Pyridine-Derived N-Heterocyclic Carbenes: An Experimental and Theoretical Evaluation of the Bonding in and Reactivity of Selected Normal and Abnormal Complexes of Nickel(II) and Palladium(II)

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We report a thorough investigation of a series of isomeric complexes with the general formula trans-(pyridylidene)M(PPh3)2Cl (M = Pd, Ni). For the first time, a systematic comparison of normal, abnormal, and remote bonding modes is presented. X-ray structural and 13C NMR data indicate the importance of carbeneoid mesomeric contributions in their compound class. The catalytic performance of the palladium complexes trans-(pyridylidene)Pd(PPh3)2Cl as precursors in Suzuki–Miyaura-type cross-coupling suggests a correlation of remote bonding with catalyst robustness and effectivity. When metal precursors M(PPh3)4 are reacted with 2,4-dichloropyridinium salts, preferential formation of remote carbene complexes occurs and indications are that electronic parameters rather than steric influences are responsible for the observed selectivity. Calculations at the BP86/TZ2P level of theory support interpretation of the results.

Introduction

The chemistry of N-heterocyclic carbenes (NHCs) has seen an explosive development during the last number of years.1–5 However, despite the vast number of possible N-heterocycles that could be classified as carbenes, the activity in NHC chemistry has concentrated by and large on 2-imidazolylidenes, often called “Arduengo” carbenes.19 The mo-
both normal and abnormal carbones arising in a remote position (II, III). We have extended Crabtree’s terminology\(^{6,7}\) by using the term abnormal whenever it is not possible to illustrate the carbene structure without charge separation (in contrast to Ia and IIIa).\(^{15}\) Remote denotes a carbene that contains no stabilizing heteroatom directly adjacent to the carbene carbon. Accordingly, isomer II is abnormal and remote, whereas isomer III is normal and remote.

Previous theoretical investigations of the free ligands indicate that pyridine is by far more stable (0.0 kcal/mol) than the most stable carbenoid isomer I (ca. 40 kcal mol\(^{-1}\)), while the remote species II and III are even higher in energy (both ca. 55 kcal mol\(^{-1}\)).\(^{24-27}\) Interestingly, calculations of isodesmic reactions by Kassae et al. suggest a similar stabilization of the methylene fragment in 2- and 4-pyridylidenes.\(^{28}\) Significant barriers for intramolecular interconversion allowed for detecting the coexistence of isomers I and II under high-vacuum conditions.\(^{26,27}\) In the condensed phase, intermolecular interconversion is more facile, and pyridilenes have thus far been observed only in complexes, i.e., stabilized by a metal center.\(^{29}\) Such metal-stabilized pyridilenes have been accessible in a few cases by a ligand isomerization process involving a formal proton shift from carbon to nitrogen. Depending on the ring substitution pattern, both 2- and 4-pyridylidenes have been prepared by such a rearrangement from N-protonated pyridinium salts.\(^{30-34}\) In contrast, C—H activation of N-alkylated pyridinium precursors that could allow for C2- or C4-coordination exclusively leads to metalation at the 4-position.\(^{35-39}\) This observation has been attributed to the steric bulk of the N-alkyl group.

We first carried out a thorough investigation of a series of isomeric complexes with the general formula trans-(pyridylidene)M(PPh\(_3\))\(_2\)Cl (M = Pd, Ni) using various experimental and computational parameters. We were particularly interested in evaluating whether certain mesomeric contributions would be particularly significant and if the concept of abnormal carbene bonding, which is defined on the basis of simple valence bond considerations, transfers to experimental observations. Second, the catalytic performance of the palladium complexes trans-(pyridylidene)Pd(PPh\(_3\))\(_2\)Cl as precursors in Suzuki—Miyaura-type cross-coupling reactions was studied in order to elucidate the influence of normal, abnormal, or remote carbene bonding. Finally, we investigated preferential carbene complex formation by oxidative addition using low-valent metal precursors and 2,4-dichloropyridinium salts. DFT calculations were used to support our interpretation of the results. As an extension of our studies on quinolylidene complexes,\(^{20,21,23,40-42}\) we also determined the reactivity of M(PPh\(_3\))\(_2\) (M = Pd, Ni) toward 4,7-dichloroquinolinium salts, wherein both chloro substituents are located three bonds away from the nitrogen atom.

Throughout this article, carbene complexes are drawn with M≡C double bonds where applicable. Our choice of representation should not be regarded as a statement concerning the actual bond order; it merely helps the reader to identify formal (normal) carbene metal bonds.

**Results and Discussion**

**a. Synthesis of 2-, 3-, and 4-Pyridylidene Metal Complexes.** The synthetic routes used to prepare two complete series of ionic 2-, 3-, and 4-pyridylidene metal complexes 3 and 4 are summarized in Scheme 2 and follow our established strategy that has been reported earlier.\(^{23}\) Pyridinium triflates 2 (triflate = OTf = trifluoromethanesulfonate) were prepared from the corresponding chloropyridines 1a–c with one equivalent of methyltriflate in dry dichloromethane. Subsequent oxidative addition of the ligand precursor salts to Ni(PPh\(_3\))\(_2\) in THF at room temperature afforded the desired yellow cationic complexes 4 in good yields. Similar procedures in toluene at 60 °C were followed to obtain the corresponding colorless palladium complexes 3. The oxidative addition leading to the abnormal complex 3b occurred significantly slower than the corresponding reaction for normal carbones.

**b. Single-Crystal Structure Determinations.** The ORTEP drawing of the molecular structure of the nickel complex 4b in Figure 1 is representative for the square-planar geometry generally observed for complexes 3 and 4, as previously established for BF\(_3\) analogues of the 2- and 4-pyridylidene metal complexes.\(^{20,21}\) The phosphate ligands adopt the usual trans configuration. Unlike the corresponding complexes 3a and 4a or 3c and 4c (in the BF\(_3\) salt), which crystallize in distinct packing arrangements,\(^{20,21}\) crystals of 3b and 4b (in the OTf salt) are isomorphous. Relevant parameters for the entire

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**Scheme 1. Isomeric Pyridine and Pyridylidenes**

[Diagram showing isomeric pyridine and pyridylidenes, including structures Ia, Ib, IIb, IIIa, and IIIb.]
Bercaw and co-workers have discussed the bonding situation for *normal* pyridylidene complexes in terms of the bond alternation within the heterocyclic carbene ligand.\(^4\) We followed a similar approach in our efforts to identify relevant contributing structures for complexes 4 (Scheme 3).\(^5\)

The 2-pyridylidene moiety in 4a shows a significant increase in the N1–C6 and C2–C3 distances compared to free pyridine (Figure 2). However, the N1–C2 bond remains short. These observations could indicate the relative importance of contributing structures such as IVa and IVe in Scheme 3. A weak diene-type character of 2-pyridylidenes has been suggested earlier by others.\(^6\) Remarkably, examination of available structural data on 2-pyridone reveals a rather similar bond distribution pattern therein (Figure 2).

