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# Synthesis of Complexes with Protic NH,NR-NHC Ligands by Oxidative Addition of *N*-Alkyl-2-iodoimidazoles to [M(PPh$_3$)$_4$] (M = Pd, Pt) Complexes

**Hanpeng Jin, Peter Kluth and F. Ekkehardt Hahn***

**Abstract:** The oxidative addition of *N*-methyl-2-iodoimidazole **1** or *N*-benzyl-2-iodoimidazole **2** to complexes [Pd(PPh$_3$)$_4$] or [Pt(PPh$_3$)$_4$] followed by the protonation of the unsubstituted imidazolato ring-nitrogen atom yielded complexes *trans*-[M(NH,NMe-NHC)(PPh$_3$)$_2$I]PF$_6$ (M = Pd: *trans*-[**3**]PF$_6$; M = Pt: *trans*-[**4**]PF$_6$) and *trans*-[M(NH,NBz-NHC)(PPh$_3$)$_2$I]PF$_6$ (M = Pd: *trans*-[**5**]PF$_6$); M = Pt: *trans*-[**6**]PF$_6$ bearing imidazole derived protic NH,NR-NHC (*p*NHC) ligands. In the absence of a proton source, the reaction of **1** with [Pd(PPh$_3$)$_4$] yielded the dinuclear dipalladium complex [**7**] featuring bridging imidazolato ligands metalated at the C2 ring-carbon atom and the N3 ring-nitrogen atom. Palladium complex *trans*-[**3**]PF$_6$ undergoes halogen abstraction with AgPF$_6$ to give acetonitrile complex *trans*-[Pd(NCCH$_3$)(NH,NMe-NHC)(PPh$_3$)$_2$](PF$_6$)$_2$ *trans*-[**8**](PF$_6$)$_2$. This complex reacted further with 1,10-phenanthroline (phen), affording complex [Pd(NH,NMe-NHC)(PPh$_3$)(phen)](PF$_6$)$_2$ [**9**](PF$_6$)$_2$.

## Introduction

The last two decades have experienced intensive research on stable N-heterocyclic carbenes (NHCs) first described by Arduengo *et al*.[1] Conventional NHCs bearing alkyl substituents at both ring-nitrogen atoms (type **A** in Figure 1)[2] exhibit superb donor properties and their complexes have consequently found multiple applications in homogeneous catalysts[3] and diverse other areas.[4] Recently, complexes of protic NHCs, *i.e.* of NHCs with an NH,NR (type **B**)[5] or NH,NH substitution pattern (type **C**),[6] have attracted attention. The N-H group found in these protic NHC ligands has proven useful for the subsequent substitution (N-alkylation) of the coordinated *p*NHC ligand,[7] as molecular recognition unit[8] and in the activation of molecular hydrogen and catalytic hydrogenation reactions.[9]

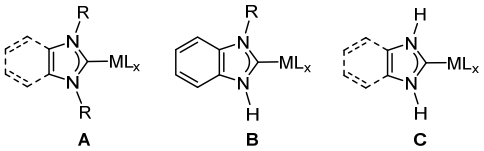


Figure 1. Complexes with classical NHC (**A**) and protic NH,NR- (**B**) and NH,NH-NHC ligands (**C**).

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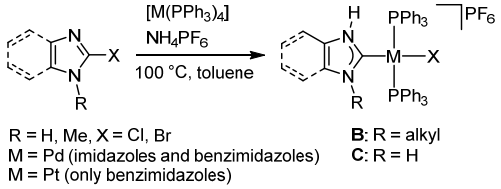
Early on, complexes bearing protic NHC ligands have been obtained by the template controlled cyclization of *β*-functionalized isocyanides.[7],[10] More recently, the oxidative addition of *N*-alkyl-2-halogenobenzimidazoles[5] or 2-halogenoazoles[6a,b] to complexes of low-valent transition metal has been developed. These reactions initially yield complexes bearing azolato ligands, which in the presence of a proton source give the complexes with the protic NHC ligands (types **B** or **C** Scheme 2). The initially formed azolato complexes have occasionally been isolated.[5c,d]




Scheme 1. Synthesis of complexes with *p*NHC ligands by oxidative addition of the C2–X bond of 2-halogenoazoles.

Since the C2–I bond of azoles is the weakest one in the series of C2–X (X = Cl, Br, I) bonds, we intuitively assumed that the oxidative addition of this bond to low-valent transition metals would be most facile. This was, however, not observed. So far the C2–I oxidative addition was only observed in two cases with Pd$^0$ and unsubstituted 2-iodoimidazole or 2-iodobenzimidazole to give NH,NH-NHC complexes of type **C**. The oxidative addition of 2-iodoimidazole to Pt$^0$ yields only decomposition products while the oxidative addition of *N*-alkyl-2-iodoazoles has not been studied yet.

Herein we describe the synthesis of two *N*-alkyl-2-iodoimidazoles, their oxidative addition to complexes of type [M(PPh$_3$)$_4$] (M = Pd, Pd) followed by protonation of the initially formed azolato ligand and some ligand substitution reactions with the complex of type [Pd(*p*NHC)(PPh$_3$)$_2$I].

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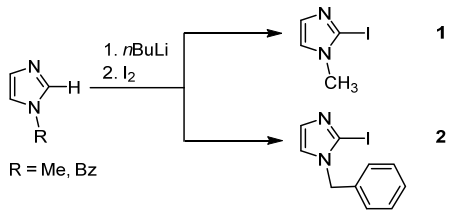
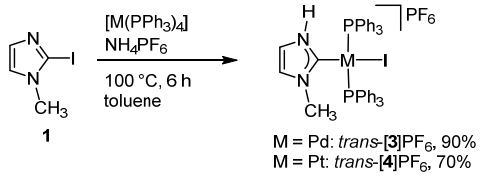
## Results and Discussion

Using previously described procedures,[11] we initially prepared the *N*-methyl-2-iodoimidazole **1** and *N*-benzyl-2-iodoimidazole **2** by iodation of the *N*-alkylimidazoles with elemental iodine (Scheme 2).




Scheme 2. Synthesis of *N*-alkyl-2-iodomimidazoles **1** and **2**.

Next, the oxidative addition of **1** to complexes $[M(PPh_3)_4]$ (M = Pd, Pt) in the presence of an excess of $NH_4PF_6$ as proton source was studied. These reactions proceed smoothly in toluene at 100 °C over 6 hours to give complexes *trans*-[**3**]$PF_6$ and *trans*-[**4**]$PF_6$ in good yields of 90% and 70%, respectively (Scheme 3). In both cases, only the *trans*-complexes were obtained in contrast to the oxidative addition of *N*-methyl-2-chlorobenzimidazole to $[Pt(PPh_3)_4]$ which always yielded some of the *cis*-complex.[5a,c] The reaction time for the completion of the oxidative addition drops from 6 d for *N*-methyl-2-chlorobenzimidazole[5a] to only 6 h for the *N*-methyl-2-iodoimidazole.




Scheme 3. Synthesis of complexes *trans*-[**3**]$PF_6$ and *trans*-[**4**]$PF_6$.

