# Synthesis of Aminoiminophosphoranate Complexes of Palladium and Platinum and X-ray Diffractional Investigation of the Weak C-H···Pd Interactions Affecting the Geometry of the PdNPN Metallacycles

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New aminoiminophosphoranate ( $\kappa^2$ -(N,N)-(NC<sub>6</sub>H<sub>4</sub>*i*-Pr-*p*)<sub>2</sub>PPh<sub>2</sub>, NPN) complexes (NPN)Pd(PPh<sub>3</sub>)Cl, (NPN)<sub>2</sub>Pd, (NPN)Pt( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)Cl, and (NPN)Pt(PPh<sub>3</sub>)Cl were prepared in high yields from anionic [NPN]Li and the corresponding transition metal chloride precursors. Reaction of (PhCN)<sub>2</sub>PdCl<sub>2</sub> with aminoiminophosphorane [NPN]H afforded bis-imino complex Pd{[NPN]H}<sub>2</sub>Cl<sub>2</sub> in 82% yield. X-ray structures of all palladium complexes were reported, and the specific weak interactions C-H···Pd were detected in the crystals of both (NPN)Pd(PPh<sub>3</sub>)Cl (intramolecular) and (NPN)<sub>2</sub>Pd (intermolecular). The topological analysis of electron density function  $\rho(r)$  within the AIM theory performed for (NPN)<sub>2</sub>Pd allowed us to analyze the peculiarities of the chemical bonding of the NPN ligand and to estimate the energy of the intermolecular C-H···Pd interaction as 0.8 kcal/mol. The plausible influence of these weak interactions on the bending of the PdNPN metallacycle was discussed.

# Introduction

During last 15–20 years the interest in complexes of transition metals and lanthanides with chelating NNN (triazenide), NCN (amidinate), and NPN (aminoiminophosphoranate) ligands (Chart 1) has been growing considerably in light of their versatile applications in homogeneous catalysis.<sup>1</sup> Among these types of compounds the coordination chemistry of amidinate complexes has been mostly developed,<sup>2</sup> whereas aminoimino-phosphoranate complexes remain far less studied, though the application of such systems as precatalysts for alkene cyclo-propanation<sup>3</sup> and polymerization<sup>4</sup> is well recognized. Some representative examples of aminoiminophosphoranate complexes are known for metals of each row of the periodic table, but systematic investigations of their structure and reactivity have

 $\begin{array}{c|c} & & & \\ & & & \\ R'C \begin{pmatrix} - & & \\ - & & \\ NR & & NR & \\ & & NR & \\ & & NR & & NR \\ & & & NN & & NPN \\ \end{array}$ 

never been carried out. Particularly, scarce information is available for NPN complexes of late transition metals: several complexes of copper,<sup>3a-c,5</sup> cobalt,<sup>6</sup> and nickel<sup>4a,e,6</sup> and only single examples of ruthenium,<sup>7</sup> palladium,<sup>4a</sup> and platinum<sup>8</sup> compounds were reported.

Analysis of the aminoiminophosphoranate complexes reported to date can provide some information on their structural features: longer P–N bonds (average 1.60 Å) compared to C–N bonds in amidinate complexes (average 1.33 Å) cause the increase of the natural bite angle N–M–N (ca. 70° for aminoiminophosphoranate complexes vs ca. 64° for amidinate). As a result, aminoiminophosphoranate ligands are typically coordinated to the metal atom in chelate mode (only one example of the bridging coordination was reported

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for  $[Cu{Ph_2P(NSiMe_3)_2}]_2^{5c})$ , which is in sharp contrast with amidinate complexes of late transition metals. Amidinate ligands display either a chelating (for example for Ru complexes<sup>9a,b</sup>) or bridging mode of coordination (characteristic for Pd and Pt complexes<sup>10</sup>), and even mixed mode in the case of dimeric complex  $Pd_2(dpb)_4$  (dpb = N,N'-diphenylbenzamidinate), containing two chelate and two bridging *dpb* ligands.<sup>10c</sup> It is also noteworthy that the geometry of the MNCN metallacycle in some chelating amidinate complexes is considerably nonplanar, with the strongest bending up to ca.  $50^{\circ}$  (the dihedral angle between NMN and NCN planes) observed for complexes having additional  $\pi$ -coordination of the NCN ligand with the metal atom.9 In contrast, the geometry of the MNPN metallacycle in aminoiminophosphoranate complexes reported to date is usually slightly nonplanar with the dihedral angle between NMN and NPN planes rarely reaching ca. 15°.<sup>4e,6b,7,11</sup> Several attempts were made to explain the reason for such distortion for complexes of alkaline earth metals (interaction of M<sup>2+</sup> cations with delocalized  $\pi$ -electron density of the NPN ligand<sup>11a</sup>), zirconium (trans-annular influence of the substituents and great strength of the crystal field<sup>11b</sup>), and ruthenium (partial contribution of the  $\pi$ -pseudoallyl bonding between NPN ligand and metal<sup>7</sup>). All of these suggestions were based on the similarity of the amidinate and aminoiminophosphoranate ligands, but the contribution of delocalized  $\pi$ -electron density into the structure of NPN ligands is rather doubtful and speculative.<sup>12</sup>

Thus at present no systematic studies on electronic properties of the NPN ligands and their complexes have been accomplished, which makes it impossible to unravel the factors affecting the bending of the MNPN cycle and the influence of the NPN ligand flexibility on catalytic properties of their complexes. At the same time the ability of aminoiminophosphoranate ligands to stabilize coordinatively unsaturated species<sup>7,13</sup> owing to their high  $\sigma$ - and  $\pi$ -donor properties<sup>5a</sup> is well documented, demonstrating clearly the importance of further investigations in this area.

Here we began a systematic study of electronic and structural properties of aminoiminophosphoranate complexes of platinum group metals. In this article we present the synthesis of novel NPN complexes of palladium and platinum, the structural study of three palladium complexes by X-ray diffraction and determination of the influence of the ligand environment on the extent of distortion of the NPNM metallacycles. Square-planar complexes of Pd(II) and Pt(II) are fully coordinatively saturated and have a formal d<sup>8</sup> electron configuration, meaning that the NPN ligands in them act exclusively as 4 e donors, and therefore all possible distortions of the MNPN fragments are produced only by the nature of the auxiliary ligands.

