Using the strategy of transition metal coordination together with that of large \(\pi\)-coordinating ligand complexation for planar tetracoordinate carbon (ptC) atoms, we present in this work a systematical DFT investigation on the possibility of ptC centers in \(M_4C\) square sheets sandwiched in \([C_8H_8]M_4C[C_nH_m]^+\) complexes (\(M = \text{Ni, Pd, Pt}\); \(n, n' = 8, 9\)) with the planar \(\pi\)-coordinating ligands \([C_8H_8]^n\) and \([C_9H_9]^n\). Introduction of a ptC center into an \(M_4\) square sheet to form four effective ptC–M bonds helped to stabilize the \([C_nH_m]M_4C[C_n'\pi H_m']\) complexes thermodynamically, and the \(\pi\)-coordinating \([C_8H_8]^n\) and \([C_9H_9]^n\) ligands were found to match the M\(_4\)C middle decks both geometrically and electronically. Planar tetracoordinate boron (ptB) and nitrogen (ptN) behave similarly to ptC in these sandwich structures. These model sandwich complexes invite experimental syntheses and characterizations in order to open up a new area in coordination chemistry for planar tetracoordinate carbon and other non-metal atoms.

**Introduction**

Considerable and continuous efforts have been made to predict and produce planar tetracoordinate carbon (ptC) and planar hypercoordinate carbon atoms during the past forty years since the pioneering work by Hoffmann and co-workers in 1970.\(^{[1,2]}\) ptC centers were observed by X-ray crystallography in stable anti-van’t Hoff/LeBel compounds,\(^{[3]}\) as exemplified by \(V_2(2,6\text{-dimethoxyphenyl})_4\) THF,\(^{[3a]}\) \(\text{Ca}_4\text{Ni}_3C_5\),\(^{[3b,3c]}\) and \(\text{Cp}_2\text{Zr}(\mu-\eta^1,\eta^2-Me_2\text{SiCCPh})_2(\mu-\text{Cl})\text{AlMe}_2\).\(^{[3d]}\) Various electronic, mechanical, and combined approaches have been used to achieve ptCs\(^{[4,5]}\) including the theoretically predicted ptC-containing pentatomic molecules,\(^{[5]}\) which were later confirmed in the gas phase by photoelectron spectroscopy.\(^{[6]}\) Our group proposed the possibility of transition metal coordinated ptCs in \(D_{4h}\) \(M_4H_4\) hydridometal compounds (\(M = \text{Cu, Ni}\))\(^{[7]}\) ptCs centered in the bared \(\text{Cu}_4\)\(^{2+}\) cluster and in \(\text{Cu}, \text{Ag},\) and \(\text{Au}\) organometallic compounds were also investigated in theory.\(^{[8]}\) The very recent discovery of the highly stable \([C_8H_8]\text{Pd}_4[C_8H_8]^+\) complex\(^{[9]}\) with a nearly equilateral \(\text{Pd}_4\) square sheet sandwiched between the large \(\pi\)-coordinating ligands \([C_8H_8]^2-\) and \([C_9H_9]^2-\) prompted us to insert a C atom at the center of the \(\text{Pd}_4\) unit to form a ptC-centered \([C_8H_8]_2\text{Pd}_4[C_3H_5]^+\) complex. This unusual sandwich complex with the formal total valence-electron count of 60 e turned out to be a true minimum. Using the strategy of transition metal coordination together with that of large \(\pi\)-coordinating ligand complexation, we systematically investigated the possibility of forming ptC centers in group 10 transition metal squares sandwiched in \([C_8H_8]M_4C[C_nH_m]\) and \([C_9H_9]M_4C[C_nH_m]\) complexes (\(M = \text{Ni, Pd, Pt}\)) at density functional theory (DFT) level in this work. Introducing a ptC into an \(M_4\) square to form four effective ptC–M bonds helped to stabilize the \([C_nH_m]M_4C[C_n'\pi H_m']\) complexes thermodynamically, and the \(\pi\)-coordinating \([C_8H_8]^n\) and \([C_9H_9]^n\) ligands were found to match the \(M_4\)C middle decks both geometrically and electronically. Planar tetracoordinate boron (ptB) and nitrogen (ptN) behave similarly to ptC in these sandwich structures. These model sandwich complexes invite experimental syntheses and characterizations in order to open up a new area in coordination chemistry for planar tetracoordinate carbon and other non-metal atoms.