Evidence for a diene-like contribution such as VIe (Scheme 3) is also found in the 4-pyridylidene ligand of 4c. The lateral bonds C2–C3 and C5–C6 are significantly (4.3 Å) shorter than those of C3–C4 and C4–C5 (Figure 2). Related bond variations are also found for 4-pyridylidene tungsten\(^2\) and platinum complexes.\(^3\) The latter comprise a short Pt–C bond and a 13C carbene resonance as high as 324 ppm. Again, a similar geometry is featured by the corresponding 4-pyridone (Figure 2).

In contrast to the heterocyclic rings of the two *normal* pyridylidene ligands in 4a and 4c, where internal distances qualitatively support carbenoid mesomers (IVe and VIe, respectively), the *abnormal* bonding in complex 4b entails bond length variations that cannot be readily described in terms of simple valence bond resonance theory. Nevertheless, consistent with the examples above, bonds that involve the nitrogen atom are relatively short (N1–C2, N1–C6), while bonds from the carbene carbon atom are rather long (C2–C3, C3–C4).

Such findings are particularly relevant when considering that the bond length variations found in complexes 4 are not observed in the corresponding chloropyridinium precursor salts (see Supporting Information for details). In contrast to the situation in the metal complexes, the atom separations are not significantly dependent on the substitution pattern and are closely related to those in unsubstituted pyridinium salts. We therefore conclude that metalation, rather than alklylation, has the greatest influence on the bonding within the heterocyclic ligands during ylidene formation from chloropyridines. Furthermore, this influence of the metal fragment seems to be related to the effect that a doubly bound oxygen exerts in pyridines. These arguments all point toward a non-negligible double-bond character of the metal carbon bonds in the *normal* pyridylidene complexes.

\[(\text{Scheme 3})\]

\[
\begin{align*}
(\text{Sof 0.2), which was not found when the result was published initially.}\quad (43)\end{align*}
\]

\[
\text{The updated structure and selected data can be found in the Supporting Information. However, the disorder compromises a closer examination of the bond distances and angles in the carbene ligand, and we shall therefore concentrate on the nickel complexes, which also, in general, offered better data.}\quad (44)
\]

\[
\text{We mention that reinvestigation of the crystal structure of 3a (in the tetrafluoroborate salt) revealed disorder of the pyridylidene ligand (sof 0.2), which was not found when the result was published initially.}\quad (46)
\]

\[
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\]

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\]

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\]

\[
\text{Such findings are particularly relevant when considering that the bond length variations found in complexes 4 are not observed in the corresponding chloropyridinium precursor salts (see Supporting Information for details). In contrast to the situation in the metal complexes, the atom separations are not significantly dependent on the substitution pattern and are closely related to those in unsubstituted pyridinium salts. We therefore conclude that metalation, rather than alklylation, has the greatest influence on the bonding within the heterocyclic ligands during ylidene formation from chloropyridines. Furthermore, this influence of the metal fragment seems to be related to the effect that a doubly bound oxygen exerts in pyridines. These arguments all point toward a non-negligible double-bond character of the metal carbon bonds in the *normal* pyridylidene complexes.}\quad (7)
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\[
\text{Information. However, the disorder compromises a closer examination of the bond distances and angles in the carbene ligand, and we shall therefore concentrate on the nickel complexes, which also, in general, offered better data.}\quad (7)
\]

\[
\text{We mention that reinvestigation of the crystal structure of 3a (in the tetrafluoroborate salt) revealed disorder of the pyridylidene ligand (sof 0.2), which was not found when the result was published initially.}\quad (46)
\]

\[
\text{The updated structure and selected data can be found in the Supporting Information. However, the disorder compromises a closer examination of the bond distances and angles in the carbene ligand, and we shall therefore concentrate on the nickel complexes, which also, in general, offered better data.}\quad (47)
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Table 1. Selected Structural Parameters of the Series of Pyridylidene Complexes

<table>
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<tr>
<td>3a</td>
<td>2.002(3)′</td>
<td>2.3638(8)</td>
<td>116.22′</td>
<td>88.60′</td>
<td>0.628′</td>
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<tr>
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<td>2.371(2)</td>
<td>117.82</td>
<td>85.21</td>
<td>0.572</td>
</tr>
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<td>3c′</td>
<td>1.979(7)</td>
<td>2.3938(17)</td>
<td>116.44</td>
<td>77.84</td>
<td>0.155</td>
</tr>
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<td>4a′</td>
<td>1.861(5)</td>
<td>2.203(1)</td>
<td>116.84</td>
<td>90.00</td>
<td>1.161</td>
</tr>
<tr>
<td>4b</td>
<td>1.874(3)</td>
<td>2.2055(8)</td>
<td>116.23</td>
<td>88.81</td>
<td>0.698</td>
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<tr>
<td>4c′</td>
<td>1.863(5)</td>
<td>2.2172(13)</td>
<td>115.04</td>
<td>83.46</td>
<td>0.228</td>
</tr>
</tbody>
</table>

* Angle between the mean square planes defined by (i) the six atoms of the heterocycle (plane1) and (ii) the metal center and the four atoms bound to the metal (plane2). † Distance of the metal-bound carbon atom from plane2 as a probe for the distortion of the square-planar geometry. ‡ Inaccurate, due to disorder of the ligand (cf. Supporting Information). § Ref 20. ¶ Ref 21.