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### **Results and Discussion**

Diaminophosphonium salts  $[R_2P(NHR')_2]^+X^-$  usually serve as versatile starting compounds for the synthesis of NPN complexes<sup>4e,6b,8</sup> because their stepwise deprotonation leads consecutively to the corresponding aminoiminophosphorane R<sub>2</sub>P(NHR')(NR') and lithium aminoiminophosphoranate  $[R_2P(NR')_2]Li$ , which are direct precursors for creating an aminoiminophosphoranate ligand framework.<sup>14</sup> We have reported recently a convenient method for the synthesis of the di(arylamino)phosphonium salts based on direct aminolysis of diphenyltrihalophosphorane with substituted anilines,<sup>15</sup> thus providing access to many NPN ligands with various electronwithdrawing and electron-releasing properties. In this paper we used diaminophosphonium salt  $[Ph_2P(NHC_6H_4i-Pr-p)_2]^+Br^-(1)$ , containing *para*-isopropyl groups, to increase the solubility of the resulting aminoiminophosphoranate complexes. Deprotonation of 1 with 1 equiv of n-BuLi or Et<sub>3</sub>N leads smoothly to the corresponding aminoiminophosphorane [Ph2P(NHC6H4i-Prp)(NC<sub>6</sub>H<sub>4</sub>*i*-Pr-p)] (2) (Scheme 1).

In the <sup>31</sup>P NMR the phosphorus resonance in 2 (-4.75 ppm) is shifted downfield compared to that of diaminophosphonium salt 1 (26.6 ppm). Analogously, all proton resonances in 2 are downfield shifted (by 0.2-0.4 ppm compared to 1), obviously due to the decrease of the positive charge at the phosphorus atom. The full equivalency of the aryl substituents in 2 together with the absence of a NH signal in the <sup>1</sup>H NMR assumes that fast proton exchange between amino- and imino-nitrogen atoms occurs in solution at room temperature.<sup>16</sup>

Aminoiminophosphoranate complexes 4-8 were prepared by the replacement of the chloride ligand in the transition metal precursor with anionic lithium aminoiminophosphoranate 3, generated *in situ* by deprotonation of 1 or 2 with an appropriate quantity of *n*-BuLi.<sup>17</sup>

Reaction of  $[Ph_2P(NC_6H_4i-Pr-p)_2]^-Li^+$  (3) with Zeise's salt dimer  $[Pt(\eta^2-C_2H_4)Cl(\mu-Cl)]_2$  leads to NPN platinum ethylene complex 4 in high yield (Scheme 2). Importantly, the lithium salt 3 should be prepared strictly from the pure aminoiminophosphorane 2, not from the diaminophosphonium salt 1. In the latter case the presence of LiBr in the reaction mixture caused the formation of the inseparable mixture of chloro- and bromo-substituted platinum complexes 4 and 4' (ratio 1:3).

The substitution of one of two chloride ligands in dimeric complexes  $[M(PPh_3)Cl(\mu-Cl)]_2$  (M = Pd, Pt) proceeds analo-

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substituents at the phosphorus atom and two different sets of signals belonging to the coordinated and noncoordinated nitrogen fragments. It is noteworthy that the signal of the NH proton observed is broad probably due to the formation of intramolecular hydrogen bonding with the chloride ligand.

**X-ray Diffractional Study.** Palladium complexes **5**, **7**, and **8** have been crystallographically characterized to provide valuable structural information on the geometry of these complexes in the solid state, particularly on correlation between the geometry of the coordinated NPN ligand and the secondary interactions with the co-ligands. The structures of complexes **5**, **7**, and **8** are shown in Figures 1–3, respectively; the main bond lengths and angles are given in Table 3.

In the crystal of **8** the palladium atom is bound to two chloride ions and two monodentate aminoiminophosphorane ligands. In crystalline **8** the molecule occupies a special position with the inversion center coinciding with the palladium atom. The P–N bonds in **8** significantly differ with pronounced elongation of the uncoordinated one (1.597(2) vs 1.667(2) Å). The nitrogen atoms in **8** are almost planar, with the N(1) atom being slightly pyramidalizied (the sum of bond angles including N(1) is  $357.1(2)^\circ$ ). The additional stabilization of complex **8** is attained by the intramolecular N–H···Cl hydrogen bond (N(2)···Cl 3.138(2) Å, H(2N)···Cl(1) 2.17 Å, NHCl 152°), leading to the formation of a six-membered cycle.

In complexes 5 and 7 aminoiminophosphoranate serves as a bidentante ligand (Figures 2 and 3, respectively). The Pd-N bond lengths vary in the narrow range of 2.054(2) - 2.0604(6)Å, with the only exception of Pd(1)-N(2) (2.146(2) Å) in complex 5. The latter increased value can be attributed to the trans-effect of the PPh<sub>3</sub> ligand. The interesting geometrical feature of both complexes is the significant difference in the nitrogen atoms' configuration, one of the nitrogen atoms being almost planar ( $\sum_{N1}$  is 357.24(4)-359.9(1)°), while the other one is significantly pyramidalized ( $\sum_{N2}$  is 347.9(1)-350.57(4)°). In the crystal of 7 the molecule is centrosymmetric; hence the above variation of nitrogen atom configuration is not due to a trans-effect. Furthermore, the degree of pyramidalization cannot be related to the conjugation with the aryl substituent. Indeed, in the crystal of 5 the maximum overlap of the electron lone pair of the N atom with the  $\pi$ -system of the aryl group according to the PNCC torsion angle is observed for the pyramidalized N(2) (ca. 17°) atom rather than for the flat N(1) (ca. 50°). Moreover, the P-N bond lengths in each complex are independent of the nitrogen atom configuration and nature of the trans-substituent in the case of 5.

In both complexes 5 and 7 the PdNPN cycles deviate from planarity. The bending of the PdNPN cycle, described by the dihedral angle between Pd(1)N(1)N(2) and P(1)N(1)N(2) planes, is equal to  $23.4(1)^{\circ}$  and  $5.23(7)^{\circ}$  in 5 and 7, respectively. Although the nature of the bending of the MNPN metallacycle in aminoiminophosphoranate complexes has not been specified so far, the weak C-H···Pd intramolecular interactions appeared to be responsible for this effect in 5.

Analysis of intramolecular interactions in complex **5** has revealed the presence of two types of interactions, i.e.,  $C(23)H(23)\cdots Cl(1)$  (H····Cl 2.53 Å, CHCl 140°) and two  $C-H\cdots Pd$  (both H(42A)····Pd and H(6A)····Pd distances are 2.87 Å with the angles CHPd 118° and 130°, respectively). At least  $C-H\cdots Cl$  contacts may be rather strong, and according to a recent investigation of the trimeric palladium complex, in which similar intramolecular  $C-H\cdots Cl$  contacts (H····Cl ~2.72 Å, CHCl 112°) are present, their energies can be as much

gously, affording monomeric complexes **5** and **6** with a chelating NPN ligand in more than 90% yield (Scheme 3).

