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Cyclic six-membered palladium complexes derived from palladium mediated C–N coupling of organonitrile and formamidine†

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Reactions of *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinium chloride (**1**) with palladium acetate in acetonitrile or propanenitrile results in the formation of cyclic six-membered triazapentadiene-palladium dichloride complexes (**4** and **5**). The reaction of formamidinium salt containing non-coordinating anions, such as $(BF_4)^-$ (**2**) and $(PF_6)^-$ (**3**) with palladium acetate in acetonitrile or propanenitrile leads to the formation of cationic bis(1,3,5-triazapentadiene)palladium complexes **6**, **7** or **8**, **9** respectively. However, the reaction with acrylonitrile afforded an unprecedented cyclic and anionic six-membered palladacycle complex (**10**). In addition a reaction of **1** with $Pd(OAc)_2$ in THF afforded an acyclic palladium complex (**11**), which is a possible intermediate formed before conversion to the cyclic six-membered palladium complexes (**4**, **5** and **10**) in presence of organonitriles.

Introduction

The metal mediated activation of the C–N bond in organonitrile is of great interest as it can provide an easier and accessible route to the corresponding organo-derivatives. Compared to the unactivated organonitrile, the metal coordinated organonitrile reactions are facilitated by enhancing the electrophilic/nucleophilic character of the unsaturated nitrile carbon of the organonitriles in the presence of a Lewis/Bronsted acidic or basic medium. Depending upon the nature of the oxidation state of the metal ion, an eletrophilic (low oxidation state of metal ions) or a nucleophilic (high or medium oxidation state of metal ions) addition can be achieved at the carbon centre of nitrile group.[1] Among them the nucleophilic addition of organonitrile has been widely studied for the past two decades due to the simple method of preparation of compounds containing new C–C and C–X (X = N, O, P, S) bonds. An extension of this work was also carried out by using multi-functional nitriles or nucleophilic reagents to obtain various C–N coupled products. As an example, the nickel mediated bifunctional nitrile undergoes C–N coupling with oximes to form the phthalocyanines.[1j] Similarly, metal mediated coupling reactions of organonitrile with mono- or di-imino derivatives resulted in (1,3,5-triazapentadienyl)-metal complexes.[1c–j] Among them, the synthesis of triazapentadiene (tap) through metal mediated coupling has received considerable attention in last three decades. Besides, tap is found to be an alternative ligand for the beta-diketaminato ligands and hence the synthesis of metal complexes using the former ligand has been carried out.[2]

So far, preparations of metal mediated tap–metal complexes have been carried out by at least seven different synthetic methods. In almost all cases the amidines were found to be an important intermediate formed before coupling. Subsequently, tap complexes were synthesized using metal mediated coupling of organonitrile with different amidine or guanidine derivatives. So far, this study has been restricted to divalent Mn(II), Co(II), Ni(II), Cu(II), Pd(II), Pt(II) or tetravalent Pt(IV) metal centers.[1] In contrast, the reactions of acrylonitrile undergo Michael-type addition with amines. Using this procedure a large number of CN coupled β-amino products have been synthesized.[3] In addition the palladium catalyzed reactions of acrylonitrile, either in the copolymerization of ethylene or an enantioselective product formation using imines as nucleophile in aza-Morita–Baylis–Hillman reaction, have been widely studied.[4] In these reactions, the acrylonitrile coordinates to the palladium centre either through CN or by the alkene group which is a key intermediate before the product formation.[4a,b] Among these reactions there are only two examples describing the C-bound or an example of N-bound σ-bonded acrylonitrile derivatives of palladium complexes which were structurally characterized.[4c,d] Inspired by the variable coordination modes of binding to palladium and the

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†Electronic supplementary information (ESI) available: Additional figures and X-ray crystallographic data in CIF format have been deposited with the Cambridge Structural Database. CCDC 1014314–1014318 for (**1**), (**4**), (**5**), (**10**) and (**11**), 1020744–1020747for (**6**), (**7**), (**8**) and (**9**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt02721c

control over the product formation, the reaction of **1** with palladium acetate in various organonitriles was carried out. Herein, we report the synthesis and structural characterization of **4–11** and the conversion of **11** to **4**, **5** and **10**. Even though metal mediated organonitrile and amidine coupling are known, no example of palladium mediated coupling reactions of this type have been reported. Moreover, to the best of our knowledge, complex **10** is the first example of anionic palladacyle derived from acrylonitrile.

