Theoretical Studies on the Fe–M Interactions and \( ^{31}P \) NMR in Fe(CO)\(_3\)(EtPhPpy)\(_2\)MX\(_2\) (X=NCS, SCN, Cl; M=Zn, Cd, Hg)

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To study the Fe–M interactions and their effects on \( ^{31}P \) NMR, the structures of Fe(CO)\(_3\)(EtPhPpy)\(_2\) 1, Fe(CO)\(_3\)(EtPhPpy)\(_2\)M(NCS)\(_2\) 2 (M=Zn, Cd; M=Hg) and Fe(CO)\(_3\)(EtPhPpy)\(_2\)CdX\(_2\) 5 (X=Cl, 6: X=SCN) were investigated by density functional theory (DFT) PBE0 method. The stabilities \( S \) of complexes follow \( S(2) > S(3) > S(4) \) and \( S(3) \approx S(6) > S(5) \), indicating that 6 is stable and may be synthesized. The complexes with thiocyanate are more stable than that with chloride in Fe(CO)\(_3\)(EtPhPpy)\(_2\)CdX\(_2\). The strength \( I \) of Fe–M interactions follows \( I(2) \approx I(3) < I(4) \). The Fe-Cd interactions of 3 and 6, which contain thiocyanate, are stronger than that of 5 with chloride. The charge-transfer, which enhances with the increasing of Fe–M interaction strength, comes from Et, Ph, py, CO groups towards P, Fe, and M atoms. Because the delocalization of thiocyanate disperses the charge of Fe\(^{2+}\), the charge-transfer of the complexes with thiocyanate is stronger than that with chloride. There is a \( \sigma \)-bond between Fe and Hg atoms in 4. However, in binuclear complexes except 4, the Fe–M interactions act as \( \sigma_{Fe-C} \rightarrow \sigma_{M} \) and \( \sigma_{C-Fe} \rightarrow \sigma_{M} \) delocalization, and the N-M interactions mainly act as \( \sigma_{N-C} \rightarrow \sigma_{M} \) delocalization. In binuclear complexes, due to the Fe–M interactions, the strong \( \sigma_{Fe-C} \rightarrow \sigma_{M} \) or \( \sigma_{M} \rightarrow \sigma_{C-Fe} \) delocalization and the charge-transfer, the electron density on P nucleus is increased, and thus upfield \( ^{31}P \) chemical shifts are caused (compared with mononuclear complex 1).

Key words: DFT, \(^{31}P \) NMR, Metal-metal interaction, Nature bond orbital

I. INTRODUCTION

The coordination chemistry of the heterometallic complexes containing metal-metal bond is a focus of extensive interest owing to their novel structures, reactivities and properties including spectroscopy [1-5] and catalysis [2,6]. Much interest and recent efforts have been concentrated in polydentate ligands with P or N donor atoms that are able to form various polynuclear complexes, such as 2-(diphenylphosphinomethyl)pyridine (Ph2Ppy) [1,2,7,8], 2-(ethylphosphinomethyl)pyridine (EtPhPpy) [9], and bis(dimethylphosphino)methane (dmpp) [10]. EtPhPpy is a bidentate ligand with a nitrogen and a phosphorus donor atoms, which can easily connect two metal centers to form a complex containing a metal-metal bond. The heterometallic complexes Fe(CO)\(_3\)(EtPhPpy)\(_2\)M(NCS)\(_2\) 2 (M=Zn, Cd; M=Hg) were synthesized by mononuclear complex Fe(CO)\(_3\)(EtPhPpy)\(_2\) 1 reacting with M(SCN)\(_2\) (M=Zn, Cd, Hg) [9]. Their IR spectra and \(^{31}P \) chemical shifts were further studied. It was also shown by X-ray diffraction that the thiocyanate in complex 3 was bonded to Cd atom in NCS\(^-\) mode rather than in a SCN\(^-\) one. Meanwhile, contrasted to mononuclear complex 1, there were upfield \(^{31}P \) NMR chemical shifts in the binuclear complexes. Moreover, Zhang group synthesized binuclear complexes Fe(CO)\(_3\)(Ph2Ppy)\(_2\)MX\(_2\) (M=Zn, Cd, Hg; Mn; X=Cl, I, SCN) [7]. Xi et al. also found that the thiocyanate in the crystal structure of Fe(CO)\(_3\)(Ph2Ppy)\(_2\)Hg(SCN)\(_2\) was bonded to the Hg atom in a SCN\(^-\) mode [8]. What is the nature of the Fe–M interactions and how do they affect the \(^{31}P \) NMR chemical shifts? How do the different anions X(Cl, SCN, NCS) affect the Fe–M interactions? Up to now, there have been neither experimental nor theoretical studies on these problems.