This method can be efficiently applied to the preparation of the bis-chelate NPN derivatives, which was demonstrated for the palladium complex 7 (Scheme 4). It is noteworthy that in the absence of base or on using a base of insufficient strength (for example, Et<sub>3</sub>N instead of *n*-BuLi) aminoiminophsphorane 2 undergoes only monodentate coordination to the palladium atom via the imine group and the bis-imino complex 8 was isolated in 80% yield (Scheme 4). This compound cannot be transformed to bis-chelate NPN complex 5 in the absence of *n*-BuLi even at elevated temperatures. Its stability toward deprotonation is probably caused by strong intramolecular hydrogen bonding between amine protons and chloride ligands, clearly shown in the solid state by X-ray diffraction (see below).

NMR spectroscopy data of complexes **4–8** are presented in Tables 1 and 2. Complexes **4–6** contain equivalent phenyl groups at the phosphorus atom and nonequivalent aryl substituents at the nitrogen atoms, clearly indicating the presence of a MNPN plane of symmetry. Characteristic satellite signals with isotope <sup>195</sup>Pt were observed in <sup>31</sup>P and <sup>13</sup>C NMR spectra of platinum complexes **4** ( ${}^{2}J_{P-Pt} = 252$  Hz,  ${}^{1}J_{C-Pt} = 118$  Hz) and **6** ( ${}^{1}J_{P-Pt} = 3996$  Hz,  ${}^{2}J_{P-Pt} = 234$  Hz). The presence of a  $\eta^{2}$ -coordinated ethylene ligand was confirmed by characteristic broad singlets in the <sup>1</sup>H ( $\delta$  4.06) and <sup>13</sup>C ( $\delta$  64.4) NMR spectra, demonstrating free rotation of the ligand at room temperature. Similar observations (inequivalence of the N-substituents of the NPN ligand and rotation of the  $\eta^{2}$ -ethylene ligand) were found earlier for platinum complex [ $(\eta^{2}$ -C<sub>2</sub>H<sub>4</sub>)Pt{Me<sub>2</sub>P(NMe)<sub>2</sub>}Cl].<sup>8</sup>

Highly symmetric complex 7 displays in NMR spectra only one type of phenyl and aryl rings. NMR spectra of bis-imino complex 8 show the presence of two equivalent phenyl

Table 1. <sup>1</sup> H and <sup>31</sup> P NMR Spectra of Complexes 4–8 (CL	$DCI_3, \partial)^{\prime\prime}$	
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complex	Ph	$C_6H_4$	Pr <sup>i</sup>	L	<sup>31</sup> P NMR
4	7.87 (dd, $J = 11.8$ , $J = 7.4$ , 4H, o-H) 7.62 (t, $J = 7.4$ , 2H, p-H) 7.48 (td, $J = 7.4$ , $J = 2.8$ , 4H, m-H)	6.96 (d, <i>J</i> = 8.3, 2H) 6.88 (d, <i>J</i> = 8.3, 2H) 6.83 (d, <i>J</i> = 8.1, 2H) 6.54 (dd, <i>J</i> = 8.1, <i>J</i> = 1.5, 2H)	2.72 (hept, $J = 6.9$ , 1H, CH) 2.70 (hept, $J = 6.8$ , 1H, CH) 1.11 (d, $J = 6.9$ , 6H, Me) 1.09 (d, $J = 6.8$ , 6H, Me)	3.82 (br s, 4H, C <sub>2</sub> H <sub>4</sub> )	73.7 ( $J_{\rm PPt} = 252$ )
5	7.74 (ddd, $J = 11.3$ , $J = 7.7$ , $J = 1.4$ , 4H, o-H) 7.46 (td, $J = 7.5$ , $J = 1.4$ , 2H, p-H) 7.34 (td, $J = 7.7$ , $J = 2.7$ , 4H, m-H)	$\begin{array}{l} 6.98 \; (\mathrm{d},  J=8.4,  2\mathrm{H}) \\ 6.80 \; (\mathrm{d},  J=8.4,  2\mathrm{H}) \\ 6.18 \; (\mathrm{d},  J=8.3,  4\mathrm{H}) \\ 6.17 \; (\mathrm{d},  J=8.3,  4\mathrm{H}) \end{array}$	2.68 (hept, $J = 6.8$ , 1H, CH) 2.44 (hept, $J = 6.8$ , 1H, CH) 1.09 (d, $J = 6.8$ , 1H, CH) 1.09 (d, $J = 6.8$ , 6H, Me) 0.94 (d, $J = 6.8$ , 6H, Me)	7.70 (ddd, $J = 11.6$ , $J = 7.7$ , $J = 1.3$ , 6H, o-H) 7.32 (td, $J = 7.4$ , $J = 1.4$ , 3H, p-H) 7.23 (td, $J = 7.6$ , $J = 2.3$ , 6H, m-H)	26.5 (s, PPh <sub>3</sub> ) 57.5 (s, PPh <sub>2</sub> )
6	7.77 (ddd, $J = 11.5$ , $J = 7.7$ , $J = 1.3$ , 4H, o-H) 7.48 (td, $J = 7.5$ , $J = 1.4$ , 2H, p-H) 7.36 (td, $J = 7.5$ , $J = 2.7$ , 4H, m-H)	7.02 (dd, $J = 8.4$ , $J = 1.3$ , 2H) 6.82 (d, $J = 8.2$ , 2H) 6.26 (dd, $J = 8.4$ , $J = 2.3$ , 2H) 6.17 (d, $J = 8.2$ , 2H)	2.69 (hept, $J = 6.8$ , 1H, CH) 2.43 (hept, $J = 6.8$ , 1H, CH) 1.09 (d, $J = 6.8$ , 6H, CH) 1.09 (d, $J = 6.8$ , 6H, Me) 0.93 (d, $J = 6.8$ , 6H, Me)	7.72 (ddd, $J = 11.6$ , $J = 7.7$ , $J = 1.5$ , 6H, o-H) 7.28 (td, $J = 7.7$ , $J = 1.4$ , 3H, p-H) 7.22 (td, $J = 7.7$ , $J = 2.3$ , 6H, $m$ -H)	2.6 ( $J_{\text{PPt}} = 3996$ , PPh <sub>3</sub> ) 66.1 ( $J_{\text{PPt}} = 234$ , PPh <sub>2</sub> )
<b>7</b> <sup>b</sup>	8.17 (m, 8H, <i>o</i> -H) 7.07 (m, 12H, <i>m</i> -H + <i>p</i> -H)	7.15 (d, $J = 8.1, 8H$ ) 6.71 (d, $J = 8.1, 8H$ )	2.59 (hept, $J = 6.9$ , 4H, CH) 1.08 (d, $J = 6.9$ , 24H, Me)		54.0
8	7.81 (dd, $J = 12.6$ , $J = 7.5$ , 8H, o-H) 7.41 (t, $J = 7.6$ , 4H, p-H) 7.24 (dd, $J = 7.6$ , $J = 3.5$ , 8H, m-H)	7.04 (d, $J = 8.3, 4$ H) 6.82 (d, $J = 8.5, 4$ H) 6.71 (d, $J = 8.3, 4$ H) 6.47 (d, $J = 8.3, 4$ H)	2.72 (hept, $J = 6.7$ , 2H, CH) 2.73 (hept, $J = 6.7$ , 2H, CH) 1.17 (d, $J = 6.7$ , 2H, CH) 1.17 (d, $J = 6.7$ , 12H, Me) 1.15 (d, $J = 6.7$ , 12H, Me)	7.39 (br s., 2H, NH)	26.4