**Theoretical Methods**

Structural optimizations, vibrational analyses, and natural bond orbital (NBO) analyses were performed by using the hybrid B3LYP method\(^{[10]}\) with the standard Gaussian basis of 6-311+G(3df,p) on H, B, C, N, and Ni, and with the Stuttgart quasi-relativistic pseudo-potentials and basis sets (Stuttgart RSC 1997 ECP) augmented with 2f and 1g
functions\textsuperscript{11} on Pd and Pt. In order to check the π-electron ring-current effects of the C\textsubscript{n}H\textsubscript{n} ligands, the total isotropic nucleus-independent chemical shifts (NICS) and their out-of-plane components (NICS\textsubscript{zz})\textsuperscript{12} were calculated at points 0.0–5.0 Å above the ring centers along the molecular axes perpendicular to the ligand planes. NICS\textsubscript{zz} components are considered to better reflect the π-electron effects than NICS values at points above the ring centers where π contributions dominate\textsuperscript{12d–12g}.

The optimized ptC-centered sandwich complexes of Cu[C\textsubscript{n}H\textsubscript{n}]Pd\textsubscript{4}C[C\textsubscript{n}H\textsubscript{n}]\textsuperscript{+} and D\textsubscript{abh} [C\textsubscript{4}H\textsubscript{4}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}] compared with the corresponding [C\textsubscript{n}H\textsubscript{n}]Pd\textsubscript{4}[C\textsubscript{n}H\textsubscript{n}] complex, which are all true minima without imaginary frequencies at the B3LYP level, are depicted in Figure 1. The primarily ptC-related molecular orbitals (MOs) of the high-symmetry D\textsubscript{4h} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}] complex is shown in Figure 2. The detailed valence MOs of D\textsubscript{abh} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}] are depicted in the Supporting Information. The NICS and NICS\textsubscript{zz} scans of the Pd\textsubscript{4}C-containing C\textsubscript{4} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}]\textsuperscript{+} and D\textsubscript{abh} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}] complexes are given in Figure 3. The calculated electronic properties of the concerned complexes, including the eigenvalues of the highest occupied MOs (HOMOs), and the energy gaps between the HOMOs and the lowest unoccupied MOs (LUMOs) are given in Table 1. The first vertical ionization potentials of the concerned complexes are given in Figure 3.

![Figure 1](image1.png) Optimized geometries of the M\textsubscript{4}C-centered C\textsubscript{4} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}]\textsuperscript{+} and D\textsubscript{abh} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}] sandwich complexes with the bond lengths around the ptC centers indicated in Å. The corresponding empty-centered [C\textsubscript{n}H\textsubscript{n}]Pd\textsubscript{4}[C\textsubscript{n}H\textsubscript{n}] complexes are depicted for comparison.

![Figure 2](image2.png) Primarily ptC-related molecular orbitals of D\textsubscript{4h} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}].

![Figure 3](image3.png) NICS and NICS\textsubscript{zz} scans of (a) C\textsubscript{4} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}]\textsuperscript{+} (2) and (b) D\textsubscript{abh} [C\textsubscript{8}H\textsubscript{8}]Pd\textsubscript{4}C[C\textsubscript{8}H\textsubscript{8}] (4) compared with those of the free D\textsubscript{abh} [C\textsubscript{8}H\textsubscript{8}] and D\textsubscript{abh} [C\textsubscript{8}H\textsubscript{8}]\textsuperscript{+} ligands, with the NICS and NICS\textsubscript{zz} values in ppm and the distances (d) from the ring centers in Å.
zation potentials (IPs) of the neutrals were calculated as the energy differences between the neutrals and the corresponding cations in the optimized neutral structures. We mainly focused on the ptC-containing M4C complexes (M = Pd, Ni, Pt) in the following discussions, and especially on the experimentally closely related PdTc series. Results on ptB-centered M4B and ptN-centered M4N complexes are also summarized in the Supporting Information. All the calculations in this work were carried out by using the Gaussian 03 program.[13]