In this work, we study about the effects of different period atoms Zn, Cd, and Hg in IIB group and different anions X(Cl, SCN, NCS) on the Fe–M interactions, \(^{31}P \) NMR chemical shifts, and stabilities by using theoretical methods.

II. COMPUTATIONAL METHODS

Density function theory (DFT) has been greatly developed and proved to have a comparatively high level of theory, which is similar to the MP2 method [11]. The application of density functional theory has been especially useful for large organic molecules or molecules with transition metal atoms [12-14]. The DFT-PBE0 method [15,16] and the SDD basis set [17] for metal atoms could be applied successfully to calculate the complexes Ru(CO)\(_3\)(Ph2Ppy)\(_2\)MCl\(_2\) (M=Zn, Cd, Hg) [18] and Fe(CO)\(_3\)(Ph2PR)\(_2\)(HgCl\(_2\))...

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III. RESULTS AND DISCUSSION

A. The structures of complexes

The optimized structures are shown in Fig. 1, and the important bond lengths and angles are listed in Table I. From Table I, we can see that the calculated geometries of 3 accurately reproduce the experimental geometrical parameters determined by X-ray diffraction [9]. The calculated Fe–Hg distance (0.2632 nm) in complex 4 is also close to that in Fe(CO)$_3$(Ph$_2$Ppy)$_2$Hg(SCN)$_2$ (0.2648 nm) [8], which has been determined by X-ray diffraction. These results suggest that the basis sets and method adopted in this work are reasonable. Compared with mononuclear complex, the distances of Fe–P and Fe–C in binuclear complexes are a bit elongated. The calculated Fe–M distances in 2–6, in the range of 0.2578–0.2749 nm, are longer than the sums of covalent radii but shorter than those of van der Waals radii of Fe and M atoms. This implies that there are weak interactions between Fe and M in binuclear complexes. The bond angle of C1–Fe–C3 changes from 111.6° in mononuclear complex 1 to the range of 152.5°–156.5° in 2–6, so the hybridization of Fe changes owing to the Fe–M bond formation.

In addition, $\Delta r$, the difference between the Fe–M distances and the sums of covalent radii of Fe and M, reflects the strength of Fe–M interactions. The sums of covalent radii of Fe–M (M=Zn, Cd, Hg) are 0.2415, 0.2575, and 0.2605 nm [25], respectively, so the $\Delta r$ follows the order of $\Delta r(2)$(0.0163 nm)$\approx\Delta r(3)$ (0.0137 nm)$>\Delta r(4)(0.0027$ nm), which means that Fe–Hg interactions are the strongest in com-

FIG. 1 Optimized structures of complexes 1–6.
plexes Fe(CO)$_3$(EtPhPpy)$_2$M(NCS)$_2$ (M=Zn, Cd, Hg). This strength order of Fe–M interactions is consistent with that of Ru–M interactions in Ru(CO)$_3$(Ph$_2$Ppy)$_2$(MC$_2$) (M=Zn, Cd, Hg) [18]. Moreover, the Fe–Cd distances (L) follow the order of $L(3)(0.2712 \text{ nm})<L(6)(0.2722 \text{ nm})<L(5)(0.2749 \text{ nm})$, suggesting that the Fe–Cd interactions of the complex with Cl$^-$ are weaker than that with SCN$^-$ or NCS$^-$.

