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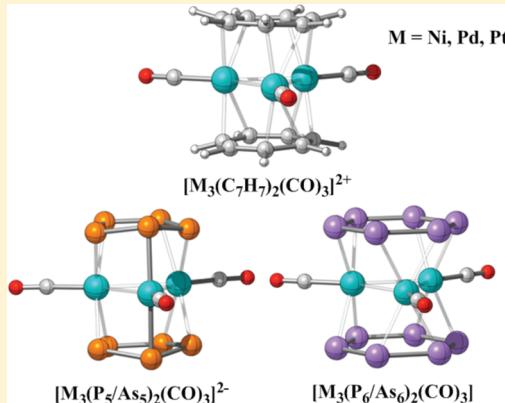
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 Supporting Information

ABSTRACT: On the basis of the 18-electron rule, we theoretically designed a series of sandwich complexes [M₃L₂(CO)₃]^q (M = Ni, Pd, Pt; L = C₇H₇, P₅, P₆, As₅, As₆; q = 2+, 0, or 2-) by means of density functional theory computations. These sandwich structures are of high stability, revealed by their strong donating and back-donating metal–ligand interactions, considerable aromatic characters as well as sizable energy gaps. All these proposed sandwich structures might serve as promising building blocks for new nanomaterials.



1. INTRODUCTION

Sandwich complexes have been investigated extensively since the discovery of ferrocene, [Fe(η^5 C₅H₅)₂], in the 1950s.¹ Metallocenes not only introduced new bonding characteristics of fundamental importance to organometallic chemistry, but also found many remarkable applications such as in catalysis, magnetic and optical materials, polymers, molecular recognition, medicine and nanodevices.^{1,2} Thus far, various intriguing findings have been reported in this field. For example, earlier studies suggested that the structures of the complexes constructed by transition metal (M) atoms and benzene (Bz) (M_n–Bz_{n+1}) prefer different forms (linearly multidecked or rice-ball) depending on the diverse metals.^{3–14} Especially, the unpaired electrons on the metal atoms are proposed to couple ferromagnetically in the multidecker V_n(Bz)_{n+1} clusters both experimentally and theoretically.^{6–10,15,16} Such ferromagnetic sandwich clusters are expected to serve as nanomagnetic building blocks in applications such as high-density information storage and quantum computing. Moreover, recent density functional theory (DFT) computations suggested that the one-dimensional [M(Bz)]_∞ polymers, especially [V(Bz)]_∞ and [Mn(Bz)]_∞, would be ideal materials for promising spin-polarized transport,^{15,16} the M_n(ferrocene)_{n+1} (M = Sc, Ti, V, Mn) sandwich clusters and nanowires ($n = \infty$) have tunable magnetic properties,¹⁷ while the Cp–Fe nanowire is half-metallic, has negative differential resistance and sign-reversible high spin-filter.¹⁸ Interestingly, several mixed inorganic/organic ligand sandwich clusters, BzMC₆₀ (M = Sc–Co), were also theoretically investigated.¹⁹ More significantly,

the first linear homoleptic triple-decker sandwich complex of an f-element, namely Nd₂(COT^{II})₃ (COT = η^8 -cyclooctatetraenyl) has been successfully synthesized.²⁰ These fascinating achievements considerably enriched our knowledge of the metallocene family.

So far most discrete sandwich complexes possess only a mono-nuclear M center between two carbocyclic ligands. *Is it possible to put more metal atoms between two aromatic ligands?* The answer is yes! Theoretically, Burdett and Canadell²¹ designed “extended polynuclear sandwich compounds” in 1985; while experimentally Murahashi et al. successfully synthesized compounds with four-atom palladium chain as well as monolayer palladium sheets in 2003²² and 2006,²³ respectively. Inspired by these pioneering works, several more similar complexes were realized or theoretically investigated in past few years.^{24–33}

Sandwich complexes are not only limited to carbon-containing ligands. In 2002, the first inorganic metallocene sandwich ion [Ti(η^5 P₅)₂]²⁻ was realized experimentally and characterized by X-ray diffraction in the salt form [K(18-crown-6)]₂[Ti(η^5 P₅)₂].³⁴ Despite its electron-deficiency (16 electrons) and formally zero-valent titanium, this salt is highly stable toward heat and air, both in solution and in the solid state. DFT computations showed that the pentaphosphacyclopentadienyl unit, P₅, functions as an unusually

