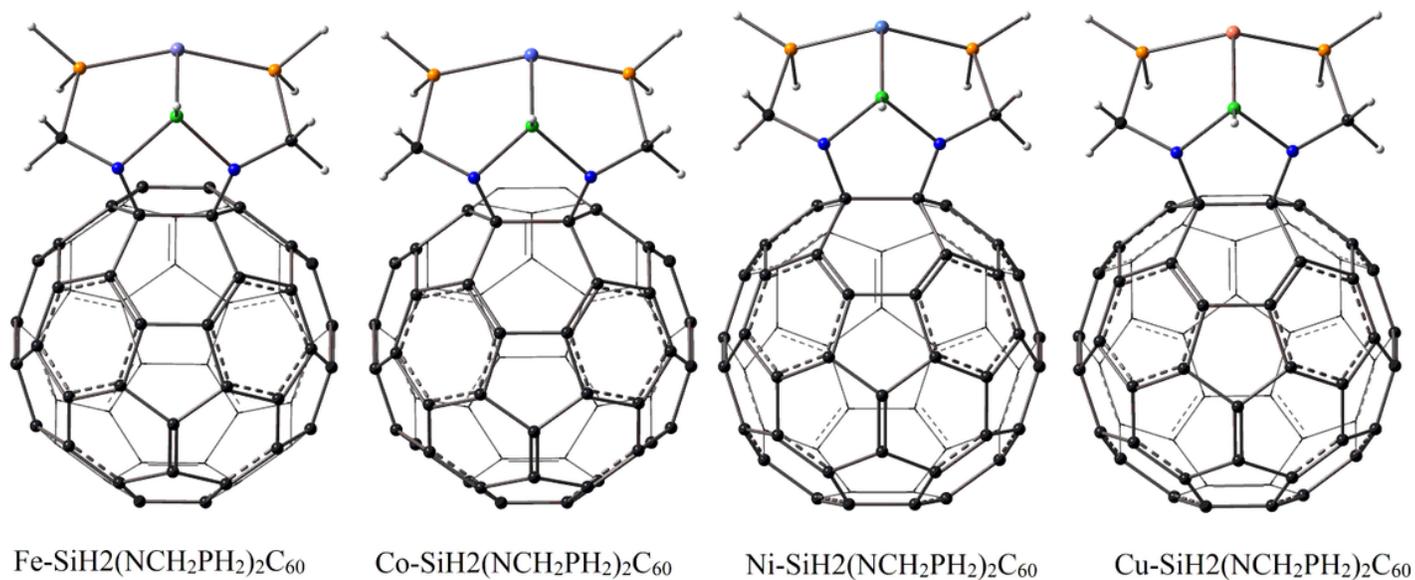


Figure 6

The optimized geometries of the pincer-ligated metal complexes obtained by the addition of a transition metal (Fe, Co, Ni and Cu) to the pincer bites.

Supplementary Files

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- [TableS1.docx](#)