### B. The stability of complexes

The interaction energies $\Delta E$ between MX$_2$ and Fe(CO)$_3$(EtPhPpy)$_2$ are calculated with counterpoise corrections for BSSE according to Eq.(1):

$$\Delta E = (E_T^a + E_T^b) - E_T^{ab}$$  

(1)

The $\Delta E$ involves not only Fe–M interactions but also N–M–N interactions. Thus, in order to analyze the strength of Fe–M interactions, five simplified model complexes Fe(CO)$_3$(EtPhP)$_2$MX$_2$ (X=NCS, Cl, SCN), obtained by replacing the py groups in 2-6 with H atoms, are also studied. The interaction energies $\Delta E_H$ between Fe(CO)$_3$(EtPhP)$_2$ and MX$_2$ fragments, calculated according to Eq.(1), can approximately represent the Fe–M interactions. Also, $\Delta E_{N-M-N}$, the difference between $\Delta E$ and $\Delta E_H$, reflects the N–M–N interactions of binuclear complexes.

In Table II, the $\Delta E$ between Fe(CO)$_3$(EtPhPpy)$_2$ and MX$_2$ suggests that complexes 2-4 are all stable and the stabilities are $S(2)(396.31 \text{ kJ/mol})>S(3)(369.91 \text{ kJ/mol})>S(4)(341.62 \text{ kJ/mol})$. The $\Delta E_H$ of 4 (277.86 kJ/mol) is larger than that of 2 (265.68 kJ/mol) and 3 (251.75 kJ/mol), indicating that Fe–Hg interactions are stronger than Fe–Cd and Fe–Zn. The least Fe–Hg interactions are the strongest in 2-4, while the least $\Delta E_{N-M-N}$ value (63.76 kJ/mol) leads to the least stability of 4.

The $\Delta E$ in complexes 3, 5, and 6 with different anion follows the order of $\Delta E(3)(369.91 \text{ kJ/mol}) \approx \Delta E(6)(363.84 \text{ kJ/mol}) > \Delta E(5)(310.91 \text{ kJ/mol})$. This implies that 6 is similar to 3 and higher than 5 in terms of stability. As a result, complex 6 can be obtained experimentally as Fe(CO)$_3$(Ph$_3$Ppy)$_2$Hg(SCN)$_2$. The values of $\Delta E_R$ and $\Delta E_{N-M-N}$ also have the same order as $\Delta E$, implying that the strength orders of Fe–Cd and Cd–N interactions are all $I(3) > I(6) > I(5)$. This means that the S or N atoms in thiocyanate connected to Cd will not affect the strength of Fe–Cd and Cd–N interactions. Moreover, the Fe–Cd and Cd–N interactions in complexes with SCN$^-$ or NCS$^-$ are stronger than that with Cl$^-$. In all binuclear complexes, the $\Delta E_{N-M-N}$ ranging from 63.76 kJ/mol to 130.62 kJ/mol is less than $\Delta E_R$ ranging from 216.65 kJ/mol to 277.86 kJ/mol, suggesting that the interactions of N–M–N are weaker than that of Fe–M. Therefore, the stabilities of complexes mostly come from the Fe–M interactions, which is in accord with the conclusion drawn from the Ru–M and M–N interactions of the complexes Ru(CO)$_3$(Ph$_2$Ppy)$_2$(MC$_2$) [18].