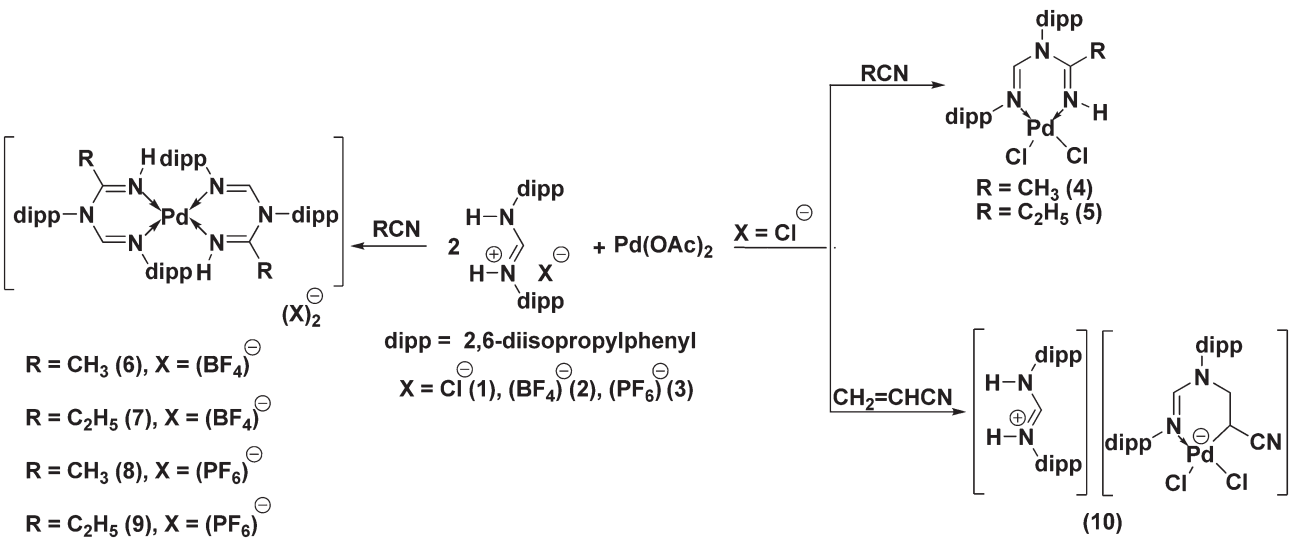
Results and discussion

Acidification of *N*,*N*′-bis(2,6-diisopropylphenyl)formamidine with hydrochloric acid resulted in the formation of *N*,*N*′-bis-(2,6-diisopropylphenyl)formamidinium chloride (**1**) as colourless solid in good yield.[5] The structure of **1** was confirmed by spectroscopic, spectrometric and analytical methods. Compared to the dipp containing formamidine,[6] the ^{1}H NMR shows a single doublet (1.26 ppm) and a septet (3.29 ppm) for the isopropyl groups of dipp indicating the symmetry of **1**. Furthermore, **1** was also characterized by X-ray crystal structure analysis which showed the expected structure. The dipp groups are oriented *trans* to each other with respect to the central carbon atom and these iminium protons interact with the chloride ions to form a chain like structure (Fig. S1 and S2; Table S1, ESI†). The C–N bond distances in **1** are similar (1.293 (4) Å and 1.314(5) Å) indicating a possible delocalization of the bond between N–C–N in **1**. Previously it has been proposed and demonstrated that the C-bound metal formamidinium complex undergoes isomerization to give the N-bound metal formamidine complex, which is similar to that of a metal-imidazole isomerisation between a C-bound and N-bound metal centre.[7] With this in mind, a reaction of **1** with palladium acetate was carried out to generate the palladium complex of acyclic diaminocarbene, even though such metal complexes have been generally prepared by the nucleophilic addition of imines to metal coordinated isocyanides.[8]

The reaction of **1** with palladium acetate in acetonitrile or propanenitrile affords a yellow coloured product (**4** or **5**) (Scheme 1).[9] The ^{1}H NMR spectra of **4** and **5** show two different doublets and septets for isopropyl C*H*$_3$ and C*H* groups respectively, indicating the unsymmetrical position of dipp in the final product. ^{13}C NMR resonances show additional peaks, besides dipp carbons, between 120–160 ppm. Moreover, the base peak in the ESI-MS spectra for **4** and **5** recorded in positive ion mode corresponds to the formamidinium cation. Furthermore, single crystals of **4** and **5** were obtained in acetonitrile and chloroform–ethyl acetate mixture, respectively, and were subjected to X-ray diffraction analysis.