Scheme 3. Various Mesomeric Structures of Normal (IV, VI) and Abnormal (V) Pyridylidene Complexes, Some of Them Remote (V, VI)

Interestingly, the nonmethylated 4-pyridyl ligand in palladium complex A (Figure 3) displays similar features to those of the pyridylidene ligand in 4c, i.e., short lateral bonds. It could be reasoned that coordination to the metal center already induces localization of double bonds in a carbeneoid fashion (A'). Indeed, according to electron decomposition analysis (EDA), σ and π orbital contributions in pyridyl—metal and pyridylidene—metal bonds are remarkably similar. This result also provides an explanation for the increased basicity of the nitrogen in pyridyl metal complexes, which can even lead to the activation of dichloromethane.

c. NMR Spectroscopic Characterization. Similar to the difficulties experienced when attempting to determine “carbene character” from metal—carbene bond lengths, a comparison of absolute carbene carbon NMR shift values also does not give clear answers. We have previously noted that correlation of NMR data with data of other analytical techniques, e.g., IR and CO stretching frequencies, is often poor, thus requiring cautious interpretation. In the series of complexes 3 and 4, significantly lower chemical shifts are observed for the abnormal complexes 3b and 4b (δC 165 and 174, respectively) than for the normal congeners (δC > 190). When compared to the corresponding carbon resonances in the precursor pyridinium salts, deshielding between 30 and 50 ppm occurs upon formal carbene formation. For both metals, abnormal C3 bonding induces the smallest and normal remote C4 bonding the largest shift difference. Nickel bonding shows consistently a stronger deshielding effect than palladium coordination.

In order to correlate the structural investigations with solution properties, we also elucidated the electronic influence of alkylation and metalation on the heterocyclic ring by NMR spectroscopy. Comprehensive interpretation of the 1H NMR chemical shifts is hampered by the phosphine signals in the aromatic region that overlap with the protons of the heterocycle. Hence, we concentrated on 13C NMR data, which are known to be less affected by long-range magnetic and solvent effects and which correlate well with 1H data in aromatic systems. Figure 4 summarizes the most relevant chemical shifts.

Linear correlations between the chemical shift and the charge density on a given atom in a homologous series of compounds are often used for the interpretation of NMR results. Using calculated charge densities, such a dependence has been shown to exist for azine derivatives, as well as...
Figure 2. Bond distances (Å) in 4a, 4b, and 4c (top) in comparison to those in free pyridine and pyridones. (Bottom) Data derived from CCSD.  

![Figure 2](http://doc.rero.ch)

Figure 3. Metal-induced carbenoid electron distribution prior to formal carbone formation (via methylation or protonation).

![Figure 3](http://doc.rero.ch)

On the basis of these considerations, nitrogen methylation of the chloropyridines 1a–c affects mostly the region remote to the nitrogen atom. Evidently, the heteroatom — now with increased effective electronegativity — compensates for the loss of its lone pair by draining electron density from the ring and thus decreases the electron density especially at the 4-position significantly in the pyridinium salts 2 regardless of the chloro-substitution pattern. Even though the upfield shift for C2 and C6 is marginal, it might be attributed to a decrease in the N1–C2 and N1–C6 bond orders.  

Subsequent metal insertion at the 2-position of 2a to form 3a or 4a induces a drift of the positive charge in the ring toward the vicinity of the metal, thus indicating contributions from resonance structures IVa, IVd, and IVe (cf. Scheme 3). Simultaneously, a secondary process apparently increases the electron density at the carbon atoms that are remote to the coordination site. Owing to this effect, the $^{13}$C NMR chemical shifts of the neutral starting compound 1a are somewhat restored in the ligand backbone, which is in agreement with predominant charge stabilization within the N–C$_{carbene}$–M moiety.

The importance of contributing structures similar to VIc and Vle (Scheme 3) for the remote 4-pyridylidene complexes 3c and 4c is reflected by a significant charge redistribution within the heterocycle upon carbone formation. Again, metal insertion effects deshielding of the carbon atoms adjacent to the metal-bound carbon and concurrent shielding of the remote nuclei. Even the nitrogen atom possibly becomes less positively charged, as is shown by a small upfield shift for the attached methyl group. Due to the mutual trans arrangement of nitrogen and carbene carbon atoms, the polarization in the complex is sufficiently large to render the carbons in ortho and meta position almost magnetically equivalent. This result lends further support to the carbone character of C4-pyridylidene complexes (Vle, cf. X-ray discussion), and it is also in agreement with NBO analysis, which revealed that a Lewis structure resembling IIIa (Scheme 1) is most appropriately describing a free 4-pyridylidene.

For abnormal C3-pyridylidene complexes, interpretation of the NMR results in terms of valence bond theory is not straightforward, thus paralleling the solid-state conclusions. However, the $^{13}$C NMR data indicate consistently for all pyridylidenes that metatation induces a deshielding effect in the vicinity of the metal combined with shielding of the remote heterocyclic nuclei. Similar observations have also been made by Isobe and co-workers for neutral non-methylated bromopyridines upon insertion of Pd(PEt$_3$)$_2$ into the carbon–halide bond. This effect may thus be independent of the coordination mode of the ligand (normal vs abnormal) or its partial charge (pyridylidene vs pyridyl). Computational studies support such a conclusion, since the σ and π orbital contributions in pyridyl–metal and pyridylidene–metal bonds have been calculated to be remarkably similar.  

Consistent with our conclusions from crystallographic analyses, the observed influence of the metal fragment on the heterocycle might be rationalized by non-negligible M$\rightarrow$L π-back-donation. In general, an essentially similar but stronger shielding/deshielding behavior is observed for the nickel(II) fragment compared to palladium(II).
This effect may tentatively be assigned to a larger $M\equiv C$ double-bond character in 4 than in the corresponding palladium complexes 3.

Singlets in the $^{31}P$ NMR spectra of all complexes indicate the equivalence of both phosphine ligands, hence confirming a mutual trans arrangement also in solution (Scheme 2). Even though the resonances for complexes 3 and 4 fall in a narrow range ($\delta P$ 22.7–24.9 and 21.2–23.0, respectively), both series show a common trend, i.e., 2- $<$ 4- $<$ 3-pyridylidene, suggesting an increasing donor strength of the carbene ligand in this order.68

c. Computational Studies. Calculations for the series of isomeric palladium and nickel model complexes $M_3$ and $M_4$ comprising PH$_3$ ligands instead of PPh$_3$ (as in Scheme 2) were conducted at the BP86/TZ2P level of theory to verify and extend our interpretation of experimental results (Table 2). The calculated $M\equiv C$ bonds are slightly shorter than the experimental values, while the theoretical $M\equiv Cl$ distances are a bit longer than the X-ray data, but the differences are not very large. The very small changes observed in the $M\equiv C$ and $M\equiv Cl$ bond lengths are within the error range of the theoretical and experimental data, and thus, they do not exhibit a significant trend. The theoretical and experimental CCX bond angles agree well. Also bond length variations within the rings, which were discussed in section b, are qualitatively reproduced. The calculated data of the model compounds may thus be used for the interpretation of the experimental results.