### C. NBO analysis

As shown in Table III, in contrast to mononuclear complex, the negative charge of EtPhpy and CO groups in binuclear complexes decreases, whereas the positive charge on P atoms decreases and the negative charge on Fe atoms increases. These changes of the charge indicate that the negative charge transfers from Et, Ph, py, CO groups towards P, Fe, and M atoms through Fe–M interactions. The NPA charge on the MX$_2$ fragment is negative, implying that the negative charge transfers from Fe(CO)$_3$(EtPhPpy)$_2$ to MX$_2$. The negative charge (C) on MX$_2$ follows the order of $C(2)(0.250)<C(3)(0.252)<C(4)(0.412)$ and $C(3)(0.252)<C(6)(0.261)<C(5)(0.204)$ which are consistent with the strength of Fe–M interactions. The larger charge-transfer indicates the stronger metal-metal interactions. Moreover, the charge on py groups can also shift to M atoms through N–M interactions.

The Fe–Cd interactions in 5 are the weakest due to the fewest negative charge transfers to MC$_2$, although the electronegativity of chlorine in 5 is higher than that of nitrogen and sulfur in 3 and 6. From NBO analyses, the NCS$^-$ and SCN$^-$ in complexes 3 and 6 are delo-

<table>
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<td>0.2712</td>
<td>0.2684</td>
<td>0.2632</td>
<td>0.2749</td>
<td>0.2722</td>
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<tr>
<td>Fe–P</td>
<td>0.2198</td>
<td>0.2238</td>
<td>0.2251</td>
<td>0.2247</td>
<td>0.2273</td>
<td>0.2245</td>
</tr>
<tr>
<td>Fe–C1</td>
<td>0.1764</td>
<td>0.1772</td>
<td>0.1777</td>
<td>0.1776</td>
<td>0.1786</td>
<td>0.1778</td>
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<tr>
<td>Fe–C2</td>
<td>0.1753</td>
<td>0.1769</td>
<td>0.1766</td>
<td>0.1790</td>
<td>0.1765</td>
<td>0.1764</td>
</tr>
<tr>
<td>N–M</td>
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<td>0.2464</td>
<td>0.2412</td>
<td>0.2624</td>
<td>0.2488</td>
<td>0.2517</td>
</tr>
<tr>
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<td>111.6</td>
<td>153.0</td>
<td>153.9</td>
<td>156.5</td>
<td>155.2</td>
<td>152.5</td>
</tr>
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</table>

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calized. Three natural bond orbitals are detected for the C–N bond, and one for the S–C bond. The lone pair 3p orbital of sulfur atom leads to the formation of a large π bond with the C≡N. As a result, in complexes 3 and 6, the Wiberg bond indices of S–C are 1.6085 and 1.2743, respectively, while those of C≡N bonds are only 2.3361 and 2.6914. The delocalization of the NCS− and SCN− may disperse the charge of the M2+4, stabilize the complexes, and lead to the stronger charge-transfer and Fe–Cd interactions.

As shown in Table II, in 2–4, the largest Wiberg bond index of Fe–Hg (0.1778), which is about twice as that of Fe–Zn or Fe–Cd, implies that the Fe–Hg interactions are the strongest. Compared with 3 and 6, the least Wiberg bond index of Fe–Cd in 5 (0.0807) suggests that the Fe–Cd interactions of 5 containing Cl− are weaker than that of complexes containing NCS− or SCN−. In binuclear complexes 2–6, the Wiberg bond indices of M–N are a little less than that of Fe–M, except for 4. This shows that the Fe–M interactions play a significant role on the stabilities of binuclear complexes, but it can be ignored in 4. This is in accordance with the conclusion drawn from the interaction energies.

From NBO analyses, in complex 4, there is a σ-bond between Fe and Hg atoms, described as 0.8962s0.30Fe+0.4436sp0.02Hg, resulting from the overlap of 4s, 3d hybrid on Fe with 6s on Hg. This Fe–Hg σ bond is polarized towards Fe. However, in 2, 3, 5, and 6, there are only weak Fe–M interactions which can be explained by means of the second-order perturbation stabilization energy $E(2)$ [26] according to Eq.(2), for a general donor NBO ($i$) and an acceptor NBO ($j$):

$$E(2) = E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

where $q_i$ is the donor orbital occupancy, $\varepsilon_i$ and $\varepsilon_j$ are diagonal elements (orbital energies), and $F(i,j)$ is the off-diagonal element in NBO Fock matrix. The second-order perturbation stabilization energy $E(2)$ has already succeeded in explaining the charge-transfer of adjacent atoms, the weak bonding interactions and NMR chemical shifts [27].