Complexes *trans*-[**3**]$PF_6$ and *trans*-[**4**]$PF_6$, were completely characterized by NMR spectroscopy and mass spectrometry. In the $^1$H NMR spectra, the characteristic resonances for the N-H ring protons in these complexes were observed as singlets at $\delta$ = 10.00 and $\delta$ = 9.75 ppm, respectively. The chemical shifts for these resonances fall in the range previously observed for the N-H resonances of palladium and platinum complexes of types $[M(NH,NR\text{-}NHC)(PPh_3)_2X]$[5] and $[M(NH,NH\text{-}NHC)(PPh_3)_2X]$.[6] The protons on the triphenylphosphine ligands appeared in the range of $\delta$ = 7.64–7.57 ppm (m, 12H, Ph–$H_{ortho}$), 7.50–7.45 ppm (m, 6H, Ph–$H_{para}$) and 7.45–7.38 ppm (m, 12H, Ph–$H_{meta}$) for *trans*-[**3**]$PF_6$ and at very similar chemical shifts for *trans*-[**4**]$PF_6$. The $^{13}C\{^1H\}$ NMR spectrum of *trans*-[**3**]$PF_6$ spectrum exhibited a triplet at $\delta$ = 161.7 ppm ($^2J_{C,P}$ = 9.8 Hz) for the $C_{pNHC}$ carbon atom while the equivalent resonance for platinum complex *trans*-[**4**]$PF_6$ was recorded upfield at $\delta$ = 149.8 ppm ($^2J_{C,P}$ = 9.7 Hz). The triplets for the $C_{pNHC}$ resonances indicate coupling to two chemically equivalent phosphorus atoms and this implies that the complexes possess the *trans*-geometry. Consequently, only one signal for the two equivalent $PPh_3$ ligands was recorded in the $^{31}P\{^1H\}$ NMR spectra of *trans*-[**3**]$PF_6$ ($\delta$ = 18.3 ppm) and *trans*-[**4**]$PF_6$ ($\delta$ = 13.5 ppm, Pt-satellites, $^1J_{Pt,P}$ = 2455 Hz), respectively. The high-resolution electrospray ionization (HR-ESI) mass spectra for *trans*-[**3**]$PF_6$ and *trans*-[**4**]$PF_6$ (positive ions) showed peaks with the highest intensity peaks at *m*/*z* = 839.0453 (calcd 839.0448 for cation [**3**]$^+$) and at *m*/*z* = 928.1040 (calcd 928.1049 for cation [**4**]$^+$), both with the correct isotope distribution for the respective cations.

The composition and coordination geometry of complexes *trans*-[**3**]$PF_6$ and *trans*-[**4**]$PF_6$ was unequivocally established by X-ray diffraction studies (Figure 2). Crystals of the composition *trans*-[**3**]$PF_6 \cdot CH_2Cl_2$ and *trans*-[**4**]$PF_6 \cdot CH_2Cl_2$ were obtained by slow vapor diffusion of diethyl ether into saturated dichloromethane solutions of the complexes at ambient temperature. The structure analyses confirmed the *trans*-arrangement of the two phosphine ligands in both complexes. A slightly distorted square-planar coordination geometry around the metal atoms was observed for both complexes with bond angles P1–M–P2 (M = Pd: 176.42(7)°; M = Pt: 175.98(5)°) and I–Pd–C2 (M = Pd: 176.6(2)°; M = Pt: 177.03(13)°). In both complexes, the plane of the NHC ligand i oriented almost perpendicular relative to the $MCP_2I$ plane. Th M–C2 bond length (M = Pd: 1.989(7) Å; M = Pt: 1.983(4) Å) fall i the typical range for mononuclear palladium[5a] and platinum[5 complex cations of type *trans*-$[M(NH,NR\text{-}NHC)(PPh_3)_2X]^+$ c *trans*-$[M(NH,NH\text{-}NHC)(PPh_3)_2X]^+$.[6b] The iodo ligand in *trans* position to the *p*NHC ligand does not lead to a significant change c the M–C2 bond lengths when compared to similar complexe bearing an chlorido or bromo ligand in *trans*-position to the *p*NH ligand. The N1–C2–N3 bond angles of 104.7(6)° (M = Pd) an 104.5(4)° (M = Pt) fall in the typical range for classical NR,NR NHC ligands and the N1–C2 and N3–C2 bond lengths in bot cations are identical within experimental error. These observation indicate that the *p*NHC ligands feature metric parameters an bonding characteristics rather similar to those of classical NR,NR NHCs.[2]

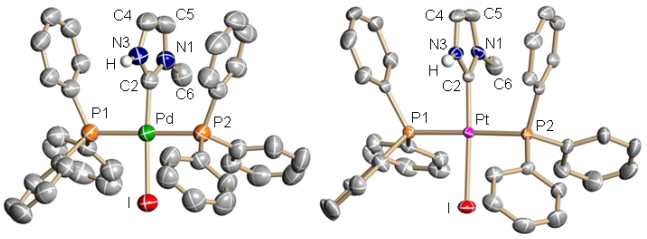
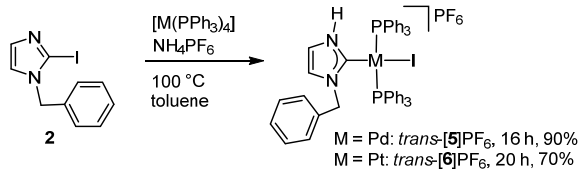



Figure 2. Molecular structures of *trans*-[**3**]$^+$ in *trans*-[**3**]$PF_6 \cdot CH_2Cl_2$ (left) an *trans*-[**4**]$^+$ in *trans*-[**4**]$PF_6 \cdot CH_2Cl_2$ (right). Hydrogen atoms, except for th N–H protons, have been omitted for clarity. Selected bond lengths [Å] an angles [°] for *trans*-[**3**]$^+$ (M = Pd) and [*trans*-[**4**]$^+$ (M = Pt)]: M–I 2.6170(6 [2.6282(4)], M–P1 2.341(2) [2.3189(12)], M–P2 2.331(2) [2.3228(12)], M C2 1.989(7) [1.983(4)], N1–C2 1.361(10) [1.352(6)], N3–C2 1.353(9 [1.337(6)]; I–M–P1 91.77(4) [87.75(3)], I–M–P2 88.16(5) [91.23(3)], I–M C2 176.6(2) [177.03(13)], P1–M–P2 176.42(7) [175.98(5)], P1–M–C 91.3(2) [89.48(14)], P2–M–C2 88.9(2) [91.61(14)], N1–C2–N3 104.7(6 [104.5(4)].

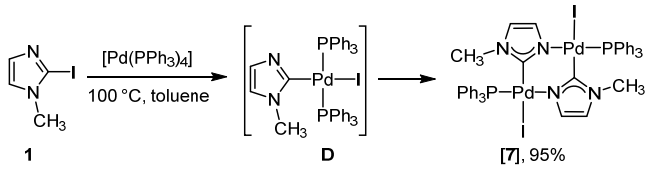
In order to demonstrate the general applicability of the oxidativ addition of the C2–I bond of *N*-alkyl-2-iodoimidazoles for th preparation of *p*NHC complexes, we have also prepared *N*-benzyl-2-iodoimidazole **2** (Scheme 1). Ligand precursor **2** was reacted with complexes $[M(PPh_3)_4]$ (M = Pd, Pt) in the presence of an excess of $NH_4PF_6$ in toluene to give, after a reaction time of 16 h (M = Pd) or 20 h (M = Pt), complexes *trans*-[**5**]$PF_6$ and *trans*-[**6**]$PF_6$, respectively, in good yields (Scheme 4). Again, only the formation of the *trans*-complexes was observed. The reaction time for completion of the reaction was significantly longer than observed for the oxidative addition of *N*-methyl-2-iodoimidazole, possibly due to the larger steric demand of the *p*NHC resulting from ligand precursor **2** and a slightly different electronic situation.