<sup>a</sup> J constants are given in Hz. <sup>b</sup> Spectra of 7 were registered in C<sub>6</sub>D<sub>6</sub>.

as 1.4-2.1 kcal/mol.<sup>18</sup> Furthermore, the stabilizing role of the above Pd····H contacts may be indirectly proved by the fact that both phosphorus atoms (P(1) and P(2)) in **5** deviate by 0.42 and 0.20 Å from the Pd(1)Cl(1)N(1)N(2) plane toward the above shortened contacts (Figure 2). The pyramidalization of the N(2) in **5** can be then a secondary effect caused by the necessity to decrease conjugation between an occupied  $\pi$ -orbital of N(2) and the  $\pi$ -system of the aryl group to enhance the positive charge at H(23A), to make the C-H···Cl interaction stronger. It is noteworthy that similar C-H···Ni contacts of 2.81Å (angle C-H-Ni is 121°) of the *ortho*-H of the triphenylphosphine ligand were reported for the complex [Ni{PPh<sub>2</sub>(NSiMe<sub>3</sub>)<sub>2</sub>}Ph-(PPh<sub>3</sub>)]; however such interaction alone did not induce significant bending of the NiNPN plane (3.5°).<sup>4e</sup>

In the crystal of 7, instead of intramolecular C–H···Pd contacts, there are two symmetrically equivalent intermolecular Pd(1)····H(10A) interactions (Pd(1)····H(10A) 2.76 Å, C(10)-H(10A)Pd 144°). These interactions do not affect much the bending of the PdNPN cycle, perhaps because of the mutual compensation (Figure 4).

Complex 7 was chosen to analyze the peculiarities of chemical bonding by performing a topological analysis of the electron density function ( $\rho(\mathbf{r})$ ). For the latter good-quality single crystals were available, and therefore, an accurate determination of the crystal structure was possible. We wish to note that such an investigation for aminoiminophosphoranate complexes has been performed for the first time.

The deformation electron density (DED) maps for the section containing the metal atom are characterized by expected features: the significant anisotropy of DED around palladium; DED accumulation in the vicinity of the nitrogen atoms that corresponds to their electron lone pairs and that on the covalent P–N and C–N bonds (Figure 5). The observed DED distribution around palladium is rather similar to those recently observed

(18) Vatsadze, S. Z.; Medved'ko, A. V.; Zyk, N. V.; Maximov, A. L.; Kurzeev, S. A.; Kazankov, G. M.; Lyssenko, K. A. *Organometallics* **2009**, 28, 1027. in pincer palladium complexes<sup>18,19</sup> and can be attributed to 4dorbitals of the palladium atom. Both the Pd–N bonds are "peak to hole" type interactions; that is, the electron lone pairs of nitrogen atoms are directed toward areas of the DED depletion in the vicinity of the Pd(1) atom (Figure 5).

The topological analysis of the electron density function  $\rho(\mathbf{r})$  within Bader's "atoms in molecules" theory  $(\text{AIM})^{20}$  revealed that Pd–N bonds correspond to the intermediate type of interactions; the values of the Laplacian of electron density  $(\nabla^2 \rho(r) \ 10.0 \text{ e} \text{ Å}^{-5})$  in the corresponding critical points (3, -1) are positive, while the local energy density  $(h_e(r))$  is negative  $(-0.0409 \ -0.0309 \ \text{au})$ . These values as well as those of  $\rho(r)$   $(0.70-0.73 \text{ e} \text{ Å}^3)$  in the above critical points (3, -1) in **7** are close to those recently observed for Pd–N bonds in the [LPdCl]<sub>3</sub> trimers (L = chiral secondary benzylamine).<sup>18</sup>

As expected, the P–N and P–C bonds in 7 correspond to a shared type of interatomic interactions with negative values of  $\nabla^2 \rho(r)$  in their corresponding critical points (3,-1). The values of ellipticity ( $\varepsilon$ ), which indicates the contribution of the  $\pi$  component, for all the P–C and P–N bonds in 7, are similar and close to zero (less than 0.10). They are comparable with  $\varepsilon$  values for the N(2)–C(22) bond (0.09), but are significantly smaller than  $\varepsilon$  for the N(1)–C(13) (0.2) one. Thus, we may conclude that the double-bond character of the P–N bonds in complex 7 is rather negligible, and therefore this bond is better described as P<sup>+</sup>–N<sup>-</sup>, similarly to what was found experimentally for the lithium picolyliminophosphoranate.<sup>12a</sup>

The atomic charges in complex 7 were obtained by integration of the  $\rho(\mathbf{r})$  function over the atomic basins ( $\Omega$ ). It was found that nitrogen atoms are characterized by rather high negative values (-1.42 and -1.52 e). For comparison, the charges of the nitrogen atom in the gadolinium-coordinated 1,10-phenan-

<sup>(19)</sup> Kozlov, V. A.; Aleksanyan, D. V.; Nelyubina, Yu. V.; Lyssenko, K. A.; Gutsul, E. I.; Puntus, L. N.; Vasil'ev, A. A.; Petrovskii, P. V.; Odinets, I. L. *Organometallics* **2008**, *27*, 4062.

<sup>(20)</sup> Bader, R. F. W. Atoms in Molecules. A Quantum Theory; Oxford: Clarendron Press, 1990.