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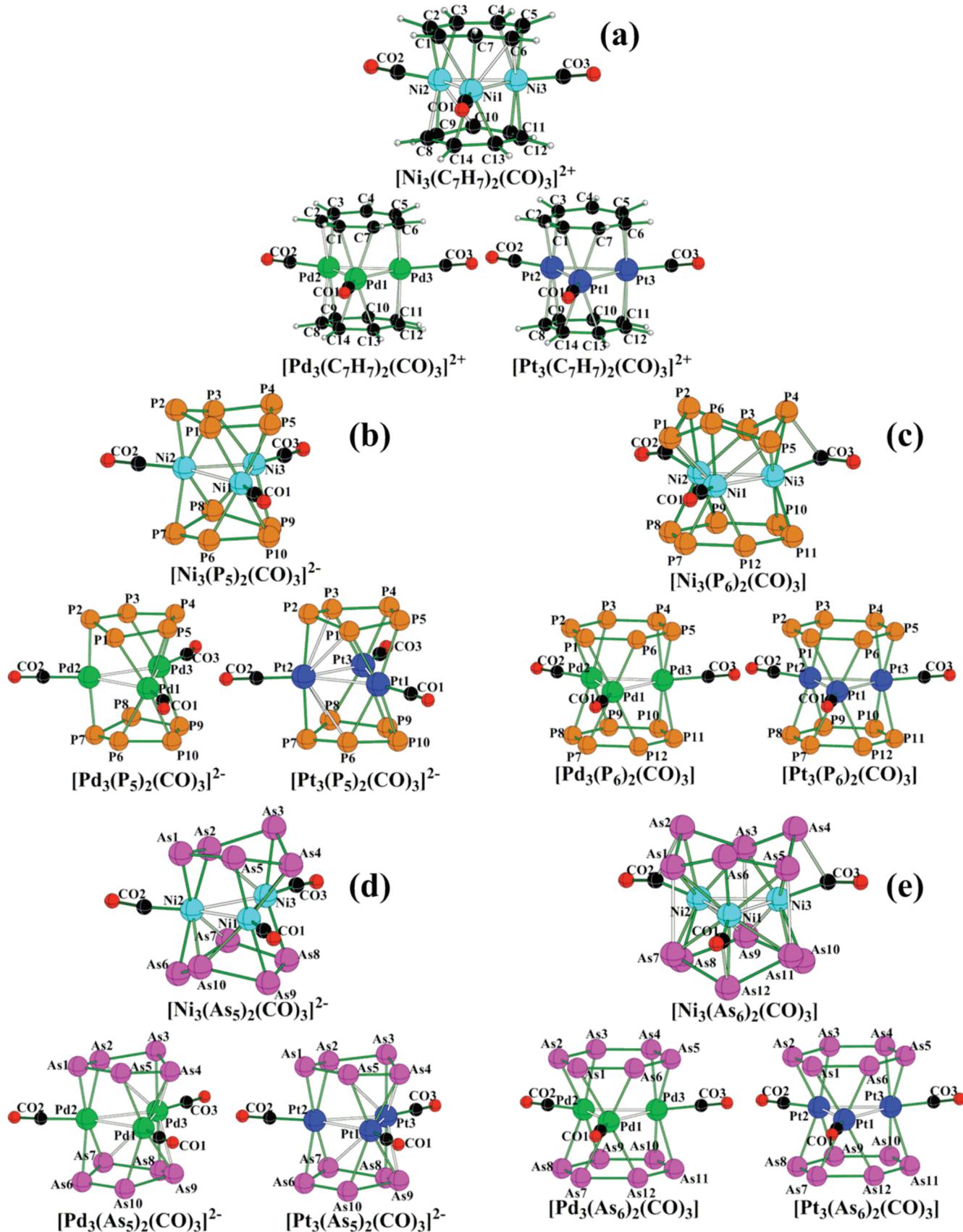


Figure 1. Geometries of (a) $[M_3(C_7H_7)_2(CO)_3]^{2+}$, (b) $[M_3(P_5)_2(CO)_3]^{2-}$, (c) $[M_3(P_6)_2(CO)_3]$, (d) $[M_3(As_5)_2(CO)_3]^{2-}$, and (e) $[M_3(As_6)_2(CO)_3]$ ($M = Ni, Pd, Pt$). Color scheme: black, C; red, O; white, H; light blue, Ni; green, Pd; dark blue, Pt; orange, P; purple, As.