Scheme 4. Synthesis of complexes *trans*-[**5**]$PF_6$ and *trans*-[**6**]$PF_6$.

Complexes *trans*-[**5**]$PF_6$ and *trans*-[**6**]$PF_6$ were also completely characterized by NMR spectroscopy and mass spectrometry. The $^1H$ spectra of *trans*-[**5**]$PF_6$ and *trans*-[**6**]$PF_6$ resemble those of *trans*-[**3**]$PF_6$ and *trans*-[**4**]$PF_6$, by featuring a strongly downfield shifted N-H proton resonance at $\delta \approx 9.8$ ppm. The $^{13}C\{^1H\}$ spectra feature triplets for the $C_{pNHC}$ carbon atom with coupling to two chemically identical phosphorus atoms thereby indicating a *trans*-configuration of the phosphine ligands. The chemical shift of the $C_{pNHC}$ resonance is not significantly affected by the change of the *N*-substituent from methyl to benzyl ($\delta$ = 161.3 ppm, $^2J_{C,P}$ = 9.3 Hz for *trans*-[**5**]$PF_6$; $\delta$ = 149.2 ppm, $^2J_{C,P}$ = 9.7 Hz) for *trans*-[**6**]$PF_6$). The high-resolution electrospray ionization (HR-ESI) mass spectrum (positive ions) showed the highest intensity peaks at *m*/*z* = 915.0754 (calcd for $[\mathbf{5}]^+$ 915.0763) and at *m*/*z* = 1004.1361 (calcd for $[\mathbf{6}]^+$ 1004.1363), both with the correct isotope distribution for the respective cations.

At this point it appears that *N*-alkyl-2-iodoimidazoles behave analogously to the other *N*-alkyl-2-halogenoazoles in oxidative addition reactions. Since $NH_4PF_6$ is normally not acidic enough to protonate *N*-alkylazoles, we assume that the formation of complexes *trans*-[**3**]$PF_6$–*trans*-[**6**]$PF_6$ proceeds by an initial oxidative addition of the C2–I bond of the imidazoles followed by protonation of the ring-nitrogen atom of the formed azolato ligand. In order to establish this reaction sequence, *N*-methyl-2-iodoimidazole was reacted with an equimolar amount of $[Pd(PPh_3)_4]$ in toluene in the absence of a proton source (Scheme 5). This reaction yielded complex [**7**] in an excellent yield of 95%.




Scheme 5. Synthesis of complex [**7**].

Complex [**7**] is highly symmetrical in solution and this leads to rather simple NMR spectra. In the $^1H$ NMR spectrum, the resonances at $\delta$ = 6.61 and 5.74 ppm were assigned to the protons attached to the NHC backbone (H5 and H4, respectively). The $^{13}C\{^1H\}$ NMR spectrum exhibited a singlet at $\delta$ = 159.5 ppm assigned to the $C_{imidazolato}$ carbon atom. Only one resonance at $\delta$ = 24.6 ppm was detected in the $^{31}P$ NMR spectrum for the triphenylphosphine ligands. The high-resolution electrospray ionization (HR-ESI) mass spectrum (positive ions) showed the peak with the highest intensity at *m*/*z* = 1154.8995 (calcd for $[[\mathbf{7}]+H]^+$ 1154.8988) with the correct isotope distribution.

The dinuclear nature of complex [**7**] was confirmed by an X-ray diffraction study (Figure 3). Crystals of composition [**7**]·$2CH_2Cl_2$ were obtained by slow vapor diffusion of diethyl ether into a saturated dichloromethane solution of complex [**7**] at ambient temperature. While complex [**7**] exhibits $C_2$-symmetry in solution as demonstrated by NMR spectroscopy, $C_i$ symmetry was observed for [**7**] in the solid state. The complex is built from two $Pd(PPh_3)I$-moieties connected by two *C*,*N*-metalated imidazolato ligands (Figure 3, right). The metric parameters measured for [**7**] fall in the expected range. The palladium atoms are coordinated in a slightly distorted square-planar geometry. Metalation of the ring-nitrogen atom of the imidazolato ligand leads to inner-ring C–N–C angles which are identical within experimental error (C2–N1–C5 109.1(2)°, C2–N3–C4 108.5(2)°; C42–N41–C45 109.0(2)°, C42–N43–C44 108.3(2)), while azolato ligands with a "free" ring-nitrogen atom (Scheme 5, **D**) feature small $C–N_{free}–C$ and larger $C–N_{alkyl}–C$ inner-ring angles.[5c,d,],[6c,d] The *C*,*N*-metalation of azolato ligands has been observed before.[5c],[12]

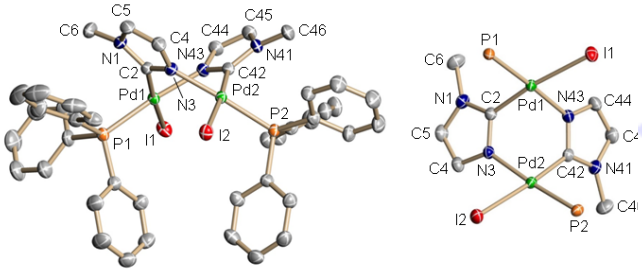



Figure 3. Molecular structure of one molecule of [**7**] in [**7**]·$2CH_2Cl_2$. Th asymmetric unit contains two almost identical units of [**7**]·$2CH_2Cl_2$, only on of which is depicted. Left: molecular structure of [**7**] with hydrogen atom omitted for clarity. Right: side view of [**7**] with P-phenyl groups an hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [° Pd1–I1 2.6640(3), Pd1–P1 2.2687(6), Pd1–N43 2.061(2), Pd1–C2 2.002(3 Pd2–I2 2.6695(3), Pd2–P2 2.2759(7), Pd2–N3 2.062(2), Pd2–C42 1.988(2 N1–C2 1.362(3), N3–C2 1.341(3), N41–C42 1.366(3), N43–C42 1.339(3 I1–Pd1–P1 92.92(2), I1–Pd1–N43 89.73(6), I1–Pd1–C2 175.37(7), P1–Pd1 N43 174.79(6), P1–Pd1–C2 91.71(7), N43–Pd1–C2 85.64(9), I2–Pd2–P 93.90(2), I2–Pd2–N3 90.15(6), I2–Pd2–C42 170.81(7), P2–Pd2–N 171.32(6), P2–Pd2–C42 92.72(7), N3–Pd2–C42 84.17(9), C2–N1–C 109.1(2), C2– N3–C4 108.5(2), C42–N41–N45 109.0(2), C42–N43–C4 108.3(2), N1–C2–N3 107.5(2), N41–C42–N43 107.7(2).

The isolation of *trans*-[**3**]$PF_6$ in the presence of a proton sourc and of [**7**] in the absence of a proton source indicates that complexe of type **D** (Scheme 5) are indeed initially formed in the oxidativ addition of the C2–I bond of *N*-alkyl-2-iodoazoles to Pd complexes. The intermediate complex **D** features an imidazolat ligand with a strongly nucleophilic ring-nitrogen atom which ca attack the metal atom of a second molecule of **D**. Such an attack after loss of two phosphine ligands, leads to dinuclear complex [**7**].