Results and Discussion

Similar to the experimentally known C1 [C8H8]Pd4[C8H8]+ (1),[8] the ptC-centered C1 [C8H8]Pd4[C8H8]+ (2) possesses a typical sandwich structure with the C8H8 ring coordinating to the nearly equilaterial Pd4C square sheet in a μ4-η2:η2:η1:η1 mode (rPd-Cl(C8H8) = 2.32–2.34 Å) and C8H8 in a μ4-η2:η2:η1:η1 mode (rPd-C(C8H8) = 2.40 and 2.47 Å for η2-Pd; rPd-Cl(C8H8) = 2.62, 2.39, and 2.85 Å for η1-Pd, with one C atom on the C8H8 ring coordinating to two Pd atoms with the longest P–C distances). The ptC-centered C2 has an average Pd–Pd distance of 2.79 Å, which is 0.07 Å longer than the measured value of 2.72 Å in C1 [C8H8]Pd4[C8H8]+.[8] The calculated Pt–C distances of rPt–Pd = 1.986 and 1.992 Å in C2 were shorter than the sum of the covalent radii of Pd and Pt (2.14 Å), indicating that effective Pt–Pd bonds have been formed around the ptC center. The calculated total atomic Wiberg bond order of WBIptC = 3.20 and the individual bond order of WBIptC–Pd = 0.59–0.60 generally agree with the ptC-related bond orders reported in the literature.[1–8] These values also indicate that multicenter interactions, which are not included in the calculation of individual WBIptC–Pd, make considerable contribution to the chemical bonding in this complex. The low natural atomic charges of qptC = −0.33 e and qPt = +0.50 to +0.51 e suggest that the ptC–Pd interactions are mainly covalent in C2. The periphery Pd atoms have the calculated total bond order of WBIptC = 1.70–1.72. Triplet and quintet sandwich isomers were found to be considerably less stable than singlet C2 at the same theoretical level. Similar results have been obtained for C1 [C8H8]Pt4[C8H8]+ with rPt–C = 1.813 and 1.820 Å and C1 [C8H8]Pt4[C8H8]+ with rPt–Pt = 2.053 and 2.067 Å. Flanking a Pd4 square with two equivalent C8H8 rings in a μ4-η2:η2:η1:η1 mode produces the sandwich-like D4h [C8H8]Pd4[C8H8] (3) that has a Pd–Pd bond length of rPd–Pd = 2.730 Å. Inserting a ptC at the center of D4h 3, the highly symmetrical D4h [C8H8]Pd4[C8H8] (4), which contains a perfect Pd4C square, is obtained. The ptC-centered D4h 4 has 60 valence electrons and possesses bond lengths of rPd–Pd = 2.799 Å and rptC–Pd = 1.975 Å and bond orders of WBIptC = 1.73, WBIptC = 3.15, and WBIptC–Pd = 0.59. Typical coordination bonds are formed between the Pd4C core and the two [C8H8]2− ligands (rPd–Cl(C8H8) = 2.392 Å and WBIptC–C(H8) = 0.16). Interestingly, the two C8H8 rings in D4h 4 exhibit certain bond length alternations (rC–C = 1.402 Å and rC–C = 1.458 Å) with an averaged C–C distance of rC–C = 1.430 Å, which is 0.016 Å longer than the corresponding value of rC–C = 1.414 Å in a perfect D4h [C8H8]2− dianion[14] at the same B3LYP level. The C–C bond-length alternation in [C8H8]M4(C8H8) complexes studied in this work is related to the fact that each periphery transition metal atom in these M4C square sheets is coordinated at a η2 mode to two C–C π–π bonds above and below it (see Figure 1). The perfect D4h [C8H8]Ni4[C8H8] complex and the slightly distorted C4h [C8H8]Pt4[C8H8] complex behave similarly to D4h 4. A perfect D4h [C8H8]Pt4[C8H8] complex proved to be a transition state leading to the C4 symettry that contains a quasi-ptC center lying 0.271 Å above the Pt4 plane (see detailed coordinates in Supporting Information).