Table 1. Symmetry (sym), Metal–Metal Bond Lengths (R_{M-M}) and WBIs (in Parentheses), Average Geometric Center Distances between M_3 and Ligands (R_{M-L}), Average Dihedral Angles (Φ_L) of the ligands, and HOMO–LUMO Gap Energies (gap) of the Sandwich Clusters

sandwiches	sym	R_{M-M} (Å)			R_{M-L} (Å)	Φ_L (deg)	gap (eV)
		M1–M2	M1–M3	M2–M3			
$[\text{Ni}_3(\text{C}_7\text{H}_7)_2(\text{CO})_3]^{2+}$	C_1	2.70 (0.323)	2.65 (0.328)	2.68 (0.326)	1.90	15.33	2.26
$[\text{Pd}_3(\text{C}_7\text{H}_7)_2(\text{CO})_3]^{2+}$	C_2	2.89 (0.186)	2.89 (0.186)	2.99 (0.168)	2.18	3.33	2.14
$[\text{Pt}_3(\text{C}_7\text{H}_7)_2(\text{CO})_3]^{2+}$	C_2	2.86 (0.269)	2.86 (0.269)	3.01 (0.213)	2.17	3.96	2.16
$[\text{Ni}_3(\text{P}_5)_2(\text{CO})_3]^{2-}$	C_s	3.02 (0.280)	3.02 (0.280)	2.59 (0.356)	2.09	16.05	1.68
$[\text{Pd}_3(\text{P}_5)_2(\text{CO})_3]^{2-}$	C_{2v}	3.10 (0.157)	3.18 (0.148)	3.10 (0.157)	2.34	10.90	1.83
$[\text{Pt}_3(\text{P}_5)_2(\text{CO})_3]^{2-}$	C_{2v}	3.05 (0.231)	3.10 (0.227)	3.05 (0.231)	2.34	11.21	2.02
$[\text{Ni}_3(\text{P}_6)_2(\text{CO})_3]$	C_1	2.80 (0.314)	2.71 (0.313)	2.80 (0.312)	1.93	31.17	1.84
$[\text{Pd}_3(\text{P}_6)_2(\text{CO})_3]$	D_{3h}	3.06 (0.185)	3.06 (0.185)	3.06 (0.185)	2.29	0.00	2.11
$[\text{Pt}_3(\text{P}_6)_2(\text{CO})_3]$	D_{3h}	3.02 (0.268)	3.02 (0.268)	3.02 (0.268)	2.29	0.00	2.28
$[\text{Ni}_3(\text{As}_5)_2(\text{CO})_3]^{2-}$	C_1	2.73 (0.320)	2.73 (0.320)	2.70 (0.320)	2.06	29.40	1.54
$[\text{Pd}_3(\text{As}_5)_2(\text{CO})_3]^{2-}$	C_{2v}	3.14 (0.180)	3.15 (0.162)	3.15 (0.162)	2.39	14.20	1.85
$[\text{Pt}_3(\text{As}_5)_2(\text{CO})_3]^{2-}$	C_{2v}	3.07 (0.276)	3.09 (0.236)	3.09 (0.236)	2.40	12.70	1.98
$[\text{Ni}_3(\text{As}_6)_2(\text{CO})_3]$	C_1	2.70 (0.327)	2.70 (0.326)	2.71 (0.324)	1.89	57.56	1.30
$[\text{Pd}_3(\text{As}_6)_2(\text{CO})_3]$	D_{3h}	3.11 (0.200)	3.11 (0.200)	3.11 (0.200)	2.35	0.00	2.13
$[\text{Pt}_3(\text{As}_6)_2(\text{CO})_3]$	D_{3h}	3.06 (0.292)	3.06 (0.292)	3.06 (0.292)	2.35	0.00	2.21

effective acceptor ligand thereby making this sandwich ion extremely stable.^{34a}

Such inorganic sandwich complexes equally interest theoreticians. Several inorganic sandwich complexes such as $[\text{Ti}(\eta^5\text{E}_5)_2]^{2-}$ ($\text{E} = \text{CH}, \text{N}, \text{P}, \text{As}, \text{Sb}$),³⁵ the isoelectronic analogues of $[\text{Ti}(\eta^5\text{P}_5)_2]^{2-}$, as well as the ferrocene derivatives with group-15 heteroligands $\text{Fe}(\eta^5\text{E}_5)_2$ ($\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}$) have been designed computationally.³⁶ Recently, the sandwich complexes containing other inorganic ligands, i.e., *cyclo-N*₄, P₆, P₅, P₄, As₅, or Sb₄ were also investigated.^{37–46}