The relative energies of the model systems $M_3$ and $M_4$ follow the trend 2-pyridylidene $\approx$ 3-pyridylidene $<$ 4-pyridylidene, which is the same order that has been reported for the corresponding free carbene isomers of pyridine, in which one proton is located on the nitrogen atom.24,27,28 However, the energy differences are much smaller in the complexes and

Table 2. Computational Results at the BP86/TZ2P Level and Comparison with Experimental Values, Which Are Given in Italicsa

<table>
<thead>
<tr>
<th>$d(M\equiv C)$ [Å]</th>
<th>$d(M\equiv Cl)$ [Å]</th>
<th>CCX angle [deg]</th>
<th>$E_{cat}$ [kcal mol$^{-1}$]</th>
<th>$E_{int}$ [kcal mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_3a$</td>
<td>2.021</td>
<td>2.342</td>
<td>116.23</td>
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<tr>
<td>$M_3b$</td>
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<td>2.347</td>
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<td>$M_4a$</td>
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<td>$M_4b$</td>
<td>1.861(5)</td>
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<td>$M_4c$</td>
<td>1.877</td>
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<td>115.13</td>
<td>3.72</td>
</tr>
</tbody>
</table>

a Compared to experimental values (cf. Table 1). b Relative minimized energies. c Metal–carbene interaction energies.

Scheme 4. Suzuki–Miyaura-Type Test Reactions

This effect may tentatively be assigned to a larger $M\equiv C$ double-bond character in 4 than in the corresponding palladium complexes 3.

Singlets in the $^{31}P$ NMR spectra of all complexes indicate the equivalence of both phosphate ligands, hence confirming a mutual trans arrangement also in solution (Scheme 2). Even though the resonances for complexes 3 and 4 fall in a narrow range ($\delta P$ 22.7–24.9 and 21.2–23.0, respectively), both series show a common trend, i.e., 2- $<$ 4- $<$ 3-pyridylidene, suggesting an increasing donor strength of the carbene ligand in this order.68

probably due to a predominantly heterogeneous mode of action. Between the precatalysts, palladium black even at very low temperatures, and no discrimination could show that thus the HOMO, i.e., the σ-lone-pair orbital of the carbene and thus the σ-donor properties of a given ligand.

can be rationalized by the calculated stronger interactions in 3- and 4-pyridylidene complexes, partly compensating the energy difference in the free pyridylidenes. The energy decomposition analysis of the metal–carbon bonds reveals increasing interaction energies ($E_{\text{int}}$) in the order 2-pyridylidene < 3-pyridylidene < 4-pyridylidene. In an extensive EDA study of pyridylidene and quinolylidene M–C bonds we could show that $E_{\text{int}}$ correlates very well with the energy of the HOMO, i.e., the σ-lone-pair orbital of the carbene and thus the σ-donor properties of a given ligand.

e. Catalysis. In order to determine the influence of abnormal and remote pyridylidene bonding modes on catalytic performance, the palladium complexes 3 were used in Suzuki–Miyaura cross-coupling reactions (Scheme 4). Results of preliminary experiments under standard conditions indicated small but distinct differences in the catalytic activity. As a general trend, increasing remoteness enhanced the conversion of the biaryl product followed the trend 3e (86%) > 3b (82%) > 3a (78%). All complexes displayed better performance than the reference complex Pd(PPh3)4 (71%). The trend was slightly more pronounced when using milder reaction temperatures and working under an inert atmosphere (Figure 5; also see Supporting Information).

No palladium black was observed during catalysis, thus suggesting a homogeneous mode of action. This assumption is further supported by the pertinent time–conversion profiles, which do not show any induction time or sigmoidal substrate conversion. Time-dependent monitoring also unveiled further subtle differences between the pyridylidene-based catalytic systems (Figure 5). The initial catalytic activity during the first two hours is very similar for all three complexes, perhaps slightly higher for the normal carbene complex 3a. However, this complex seems to be the least robust and deactivates after extended periods of reaction time, thus not reaching high conversions. In contrast, the remote pyridylidene complexes 3b and 3c remain active even after 20 h of activity. Hence the general trends stated above need to be refined. While the normal pyridylidene complexes 3a and 3c are slightly more active than abnormal 3b, the remote complexes 3e and 3b are more robust than 3a. Since the differences observed here are only small, further tests will be needed in order to substantiate the deduced trends.

f. Regioselectivity of the Oxidative Addition of Pyridylidium Salts. In addition to comparing the possible bonding modes of pyridylidenes, we were also interested in determining how carbene formation would preferentially occur when the metal complex reactant was presented with two active Cl-containing sites on the pyridinium ring. Reactions of M(PPh3)4 (M = Pd, Ni) with the dichloromethylpyridinium salt 5 in toluene (Scheme 5) yielded, according to $^1$C and $^1$H NMR, exclusively the 4-pyridylidene complexes 6 and 7. In comparison with the unsubstituted analogue 3c, complex 6 shows a ca. 5 ppm downfield shift of the carbene resonance, which can be attributed to the meta influence of the chloride substituent. The $^{31}$P signals differ only insignificantly.

X-ray crystal structure determinations of 6 and 7 unambiguously confirmed the coordination sites deduced by NMR spectroscopy (Figure 6). The observed features are generally similar to those discussed above. Notably, the M–C distances of 1.972(4) and 1.855(2) Å for 6 and 7, respectively, both represent the shortest bonds in the series of pyridylidene complexes discussed in this article. The M–Cl bonds are within the range described.

On the basis of the steric shielding effect of the N-methyl group in 5 and with reference to the seminal work by Carmona and co-workers, the observed regioselectivity of metatation might be ascribed to steric discrimination. However, the same selectivity was observed when the
that the relative stability of the 2- and 4-substituted systems isomers is indeed observed. Accordingly, preferential attack at the most electron-deficient position can be assumed and is indeed observed. The fact that metal attack occurs preferentially at the remote position can be understood against the background of the selective formation of the C4-bound isomer. Obviously, metatation of the remote 4-position is not sterically triggered but is electronically preferred.