Next, the reactivity of *p*NHC complex *trans*-[**3**]$PF_6$ wa investigated. Removal of the iodo ligand was achieved by reactio of *trans*-[**3**]$PF_6$ with an equimolar amount of $AgPF_6$ in acetonitrile The vacant coordination site was then occupied by an acetonitril molecule to give complex *trans*-[**8**]$(PF_6)_2$ in 96% yield (Scheme 6 Complex *trans*-[**8**]$(PF_6)_2$ was characterized by NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectrum features the $C_{pNHC}$ resonance as a triplet at $\delta$ = 149.2 ppm upfield shifted from the equivalent resonance observed for *trans*-[**3**]$PF_6$ ($\delta$ = 161.7 ppm). The resonances for the carbon atoms of the acetonitrile ligand were recorded at $\delta$ = 127.2 and 1.8 ppm, clearly downfield from the resonances of free acetonitrile.

Substitution of a phosphine ligand from *trans*-[**8**]$(PF_6)_2$ was achieved by reaction of with anhydrous 1,10-phenantroline in dichloromethane. This reaction yielded complex [**9**]$(PF_6)_2$ in 90% yield (Scheme 6).

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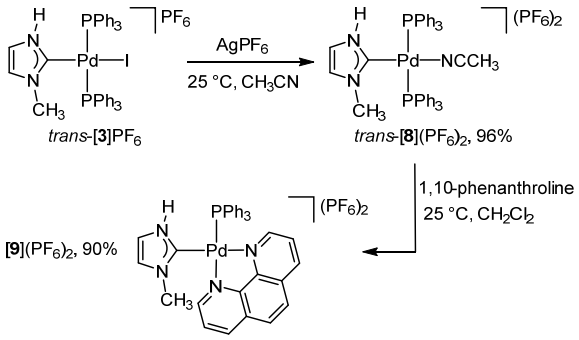



Scheme 6. Synthesis of complexes *trans*-[**8**]$(PF_6)_2$ and [**9**]$(PF_6)_2$ by ligand exchange.

Formation of compound [**9**]$(PF_6)_2$ was confirmed by NMR spectroscopy. The $^1$H NMR spectrum features the resonance for the N-H proton of the NH,NMe-NHC ligand at $\delta$ = 10.93 ppm slightly downfield shifted from the resonance for *trans*-[**3**]$PF_6$ ($\delta$ = 10.00 ppm). The $^{13}C\{^1H\}$ NMR spectrum exhibited a doublet at 152.5 ppm ($^2J_{C,P}$ = 16.1 Hz) for the carbene carbon with coupling to the phosphorus atom. This resonance is downfield shifted relative to the equivalent resonance in the starting material *trans*-[**3**]$PF_6$ ($\delta$ = 161.7 ppm).[13] All resonances for the 1,10-phenanthroline ligand were observed and assigned. The high-resolution electrospray ionization (HR-ESI) mass spectrum (positive ions) featured the most intense peak at *m/z* = 315.0579 (calcd for $[\mathbf{9}]^{2+}$ 315.0588) with the correct isotope distribution.

The composition and coordination geometry of [**9**]$(PF_6)_2$ was established by an X-ray diffraction study (Figure 4). Crystals of composition [**9**]$(PF_6)_2 \cdot 2CH_2Cl_2$ were obtained by slow vapor diffusion of diethyl ether into a saturated dichloromethane solution of [**9**]$(PF_6)_2$. The structure analysis revealed a slightly distorted square-planar coordination geometry around the palladium atom with bond angles N4–Pd–C2 172.79(12)° and P–Pd–N5 178.14(8)°. The 1,10-phenanthroline ligand maintains a planar structure in plane with the palladium coordination plane. The *p*NHC ligand is oriented roughly perpendicular to the coordination plane as was observed for the other *p*NHC complexes described before. The metric parameters of the NH,NMe-NHC ligand fall into the range observed previously for protic NHC ligands. The Pd–P bond distance (2.2716(8) Å) is shorter than in the *trans*-diphosphine complex *trans*-[**3**]$PF_6$.

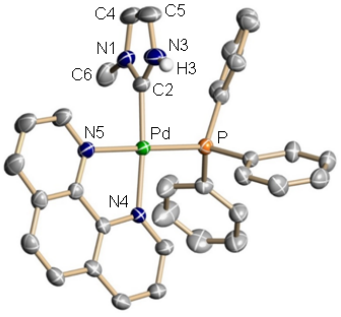



Figure 4. Molecular structure of $[\mathbf{9}]^{2+}$ in [**9**]$(PF_6)_2 \cdot 2CH_2Cl_2$. Hydrogen atoms, except for the N-H proton, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd–P 2.2716(8), Pd–N4 2.105(3), Pd–N5 2.090(3), Pd–C2 1.977(3), N1–C2 1.337(5), N3–C2 1.340(5); P–Pd–N4 99.26(7), P–Pd–N5 178.14(8), P–Pd–C2 87.60(9), N4–Pd–N5 80.13(10), N4–Pd–C2 172.79(12), N5–Pd–C2 92.94(12), N1–C2–N3 105.5(3).

## Conclusion

We have shown that *N*-alkyl-2-iodoimidazoles in the presence of $NH_4PF_6$ react in an oxidative addition reaction with $[M(PPh_3)_4]$ (M = Pd, Pt) in a similar fashion as the previously studied *N*-alkyl-2-chloro- and *N*-alkyl-2-bromoazoles. Only complexes of type *trans*-[M(NH,NR-NHC)$(PPh_3)_2$I] were isolated with no *cis*-complexes detectable. The oxidative addition of the C2−I bond proceeds faster than that of the related C2−X (X = Cl, Br) bonds. In the absence of a proton source, *N*-methyl-2-iodoimidazole reacts with $[Pd(PPh_3)_4]$ to give the dinuclear complex [**7**] containing two bridging *C*,*N*-metalated imidazolato ligands. Ligand substitution reactions were performed with palladium complex *trans*-[**3**]$PF_6$ bearing a *p*NHC ligand. Removal of the iodo ligand with $AgPF_6$ led to th acetonitrile adduct [**8**]$(PF_6)_2$. Reaction of [**8**]$(PF_6)_2$ with 1,10 phenanthroline proceeded under substitution of one of the phosphin ligands to give [**9**]$(PF_6)_2$.

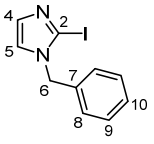
## Experimental Section

**General Procedures.** All preparations were carried out under an argo atmosphere using conventional Schlenk techniques or in a glovebo Solvents were dried and degassed by standard methods prior to use. NM spectra were recorded on a Bruker Avance I 400 or a Bruker Avance III 40 NMR spectrometer. Chemical shifts ($\delta$) are expressed in ppm downfiel from tetramethylsilane by using the residual protonated solvent signals a internal standard. Coupling constants are expressed in Hertz. ESI-HRM spectra were obtained with an Orbitrap LTQ XL (Thermo Scientific spectrometer. Imidazole, *N*-methylimidazole, 1,10-phenanthrolin $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_4]$ were purchased from commercial sources an were used as received. For assignment of the NMR resonances see th numbering at the molecular plots. Satisfactory elemental analyses c compounds *trans*-[**3**]$PF_6$ − [**9**]$(PF_6)_2$ were difficult to obtain due to th sensitivity of the compounds towards oxygen and moisture and the presenc of $PF_6^-$ anions. A complete set of NMR spectra and ESI-HRMS mass spectr is provided in the Supporting Information instead.