As the $E(2)$ listed in Table IV says, the Fe→M interactions in 2, 3, 5, and 6 include direct (acting as $n_{Fe}→\sigma_{M}$ charge-transfer) and indirect (acting as $\sigma_{P→Fe}→\pi_M$, $\sigma_{C→Fe}→\pi_M$ charge-transfer) interactions. The types of Fe→M interactions are similar in binuclear complexes except 4. Taking complex 3 as an example, the $E(2)$ values, produced by the delocalization of P–Fe and C–Fe σ bonding orbital into the 5σ orbital of Cd, amount to 91.46 and 187.69 kJ/mol, respectively. However, the $n_{Hg}→\sigma_{Fe}$ direct interactions, which are the delocalization from the 3d orbital of Fe into the 5σ orbital of Cd, only amount to 3.93 kJ/mol. This shows that the indirect interactions, $\sigma_{P→Fe}→\pi_M$, $\sigma_{C→Fe}→\pi_M$ donor-acceptor interactions, play the dominant role in binuclear complexes except 4.

In complexes 2, 3, 5, and 6, the N–M interactions $n_{N}→\sigma^{*}_{M}$, acting as the delocalization from the N lone
pair orbital into the 4s orbital of Zn and 5s orbital of Cd, produces $E(2)$ in the range of 61.13-71.38 kJ/mol. However, the N–M interactions of 4 act as a weak delocalization of $n_{N} \rightarrow \sigma^{*}_{\text{Fe-Hg}}$ with the $E(2)$ amounting to 22.80 kJ/mol. Thus, the interactions of N–M are weaker than that of Fe–M, suggesting that Fe–M interactions play a more important role than N–M interactions on the stabilities of binuclear complexes.

D. $^{31}$P chemical shifts

Recently, nuclear magnetic resonance (NMR) spectroscopy is becoming increasingly important in studies of intermolecular and weak interaction. In the past decades, it has become possible to carry out calculations on NMR chemical shifts with increasing accuracy [28].

On the basis of optimized geometries, phosphorus isotropic chemical shielding ($\sigma$) of complexes 1-6 and reference $\text{H}_3\text{PO}_4$ is calculated using PBE0-GIAO method. The calculated $^{31}$P chemical shielding (306.82 ppm) in $\text{H}_3\text{PO}_4$ is close to 315.5 ppm calculated by Ziegler using DFT(BP-LDA)-GIAO method [29]. Hence the $^{31}$P chemical shifts $\delta$ relative to the reference $\text{H}_3\text{PO}_4$ can be given by $\delta=\sigma_{\text{H}_3\text{PO}_4}-\sigma_{\text{complex}}$.

It can be seen from Table V that the calculated $^{31}$P chemical shifts ($\delta_{\text{cal}}$) in 1-4 are in approximate agreement with experimental values ($\delta_{\text{exp}}$) [9]. The deviations, ranging from 0.15 ppm to 7.18 ppm, are much less than those calculated by Ziegler and Eichele [29,30]. In addition, the order of calculated $^{31}$P chemical shifts ($P$) coincides with the experiment results as $P(1)\approx P(2)>P(3)>P(4)$. So the PBE0-GIAO method adopted in this work is valid and thus is employed to predict the $^{31}$P chemical shift of 5 and 6 with 73.34 and 72.98 ppm, respectively. Upon comparison of mononuclear complex with binuclear complexes, there are all upfield $^{31}$P chemical shifts in 2-6. The stronger Fe–M interactions result in larger upfield $^{31}$P chemical shifts in 2-4. However, because the X– groups are far from the P atoms, the $^{31}$P chemical shifts in complexes 3, 5, and 6 are similar to each other. This suggests that the X– groups do not affect the $^{31}$P chemical shifts.