Conclusions

While X-ray structural data and $^{13}$C NMR measurements of the normal (both adjacent and remote to N) complexes within a complete set of pyridine-derived carbene complexes consistently support a carbenden-type bonding (i.e., partial M=C double-bond character), results for the abnormal examples cannot be described in terms of simple valence bond resonance theory. However, close examination reveals a coherent and consistent influence of the metal fragments on the heterocyclic ligand in all bonding modes. Due to an apparent influence of remote carbene bonding on catalytic robustness, this concept seems slightly more relevant for catalytic application than the variation between normal and abnormal bonding situations. In an investigation of competitive carbene complex formation by oxidative insertion, remote 4-pyridylidene formation is favored over that of 2-pyridylidene formation even in the absence of steric shielding at nitrogen. Overall, we conclude that the concepts of remote and (ab)normal carbene bonding are useful and their does not depend on the steric requirements of the ligand. We also calculated the computationally less demanding 4-substituted model compounds $M_8/M_9$ and their 2-substituted congeners $M_8'/M_9'$ and found a similar energy difference in favor of the latter isomers, as for the bulkier compounds (Table 3). Energy decomposition analysis on these simpler models further shows that the stronger interaction occurs in the para position ($E_{int}$ in Table 3). These findings are consistent with the results shown in Table 2 and with our previous EDA studies on pyridylidene.

The theoretically predicted higher stability of the 2-pyridylidene complexes $M_6'$ and $M_7'$ and the experimental finding that only the 4-congeners 6 and 7 are formed indicate that these less stable isomers are the products of a kinetically controlled reaction. This is a very important result, which we shall investigate in a future study.

As an extension of our studies on quinolylidene,20,21,23,40–42 we also compared the reactivity of M(PPh$_3$)$_4$ toward dichloroquinolinium salts 8 where both chloro substituents (Scheme 6) are three bonds removed from the methylated (R = Me) or protonated (R = H) nitrogen atom. Again, only one of the possible products was formed in each reaction. Consistent with the expected electrophilicity derived from the $^{13}$C NMR spectra of the precursors (C4: $d$C: 155; C7: $d$C: 144), metatation is preferred within the N-containing ring to yield complexes 9 and 10. In comparison with the mononuclear congeners in 3e and 4e, the quinolylidene carbene signals are shifted about 10 ppm downfield, while the $^{31}$P NMR shifts remain essentially identical.

No traces of any dinuclear complexes were found even when using an excess of metal precursor. Figure 8 depicts the crystal structure of 9a, indicating that the presence of bulky phosphine ligands excludes the formation of dinuclear products.
The phase was washed with brine, dried with MgSO₄, and concentrated in a brown Schlenk tube. The oil (2.18 g, 19.2 mmol) was dissolved in CH₂Cl₂ and cooled to −78 °C, and methyl trifluoromethanesulfonate (3.46 g, 2.40 mL, 21.1 mmol) was added dropwise. The mixture was stirred overnight while it was allowed to warm to room temperature. The solvent was removed in vacuo, and the resulting product was washed once with 10 mL of THF and twice with 10 mL of diethyl ether.

**Procedure B: Preparation of Protonated Triflate Salts.** The hydopyridinium triflate salts were obtained by reacting the ligand precursor with a small excess (1.1 molar equiv) of CF₃SO3H in 20 mL of CH₂Cl₂ at room temperature for 18 h. Diethyl ether (20 mL) was added and a white precipitate formed. The solvent was removed via a cannula and the resulting solid washed with 4 × 20 mL of diethyl ether and dried in vacuo.

**Procedure C: Preparation of trans-Chloro-pyridylidene-bis(triphenylphosphine)/palladium(II) Triflate Complexes.** The respective triflate salts and a small excess (1.01 molar equiv) of Pd(IPPh₃)₄ were suspended in 30 mL of toluene and stirred for 17 h at 60 °C (in the case of 3b, the reaction mixture was stirred for 64 h). The white suspension in a light yellow solution was allowed to cool to room temperature and filtered through Celite. The solid on the filter was washed with 4 × 5 mL of toluene, and the product was dissolved in CH₂Cl₂ and filtered, to yield after solvent evaporation in vacuo the microcrystalline palladium complexes.

**Procedure D: Preparation of trans-Chloro-pyridylidene-bis(triphenylphosphine)/nickel(II) Triflate Complexes.** A small excess (1.1 molar equiv) of Ni(PPh₃)₄ and the respective triflate salt were suspended in THF (20 mL), and the mixture was stirred at room temperature for 17 h. The resulting yellow precipitate in a brown solution was filtered through Celite and washed with 3 × 5 mL of toluene. The product was dissolved in CH₂Cl₂, filtered, and dried under high vacuum.

### 2-Chloro-1-methylpyridinium Triflate. 2a.

According to procedure A: 88.0% yield of colorless microcrystalline material; mp 163.3–165.0 °C. 1H NMR (CD₂Cl₂, 200 MHz): δ 4.49 (3H, s, NMe), 8.02 (1H, m, H7), 8.06 (1H, dd, J = 8.3 Hz, J = 1.7 Hz, H6), 8.45 (1H, td, J = 8.3 Hz, J = 1.7 Hz, H5), 9.18 (1H, dd, J = 6.2 Hz, J = 1.7 Hz, H4). 13C{1H} NMR (CD₂Cl₂, 200 MHz): 17.4 (s, C1), 127.1 (s, C6), 130.0 (s, C3), 147.3 (s, C5), 149.4 (bs, C7 and C8), CF₃ not observed. Anal. Calcd for C₉H₇NO₃SClF₃: 277.65 g·mol⁻¹: C 30.28, H 2.54, N 5.04. Found: C 30.01, H 2.41, N 4.93.

### 3-Chloro-1-methylpyridinium triflate. 2b.

According to procedure A: 98.5% yield of colorless microcrystalline material; mp 60.8–62.3 °C. 1H NMR (CD₂Cl₂, 200 MHz): δ 4.63 (3H, s, NMe), 8.29 (1H, dd, J = 8.3 Hz, J = 6.3 Hz, H7), 8.81 (1H, dm, J = 8.3 Hz, J = 0.5 Hz, H6), 9.15 (1H, dd, J = 6.3 Hz, H5), 9.38 (1H, dd, J = 0.5 Hz, H4). 13C{1H} NMR (CD₂Cl₂, 200 MHz): 49.7 (s, NMe), 130.1 (s, C6), 146.4 (s, C5), 146.7 (s, C2), CF₃ not observed. MS (FAB): m/z (%): 131.0 (35) [M − CF₃SO3⁺], 128.1 (100) [M − CF₃SO₂⁺], 125.1 (35Cl). Anal. Calcd for C₉H₇NO₃SClF₃: 277.65 g·mol⁻¹: C 30.28, H 2.54, N 5.04. Found: C 30.00, H 2.30, N 5.09.