With one less and one more valence electron than C both B and N, respectively, can be used to substitute the ptC centers in C2 and D4h 4 to produce the isoelectronic ptB-containing C2 [C8H8]Pd4[B8H8] complex, the slightly distorted ptN-containing C1 [C8H8]Pd4[N4C8H8]+ complex, the ptB-containing D2h [C8H8]Pd4[B8H8] complex, and the ptN-containing D2d [C8H8]Pd4[N4C8H8]+ complex (see details in Supporting Information). These ptB- and ptN-containing sandwich complexes all were found to be true minima similar to the corresponding ptC-containing complexes. For example, the bond lengths and the bond orders in the high-symmetry [C8H8]Pd4X2[C8H8] complexes (X = B, C, N) (rPd–Pd = 2.819 Å, rPd–Pd = 1.993 Å, WBIptB = 3.20, and WBIptB–Pd = 0.54 for D2d [C8H8]Pd4[B8H8]; rPd–Pd = 2.857 Å, rptB–Pd = 2.020 Å, WBIptB = 2.47, and WBIptB–Pd = 0.41 for D2d [C8H8]Pd4[N4C8H8]+ compare

### Table 1. Calculated natural atomic charges (qptC, qptB) and the total Wiberg bond indices (WBIptC, WBIptB) of the ptC centers and periphery transition metal atoms M, the Wiberg bond indices of the ptC–M interactions (WBIptC–M), NICS(1) and NICS(1)c values in ppm, HOMO energies (E_{HOMO})/eV, and HOMO–LUMO energy gaps (ΔE_{gap})/eV of the [C8H8]M4[C8H8] complexes at B3LYP level. The IP values of the neutrals are also indicated in eV.

<table>
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<th></th>
<th>qptC</th>
<th>WBIptC</th>
<th>qptB</th>
<th>WBIptB</th>
<th>WBIptC–M</th>
<th>NICS(1)</th>
<th>NICS(1)c</th>
<th>E_{HOMO}</th>
<th>ΔE_{gap}</th>
<th>IP</th>
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<td>C1 [C8H8]Pd4[C8H8]+</td>
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<td>1.612 to 1.614</td>
<td>+0.59 to +0.60</td>
<td>9.96</td>
<td>26.23</td>
<td>8.16</td>
<td>1.89</td>
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<tr>
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<td>1.88 to 1.90</td>
<td>0.59 to 0.62</td>
<td>9.13</td>
<td>19.07</td>
<td>8.25</td>
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<tr>
<td>C1 [C8H8]Pt4[C8H8]+</td>
<td>+0.56 to +0.53</td>
<td>2.14 to 2.16</td>
<td>0.58 to 0.62</td>
<td>8.02</td>
<td>21.47</td>
<td>8.16</td>
<td>2.30</td>
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<tr>
<td>D4h [C8H8]Pt4[C8H8]</td>
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<td>1.57</td>
<td></td>
<td>+1.52</td>
<td>+10.31</td>
<td>5.25</td>
<td>6.71</td>
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<tr>
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<td>+0.47</td>
<td>1.88</td>
<td></td>
<td>0.59</td>
<td>5.15</td>
<td>7.01</td>
<td>2.27</td>
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<tr>
<td>D4h [C8H8]Pt4[C8H8]+</td>
<td>−0.57</td>
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<td>0.60</td>
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<td>12.75</td>
<td>−4.33</td>
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favourably with those obtained for $D_{4h}$ [C₈H₈]Pd₄C[C₈H₈] (4) \((r_{Pd-Pd} = 2.793 \, \text{Å}, \, r_{Pd-C} = 1.975 \, \text{Å}, \, WBI_{Pd-C} = 3.15, \, \text{and} \, WBI_{Pd-Pd} = 0.59)$. The low covalent bond order of the ptN center can be explained by the relatively strong ionic interaction formed between the highly negatively charged ptN center \((q_{ptN} = -0.97 \, |e|)\) and the four positively charged Pd periphery atoms \((q_{ptd} = +0.65 \, |e|)\). Similar situations exist for the low-symmetry [C₈H₈]Pdₓ[X][C₈H₈] series \((X = B, C, N)\).