The asymmetric unit of complex **4** is shown in Fig. 1 (**5** in Fig. S3†) and crystallographic parameters are given in Table S1 (ESI†). Surprisingly, the molecular structures of **4** and **5** consist of an unsymmetrically substituted cyclic six-membered 1,3,5-triazapentadiene-palladium dichloride complex, where palladium is in distorted square planar geometry surrounded by neutral triazapentadiene (tap), which acts as a *N*,*N*-bidentate chelating ligand, and two chloride ions occupy the *cis* position. Due to the unsymmetrical substitution, two different bond distances 2.024(2) Å and 1.972(2) Å (**4**); 2.019(3) Å and 1.978(3) Å (**5**) (Table S1† and Table 1) were observed, which are in the expected range with the similarly known compounds[9] and also the splitting of peaks was observed in the ^{1}H and ^{13}C NMR spectra.

During the course of investigation of the possible formation of C-bound palladium acyclic diaminocarbene (ADC)[8f] using *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinium chloride (**1**) and palladium acetate in acetonitrile or propanenitrile, neutral six-membered tap–palladium dichloride complexes (**4** and **5**) were obtained. Kukushkin and others reported the preparation of tap–metal complexes starting from the nucleophilic



Scheme 1 Synthesis of compounds **4–10**.

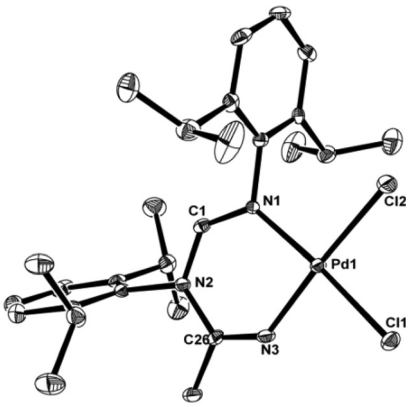


Fig. 1 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **4**. Hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths [Å] and angles (°) for compound **4** and **5**

	4	**5**
Pd(1)–N(1)	2.024(2)	2.019(3)
Pd(1)–N(3)	1.972(2)	1.978(3)
C(1)–N(1)	1.286(4)	1.284(4)
C(1)–N(2)	1.369(4)	1.385(4)
C(26)–N(2)	1.392(4)	1.400(4)
C(26)–N(3)	1.273(4)	1.282(4)
N(3)–Pd(1)–N(1)	88.51(9)	87.27(9)
N(3)–C(26)–N(2)	120.3(3)	120.1(3)
C(1)–N(2)–C(26)	125.4(2)	123.8(2)
N(1)–C(1)–N(2)	128.7(3)	127.4(3)
C(1)–N(1)–Pd(1)	123.7(2)	123.6(2)