### 4-Chloro-1-methylpyridinium triflate, 2c.

According to procedure A: 55.5% yield of colorless microcrystalline material; mp 135.1–136.6 °C. 1H NMR (CD₂Cl₂, 200 MHz): δ 4.45 (3H, s, NMe), 8.11 (1H, d, J = 6.3 Hz, H7), 8.13 (1H, dd, J = 8.3 Hz, J = 0.5 Hz, H6), 9.15 (1H, dd, J = 6.3 Hz, H5), 9.38 (1H, dd, J = 0.5 Hz, H4). 13C{1H} NMR (CD₂Cl₂, 200 MHz): 49.7 (s, NMe), 130.1 (s, C6), 146.4 (s, C5), 146.7 (s, C2), CF₃ not observed. MS (FAB): m/z (%): 131.0 (35) [M − CF₃SO⁺], 128.1 (100) [M − CF₃SO₂⁺], 125.1 (35Cl). Anal. Calcd for C₉H₇NO₃SClF₃: 277.65 g·mol⁻¹: C 30.28, H 2.54, N 5.04. Found: C 30.00, H 2.30, N 5.09.

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8.01 (2H, d, J = 6.8 Hz, H' and H''), 8.82 (2H, d, J = 6.8 Hz, H' and H'''). 13C(NMR CDCl3, 20 °C): δ 49.0 (s, NMe), 129.5 (s, C' and C''), 147.0 (bs, C' and C''), 153.3 (s, C'), CF3 not observed. Anal. Calcld for C32H25NO3SClF3Ni: C 59.99, H 4.10, N 1.54. Found: C 59.99, H 4.10, N 1.54.

trans-Chloro-2-hydro-1-methyl-2-pyridylidene/bis(triphenylphosphine)nickel(II) Triflate, 4a. According to procedure C: 99.8% yield of yellow microcrystalline material; mp (dec): 187 °C. H NMR (CDCl3, 20 °C): δ 3.80 (3H, s, NMe), 7.16 (2H, d, J = 6.4 Hz, H' and H''). 7.39 (14H, m, PPh with observed H' and H''), 7.50, 7.62 (18H, m, PPh). 13C(NMR CDCl3, 20 °C): δ 46.5 (s, NMe), 129.2 (m, PPhmeta), 130.0 (m, PPhortho), 131.7 (s, PPhortho), 135.2 (m, PPhortho), 136.8 (bs, C' and C''), 137.4 (s, C' and C''). 197.7 (t, J = 6.5 Hz, C'). CF3 not observed. 31P{1H} NMR (CDCl3, 20 °C): δ 24.9 (s, PPh3). MS (FAB): m/z (%): 796.5 (52) [M − CF3SO3]+, 31P{1H} NMR (CDCl3, 20 °C): δ 23.6 (s, PPh3). Anal. Calcld for C32H25NO3SClF3Ni (860.91 g mol−1): C 56.84, H 4.10, N 1.54. Found: C 56.61, H 4.01, N 1.60.

trans-Chloro-2-hydro-1-methyl-2-pyridylidene/bis(triphenylphosphine)nickel(II) Triflate, 4a. According to procedure C: 59.8% yield of yellow microcrystalline material; mp (dec): 189 °C. H NMR (CDCl3, 20 °C): δ 3.80 (3H, s, NMe), 7.16 (2H, d, J = 6.4 Hz, H' and H''). 7.39 (14H, m, PPh with observed H' and H''), 7.50, 7.62 (18H, m, PPh). 13C(NMR CDCl3, 20 °C): δ 46.5 (s, NMe), 129.2 (m, PPhmeta), 130.0 (m, PPhortho), 131.7 (s, PPhortho), 135.2 (m, PPhortho), 136.8 (bs, C' and C''), 137.4 (s, C' and C''). 197.7 (t, J = 6.5 Hz, C'). CF3 not observed. 31P{1H} NMR (CDCl3, 20 °C): δ 24.9 (s, PPh3). MS (FAB): m/z (%): 796.5 (52) [M − CF3SO3]+, 31P{1H} NMR (CDCl3, 20 °C): δ 23.6 (s, PPh3). Anal. Calcld for C32H25NO3SClF3Ni (860.91 g mol−1): C 56.84, H 4.10, N 1.54. Found: C 56.61, H 4.01, N 1.60.

trans-Chloro-2-hydro-1-methyl-2-pyridylidene/bis(triphenylphosphine)nickel(II) Triflate, 4a. According to procedure C: 74.3% yield of colorless crystals; mp (dec) 200 °C. H NMR (CDCl3, 20 °C): δ 3.82 (3H, s, NMe), 7.16 (2H, d, J = 6.4 Hz, H' and H''). 7.39 (14H, m, PPh with observed H' and H''), 7.50, 7.62 (18H, m, PPh). 13C(NMR CDCl3, 20 °C): δ 46.5 (s, NMe), 121.5 (s, C'), 128.9 (m, PPhmeta), 129.4 (m, PPhmeta), 131.8 (s, PPhmeta), 134.5 (m, PPhortho), 134.7 (s, C'), 138.2 (bs, C'), 146.0 (s, C'), 193.6 (t, J = 33.0 Hz, C'). CF3 not observed. 31P{1H} NMR (CDCl3, 20 °C): δ 21.2 (s, PPh3). Anal. Calcld for C32H25NO3SClF3Ni (860.91 g mol−1): C 59.99, H 4.33, N 1.63. Found: C 60.32, H 4.24, N 1.49.