				Table 2. <sup>13</sup> C N	<b>WMR Spectra of Com</b>	plexes 4-8 (CDCl <sub>3</sub>	, δ) <sup>a</sup>			
complex	<i>i</i> -Ph	o-Ph	m-Ph	p-Ph	0-C <sub>6</sub> H <sub>4</sub>	m-C <sub>6</sub> H <sub>4</sub>	<i>i</i> -C-N	<i>i</i> -C-Pr <sup>i</sup>	$Pr^{i}$	L
4	130.7 (d, $J = 92.9$ )	132.8 (d, $J = 11.1$ )	128.8 (d, $J = 12.2$ )	133.2 (d, $J = 3.3$ )	123.3 (d, $J = 10.0$ ) 128.8 (d, $J = 5.5$ )	126.2(s) 126.7 (s)	141.8 (d, $J = 2.2$ ) 145.3 (d, $J = 3.3$ )	137.3 (s) 142.0 (s)	23.8 (s, Me) 24.0 (s, Me) 33.4 (s, CH) 33.2 (s, CH)	64.4 (s) $(J_{\rm CPt} = 118)$
N	131.9 (d, $J = 91.4$ )	132.6 (d, <i>J</i> = 9.6)	127.9 (d, <i>J</i> = 8.8)	131.7 (d, $J = 2.0$ )	123.4 (dd, J = 14.0) 128.4 (d, J = 6.0)	125.2 (d, $J = 2.4$ ) 125.8 (s)	142.2 (d, $J = 3.6$ ) 141.3 (s)	139.5 (s) 143.2 (s)	23.9 (s, Me) 23.9 (s, Me) 33.0 (s, CH) 33.0 (s, CH)	127.7 (d, $J_{CP} = 10.7$ , m-C) 129.6 (d, $J_{CP} = 51.5$ , i-C) 130.2 (d, $J_{CP} = 2.4$ , p-C) 134.5 (d, $J_{CP} = 2.4$ , p-C) 134.5 (d, $J_{CP} = 10.8$ , o-C)
Q	131.7 (d, <i>J</i> = 92.6)	132.6 (d, <i>J</i> = 9.6)	128.1 (d, <i>J</i> = 11.2)	132.0 (s)	123.9 (d, $J = 8.0$ ) 128.1 (d, $J = 6.2$ )	125.0 (d, $J = 2.2$ ) 125.7 (s)	141.3 (s) $142.3$ (d, J = 3.6)	140.4 (s) 142.4 (s)	23.9 (s, Me) 23.9 (s, Me) 32.9 (s, CH) 33.0 (s, CH)	127.5 (d, $J_{CP} = 11.1$ , m-C) 129.9 (d, $J_{CP} = 61.1$ , 61.1, <i>i</i> -C) 129.9 (s, <i>p</i> -C) 134.4 (d, $J_{CP} = 10.4$ , <i>o</i> -C)
$^{q}$ L	$\sim$ 132.5 (d, $J \sim 90)$	132.8 (d, $J = 10.0$ )	128.4 (d, $J = 11.5$ )	132.1 (s)	124.5 (d, $J = 9.2$ )	125.8 (s)	139.9 (s)	142.8 (s)	24.2 (s, Me) 33.4 (s, CH)	
×	126.0 (d, <i>J</i> = 125)	133.8 (d, $J = 10.0$ )	128.1 (d, <i>J</i> = 13.2)	132.4 (s)	118.9 (d, $J = 6.0$ ) 128.7 (d, $J = 9.2$ )	125.9 (s) 126.6 (s)	138.8 (d, $J = 3.0$ ) 141.7 (s)	142.2 (s) 143.7 (s)	23.8 (s, Me) 23.9 (s, Me) 33.0 (s, CH) 33.4 (s, CH)	
a I con	tants are given in Hs	r b Snectra of 7 were	registered in C.D.							



**Figure 1.** ORTEP drawing of **8** (thermal ellipsoids set at the 50% probability level).



**Figure 2.** ORTEP drawing of **5** (thermal ellipsoids set at the 50% probability level).

traline ligand are -1.12 to -0.94 e.<sup>21</sup> The positive atomic charge within the ligand is mainly located on the P(1) atom (1.74 e), while that of the Pd(1) atom is very small (0.32 e) and is close to that (0.65 e) observed for the palladium pincer complex in which Pd is bound to two sulfur atoms, chlorine, and the carbon atom of the aromatic ring.<sup>19</sup>

Among the intermolecular contacts in addition to numerous weak  $H \cdots H$  and  $C \cdots H$  ones we can identify the abovementioned  $Pd \cdots H$  interactions; the critical point search unambiguously revealed the presence of the latter.

These interactions are weak and characterized by a rather small value of  $\rho(r)$  (0.038 e Å<sup>-3</sup>) in the critical point (3, -1). The analysis of DED in their area revealed that hydrogen atoms of the phenyl group are directed toward a maximum DED corresponding to 4d-orbitals of the Pd(1) atom (Figure 6). The interaction energy for these Pd····H contacts was estimated by

<sup>(21)</sup> Puntus, L. N.; Lyssenko, K. A.; Antipin, M. Yu.; Bünzli, J.-C. G. Inorg. Chem. 2008, 47, 11095.



**Figure 3.** ORTEP drawing of **7** (thermal ellipsoids set at the 50% probability level).

Table 3. Main Geometrical Parameters of Complexes 5, 7, and 8

	5	7	8
Pd(1)-N(1)	2.055(2)	2.0604(6)	2.054(2)
Pd(1) - N(2)	2.146(2)	2.062(6)	n/a
P(1) - N(1)	1.631(2)	1.6223 (6)	1.597(2)
P(1) - N(2)	1.636(2)	1.6208(6)	1.667(2)
N(1)-C	1.394(3)	1.3972(8)	1.430(3)
N(2)-C	1.425(3)	1.4074(8)	1.417(3)
N(1)P(1)N(2)	97.4(1)	97.15 (3)	111.35 (2)
N(1)Pd(1)N(2)	71.51 (8)	72.30 (2)	n/a
NPN/NPdN	23.4(1)	5.23(7)	n/a
$\Sigma_{\rm N1}$	359.9(1)	357.24(4)	357.1(2)
$\Sigma_{\rm N2}$	347.9(1)	350.57(4)	359.8

means of Espinosa's correlation scheme,<sup>22</sup> which according to various theoretical<sup>23</sup> and experimental<sup>24</sup> investigations allows estimating the energy ( $E_{cont}$ ) for closed-shell interactions with rather high accuracy. The energy of the Pd····H interactions in 7 is equal to 0.8 kcal/mol, which is comparable with that for the Ru····H contacts recently located in the crystal of rutenocene.<sup>25</sup> Although the Pd····H interactions are extremely weak, we have to mention that the energy of two of them, as observed in the case of 5, reaches ca. 1.5 kcal/mol and even ca. 3.5 kcal/mol taking into account the energy of the C–H····Cl interaction, which can be more than sufficient to stabilize the nonplanar conformation of the palladacycle.