It is known that the shielding arising from more electron density of phosphorus moves $^{31}$P chemical shifts upfield. Metal-metal interactions have a remarkable effect on the $^{31}$P chemical shifts [31]. Although the NPA charge around the P nucleus in 2-6 is almost unchanged compared with mononuclear complex 1, the deviation of $^{31}$P chemical shifts can be illustrated by means of the second-order perturbation energy $E(2)$.

As seen from Table III, through Fe–M interactions, the negative charge transfers from Et, Ph, CO groups towards P, Fe, and M atoms, so the decreasing of positive charge on P atoms in binuclear complexes (from 1.196 in 1 to the range of 1.171-1.185 in 2-6) leads to the upfield $^{31}$P chemical shifts.

In 2, 3, 5, and 6, it can be seen from Table IV that the deshielding for the P nucleus is derived from the $\sigma_{P-\text{Fe-Hg}}$ delocalization with the $E(2)$ amount-

### Table IV: The second order perturbation stabilization energies $E(2)$ of 1-6.

<table>
<thead>
<tr>
<th>Donor NBOs</th>
<th>Acceptor NBOs</th>
<th>$E(2)$ (kJ/mol)</th>
<th>Donor NBOs</th>
<th>Acceptor NBOs</th>
<th>$E(2)$ (kJ/mol)</th>
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<tr>
<td>1 $\sigma_{P-\text{Fe}}$ $\sigma^{*}_{\text{C-Fe}}$</td>
<td>$\sigma^{*}_{\text{P-Fe}}$</td>
<td>313.72</td>
<td>4 $\sigma_{\text{C-Fe}}$ $\sigma^{*}_{\text{Fe-Hg}}$</td>
<td>$\sigma^{*}_{\text{P-Fe}}$</td>
<td>120.83</td>
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<td>$\sigma_{\text{C-Fe}}$</td>
<td>$\sigma^{*}_{\text{P-Fe}}$</td>
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<td>$\sigma_{\text{Fe-Hg}}$</td>
<td>$\sigma^{*}_{\text{P-Fe}}$</td>
<td>788.31</td>
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<tr>
<td>2 $\sigma_{\text{P-Fe}}$ $n$(Zn,4s)</td>
<td>$n$(Zn,4s)</td>
<td>118.57</td>
<td>5 $\sigma_{\text{P-Fe}}$ $n$(Cd,5s)</td>
<td>$\sigma^{*}_{\text{C-Fe}}$</td>
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<td>$n$(Fe,3d)</td>
<td>$n$(Zn,4s)</td>
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<td>$\sigma_{\text{C-Fe}}$</td>
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<td>3 $\sigma_{\text{P-Fe}}$</td>
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<td>$\sigma_{\text{C-Fe}}$</td>
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<td>$n$(N)</td>
<td>$n$(Cd,5s)</td>
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<td>$\sigma_{\text{P-Fe}}$</td>
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<td>4 $\sigma_{\text{P-Fe}}$</td>
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<td>108.37</td>
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### Table V: The $^{31}$P NMR chemical shift $\delta$ for 1-6.