**Synthesis of *N*-methyl-2-iodoimidazole 1.**[11] Under an argon atmosphere

*N*-methylimidazole (2.87 g, 2.8 mL, 35 mmol) wa dissolved in THF (150 mL) and the solution was cooled t −78 °C. Over 1 h, a THF solution of *n*-butyl lithium (3 mmol, 21.9 mL of a 1.6 M solution) was added dropwis and the mixture was stirred for 2 h at −78 °C Subsequently, a THF solution of iodine (10.7 g, 42 mmol in 40 mL of THF was added slowly and the reaction mixture was allowed to warm up t ambient temperature over 3 h. The reaction was stopped by addition of saturated aqueous solution of $Na_2S_2O_3$ (1 mL). The solvent was removed *i vacuo* and the solid residue was extracted twice with chloroform (20 m each). The combined organic phase was washed twice with saturate aqueous solutions of $Na_2S_2O_3$ (30 mL each) and brine (20 mL each) and wa then dried over $Na_2SO_4$. Removal of the solvent *in vacuo* followed b column chromatography (silica gel, $CHCl_3$:MeOH = 10:1, v:v) gave **1** as a off-white solid. Yield: 6.3 g (30.3 mmol, 87%). $^1$H NMR (400 MHz, $CDCl_3$ $\delta$ = 7.02 (d, $^3J_{H,H}$ = 1.1 Hz, 1H, H4), 6.99 (d, $^3J_{H,H}$ = 1.1 Hz, 1H, H5), 3.58 ( 3H, H6). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ = 132.3 (C4), 124.0 (C5), 90. (C2), 36.6 (C6). HRMS (ESI, positive ions): *m/z* = 230.9391 (calcd for $[\mathbf{1}+Na]^+$ 230.9395).

**Synthesis of *N*-benzyl-2-iodoimidazole 2.**[11] To a solution of imidazole



(2.73 g, 41 mmol) in DMF (20 mL) was added NaH (1.76 g, 60% in paraffin, 44 mmol) in small portions at 0 °C. The mixture was stirred for 1 h at 0 °C. Then benzyl bromide (6.85 g, 4.76 mL, 40 mmol) was added to the mixture in one portion. The solution was allowed to warm up ambient temperature and was stirred at this temperature stirred for 5 h. Removal of the solvent *in vacuo* gave a solid residue which was isolated, dissolved in dichloromethane and washed with brine. Further

10.1002/ejic.201700403

purification was achieved by recrystallization from $CH_2Cl_2$/hexane. *N*-benzylimidazole was obtained as white needles. Yield: 3.04 g (19.2 mmol, 48%). The *N*-benzylimidazole obtained from the previous reaction was used for the iodation. Under an argon atmosphere, 3.04 g of *N*-benzylimidazole were dissolved in THF (50 mL) and the solution was cooled to −78 °C. Over 1 h at −78 °C, a THF solution of *n*-butyl lithium (12.5 mL of a 1.6 M solution, 20 mmol) was added dropwise and the mixture was stirred for 2 h at −78 °C. Subsequently, a THF solution of iodine (5.1 g, 20 mmol in 40 mL of THF) was added slowly and the reaction mixture was allowed to warm up to ambient temperature and stirred for 3 h at this temperature. Then, a saturated aqueous solution of $Na_2S_2O_3$ (1 mL) was added to stop the reaction. The solvent was removed *in vacuo* and the solid residue was extracted twice with chloroform (20 mL each). The organic phase was washed twice with saturated aqueous solutions of $Na_2S_2O_3$ (30 mL each) and brine (20 mL each). The organic phase was dried over $Na_2SO_4$ and the solvent was removed *in vacuo*. Column chromatography (silica gel, $CHCl_3$:MeOH = 50:1, v:v) gave **2** as off-white solid. Yield: 3.00 g (10.6 mmol, 55.2% relative to *N*-benzylimidazole from the first reaction step. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.34 (m, 3H, H9 and H10), 6.99 (d, $J_{H,H}$ = 7.2 Hz, 2H, H8), 7.11 (d, $J_{H,H}$ = 1.1 Hz, 1H, H4), 7.00 (d, $J_{H,H}$ = 1.1 Hz, 1H, H5), 5.09 (s, 2H, H6). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 135.6 (C7), 132.9 (C4), 128.9 (C8), 128.2 (C10), 127.2 (C9), 123.3 (C5), 90.6 (C2), 53.0 (C6). HRMS (ESI, positive ions): *m/z* = 306.9710 (calcd for [**2**+Na]$^+$ 306.9708).

**Synthesis of complex *trans*-[3]PF$_6$.** A mixture of *N*-methyl-2-iodoimidazole **1** (208 mg, 1.0 mmol), [Pd(PPh$_3$)$_4$] (1155 mg, 1.0 mmol) and $NH_4PF_6$ (326 mg, 2.0 mmol) were suspended in toluene (50 mL). The reaction mixture was heated at 100 °C for 6 h. The solvent was then removed *in vacuo* and the residue was washed with pentane (3 × 20 mL) and diethyl ether (3 × 20 mL). The obtained solid was suspended in dichloromethane (20 mL) and the mixture was filtered to obtain a clear solution. After removal of the solvent *in vacuo* complex *trans*-[**3**]PF$_6$ was obtained as pale yellow powder. Yield: 887 mg (0.9 mmol, 90%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 10.00 (s, 1H, N-H), 7.64−7.57 (m, 12H, Ph-H$_{ortho}$), 7.50−7.45 (m, 6H, Ph-H$_{para}$), 7.45−7.38 (m, 12H, Ph-H$_{meta}$), 6.47 (*pseudo*-t, 1H, H4), 6.19 (*pseudo*-t, 1H, H5), 3.25 (s, 3H, H6). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 161.7 (t, $^2J_{C,P}$ = 9.8 Hz, C2), 134.8 (v-t, $^{2/4}J_{C,P}$ = 6.2 Hz, Ph-C$_{ortho}$), 131.6 (Ph-C$_{para}$), 130.9 (v-t, $^{1/3}J_{C,P}$ = 25.9 Hz, Ph-C$_{ipso}$), 129.1 (v-t, $^{3/5}J_{C,P}$ = 5.4 Hz, Ph-C$_{meta}$), 122.4 (C4, C5), 37.3 (C6). $^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$): $\delta$ = 18.3 (s, $PPh_3$), –144.2 (sept, $^1J_{F,P}$ = 712.3 Hz, $PF_6$). $^{19}$F NMR (376 MHz, $CD_2Cl_2$): $\delta$ = −72.1 (d, $^1J_{F,P}$ = 712.3 Hz, $PF_6$). HRMS (ESI, positive ions): *m/z* = 839.0453 (calcd for [**3**]$^+$ 839.0448).