(22) (a) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett.* **1998**, 285, 170. (b) Espinosa, E.; Alkorta, I.; Rozas, I.; Elguero, J.; Molins, E. *Chem. Phys. Lett.* **2001**, *336*, 457.

(23) (a) Pidko, E. A.; Xu, J.; Mojet, B. L.; Lefferts, L.; Subbotina, I. R.; Kazansky, V. B.; van Santen, R. A. *J. Phys. Chem. B* 2006, *110*, 22618.
(b) Pidko, E. A.; van Santen, R. A. *Chem. Phys. Chem.* 2006, *7*, 1657.

(24) (a) Lyssenko, K. A.; Nelyubina, Yu. V.; Kostyanovsky, R. G.;
Antipin, M. Yu. *Chem. Phys. Chem.* 2006, *7*, 2453. (b) Lyssenko, K. A.;
Korlyukov, A. A.; Golovanov, D. G.; Ketkov, S. Yu.; Antipin, M. Yu. J. *Phys. Chem. A* 2006, *110*, 6545. (c) Lyssenko, K. A.; Korlyukov, A. A.;
Antipin, M. Yu. *Mendeleev Commun.* 2005, 90. (d) Glukhov, I. V.;
Lyssenko, K. A.; Korlyukov, A. A.; Antipin, M. Yu. *Faraday Discuss.* 2007, *135*, 203. (e) Lyssenko, K. A.; Antipin, M. Yu. *Russ. Chem. Bull.* 2006, *55*, 1.





**Figure 4.** Fragment of crystal packing of 7 illustrating the formation of intermolecular  $C-H\cdots Pd$  contacts with the *para*-H atom of the phenyl ring of the other molecule of 7.



**Figure 5.** Deformation electron density distribution in the plane of the PdNN cycle of **7**. The contours are drawn with 0.1 e  $Å^{-3}$  interval; the nonpositive contours are dashed.

## Conclusion

In this work we have synthesized new complexes of palladium and platinum with the aminoiminophosphoranate ligand belonging to the type of compounds poorly described in the literature. Complexes of palladium with aminoiminophosphorane and chelating aminoiminophosphoranate ligands were investigated by X-ray diffraction. It was proposed for the first time that weak intra- and intermolecular interactions such as C-H ··· Pd can play an important role in the deviation of MNPN metallacycles from planarity. The experimental determination of deformational electron density for bis-chelate palladium complex 7 revealed low contribution of  $\pi$ -bonding in the P–N bonds, indicating potential conformational flexibility of the NPN ligand. Also the energy of the intermolecular interactions C-H···Pd in (NPN)<sub>2</sub>Pd (7) was estimated to be 0.8 kcal/mol. The experimentally determined high negative charges on the nitrogen atoms and nonbonding character of their p-orbitals allow one to consider aminoiminophosphoranates as electronically and conformationally tunable ligands for organometallic catalysis. Additional studies to clarify the influence of electronic and steric



**Figure 6.** 3D distribution of the DED within the C-H···PdN4 fragment. Isosurface of the DED equal to 0.40 e  $A^{-3}$  is shown in red.

properties of aminoiminophosphoranate ligands on the structure of NPN complexes and their relationship to the catalytic behavior of the NPN complexes are now in progress.

#### **Experimental Details**

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were purified by standard methods and distilled prior to use. <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were obtained on a Bruker AMX-400 spectrometer and referenced to the residual signals of the deuterated solvent (<sup>1</sup>H and <sup>13</sup>C) and to 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P, external standard). Elemental analyses were performed on a Carlo Erba 1106 CHN analyzer. The following compounds were prepared according to described methods: [( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)PtCl( $\mu$ -Cl)]<sub>2</sub>,<sup>26</sup> [(Ph<sub>3</sub>P)PdCl( $\mu$ -Cl)]<sub>2</sub>,<sup>27</sup> [(Ph<sub>3</sub>P)PtCl( $\mu$ -Cl)]<sub>2</sub>,<sup>28</sup> [(PhCN)<sub>2</sub>PdCl<sub>2</sub>],<sup>29</sup> Ph<sub>2</sub>P(NHC<sub>6</sub>H<sub>4</sub>*i*-Pr-*p*)<sub>2</sub>Br (1).<sup>15</sup>

Synthesis of Ph<sub>2</sub>P(NHC<sub>6</sub>H<sub>4</sub>*i*-Pr-*p*)(NC<sub>6</sub>H<sub>4</sub>*i*-Pr-*p*) (2). (a) To a suspension of the diaminophosphonium salt 1 (6.3 g, 11.8 mmol) in Et<sub>2</sub>O (200 mL) was added at 20 °C a 1.45 M solution of *n*-BuLi in hexane (9.8 mL, 14.2 mmol), and the reaction mixture was stirred for 2 h. The solvent was removed *in vacuo*, and the residue was extracted with C<sub>6</sub>H<sub>6</sub> (60 mL). The extract was filtered and concentrated to 20 mL, and the product was precipitated with 50 mL of hexane and dried, affording 5.0 g (94%) of **2** as a white solid. Anal. Calcd for C<sub>30</sub>H<sub>33</sub>N<sub>2</sub>P: C, 79.62; H, 7.35; N, 6.19. Found: C, 79.39; H, 7.38; N, 6.17. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.17 (d, 12H, CHMe<sub>2</sub>, J = 6.9 Hz); 2.77 (sept, 2H, *CH*Me<sub>2</sub>, J = 6.9 Hz); 6.96 (s, 8H, *C*<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>); 7.45 (m, 6H, *m*-H + *p*-H, Ph); 7.94 (dd, 4H, *o*-H, Ph, J = 12.4 Hz, J = 6.9 Hz). <sup>31</sup>P NMR  $\delta$ : -4.75 (CDCl<sub>3</sub>), -9.0 (C<sub>6</sub>D<sub>6</sub>).

(b) Analogously, reaction of 1 (0.53 g, 1.0 mmol) with NEt<sub>3</sub> (0.11 g, 1.1 mmol) in benzene afforded 0.38 g (84%) of **2**.