Orbital analyses can be used to explain the bonding nature of these ptC centers. The atomic electron configurations of the ptC \([\text{He}]^22p^4\) in \(C_8\) and the ptC \([\text{He}]^22p^4\) in \(C_9\) are occupied in agreement with the Wang–Schleyer ptC bonding model, which is based on conceptually on stabilization of the vacant ptC 2p orbitals, through electron transfer.\(^{[8a,15]}\) PtC serves as a σ-acceptor and a π-donor in planar tetra- and hypercoordinate carbon systems.\(^{[1–8,16]}\) As shown in Figure 2, both the HOMO-16\((a_{2u})\) and HOMO-25\((a_{2u})\) of \(D_{4h}\) [C₈H₈]Pd₄C[C₈H₈] (4) contain an in-phase π-overlap between the ptC 2p and the four equivalent periphery Pd 4d orbitals, while the delocalized π MOs of the [C₈H₈]²⁻ ligands form an antibonding interaction with the Pd₄C middle deck in the former and a bonding interaction in the latter. The all-in-phase bonding HOMO-25\((a_{2u})\) involves a weak overlap between the ptC 2p orbital and the delocalized π MOs of the ligands, which is expected to promote the ring-current effects of the C₈H₈ rings. The degenerate HOMO-26\((e_u)\) represents two equivalent σ-bonds between the ptC 2p orbitals and the Pd 4d orbitals in radial directions in the Pd₄C plane, with the corresponding antibonding orbitals LUMO+2\((e_u)\) unoccupied (see Supporting Information). The in-phase bonding MOs of HOMO-13\((b_{1g})\), the degenerate HOMO-22\((b_{1g})\), and HOMO-27\((a_{1g})\) mainly represent the Pd\((d_{xy})\)–ligand(π) coordination interactions in the vertical direction (see Supporting Information). Similar electronic configurations and ptC-related MOs exist in \(C_9\) and other ptC-centered sandwich complexes.

As shown in Figure 3, the NICS values of the free 10π [C₈H₈] (\(D_{6h}\)) and [C₈H₈]²⁻ (\(D_{4h}\)) rings increase monotonically, while their NICS₂₂ components exhibit only very shallow minima at points 0.5–1.0 Å above the ring centers, unlike the prototypical free 6π C₈H₈ \(D_{6h}\) ring, which possesses deep minima at both NICS(1) and NICS(1)₂₂.\(^{[12a]}\) The C₈H₈ ring in the C₉ complex behaves quite similarly to the free \(D_{6h}\) [C₈H₈]²⁻ ligand for both NICS and NICS₂₂ [see Figure 3(a)]. The conventional values of NICS(1) = −9.96 ppm and NICS(1)₂₂ = −26.23 ppm compare favourably, albeit systematically lower, with NICS(1) = −12.32 ppm and NICS(1)₂₂ = −38.49 ppm obtained for the free [C₈H₈]. For the C₈H₈ rings in the \(D_{4h}\) [C₈H₈]Pd₄C[C₈H₈] (4) complex, which possesses C–C bond length alternation, the calculated NICS and NICS₂₂ values are less negative than the corresponding values obtained for the free [C₈H₈]²⁻ ligand between 0.0 and 2.0 Å above the ring center [see Figure 3(b) and Table 1]. NBO analyses indicated that a π-donating C₈H₈ ring in the neutral \(D_{4h}\) [C₈H₈]Pd₄C[C₈H₈] (4) complex carries a net natural charge of \(q_{\text{C₈H₈}} = -1.08 \, |e|\), a value much smaller than the formal charge \(q_{\text{C₈H₈}} = -2.0 \, |e|\) of a free \(D_{4h}\) [C₈H₈]³⁻, which results in significantly less effective ring-current effects and therefore less negative NICS and NICS₂₂ values for the complex. The charge transfers from the M₄C middle sheets are not effective enough to fully satisfy the formal charge states of [C₈H₈]⁻ and [C₈H₈]²⁻ for the large carbocyclic ligands in the complexes. Nevertheless, the overall variation and convergence behavior of the ligands in the complexes and in the free gas states appear to be similar (Figure 3). The ptC-centered [C₈H₈]M₄C[C₉H₉] complexes have more negative NICS(1) and NICS(1)₂₂ values than the corresponding empty-centered [C₈H₈]M₄[C₉H₉] complexes (see Table 1), indicating that the ptC centers help to promote the ring-current effects of the ligands in these complexes, which is in agreement with the orbital analyses presented above.