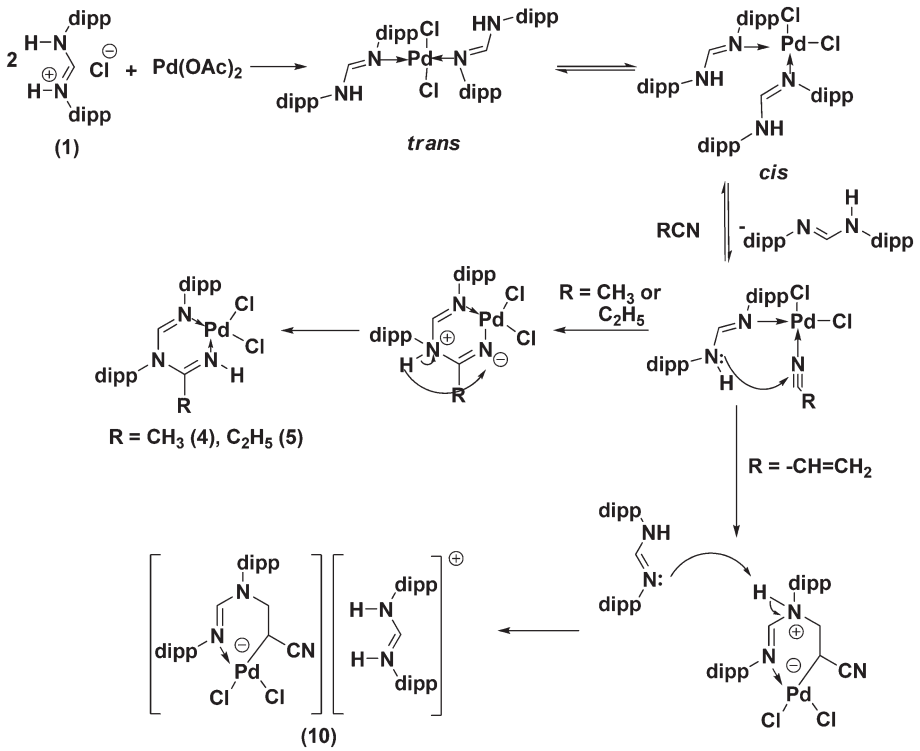
addition of amidine derivatives to the organonitrile.[1c] Based on this research, we propose that the complexes **4** and **5** must have been formed through a multistep synthesis which is shown in Scheme 2. Accordingly, the deprotonation of the formamidinium salt results in a formamidine-bound palladium chloride complex (either *trans* or *cis*). The *cis*-complex of the latter in the presence of acetonitrile loses one of the formamidine units which is replaced by an acetonitrile molecule to afford a formamidine(acetonitrile)–palladium dichloride complex. Subsequently, a C–N coupled product, tap–palladium dichloride, was obtained due to the nucleophilic addition of the amine nitrogen atom of coordinated formamidine to the electrophilic unsaturated nitrile carbon of acetonitrile. NMR analysis of the crude product of **4** supports the presence of by-product formamidine. Analysis of ESI mass spectra shows the presence of a molecular ion peak $[(M - Cl^-) + CH_3CN]^+$ for **4** and **5**. Furthermore, peaks corresponding to imine C=NH (3326 cm^{-1} (**4**) and 3335 cm^{-1} (**5**)) as well as C=N (1663 cm^{-1} (**4**) and 1663 cm^{-1} (**5**)) were also observed in the IR spectra of **4** and **5**, which supports the proposed mechanism (Scheme 2).

It has been shown previously that bis-substituted tap–platinum complexes were synthesized by reactions starting from the nitrile adduct of platinum chloride with a formamidine derivative.[10] In a similar manner it may be possible to prepare the bis-tap complexes of palladium if the counter anion for formamidine is exchanged and used as a precursor. As expected the reaction of formamidinium salt (**2** and **3**) containing $(BF_4)^-$ and $(PF_6)^-$ as counteranions with palladium acetate in acetonitrile or propanenitrile leads to the formation of cationic bis(1,3,5-triazapentadiene) palladium complexes (**6–9**; Scheme 1). The formation of these complexes was confirmed by microanalytical data, NMR, IR spectroscopy and single X-ray crystallography. The ^{1}H NMR spectra of **6–9** are similar to that of **4** and **5** except that the proton of N–CH–N in the former is slightly deshielded as compared to the latter. Also the monocationic molecular ions $[M - (BF_4)^-]^+$ for **6** and **7** or $[M - (PF_6)^-]^+$ for **8** and **9** were observed in ESI-MS. Furthermore, the structures of **6–9** were confirmed by single crystal X-ray diffraction studies.

The molecular structure of **6–9** is shown in Fig. 2 and S4–6.† It shows a cationic six-memberd bis(tap)–palladium complex in which the central Pd(II) ion is coordinated by four nitrogen atoms from tap which act as *N*,*N*-chelators, and adopts a square planar geometry.[10b] The bond distances and angles within the complexes are similar to those of **4** and **5** as well as other already reported complexes (Table 2, Fig. 2, Tables S1 and S2†).