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<tr>
<th>Complex</th>
<th>$\delta_{\text{cal}}$ (ppm)</th>
<th>$\delta_{\text{exp}}$ (ppm)</th>
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<td>66.82</td>
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<td>5</td>
<td>73.34</td>
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<tr>
<td>6</td>
<td>72.98</td>
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</table>
ing to 118.57, 91.46, 65.10, and 80.17 kJ/mol. This \( \sigma_{p-Fe} \rightarrow \sigma^*_{Fe-M} \) charge-transfer decreases the electron density on the P nucleus. However, upon the Fe–M formation, the hybridization of Fe in Fe–C σ bonds changes (from 4s3d\(^{0.30} \) to 4s3d\(^{0.29} \), 4s3d\(^{0.30} \), 4s3d\(^{0.30} \), and 4s3d\(^{0.29} \)), and the percentage of d-character of Fe bonded to CO, 47.17% in 1, increases to 68.92%-70.37%. The increase of d-character makes it easy to lose the electrons and leads to the stronger \( \sigma_{C-Fe} \rightarrow \sigma^*_{p-Fe} \) charge-transfer. In 2, 3, 5, and 6, the \( E(2) \) of \( \sigma_{C-Fe} \rightarrow \sigma^*_{p-Fe} \), which is 979.14, 741.95, 679.77, and 861.11 kJ/mol, respectively, is much larger than that of \( \sigma_{p-Fe} \rightarrow \sigma^*_{M} \). Moreover, the delocalization of \( \sigma_{C-Fe} \rightarrow \sigma^*_{p-Fe} \) is stronger than that in 1 (183.30 kJ/mol), while the \( \sigma_{p-Fe} \rightarrow \sigma^*_{C-Fe} \) is weaker than that in 1. In all, the electron density of P nucleus in 2, 3, 5, and 6 is larger than that in 1, and causes upfield \( ^{31P} \) chemical shift.

In 4, there is delocalization acting as \( \sigma_{Fe-Hg} \rightarrow \sigma^*_{p-Fe} \) and \( \sigma_{p-Fe} \rightarrow \sigma^*_{Fe-Hg} \). As the Fe–Hg σ bond is polarized towards Fe atom, the \( \sigma_{p-Fe} \rightarrow \sigma^*_{p-Fe} \) charge-transfer is stronger than the \( \sigma_{p-Fe} \rightarrow \sigma^*_{Fe-Hg} \). As seen from Table IV, the \( E(2) \) (788.31 kJ/mol) of \( \sigma_{Fe-Hg} \rightarrow \sigma^*_{p-Fe} \) delocalization is much larger than that of \( \sigma_{p-Fe} \rightarrow \sigma^*_{Fe-Hg} \) (108.37 kJ/mol) charge-transfer. This charge-transfer increases the electron density of P nucleus and causes upfield \( ^{31P} \) chemical shift compared with 1.

**IV. CONCLUSION**

The complexes 1-6 have been investigated by theoretical method. The following conclusions can be drawn: (i) The complex Fe(CO)\(_3\)(EtPhPy)\(_2\)Cd(SCN)\(_2\) is stable and could be synthesized. The complexes with thiocyanate are more stable than that with chloride. (ii) The strength order of Fe–M interactions is \( I(Fe-Zn) \approx I(Fe-Cd) < I(Fe-Hg) \) in 2-4. The Fe–Cd interactions in complexes containing thiocyanate are stronger than that in complex containing chloride. (iii) The charge-transfer from Et, Ph, py, and CO groups towards Fe, P, and M atoms enhances with the increasing of Fe–M interactions. The delocalization of the thiocyanate may disperse the charge of the M\(^{2+} \). (iv) There is a σ-bond between Fe and Hg resulting from the overlap of 6s orbital of Hg and the hybrid orbital of Fe in 4, while in other binuclear complexes, there is only a weak delocalization between Fe and M (\( \sigma_{Fe-\sigma_{M}} \), \( \sigma_{p-Fe-\sigma_{M}} \), and \( \sigma_{C-Fe-\sigma_{M}} \)), and the N–M interactions mainly act as \( n_C-\sigma_{M} \) delocalization. (v) In complexes 2-6, through Fe–M interactions, the negative charge transfer from Et, Ph, py, and CO groups towards P, Fe, and M atoms and the delocalization of \( \sigma_{Fe-C-\sigma_{p-Fe}} \) or \( \sigma_{Fe-Hg-\sigma_{p-Fe}} \) increase the electron density on P nucleus and result in upfield \( ^{31P} \) chemical shifts compared to 1.

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