Synthesis of [Pt{Ph<sub>2</sub>P(NC<sub>6</sub>H<sub>4</sub>*i*-Pr-*p*)<sub>2</sub>}( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)X] (4, X = Cl; 4', X = Br). To a suspension of 1 (1.07 g, 2.0 mmol) in Et<sub>2</sub>O (80 mL) was added a 1.40 M solution of *n*-BuLi in hexane (3.3 mL, 4.6 mmol), and the reaction mixture was stirred at 20 °C for 1.5 h. Then solid [Pt( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)( $\mu$ -Cl)Cl]<sub>2</sub> (0.59 g, 1.0 mmol) was added and the reaction mixture was stirred overnight. The solvent was removed *in vacuo* and the residue was extracted with C<sub>6</sub>H<sub>6</sub> (3 × 20 mL). The filtered benzene extract was concentrated until the product started to crystallize and was precipitated with 50 mL of hexane to give 0.70 g of a yellow solid, which consisted of 4 (25%)

and **4'** (75%) according to <sup>1</sup>H NMR data. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 1.07 (d, *J* = 6.9 Hz, 6H, CH*Me*<sub>2</sub>), 1.10 (d, *J* = 6.8 Hz, 6H, CH*Me*<sub>2</sub>), 2.60 (sept, *J* = 6.9 Hz, 1H, C*H*Me<sub>2</sub>); 2.66 (sept, *J* = 6.8 Hz, 1H, C*H*Me<sub>2</sub>), 4.06 (br s, 4H, C<sub>2</sub>H<sub>4</sub>), 6.70 (d, *J* = 7.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>i-Pr); 6.81 (d, *J* = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>i-Pr); 7.01 (m, 6H, *m*-H and *p*-H, Ph); 7.09 (d, *J* = 6.7 Hz, 2H, C<sub>6</sub>H<sub>4</sub>i-Pr); 7.54 (d, *J* = 7.8 Hz, 2H, *i*-C<sub>6</sub>H<sub>4</sub>Pr); 7.83 (dd, *J* = 7.3 Hz, *J* = 4.4 Hz, 4H, *o*-H, Ph). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 72.59 (s, *J*<sub>*p*t-*p*</sub>= 236.5 Hz); 72.98 (s, *J*<sub>*p*t-*p*</sub>= 243.4 Hz).

Synthesis of [Pt{Ph<sub>2</sub>P(NC<sub>6</sub>H<sub>4</sub>*i*-Pr-*p*)<sub>2</sub>}( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)Cl] (4). To a solution of **2** (0.45 g, 1.0 mmol) in benzene (60 mL) was added a 1.40 M solution of *n*-BuLi in hexane (0.80 mL, 1.12 mmol), and the reaction mixture was allowed to stir for 2 h at 50 °C. Then solid [Pt( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)( $\mu$ -Cl)Cl]<sub>2</sub> (0.30 g, 0.50 mmol) was added to the solution, and the reaction mixture was stirred at 50 °C for 2 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness, and the crude product was purified by recrystallization from hot hexane, affording 0.59 g (83%) of **4** as a yellow solid. Anal. Calcd for C<sub>32</sub>H<sub>36</sub>ClN<sub>2</sub>PPt: C, 54.12; H, 5.07; N, 3.94. Found: C, 54.09; H, 5.11; N, 3.75.

Synthesis of  $[Pd{Ph_2P(NC_6H_4i-Pr-p)_2}(PPh_3)Cl]$  (5). To a solution of **2** (0.45 g, 1.0 mmol) in benzene (50 mL) was added a 1.98 M solution of *n*-BuLi in hexane (0.60 mL, 1.10 mmol), and the reaction mixture was then stirred at 50 °C for 2 h. The solution was cooled to room temperature, and solid  $[Pd(PPh_3)(\mu-Cl)(Cl)]_2$  (0.44 g, 0.50 mmol) was added. The reaction mixture was stirred overnight at 20 °C and then filtered; the filtrate was concentrated to 3 mL and precipitated with 30 mL of hexane. The product was purified by recrystallization from benzene/hexane, affording 0.78 g (91%) of **5** as red solid. Anal. Calcd for  $C_{48}H_{47}ClN_2P_2Pd$ : C, 67.36; H, 5.50; N, 3.27. Found: C, 67.02; H, 5.45; N, 3.17.

Synthesis of  $[Pt{Ph_2P(NC_6H_4i-Pr-p)_2}(PPh_3)Cl]$  (6). To a solution of 2 (0.27 g, 0.60 mmol) in benzene (30 mL) was added a 1.98 M solution of *n*-BuLi in hexane (0.33 mL, 0.65 mmol), and the reaction mixture was heated at 50 °C for 2 h. The solution was cooled to room temperature, and solid  $[Pt(PPh_3)(\mu-Cl)(Cl)]_2$  (0.32 g, 0.30 mmol) was added. The reaction mixture was refluxed for 4 h, cooled to room temperature, and filtered. The filtrate was concentrated to 3 mL and precipitated with 30 mL of hexane. The product was purified by recrystallization from benzene/hexane, affording 0.41 g (72%) of **6** as a yellow solid. Anal. Calcd for C<sub>48</sub>H<sub>47</sub>ClN<sub>2</sub>P<sub>2</sub>Pt: C, 61.05; H, 4.98; N, 2.97. Found: C, 61.08; H, 5.10; N, 2.86.

Synthesis of  $[Pd{Ph_2P(NC_6H_4i-Pr-p)_2]_2]$  (7). To a suspension of the phosphonium salt 1 (0.53 g, 1.0 mmol) in Et<sub>2</sub>O (50 mL) was added at 20 °C a solution of *n*-BuLi in hexane (1.45 M, 1.7 mL, 2.5 mmol), and the reaction mixture was stirred for 1.5 h. Then, a solid of  $[PdCl_2(PhCN)_2]$  (0.19 g, 0.50 mmol) was added, and the reaction mixture was stirred overnight. The solvent was removed *in vacuo* and the residue was extracted with benzene (3 × 20 mL). The filtered extract was evaporated to dryness; the product was purified by recrystallization from hot hexane, affording 0.30 g (60%) of 7 as red solid. Anal. Calcd for C<sub>60</sub>H<sub>64</sub>N<sub>4</sub>P<sub>2</sub>Pd: C, 71.39; H, 6.35; N, 5.55. Found: C, 71.24; H, 6.26; N, 5.61.