trans-Chloro-3-hydro-1-methyl-3-pyridylidene/bis(triphenylphosphine)nickel(II) Triflate, 4b. According to procedure D: 49.6% yield of light yellow crystals; mp (dec) 135.0–138.0 °C. Yellow crystals, suitable for single-crystal X-ray structure determination, were obtained by slow diffusion of pentane into a concentrated CH2Cl2 solution at −20 °C. H NMR (CDCl3, 20 °C): δ 3.36 (3H, s, NMe), 6.69 (1H, m, H'), 7.11 (1H, bs, H' and H''), 7.40. 7.66 (31H, m, PPh with observed H'), 8.09 (1H, d, J = 4.4 Hz, H'). 13C(NMR (CDCl3, 20 °C): δ 47.7 (s, NMe), 123.0 (s, C'), 128.9 (m, PPhmeta), 129.7 (m, PPhmeta), 131.2 (s, PPhmeta), 134.7 (m, PPhmeta), 136.5. (bs, C'), 148.2 (s, C'), 150.7 (bs, C'), 174.1 (bs, C'), CF3 not observed. 31P{1H} NMR (CDCl3, 20 °C): δ 23.0 (s, PPh3). MS (FAB): m/z (%): 711.8 (6) [M − CF3SO3]+, 31P{1H} NMR (CDCl3, 20 °C): δ 43.7 (s, PPh3). Anal. Calcld for C32H25NO3SClF3Ni (860.91 g mol−1): C 59.99, H 4.33, N 1.63. Found: C 60.21, H 4.20, N 1.73.

trans-Chloro-4-hydro-1-methyl-4-pyridylidene/bis(triphenylphosphine)nickel(II) Triflate, 4c. According to procedure D: 45.7% yield of yellow microcrystalline material; mp (dec): 153 °C. H NMR (CDCl3, 20 °C): δ 3.70 (3H, s, NMe), 6.91 (2H, d, J = 5.9 Hz, H' and H''). 7.40, 7.49, 7.68 (32H, m, PPh with observed H' and H''). 13C(NMR (CDCl3, 20 °C): δ 4.66 (s, NMe), 128.8 (m, PPhmeta), 129.7 (m, PPhmeta), 131.2 (s, PPhmeta), 134.0 (s, C' and C''), 134.7 (m, PPhortho), 136.0 (bs, C' and C''), 205.0 (t, J = 31.2 Hz, C'), CF3 not observed. 31P{1H} NMR (CDCl3, 20 °C): δ 22.4 (s, PPh3). Anal. Calcld for C32H25NO3SClF3Ni (860.91 g mol−1): C 59.99, H 4.33, N 1.63. Found: C 60.21, H 4.23, N 1.54.
1H NMR (CD2Cl2, 20 °C): δ 3.71 (3H, s, NMe), 7.16 (1H, bs, H7), 7.41 (12H, m, PPh3), 7.48 (7H, m, PPh3 with obscured H8), 7.69 (12H, m, PPh3), 7.76 (1H, d, J = 6.4 Hz, H5), 7.84 (2H, m, H3/4), 13C(NMR (CD2Cl2, 20 °C)): δ 45.0 (s, NMe), 128.9 (m, PPh3), 129.4 (m, PPh3), 131.5 (s, PPh3), 133.8 (s, C13), 134.7 (m, PPh3), 136.6 (s, C8), 136.8 (s, C1), 210.8 (s, C4), CF3 not observed. 31P1H NMR (CD2Cl2, 20 °C): δ 22.5 (s, PPh3). MS (FAB): m/z (%): 746.4 (40) [M – CF3SO3]–, 13C, 58Ni; 710.8 (9) [M – Cl – CF3SO3]–, 184.0 (12) [M – PPh3 – CF3SO3]–. Anal. Caled for C47H38NO3P2SCl2F3Ni (945.42 g mol−1): C 56.84; H 3.86; N 1.41. Found: C 56.66; H 3.86; N 1.41. 

**trans-Chloro**(7-chloro-4-hydro-1-methyl-4-quinolylidene)(bis(triphenylphosphine)nickel(II)) Triflate, 10a. According to procedure D: 80.4% yield of yellow crystals; mp (dec) 176 °C. 1H NMR (CD2Cl2, 20 °C): δ 3.90 (3H, s, NMe), 7.29 (12H, m, PPh3), 7.42 (7H, m, PPh3 with obscured H8), 7.59 (13H, m, PPh3 with obscured H9), 7.66 (12H, m, PPh3 with obscured H10), 7.89 (11H, d, J = 6.3 Hz, H7), 7.89 (11H, d, J = 6.3 Hz, H8), 9.44 (11H, d, J = 8.8 Hz, H11). 13C(NMR (CD2Cl2, 20 °C): δ 43.0 (s, NMe), 117.2 (s, C2), 128.6 (m, PPh3), 128.8 (s, C7), 129.3 (m, PPh3), 130.6 (bs, C13), 131.2 (s, PPh3), 133.3 (s, C4), 134.6 (m, PPh3), 135.3 (s, C8), 136.6 (s, C9), 137.9 (s, C5), 140.9 (s, C6), 216.7 (t, JCP = 10.5 Hz, H4, C3), CF3 not observed. Anal. Calcd for C47H38NO3P2SCl2F3Ni (945.42 g mol−1): C 59.71; H 4.05; N 1.48. Found: C 59.67; H 4.26; N 1.39.

**trans-Chloro**(7-chloro-1,4-dihydro-4-quinolylidene)(bis(triphenylphosphine)nickel(II)) Triflate, 10b. According to procedure D: 68.1% yield of yellow crystals; mp (dec) 197 °C. 1H NMR (CD2Cl2, 20 °C): δ 7.28 (13H, m, PPh3 with obscured H8), 7.40 (6H, m, PPh3), 7.48 (1H, dd, J = 8.8 Hz, J = 1.9 Hz, H7), 7.55 (13H, m, PPh3 with obscured H9), 7.77 (11H, d, J = 5.8 Hz, H8), 9.19 (11H, d, J = 8.8 Hz, H11), not observed NH. 13C(NMR (CD2Cl2, 20 °C): δ 120.3 (s, C2), 126.8 (m, PPh3), 129.3 (m, PPh3), 129.6 (t, JCP = 3.7 Hz, H4), 131.3 (s, PPh3), 132.0 (s, C9), 132.0 (s, C7), 134.4 (m, PPh3), 134.7 (bs, C8), 134.9 (s, C5), 140.0 (s, C6), 216.6 (t, JCP = 30.0 Hz, H4, C3), CF3 not observed. 31P1H NMR (CD2Cl2, 20 °C): δ 22.6 (s, PPh3). MS (FAB): m/z (%): 782.1 (19) [M – CF3SO3]–, 13C, 58Ni; 746.9 (1) [M – Cl – CF3SO3]–. Anal. Calcd for C47H38NO3P2SCl2F3Ni (945.42 g mol−1): C 59.32, H 3.90, N 1.50. Found: C 59.11, H 4.02, N 1.63.