Besides, based on the “all-metal” Al₄²⁻ aromatic compounds,^{47,48} Mercero et al.⁴⁹ designed a series of all-metal sandwich complexes $[\text{Al}_4\text{MAl}_4]^{q-}$ ($q = 0–2$, and M = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W), as exemplified by $[\text{Ti}(\text{Al}_4)]^{2-}$, while Yang et al.⁵⁰ computed various non-transition-metal sandwich complexes based on Al₄²⁻. Moreover, Datta and Pati predicted that the all-metal antiaromatic molecules like Al₄M₄ (M = Li, Na and K) can be stabilized in sandwich (Al₄M₄)₂Ni complex.⁵¹

Moreover, differing from the above nonmetal–metal–nonmetal and all-metal sandwich compounds, several metal–nonmetal–metal sandwich molecules such as M₃–CO₃–M'₃ (M, M' = Li, Na, K) were also suggested theoretically.⁵²

Clearly, all these bottom-up studies reveal to us the remarkable significance of finding basic units for designing new nanomaterials. Motivated by the above fascinating achievements and based on the 18-electron rule, in this work, we computationally designed several novel sandwich complexes comprising M₃ sheets (M = Ni, Pd, and Pt) flanked by five aromatic ligand pairs, which include not only organic ring (C₇H₇) but also inorganic ones (P₅, P₆, As₅, and As₆).⁵³ Their geometric structures, electronic properties, and bonding characters as well as electron delocalization were investigated and discussed.

2. COMPUTATIONAL METHODS

The Becke–Perdew (BP86) functional⁵⁴ was employed throughout our DFT computations. A double- ζ basis set (LanL2DZ) with the effective core potential for Pd and Pt⁵⁵ and standard 6-31G* basis

set for other atoms (denoted here by 6-31G*~dz) were used. Geometries were fully optimized, followed by harmonic vibrational frequencies calculations at the same theoretical level to characterize the nature of the stationary points. Charge distributions and Wiberg bond indices (WBIs)⁵⁶ were derived from the natural bond orbital (NBO) analysis of Weinhold et al.⁵⁷ Nucleus-independent chemical shifts (NICS, in ppm)⁵⁸ were computed using the gauge-independent atomic orbital (GIAO) method⁵⁹ at the BP86/6-31G*~dz theoretical level. All the computations employed Gaussian 03 package.⁶⁰

Becke and Edgecombe's electron localization functions (ELFs)⁶¹ were evaluated to gain deeper insights into the metal–metal interactions by using DGrid program.⁶² As a property of the same-spin pair density, ELF's value is restricted to the range $0 \leq \text{ELF} \leq 1$ and reflects the probability to find electron pairs in the space of interest. The values of 0, 0.5, and 1 describe the regions with delocalized electrons, homogeneous electron gas and perfect electronic localization, respectively.

Moreover, to quantitatively describe the metal–ligand bonding, a charge decomposition analysis (CDA)⁶³ was carried out from the Gaussian results with the program QMForge.⁶⁴ In the CDA, the wave function of a donor–acceptor complex is considered as a linear combination of the fragment orbitals of the ligand and the remaining metal-containing moiety. This method dissects the following primary contributions: ligand → metal donation (*d*), ligand ← metal back-donation (*b*), and ligand ↔ metal repulsive polarization (*r*).

3. RESULTS AND DISCUSSION

3.1. Molecular Structures. All the sandwich structures were fully optimized and confirmed to be local minima without imaginary frequencies at the BP86/6-31G*~dz level of theory (Figure 1). Shorter than their corresponding sums of van der Waals radii, all the intermetallic distances (Ni–Ni, 2.59–3.02 Å; Pd–Pd, 2.89–3.18 Å; Pt–Pt, 2.86–3.10 Å) are within the range of normal M–M single bonds (Table 1), with perfect equilateral M₃ triangles formed in [M₃(P₆)₂(CO)₃] and [M₃(As₆)₂(CO)₃] (M = Pd, Pt).