**Synthesis of complex *trans*-[4]PF$_6$.** A mixture of *N*-methyl-2-iodoimidazole **1** (210 mg, 0.1 mmol), [Pt(PPh$_3$)$_4$] (125 mg, 0.1 mmol) and $NH_4PF_6$ (490 mg, 3.0 mmol) were suspended in toluene (30 mL). The reaction mixture was heated at 100 °C for 6 h. Subsequently, the solvent was removed *in vacuo* and the residue was washed with pentane (3 × 20 mL) and diethyl ether (3 × 20 mL). The obtained solid was suspended in dichloromethane (20 mL) and filtered to give a clear solution. After removal of the solvent *in vacuo* complex *trans*-[**4**]PF$_6$ was obtained as colorless powder. Further purification was achieved by recrystallization from $CH_2Cl_2$/$Et_2O$. Yield: 75 mg (0.07 mmol, 70%). $^1$H NMR (600 MHz, $CD_2Cl_2$): $\delta$ = 9.75 (s, 1H, N-H), 7.67−7.61 (m, 12H, Ph-H$_{ortho}$), 7.52−7.47 (m, 6H, Ph-H$_{para}$), 7.46-7.41 (m, 12H, Ph–H$_{meta}$), 6.36 (m, 1H, H4), 6.16 (m, 1H, H5), 3.24 (s, 3H, H6). $^{13}$C{$^1$H} NMR (150 MHz, $CD_2Cl_2$): $\delta$ = 149.8 (t, $^2J_{C,P}$ = 9.7 Hz, C2), 134.4 (v-t, $^{2/4}J_{C,P}$ = 6.0 Hz, Ph-C$_{ortho}$), 131.2 (Ph-C$_{para}$), 129.5 (v-t, $^{1/3}J_{C,P}$ = 30.0 Hz, Ph-C$_{ipso}$), 128.6 (v-t, $^{3/5}J_{C,P}$ = 5.3 Hz, Ph-C$_{meta}$), 121.1 (C5), 120.4 (C4), 36.6 (C6). $^{31}$P{$^1$H} NMR (243 MHz, $CD_2Cl_2$): $\delta$ = 13.5 (s, Pt satellites, $^1J_{Pt,P}$ = 2455 Hz, $PPh_3$), –144.2 (sept, $^1J_{F,P}$ = 712.4 Hz, $PF_6$). $^{19}$F NMR (564 MHz, $CD_2Cl_2$): $\delta$ = –72.1 (d, $^1J_{F,P}$ = 712.4 Hz, $PF_6$). HRMS (ESI, positive ions): *m/z* = 928.1040 (calcd for [**4**]$^+$ 928.1049).

**Synthesis of complex *trans*-[5]PF$_6$.** Samples of *N*-benzyl-2-iodoimidazole **2** (28 mg, 0.1 mmol), [Pd(PPh$_3$)$_4$] (115 mg, 0.1 mmol) and $NH_4PF_6$ (49 mg, 0.3 mmol) were suspended in toluene (10 mL). The reaction mixture was heated at 100 °C for 16 h. Then the solvent was removed *in vacuo* and the solid residue was washed with hexane (3 × 10 mL) and diethyl ether (3 × 10 mL). The solid was suspended in dichloromethane (20 mL) and filtered to obtain a clear solution. After removal of the solvent and drying *in vacuo*, complex *trans*-[**5**]PF$_6$ was obtained as yellow powder. Yield: 91 mg (0.09 mmol, 90%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 9.85 (s, 1H, N-H), 7.58 (m, 12H, Ph-H$_{ortho}$), 7.48 (m, 6H, Ph-H$_{para}$), 7.40 (m, 12H, Ph-H$_{meta}$), 7.26 (m, 1H, H10), 7.13 (m, 2H, H9), 6.94 (m, 2H, H8), 6.43 (m, 1H, H4), 6.20 (m, 1H, H5), 4.75 (s, 2H, H6). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 161.3 (t, $^2J_{C,P}$ = 9.3 Hz, C2), 134. (v-t, $^{2/4}J_{C,P}$ = 6.1 Hz, Ph-C$_{ortho}$), 133.1 (s, C7), 131.5 (s, Ph-C$_{para}$), 131.2 ( $^{1/3}J_{C,P}$ = 25.8 Hz, Ph-C$_{ipso}$), 129,7 (s, C10), 129.5 (s, C8), 129.5 (s, C9), 129. (t, $^{3/5}J_{C,P}$ = 5.7 Hz, Ph-H$_{meta}$), 122.5 (s, C4), 120.7 (s, C5), 55.3 (s, C6 $^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$): $\delta$ = 18.3 (s, $PPh_3$), –144.2 (sept, $^1J_{F,P}$ 712.4 Hz, $PF_6$). $^{19}$F{H} NMR (376 MHz, $CD_2Cl_2$): $\delta$ = –71.9 (d, $^1J_{F,P}$ = 712. Hz, $PF_6$). HRMS (ESI, positive ions): *m/z* = 915.0754 (calcd for [**5** 915.0763).

**Synthesis of complex *trans*-[6]PF$_6$.** A mixture of *N*-benzyl-2-iodoimidazol **2** (28 mg, 0.1 mmol), [Pt(PPh$_3$)$_4$] (125 mg, 0. mmol) and $NH_4PF_6$ (49 mg, 0.3 mmol) wer suspended in toluene (10 mL). The reactio mixture was heated at 100 °C for 20 h. Th solvent was then removed *in vacuo* and th residue was washed with hexane (3 × 10 mL and diethyl ether (3 × 10 mL). The solid wa then suspended in dichloromethane (20 mL and filtered to obtain a clear solution. Afte removal of the solvent and drying *in vacuo* complex *trans*-[**6**]PF$_6$ wa obtained as white powder. Further purification was achieved b recrystallization from $CH_2Cl_2$/$Et_2O$. Yield: 84 mg (0.07 mmol, 70%). $^1$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 9.71 (s, 1H, N-H), 7.60 (m, 12H, Ph-H$_{ortho}$ 7.48 (m, 6H, Ph-H$_{para}$), 7.40 (m, 12H, Ph-H$_{meta}$), 7.25 (m, 1H, H10), 7.11 (m 2H, H9), 6.98 (m, 2H, H8), 6.29 (*pseudo*-t, 1H, H4), 6.15 (*pseudo*-t, 1H, H5 4.75 (s, 2H, H6). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 149.2 (t, $^2J_{C,P}$ = 9. Hz, C2), 135.0 (t, $^{2/3}J_{C,P}$ = 6.0 Hz, Ph-C$_{ortho}$), 133.2 (s, C7), 131.6 (s, Ph-C$_{para}$ 130.5 (t, $^{1/3}J_{C,P}$ = 30.1 Hz, Ph-C$_{ipso}$), 129.7 (s, C10), 129.6 (s, C8), 129.5 ( C9), 129.0 (t, $^{3/4}J_{C,P}$ = 5.4 Hz, Ph-H$_{meta}$), 120.8 (s, C4), 119.8 (s, C5), 54.8 ( C6). $^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$): $\delta$ = 13.5 (s, Pt satellites $^1J_{Pt,P}$ = 2464 Hz, $PPh_3$), −144.2 (sept, $^1J_{F,P}$ = 712.2 Hz, $PF_6$). $^{19}$F NMR (37 MHz, $CD_2Cl_2$): $\delta$ = −72.0 (d, $^1J_{F,P}$ = 712.2 Hz, $PF_6$). $^{195}$Pt{$^1$H} NMR (37 MHz, $CD_2Cl_2$): $\delta$ = –4797.1 (v-t, $^1J_{Pt,P}$ = 2464 Hz). HRMS (ESI, positiv ions): *m/z* = 1004.1361 (calcd for [**6**]$^+$ 1004.1363).