**Typical Procedure for the Suzuki–Miyaura Coupling**.

The reactions were performed under inert conditions using dry and degassed reagents. Phenylboronic acid (3 mmol, 0.3658 g), bromocacetophenone (2 mmol, 0.3981 g), potassium carbonate/cesium carbonate (4 mmol, 0.5528/1.303 g), diethylene glycol-di-n-butyl ether (2 mmol, 0.4367 g, 0.5 mL), and dimethylacetamide (5 mL) were placed in a 25 mL three-neck round-bottom flask. The flask was connected to N2 and equipped with a reflux condenser and a septum. The catalyst solution was added after heating to 130 °C. Alquiols (0.2 mL) were taken at regular intervals from the reaction mixture and added to 5 mL of CH2Cl2. The organic layer was washed with 3 × 5 mL of water, dried over MgSO4, and filtered. The solvent was removed in vacuo, and the residue was analyzed by 1H NMR spectroscopy.

**Crystal Structure Determinations**.

Data associated with the crystal structures are summarized in Tables 4 and 1S, Supporting Information. Intensity data were collected at T = 100 K with a Bruker SMART Apex diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were measured using the o-scan mode and were corrected for Lorentz polarization effects. The structures were solved by direct methods (SHELSX-97) and refined by full-matrix least-squares on F2 (SHELXL-97). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions if possible. Reinvestigation of the crystal data of 3b (in the BF4 salt, previously published) yielded a so far unnoticed disorder (sof: 0.2) of the carbene ligand. Refinement of the less occupied site was supported by restraining its geometry to fit the major ligand site using SAME. All crystals were found to contain

(76) SADABS (version 2.05); Bruker AXS Inc.; Madison, WI, 2002.
(77) SAINT: Data reduction software (version 6.45); Bruker AXS Inc.; Madison, WI, 2003.
(78) SMART: Data collection software (version 5.629); Bruker AXS Inc.; Madison, WI, 2003.
by the SQUEEZE routine in PLATON. Detailed information could not be resolved due to disorder and were thus removed.

The empirical formula is C₄₆H₃₇ClNP₂Pd. All geometries were optimized under density functional theory at the BP86 level of theory, using uncontracted Slater-type orbitals (STOs) with TZ2P quality as basis functions for the SCF calculations. The bonding situation of the metal–carbene bonds was investigated by an energy decomposition analysis that was found in the CIF along with a complete list of displacement parameters and tables of interatomic distances and angles. These have been deposited with the Cambridge Crystallographic Data Centre and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif on quoting CCDC 796954 to 797119.

### Computational Section

With the exception of M₆, M₇, M₆', and M₇' (BP86/TZVP), all geometries were optimized under C₆₃-symmetry constraint using density functional theory at the BP86 level of theory.81,82,83

### Table 4. Crystal Data, Data Collection, and Structure Refinement Details

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6-2CH₂Cl₂ 7-CH₂Cl₂ 9-CH₂Cl₂

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<td>731 [R(int) = 0.034]</td>
<td>8048 [R(int) = 0.028]</td>
</tr>
<tr>
<td>refined params/restraints</td>
<td>560(9)</td>
<td>533(0)</td>
</tr>
<tr>
<td>R₁ [I ≥ 2σ(I)]</td>
<td>0.053</td>
<td>0.038</td>
</tr>
<tr>
<td>wR²</td>
<td>0.120</td>
<td>0.095</td>
</tr>
<tr>
<td>weighting scheme</td>
<td>a = 0.0457</td>
<td>a = 0.048</td>
</tr>
<tr>
<td>b = 0.179112</td>
<td>b = 3.1369</td>
<td>b = 0.000</td>
</tr>
<tr>
<td>σ hòa(max./min.)/e Å⁻³</td>
<td>1.67/–1.56</td>
<td>0.72–0.59</td>
</tr>
</tbody>
</table>

wR² = [Σ(w(Fo² − Fc²)²)/Σ(w(Fc²)²)]¹/²; w = 1/[σ²(Fo)² + (ap)² + bp]; p = (Fo² + 2Fc²)/3.

bonding analysis focuses on the instantaneous interaction energy $\Delta E_{\text{int}}$ of a bond $A-B$ between two fragments $A$ and $B$ in the particular electronic reference state and in the frozen geometry of $AB$. This interaction energy is divided into three main components [eq 1].

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$  \hspace{1cm} (1)

The term $\Delta E_{\text{elstat}}$ corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. The Pauli repulsion, $\Delta E_{\text{Pauli}}$, is the energy change associated with the transformation from the superposition of the unperturbed electron densities $\rho_A + \rho_B$ of the isolated fragments to the wave function $\Psi^0 = N \{ A \Psi_A \Psi_B \}$, which properly obeys the Pauli principle through explicit antisymmetrization ($\hat{A}$ operator) and renormalization of the product wave function.\(^{(90)}\)

The orbital interaction $\Delta E_{\text{orb}}$ accounts for charge transfer and polarization effects.\(^{(91)}\) The $\Delta E_{\text{orb}}$ term can be decomposed into contributions from each irreducible representation of the point group of the interacting system. This makes it possible to estimate the intrinsic strength of orbital interactions from orbitals having $\sigma'$ ($\sigma$) and $\pi'$ ($\pi$) symmetry quantitatively. To obtain the bond dissociation energy, $D_e$, the preparation energy, $\Delta E_{\text{prep}}$, which gives the relaxation of the fragments into their electronic and geometrical ground states, must be added to $\Delta E_{\text{int}}$ [eq 2].

$$\Delta E(= -D_e) = \Delta E_{\text{int}} + \Delta E_{\text{prep}}$$  \hspace{1cm} (2)

To calculate the dissociation energies, we calculated each fragment in its optimized geometry and derived $\Delta E$ by eq 2. Further details on the EDA can be found in the literature.\(^{(90,92)}\)

The EDA has been used by us for a comprehensive study of metal–ligand interactions in transition metal complexes.\(^{(93,94)}\)

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Supporting Information Available: Crystallographic details as CIF; ORTEP figure of 3a (in the BF$_4$ salt) with resolved disorder; correlation of calculated charges and $^{13}$C NMR data in chloropyridines; average geometries of chloropyridinium salts; Cartesian coordinates for all calculated structures.

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