The ligand pairs (organic or inorganic rings) prefer an eclipsed structure in most of the sandwich complexes, whereas staggered ones only exist in three Ni-containing structures, i.e., $[Ni_3(C_7H_7)_2(CO)_3]^{2+}$, $[Ni_3(P_6)_2(CO)_3]$ and $[Ni_3(As_5)_2(CO)_3]^{2-}$. The tropylidium (Tr) backbones slightly deviate from planarity, as indicated by the average $C_a-C_b-C_c/C_b-C_c-C_d$ dihedral angles (Φ_L) (15.33°, 3.33°, and 3.96° for Ni, Pd, and Pt, respectively; see Table 1). Similarly, nonplanar ligand motifs also exist in the $[M_3(P_5)_2(CO)_3]^{2-}$ ($\Phi_L = 16.05^\circ$, 10.90°, and 11.21° for Ni, Pd, and Pt, respectively) and $[M_3(As_5)_2(CO)_3]^{2-}$ ($\Phi_L = 29.40^\circ$, 14.20° and 12.70° for Ni, Pd, and Pt, respectively) compounds. The top P_6 motif in the $[Ni_3(P_6)_2(CO)_3]$ employs a chair conformation, whereas the bottom one is quasi-planar, leading to a larger Φ_L value of 31.17° (Figure 1). Likewise, both of the two twisted As_6 rings in the $[Ni_3(As_6)_2(CO)_3]$ exhibit chair conformation, resulting in the largest Φ_L value (57.56°) in all the sandwich complexes. In contrast, the ligands sustain planarity with $\Phi_L = 0.00^\circ$ in the cases of $[M_3(L_6)_2(CO)_3]$ ($M = Pd, Pt; L = P, As$), resulting in their high D_{3h} symmetry (Table 1). Evidently, the ligands always exhibit the largest deviation from planarity in Ni-containing sandwich complexes, whereas those interacting with Pd_3 and Pt_3 are almost the same.

The ligands all tightly bind to the M_3 sheets, as clearly indicated by the corresponding metal–ligand bonding distances (Table S1–S5) and the computed geometric center separations between the M_3 sheet and the ligands, R_{M-L} (Table 1). For example, the M–C bond lengths in the three $[M_3(C_7H_7)_2(CO)_3]^{2+}$ complexes range from 2.00 to 2.47 Å, 2.24 to 2.44 Å and 2.25 to 2.38 Å for Ni–C, Pd–C and Pt–C, respectively (Table S1). Additionally, the computed R_{M-L} values (1.90 Å for Ni, 2.18 Å for Pd and 2.17 Å for Pt) also suggest substantial metal–ligand interactions between the M_3 sheet and the Tr ligands. Note that, among the compounds with the same ligands, the Ni₃-containing complexes always hold the smallest R_{M-L} values, while Pd and Pt sheets compounds essentially have the same values.

3.2. Electron Delocalization. All the designed sandwich complexes exhibit considerable HOMO–LUMO gap energies (≥ 1.30 eV, Table 1), implying their substantial kinetic stabilities. On the other hand, as a simple and efficient method to evaluate aromaticity, NICS can help predict and understand some unique properties of a molecule, especially, its stability due to aromatic stabilization. Considering the nonplanarity of the ligands in most of the sandwich complexes, we computed the NICS values at the geometric centers of all the rings (NICS(0)) as well as at 1 Å above or below the centers of the ligands: NICS(1)⁶⁵ and their perpendicular tensors NICS(1)_{zz}.⁶⁶ The computed NICS values at the BP86/6-31G*~dz level of theory are listed in Table 2.

Evidently, the NICS values at the M_3 ring centers are all highly negative (−58.3 to −38.5 ppm), suggesting their high degree of aromaticity. For Ni₃ moiety, the maximum (−52.1 ppm) and minimum (−39.4 ppm) negative NICS values are calculated in the $[Ni_3(C_7H_7)_2(CO)_3]^{2+}$ and $[Ni_3(As_6)_2(CO)_3]$, respectively. The NICS values for the Pd_3 sheet centers range from −50.7 ($[Pb_3(As_6)_2(CO)_3]$) to −38.5 ppm ($[Pd_3(P_5)_2(CO)_3]^{2-}$). The Pt_3 ring exhibits the highest negative NICS values ($[Pt_3(C_7H_7)_2(CO)_3]^{2+}$, −58.3 ppm), with the minimum occurs in $[Pt_3(As_5)_2(CO)_3]^{2-}$ (−43.4 ppm).