**Synthesis of complex [7].** A mixture of *N*-methyl-2-iodoimidazole **1** (41 mg 0.2 mmol) and [Pd(PPh$_3$)$_4$] (231 mg, 0. mmol) were dissolved in toluene (10 mL The reaction mixture was heated at 100 °C for 2 h and then cooled down to 0 °C. Th resulting suspension was filtered and th solid was washed with hexane (2 × 10 mL and diethyl ether (2 × 10 mL). After dryin *in vacuo* complex [**7**] was obtained as yellow powder. Yield: 110 mg (0.095 mmol, 95%). $^1$H NMR (400 MHz, $CDCl_3$/DMSO-$d_6$ (1:1, v:v)): $\delta$ = 7.34−7.26 (m, 12H, Ph-H$_{ortho}$), 6.96−6.89 (m, 6H, Ph-H$_{para}$), 6.81−6.74 (m, 12H, Ph-H$_{meta}$), 6.61 (s, 2H, H5), 5.74 (s, 2H, H4), 2.51 (s, 6H, H6). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$/DMSO-$d_6$ (1:1, v:v)): $\delta$ = 159.5 (C2), 134.3 (d, $^2J_{C,P}$ = 11.0 Hz, Ph-C$_{ortho}$), 131.0 (d, $^1J_{C,P}$ = 50.9 Hz, Ph-C$_{ipso}$), 130.1 (C4), 129.6 (d, $^4J_{C,P}$ = 2.2 Hz, Ph-C$_{para}$), 12.4 (d, $^3J_{C,P}$ = 10.6 Hz, Ph-C$_{meta}$), 119.3 (C5), 34.2 (C6). $^{31}$P NMR (162 MHz, $CDCl_3$/DMSO-$d_6$ (1:1, v:v)): $\delta$ = 24.6 (s, $PPh_3$). HRMS (ESI, positive ions): *m/z* = 1154.8995 (calcd for [**7**+H]$^+$ 1154.8988).

**Synthesis of complex [8](PF$_6$)$_2$.** Samples of complex *trans*-[**3**]PF$_6$ (49 mg, 0.05 mmol) and AgPF$_6$ (13 mg, 0.05 mmol) were suspended in acetonitrile (10 mL). The reaction mixture was stirred at ambient temperature for 10 h under exclusion of light. The resulting suspension was filtered through a short pad of celite. The solvent was removed *in vacuo* to give complex *trans*-[**8**](PF$_6$)$_2$ as a white powder. Yield: 50 mg (0.048 mmol, 96%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 10.22 (s, 1H, N-H), 7.65−7.46 (m, 30H, PPh$_3$), 6.65−6.62 (m, 2H, H4 and H5), 3.23 (s, 3H, H6), 1.40 (s, 3H, H8). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 149.2 (t, $^2J_{C,P}$ = 9.0 Hz, C2), 133.9 (v-t, $^{2/4}J_{C,P}$ = 6.6 Hz, Ph-C$_{ortho}$), 132.9 (Ph-C$_{para}$), 130.2 (v-t, $^{3/5}J_{C,P}$ = 5.5 Hz, Ph-C$_{meta}$), 127.2 (C7), 126.6 (v-t, $^{1/3}J_{C,P}$ = 26.3 Hz, Ph-C$_{ipso}$), 124.3 (C5), 123.5 (C4), 37.7 (C6), 1.8 (C8). $^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$): $\delta$ = 20.5 (s, PPh$_3$), –144.2 (sept, $^1J_{F,P}$ = 711.1 Hz, PF$_6$). $^{19}$F NMR (376 MHz, $CD_2Cl_2$): $\delta$ = –72.0 (d, $^1J_{F,P}$ = 711.1 Hz, PF$_6$). HRMS (ESI, positive ions): *m/z* = 747.1082 (calcd for [**8**−CH$_3$CN+Cl]$^+$ 747.1088).

**Synthesis of complex [9](PF$_6$)$_2$.** Samples of complex *trans*-[**8**](PF$_6$)$_2$ (54 mg, 0.05 mmol) and 1,10-phenanthroline (9 mg, 0.05 mmol) were dissolved in dichloromethane (10 mL). The reaction mixture was stirred at ambient temperature for 12 h. The solvent was then removed *in vacuo* and the solid residue was washed with diethyl ether (3 × 20 mL). After drying *in vacuo* complex [**9**](PF$_6$)$_2$ was obtained as a white powder. Yield: 42 mg (0.045 mmol, 90%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 10.93 (s, 1H, N-H), 8.74 (dd, $^3J_{H16,H17}$ = 8.3 Hz, $^4J_{H16,H18}$ = 1.3 Hz, 1H, H16), 8.61 (dd, $^3J_{H9,H8}$ = 8.2 Hz, $^4J_{H9,H7}$ = 1.3 Hz, 1H, H9), 8.15 (d, $^3J_{H14,H15}$ = 8.8 Hz, 1H, H14), 8.12 ppm (d, $^3J_{H15,H14}$ = 8.8 Hz, 1H, H15), 7.86 (ddd, $^3J_{H17,H16}$ = 8.3 Hz, $^3J_{H17,18}$ = 5.2 Hz, $^5J_{H17,P}$ = 1.4 Hz, 1H, H17), 7.84−7.76 (m, 6H, Ph-H$_{ortho}$), 7.75 (1H, detected by HMBC, H7), 7.68−7.60 (m, 3H, Ph-H$_{para}$), 7.56−7.50 (m, 6H, Ph-H$_{meta}$), 7.53 (1H, detected by HMBC, H18), 7.39 (dd, $^3J_{H8,H9}$ = 8.2 Hz, $^3J_{H8,H7}$ = 5.3 Hz, 1H, H8), 7.11 (m, 1H, H4), 6.96 (m, 1H, H5), 3.80 (s, 3H, H6). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 152.5 (d, $^2J_{C,P}$ = 16.1 Hz, C2), 152.0 (d, $^3J_{C,P}$ = 3.4 Hz, C7), 151.5 (C18), 148.3 (C11), 146.9 (C12), 141.4 (C9), 141.3 (C16), 134.7 (d, $^2J_{C,P}$ = 11.7 Hz, Ph-C$_{ortho}$), 133.6 (d, $^4J_{C,P}$ = 3.0 Hz, Ph-C$_{para}$), 131.6 (d, $^4J_{C,P}$ = 2.3 Hz, C13), 131.5 (C10), 130.4 (d, $^3J_{C,P}$ = 11.7 Hz, Ph-C$_{meta}$), 128.6 (C14), 128.3 (C15), 126.9 (d, $^4J_{C,P}$ = 3.0 Hz, C17), 126.5 (d, $^1J_{C,P}$ = 56.8 Hz, Ph-C$_{ipso}$), 125.5 (d, $^4J_{C,P}$ = 1.0 Hz, C8), 124.7 (C5), 123.2 (C4), 38.3 (C6). $^{31}$P NMR (162 MHz, $CD_2Cl_2$): $\delta$ = 29.6 (s, PPh$_3$), –144.7 (sept, $^1J_{F,P}$ = 712.9 Hz, PF$_6$). $^{19}$F NMR (376 MHz, $CD_2Cl_2$): $\delta$ = −72.6 (d, $^1J_{F,P}$ = 712.9 Hz, PF$_6$). HRMS (ESI, positive ions): *m/z* = 315.0579 (calcd for [**9**]$^{2+}$ 315.0588).