To check the thermodynamic stability of the ptC-containing complexes, we calculated the “insertion energies” of the ptC centers (\(\Delta E_{ptC}\)) in the following processes.

\[
\text{[C₈H₈]M₄[C₈H₈]^+ + C = [C₈H₈]M₄C[C₈H₈]^+} \quad (1)
\]

\[
\text{[C₈H₈]M₄[C₈H₈] + C = [C₈H₈]M₄C[C₈H₈]} \quad (2)
\]

We found them to be \(\Delta E_{ptC} = -83.3, \, -51.7, \, \text{and} \, -56.0 \, \text{kcalmol}^{-1}\) in (1) and \(\Delta E_{ptC} = -74.0, \, -41.2, \, \text{and} \, -42.8 \, \text{kcalmol}^{-1}\) in (2) for M = Ni, Pd, and Pt, respectively. These negative energy changes indicate that the insertion of a ptC atom to form four effective ptC–M bonds helps to stabilize the \([C₈H₈]M₄C[C₈H₈]^+\) and \([C₈H₈]M₄C[C₈H₈]\) complexes thermodynamically. It is worth noting that the ptCs in the Ni₄C squares possess significantly higher insertion energies than in both Pd₄C and Pt₄C in these processes. An Ni₄ square best matches in size both the ptC center and the carbocyclic C₉H₉ ligands \((n = 8, 9)\) in the [C₈H₈]-M₄C[C₉H₉] series \((M = \text{Ni, Pd, and Pt})\). This observation supports the fact that ptC centers have already been observed in square Ni₄C in crystalline Ca₄Ni₃C₅ and have been predicted as possible in the hydridonickel compound Ni₄H₄C\(^{[7]}\). As indicated in Table 1, these ptC-centered complexes also possess considerably low HOMO energies \((E_{\text{HOMO}} = -4.2 \, \text{to} \, -8.3 \, \text{eV})\) and wide HOMO–LUMO energy gaps \((\Delta E_{\text{gap}} = 1.9–2.3 \, \text{eV})\), further supporting their thermodynamic stability. The [C₈H₈]M₄C[C₈H₈] neutral\(^s\) have relatively high ionization potentials, with the calculated IPs = 5.30–5.76 eV at the DFT level. Vibrational analysis showed that these ptC-containing complexes possess a characteristic ptC–M in-plane stretching vibrational frequency at approximately 500 cm\(^{-1}\), which is absent in the corresponding empty-centered systems (see Figure S1 in the Supporting Information).

**Conclusions**

In this work, we have performed a systematical DFT investigation on the possibility of ptC-centered \([C₈H₈]M₄C[C₉H₉]\) sandwich complexes \((M = \text{Ni, Pd, Pt}; \, n, n' = 8, 9)\) and have predicted them to be kinetically and thermodynamically stable. The results of the electronic structure calculations are corroborated by vibrational studies, which further support the existence of these complexes as stable intermediates in the formation of hydridonickel compounds.
with the large π-coordinating \([\text{C}_2\text{H}_2]^2-\) and \([\text{C}_6\text{H}_6]^2-\) ligands. Introduction of a PtC center into a square M₄ sheet to form four effective ptC–M bonds helps to stabilize the \([\text{C}_6\text{H}_6]^2-\text{M}_4\text{C}[\text{C}_6\text{H}_6]\) complexes thermodynamically, and the \([\text{C}_6\text{H}_6]^2-\) and \([\text{C}_6\text{H}_6]^2-\) ligands were found to match the M₄C middle decks both geometrically and electronically; ptB and ptN centers behave similarly to ptC centers with certain structural distortions. These novel sandwich complexes invite experimental syntheses and characterizations in order to open up a new area in coordination chemistry for ptC and other planar tetraatomic centers.

**Supporting Information** (see footnote on the first page of this article): Calculated IR spectra of \(\text{C}_1\left[\text{C}_6\text{H}_6]_2\text{Pt}_2_2\text{C}[\text{C}_6\text{H}_6]^2\right]\) and \(\text{C}_1\left[\text{C}_6\text{H}_6]_2\text{Pt}_2\text{C}[\text{C}_6\text{H}_6]^2\right]\), valence MOs of \(\text{D}_{2h}\text{C}_6\text{H}_6]_2\text{Pt}_2\text{C}[\text{C}_6\text{H}_6]\), lowest vibrational frequencies, zero point energies, and optimized coordinates of the \([\text{C}_6\text{H}_6]^2-\text{M}_4\text{C}[\text{C}_6\text{H}_6]\) and \([\text{C}_6\text{H}_6]^2-\text{M}_4\text{C}[\text{C}_6\text{H}_6]\) complexes (\(X = C, B, N\)).