The high degree of electronic delocalization at the M_3 rings can also be vividly revealed by the computed ELFs for the $[M_3(CO)_3]$ moieties (Figure 2). Clearly, depending on different ligands, the metal sheets present varied but significant aromaticity.

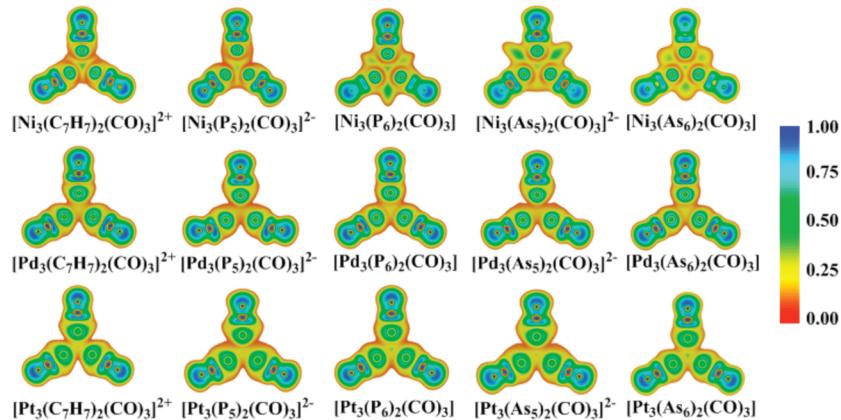
Table 2. GIAO-BP86/6-31G*~dz-Computed NICS (ppm) for the Sandwich Complexes^a

sandwiches	ring	NICS(0)	NICS(1)	NICS(1) _{zz}
$[Ni_3(C_7H_7)_2(CO)_3]^{2+}$	C_7H_7 (T)	−13.4	−4.2	−4.4
	Ni_3	−52.1	—	—
	C_7H_7 (B)	−13.3	−4.2	−4.3
$[Pd_3(C_7H_7)_2(CO)_3]^{2+}$	C_7H_7 (T)	−10.3	−3.5	−6.2
	Pd_3	−46.8	—	—
	C_7H_7 (B)	−10.3	−3.4	−6.2
$[Pt_3(C_7H_7)_2(CO)_3]^{2+}$	Pt_3	−13.8	−4.9	−10.9
	C_7H_7 (B)	−58.3	—	—
	P_5 (T)	−13.8	−4.8	−11.0
$[Ni_3(P_5)_2(CO)_3]^{2-}$	Ni_3	−45.6	—	—
	P_5 (B)	−28.1	−15.3	−29.5
	P_5 (T)	−22.2	−11.8	−23.9
$[Pd_3(P_5)_2(CO)_3]^{2-}$	Pd_3	−38.5	—	—
	P_5 (B)	−22.2	−11.7	−24.2
	P_5 (T)	−23.9	−12.7	−27.5
$[Pt_3(P_5)_2(CO)_3]^{2-}$	Pt_3	−44.2	—	—
	P_5 (B)	−23.9	−12.6	−27.6
	P_6 (T)	−16.5	−9.2	−10.2
$[Ni_3(P_6)_2(CO)_3]$	Ni_3	−41.3	—	—
	P_6 (B)	−15.4	−11.2	−20.8
	P_6 (T)	−23.2	−15.4	−31.1
$[Pd_3(P_6)_2(CO)_3]$	Pd_3	−50.6	—	—
	P_6 (B)	−23.2	−15.4	−31.1
	P_6 (T)	−23.6	−15.9	−34.6
$[Pt_3(P_6)_2(CO)_3]$	Pt_3	−57.5	—	—
	P_6 (B)	−23.6	−15.9	−34.6
	As_5 (T)	−21.2	−13.0	−20.5
$[Ni_3(As_5)_2(CO)_3]^{2-}$	Ni_3	−40.3	—	—
	As_5 (B)	−21.2	−13.0	−20.5
	As_5 (T)	−21.3	−12.2	−19.8
$[Pd_3(As_5)_2(CO)_3]^{2-}$	Pd_3	−39.2	—	—
	As_5 (B)	−21.3	−12.2	−19.8
	As_5 (T)	−22.0	−12.5	−23.0
$[Pt_3(As_5)_2(CO)_3]^{2-}$	Pt_3	−43.4	—	—
	As_5 (B)	−22.0	−12.6	−23.0
	As_6 (T)	−10.1	−6.8	−5.5
$[Ni_3(As_6)_2(CO)_3]$	Ni_3	−39.4	—	—
	As_6 (B)	−9.6	−6.1	−5.1
	As_6 (T)	−25.4	−17.9	−37.4
$[Pb_3(As_6)_2(CO)_3]$	Pd_3	−50.7	—	—
	As_6 (B)	−25.4	−17.9	−37.4
	As_6 (T)	−25.5	−18.0	−39.9
$[Pt_3(As_6)_2(CO)_3]$	Pt_3	−57.3	—	—
	As_6 (B)	−25.4	−18.0	−39.9

^a Please refer to Figure 1 for the definitions of top (T) and bottom (B) rings.