Synthesis of [Pd{Ph<sub>2</sub>P(NHC<sub>6</sub>H<sub>4</sub>i-Pr-*p*)(NC<sub>6</sub>H<sub>4</sub>i-Pr-*p*)}<sub>2</sub>Cl<sub>2</sub>] (8). A solution of [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (0.19 g, 0.50 mmol) in benzene (30 mL) was added dropwise to a solution of Ph<sub>2</sub>P(NHC<sub>6</sub>H<sub>4</sub>Pr<sup>i-</sup>*p*)(NC<sub>6</sub>H<sub>4</sub>i-Pr-*p*) (0.45 g, 1.0 mmol) in benzene (50 mL) and stirred at 20 °C overnight. The solvent was removed *in vacuo*, and the residue was washed with methanol (3 × 5 mL) and dried to give 0.44 g (82%) of **8** as red solid. Anal. Calcd for C<sub>60</sub>H<sub>66</sub>Cl<sub>2</sub>N<sub>4</sub>P<sub>2</sub>Pd: C, 66.57; H, 6.10; N, 5.18. Found: C, 66.64; H, 6.28; N, 5.11.

**X-ray Crystal Structure Determination.** Single crystals of **5**, 7, and **8** were obtained by slow diffusion of hexane to a solution of the complex in dichloromethane (**5**, **8**) or in benzene (**7**). Diffraction data for **5** and **8** were taken using a Bruker SMART 1000 CCD diffractometer [ $\lambda$ (Mo K $\alpha$ ) = 0.71072 Å,  $\omega$ -scans] and

<sup>(26)</sup> Chatt, J.; Searle, M. L.; Liu, C. F.; Wymore, C. E. Inorg. Synth. 1957, 5, 210.

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<sup>(28)</sup> Goodfellow, R. J.; Venanzi, L. M. J. Chem. Soc. 1965, 7533.
(29) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. Inorg. Synth. 1960, 6, 218.

Table 4. Crystal Data and Structure Refinement Parameters for 5,7, and 8

	5	7	8
formula	$C_{48}H_{47}ClN_2P_2Pd$	$C_{60}H_{64}N_4P_2Pd$	$C_{60}H_{66}Cl_2N_4P_2Pd$
Т, К	120	100	298
fw	855.67	1009.49	1082.41
cryst syst	triclinic	triclinic	monoclinic
space group, $Z(Z')$	$P\bar{1}, 2(1)$	$P\bar{1}, 1(0.5)$	$P2_1/n$
a (Å)	10.314(4)	9.3444(2)	9.363(2)
b (Å)	12.219(4)	11.5954(2)	22.507(5)
<i>c</i> (Å)	18.221(7)	12.9651(2)	13.716(2)
$\alpha$ (deg)	94.734(6)	85.553(1)	90
$\beta$ (deg)	94.295(7)	70.253(1)	98.309(7)
$\gamma$ (deg)	114.159(6)	79.469(1)	90
$V(Å^3)$	2073.0(13)	1299.72(4)	2860.2(10)
$F(000), D_{calc}$	884, 1.371	528, 1.290	1128,1.257
$(g \text{ cm}^{-1})$			
$\mu ({\rm cm}^{-1})$	6.25	4.61	5.14
$2\theta_{\rm max}$ (deg)	58	100	56
reflns measd	22 931	79 234	19 621
indep reflns (Rint)	10 876 (0.0246)	25 522 (0.0314)	6848 (0.0395)
obsd reflns	8564	22940	4234
$[I > 2\sigma(I)]$			
final $R(F_{hkl})$ : $R_1$	0.0423	0.0333	0.0456
$wR_2$	0.1035	0.0822	0.1023
GOF	1.080	0.978	1.028
$\Delta \rho_{\rm max},  \Delta \rho_{\rm min} \ ({\rm e} \ {\rm \AA}^{-3})$	0.776/-0.464	1.504/-0.961	0.480/-0.299

for **7** using a Bruker SMART APEX II CCD diffractometer [ $\lambda$ (Mo K $\alpha$ ) = 0.71072 Å,  $\omega$ -scans] (see Table 4). The substantial redundancy in data allows empirical absorption correction to be applied using multiple measurements of equivalent reflections with the SADABS Bruker program.<sup>30</sup> The structures were solved by direct methods and refined by the full-matrix least-squares technique against  $F^2$  in the anisotropic–isotropic approximation. The hydrogen atoms of the N–H group were located from the Fourier density synthesis and refined with a riding model, while the positions of the rest of the hydrogen atoms were calculated from the geometrical point of view. The analysis of Fourier density synthesis has revealed that one of the isopropyl groups in **8** is disordered by two positions with equal occupancies. All calculations were performed using the SHELXTL software.<sup>31</sup> Crystal data and structure refinement parameters for **5**, **7**, and **8** are given in Table 4.

The multipole refinement of **7** was carried out within the Hansen–Coppens formalism<sup>32</sup> using the XD program package<sup>33</sup>

- (31) SHELXTL, version 6.1; Bruker AXS Inc.: Madison, WI, 2005.
- (32) Hansen, N. K.; Coppens, P. Acta Crystallogr. 1978, A34, 909.

with the core and valence electron density derived from wave functions fitted to a relativistic Dirac-Fock solution. Before the refinement the C-H bond distances were normalized to ideal values of 1.08 Å according to neutron data. The level of multipole expansion was hexadecapole for metal atom and octupole for all other non-hydrogen atoms. The refinement was carried out against F and converged to R = 0.0241,  $R_w = 0.0267$ , and GOF = 0.8695 (for 22 727 merged reflections with  $I > 3\sigma(I)$ ). All bonded pairs of atoms in the ligand satisfy the Hirshfeld rigid-bond criteria, while the difference of the mean square displacement amplitude for Pd-N was  $1710^{-4}$  Å<sup>2</sup>).<sup>34</sup> The potential energy density v(r) was evaluated through the Kirzhnits approximation for the kinetic energy density function g(r).<sup>35</sup> Accordingly, the g(r) function is described as (3/  $10(3\pi^2)^{2/3}[\rho(r)]^{5/3} + (1/72)|\nabla\rho(r)|^2/\rho(r) + 1/6\nabla^2\rho(r)$ , which in conjunction with the virial theorem  $(2g(r) + v(r) = 1/4\nabla^2 \rho(r))^{20}$ leads to the expression for v(r) and makes it possible to estimate the electron energy density  $h_{\rm e}(r)$ . The total electron density function was positive everywhere, and the maxima of residual electron density for observed reflections with sin  $\theta/\lambda > 0.7$  were located in the vicinity of nuclei and were not more than 0.35 e  $Å^{-3}$ . Analysis of topology of the  $\rho(r)$  function was carried out using the WinXPRO program package.36

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**Supporting Information Available:** CIF files for complexes **5**, **7**, and **8**. X-ray data for **5**, **7**, and **8** have been also deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 721726–721728. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(34)</sup> Hirshfeld, F. L. Acta Crystallogr. 1976, A32, 239.

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