**X-Ray Diffraction Studies.** X-Ray diffraction data were collected with a Bruker APEX-II CCD diffractometer equipped with a micro source at 153(2) K using graphite monochromated Mo-K$\alpha$ ($\lambda$ = 0.71073 Å) radiation. Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97 package[14] using the heavy-atom method and were refined with SHELXL-97[14] against $F^2$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

**Crystal Data for [3]PF$_6$·CH$_2$Cl$_2$.** Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of [**3**] in dichloromethane. Formula $C_{41}H_{38}N_2Cl_2F_6IP_3Pd$, $M$ = 1069.84, yellow needle, 0.37 × 0.08 × 0.05 mm$^3$, orthorhombic, space group $P2_12_12_1$, $a$ = 10.3378(2), $b$ = 18.1780(4), $c$ = 22.9689(5) Å, $V$ = 4316.3(2) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.646 g·cm$^{-3}$, $\mu$ = 1.438 mm$^{-1}$, $\omega$- and $\varphi$-scans, 78689 intensities measured in the range 5.8° ≤ 2$\theta$ ≤ 62.0°, semiempirical absorption correction (0.001 ≤ $T$ ≤ 0.014), 13636 independent intensities ($R_{int}$ = 0.0502), 11319 observed intensities [$I \geq 2\sigma(I)$], refinement of 506 parameters against all $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, $R$ = 0.0674, $wR$ = 0.1599, $R_{all}$ = 0.0780, $wR_{all}$ = 0.1687. The asymmetric unit contains one formula unit of [**3**]PF$_6$·CH$_2$Cl$_2$.

**Crystal Data for [4]PF$_6$·CH$_2$Cl$_2$.** Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of [**4**]PF$_6$ in dichloromethane. Formula $C_{41}H_{38}N_2Cl_2F_6IP_3Pt$, $M$ = 1158.53, colorless needle, 0.46 × 0.08 × 0.05 mm$^3$, orthorhombic, space group $P2_12_12_1$, $a$ = 10.3429(3), $b$ = 18.1857(6), $c$ = 22.9299(7) Å, $V$ = 4313.0(2) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.784 g·cm$^{-3}$, $\mu$ = 4.262 mm$^{-1}$, $\omega$- and $\varphi$-scans, 78663 intensities measured in the range 6.2° ≤ 2$\theta$ ≤ 62.0°, semiempirical absorption correction (0.244 ≤ $T$ ≤ 0.815), 13663 independent intensities ($R_{int}$ = 0.0654), 12145 observed intensities [$I \geq 2\sigma(I)$], refinement of 506 parameters against all $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, $R$ = 0.0296, $wR$ = 0.0612, $R_{all}$ = 0.0377, $wR_{all}$ = 0.0635. The asymmetric unit contains one formula unit of [**3**]PF$_6$·CH$_2$Cl$_2$.

**Crystal Data for [7]·2CH$_2$Cl$_2$.** Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of [**7**] in dichloromethane. Formula $C_{46}H_{44}N_4Cl_4I_2P_2Pd$, $M$ = 1323.19, yellow cube 0.26 × 0.23 × 0.19 mm$^3$, triclinic, space group $P$–1, $a$ = 10.0745(2), $b$ 20.6752(3), $c$ = 25.2164(4) Å, $\alpha$ = 70.4510(10), $\beta$ = 83.9120(10), $\gamma$ 79.6640(10)°, $V$ = 4863.29(15) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.807 g·cm$^{-3}$, $\mu$ = 2.33 mm$^{-1}$, $\omega$- and $\varphi$-scans, 89372 intensities measured in the range 2.1° ≤ 2$\theta$ 64.0°, semiempirical absorption correction (0.506 ≤ $T$ ≤ 0.746), 3036 independent intensities ($R_{int}$ = 0.0309), 26081 observed intensities [$I \geq 2\sigma(I$ refinement of 1085 parameters against all $|F^2|$ with anisotropic therma parameters for all non-hydrogen atoms and hydrogen atoms on calculate positions, $R$ = 0.0316, $wR$ = 0.0737, $R_{all}$ = 0.0389, $wR_{all}$ = 0.0777. Th asymmetric unit contains two formula unit of [**7**]·2CH$_2$Cl$_2$.

**Crystal Data for [9](PF$_6$)$_2$·2CH$_2$Cl$_2$.** Crystals suitable for an X-ra diffraction study were obtained by slow diffusion of diethyl ether into solution of [**9**](PF$_6$)$_2$ in dichloromethane. Formula $C_{36}H_{33}N_4Cl_4F_{12}P_3Pd$, $M$ 1090.77, colorless prism, 0.42 × 0.23 × 0.19 mm$^3$, triclinic, space group $P$– $a$ = 11.9801(3), $b$ = 13.4209(3), $c$ = 14.6680(3) Å, $\alpha$ = 73.9660(10), $\beta$ 85.8570(10), $\gamma$ = 82.1390(10)°, $V$ = 2243.86(9) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.61 g·cm$^{-3}$, $\mu$ = 0.841 mm$^{-1}$, $\omega$- and $\varphi$-scans, 25872 intensities measured in th range 5.8° ≤ 2$\theta$ ≤ 60.0°, semiempirical absorption correction (0.638 ≤ $T$ 0.746), 12999 independent intensities ($R_{int}$ = 0.0228), 11171 observe intensities [$I \geq 2\sigma(I)$], refinement of 570 parameters against all $|F^2|$ wit anisotropic thermal parameters for all non-hydrogen atoms and hydroge atoms on calculated positions, $R$ = 0.0550, $wR$ = 0.1576, $R_{all}$ = 0.0634, $wR_{}$ = 0.1657. The asymmetric unit contains one formula unit of [**9**](PF$_6$)$_2$ on CH$_2$Cl$_2$ molecule and two CH$_2$Cl$_2$ molecules with SOF = 0.5.

CCDC-1543704 ([**3**]PF$_6$·CH$_2$Cl$_2$), CCDC-1543705 ([**4**]PF$_6$·CH$_2$Cl$_2$ CCDC-1543706 ([**7**]·2CH$_2$Cl$_2$) and CCDC-1543707 ([**9**](PF$_6$)$_2$·2CH$_2$Cl$_2$ contain the supplementary crystallographic data for this paper. These dat can be obtained free of charge from the Cambridge Crystallographic Dat Centre via www.ccdc.cam.ac.uk/data_request/cif.

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# FULL PAPER

**Protic NHCs**

*Hanpeng Jin, Peter Kluth and F. Ekkehardt Hahn**

***Page No. – Page No.***

**Synthesis of Complexes with Protic NH,NR-NHC Ligands by Oxidative Addition of *N*-Alkyl-2-iodoimidazole to [M(PPh$_3$)$_4$] (M = Pd, Pt) Complexes**

*N*-Alkyl-2-iodoimidazoles react in the presence of $NH_4PF_6$ in an oxidative addition with [M(PPh$_3$)$_4$] (M = Pd, Pt) to give complexes of type *trans*-[M(NH,NR-NHC)(PPh$_3$)$_2$I]PF$_6$ with a protic NH,NR-NHC ligand. Substitution reactions of only the iodo or both the iodo and one of the phosphine ligands in such complexes have been studied.