Interestingly, these trinuclear metal complexes could be considered as metal carbonyl analogues of cyclopropane, similar to the case of $Fe_3(CO)_{12}$,⁶⁷ thus their aromaticity relates to the σ -aromaticity in cyclopropane.⁶⁸

Similarly, all of the five ligands are indicative of strong aromatic behaviors, confirmed by their computed negative NICS values.

Figure 2. ELFs for the $[M_3(CO)_3]$ moieties of the sandwiches.

For example, the NICS values of the P_5 ligands, are from -28.1 to -22.2 ppm, -15.5 to -11.7 ppm, and -29.6 to -23.9 ppm for $NICS(0)$, $NICS(1)$, and $NICS(1)_{zz}$, respectively. Thus, the whole series of our sandwich systems are aromatic.

3.3. Bonding Nature. We analyzed the bonding nature of the sandwich complexes in terms of two aspects: the binding between metals in the M_3 sheet itself and the interaction between ligands and the metal sheet.

First, in consistent with the metal–metal single bonds⁵³ and the plotted ELFs, weak M–M interactions predominate the bonding in all the M_3 sheets, evidenced by their computed small WBIs (0.280 – 0.356 , 0.148 – 0.200 , and 0.213 – 0.292 for Ni_3 , Pd_3 , and Pt_3 , respectively, Table 1), which implies slightly stronger interactions between Ni atoms or Pt atoms than that of Pd_3 sheet. Note that the WBIs for transition metal–transition metal single bonds (typically 0.2 – 0.3), exemplified by unbridged Fe–Fe bonds in $Fe_3(CO)_{12}$ (WBI: 0.18),⁶⁷ are much smaller than that for carbon–carbon bonds (WBI: 1.0). Besides, although the weak intermetallic interactions suggested by the computed WBIs, sandwich complexes containing Pd_3 cores were prepared and isolated recently (WBI is 0.282 , 0.282 , and 0.258 for each Pd–Pd pair, refer to ref 23 and its supporting materials).

Herein, M–CO interactions also were investigated by examining the C–O stretching frequency changes due to the formation of the $[M_3(CO)_3]$ units. Ranging from 1890.5 to 2118.8 cm^{-1} , all the C–O stretching modes computed at the BP86/6-31G*~dz level of theory are markedly shifted toward lower wavenumbers with respect to the free carbon monoxide (2143 cm^{-1}).⁶⁹ The three Tr-containing complexes exhibit the largest wavenumbers: 2107.62 , 2118.83 , and 2110.16 cm^{-1} for Ni, Pd and Pt, respectively. Thus, all the sandwiches may be identified as classical metal carbonyls, i.e., the C–O stretch is red-shifted and CO bond is weakened due to the synergistic $OC \rightarrow M$ σ -donation and $OC \leftarrow M$ π -back-donation, which lead to the loss of bonding electron density and the gain of antibonding ones on the carbonyl groups.⁷⁰

NBO charge population analyses were further performed to examine the intramolecular bonding characters (Table S6–S8, Supporting Information). The s and p orbital populations for each atom of the M_3 moieties are larger than $2.0\ e$. For the Ni-containing complexes, the electron occupancies on most of the d orbitals are smaller than $1.80\ e$, leading to the total charge population of the d orbitals smaller than $10.0\ e$ (ca. $d^{8.5}$). Thus, d orbitals participate in and remarkably contribute to the bonding interaction in these sandwich complexes. With more

Table 3. CDA Results of the Sandwich Complexes^a

sandwiches	<i>d</i>	<i>b</i>	<i>r</i>
$[Ni_3(C_7H_7)_2(CO)_3]^{2+}$	1.819	0.863	-1.288
$[Pd_3(C_7H_7)_2(CO)_3]^{2+}$	1.622	0.929	-0.630
$[Pt_3(C_7H_7)_2(CO)_3]^{2+}$	1.386	0.863	-1.073
$[Ni_3(P_5)_2(CO)_3]^{2-}$	-0.319	0.090	-3.085
$[Pd_3(P_5)_2(CO)_3]^{2-}$	3.202	0.932	-1.291
$[Pt_3(P_5)_2(CO)_3]^{2-}$	2.203	0.518	-1.702
$[Ni_3(P_6)_2(CO)_3]$	-0.743	-0.199	-4.325
$[Pd_3(P_6)_2(CO)_3]$	2.943	1.120	-1.557
$[Pt_3(P_6)_2(CO)_3]$	1.937	0.544	-1.955
$[Ni_3(As_5)_2(CO)_3]^{2-}$	0.099	0.088	-3.993
$[Pd_3(As_5)_2(CO)_3]^{2-}$	3.366	1.111	-0.726
$[Pt_3(As_5)_2(CO)_3]^{2-}$	2.902	1.041	-1.058
$[Ni_3(As_6)_2(CO)_3]$	1.252	0.146	-4.616
$[Pd_3(As_6)_2(CO)_3]$	3.392	1.367	-1.194
$[Pt_3(As_6)_2(CO)_3]$	2.677	1.147	-1.220

^a Definitions: donation (*d*), back-donation (*b*), and repulsive polarization (*r*).

electrons located on the d orbitals (ca. $d^{9.2}$ and $d^{9.0}$ for Pd and Pt, respectively), the Pd/Pt-containing sandwiches exhibit smaller but still substantial d contribution to the chemical bondings.

Apparently, the aromaticities of the studied sandwich complexes are partially (more or less) arising from the delocalization of the d electrons of the M_3 cores. Therefore, the present systems hold substantial d-aromaticity characters. Note that aromaticities involving d orbitals are rather intriguing,⁷¹ since they may give rise to novel multiple (σ , π , and δ) aromaticity character due to the more complicated nodal structures of the d atomic orbitals.

Now, we turn to consider the metal–ligand interactions. The computed NBO charges of the sandwiches significantly deviate from their formal charges, namely $+1$, -1 , and 0 for each Tr, P_5 /As₅, and P_6 /As₆, respectively (Table S9, Supporting Information). Therefore, remarkable donating and back-donating interactions may also exist between the ligands and the middle $[M_3(CO)_3]$ moieties. Moreover, to analyze the metal–ligand bonding more quantitatively, we performed a CDA study on the BP86/6-31G*~dz geometries and summarized the results in Table 3. The CDA results show clearly that considerable charge donation and back-donation occur in most of the sandwiches, with the former always stronger than the latter. One exception is $[Ni_3(P_6)_2(CO)_3]$, its negative *d* and *b* items suggest that both the donating and

back-donating characters can be negligible. $[Ni_3(P_5)_2(CO)_3]^{2-}$ is another exception, for which the negative d ($-0.319\ e$) and small positive b values ($+0.090\ e$) are computed, implying the $(P_5)_2^{2-}$ fragment does not transfer any charge to the bonding region, and it accepts a small amount of charge back-donated from the $[Ni_3(CO)_3]$ moiety. These results are in line with the NBO charge distribution listed above.

Note that all the repulsive polarization items are significant, indicating the remarkable amount of charge in the overlapping area of the occupied molecular orbitals of the metal–ligand fragments. All the Ni-containing complexes hold the largest r values, which are consistent with their obvious structural deformation on the planarity of the ligands, as stated above (see Figure 1 and Table 1).

4. CONCLUSIONS

In summary, based on the 18-electron rule, we computationally designed 15 new members of the sandwich complex family, i.e., C_7H_7 , P_5 , P_6 , As_5 , and As_6 with monolayer Ni_3 , Pd_3 , and Pt_3 metal sheets in the middle. These novel compounds exhibit considerable stabilities due to the donating and back-donating metal–ligand interactions and the favorable aromatic stabilization in the transition metal sheets. The substantial aromaticities in these compounds are partially contributed by the d atomic orbitals of the flanked transition metals. We hope this study will stimulate future experimental efforts on realizing new nanomaterials based on the relevant sandwich structures.

■ ASSOCIATED CONTENT

S Supporting Information. Optimized coordinates, computed NBO charge populations and detailed geometric parameters of all the sandwich complexes as well as the full citation of ref 60. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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