In contrast, the reaction of **1** with $Pd(OAc)_2$ in acrylonitrile afforded a cyclometalated product (**10**) which was characterized by spectroscopic and spectrometric techniques. Unlike those of **4** and **5**, the IR spectrum of **10** shows a peak at 2199 cm^{-1} corresponding to the presence of the unreacted CN of acrylonitrile. The ^{1}H NMR spectrum of **10** exhibited multiple peaks corresponding to the CH_3 and CH protons of the isopropyl groups in dipp in the regions of 1–2 ppm and 2.8–3.3 ppm respectively. In addition the olefinic protons of acrylonitrile are shifted to the shielding region, with an AB type pattern at ~1.9 ppm corresponding to the CH_2 protons and a multiplet for the CH proton merged with septets of the isopropyl CH of dipp, which gave an indication that the C=C activated acrylonitrile derivative is formed in **10**. However, the ESI-MS spectrum, recorded in positive ion mode showed only the presence of the formamidinium moiety. Additionally, yellow crystals of **10** were obtained in dichloromethane solution by the slow evaporation method and were subjected to single crystal X-ray diffraction analysis.

The molecular structure of **10** and the crystallographic parameters are given in Fig. 3 and Table 3 (Table S2†) respectively. Unlike in compounds **4** and **5**, compound **10** consists of a cyclic and anionic six-membered palladacycle containing a PdC_3N_2 unit in which palladium is bound by a σ-bonded α-carbon, derived from acrylonitrile, and a nitrogen atom through its lone pair. In addition, two chloride ions are in the *cis* position to complete the four coordination around the palladium centre, and thus adopts a square planar type anionic complex which is stabilized by a cationic formamidinium unit. The six-membered PdC_3N_2 ring is not in a plane due to the presence of a saturated C–C single bond derived from acrylonitrile, and adopts a twisted boat conformation. Moreover, unlike in **4** and **5**, the functional group CN in acrylonitrile



Scheme 2 Proposed mechanistic pathway for the conversion of **1** into complexes **4**, **5** and **10**.

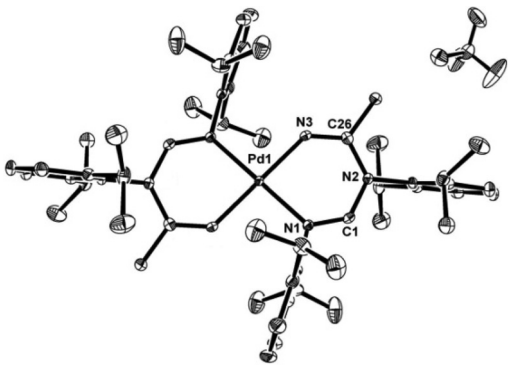


Fig. 2 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **6**. Hydrogen atoms have been omitted for clarity.

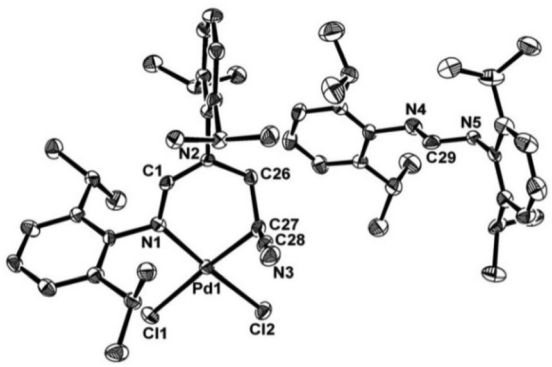


Fig. 3 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **10**. Hydrogen atoms and one solvent DCM molecule have been omitted for clarity.

Table 2 Selected bond lengths (Å) and bond angles (°) for compounds **6**, **7**, **8** and **9**

	6	**7**	**8**	**9**
Pd(1)–N(1)	2.0116(16)	2.009(3)	2.021(4)	2.017(4)
Pd(1)–N(3)	1.9920(15)	1.985(2)	1.975(4)	2.000(4)
C(1)–N(1)	1.280(2)	1.284(4)	1.275(7)	1.282(6)
C(1)–N(2)	1.368(2)	1.360(4)	1.374(6)	1.359(6)
C(26)–N(2)	1.388(2)	1.388(4)	1.390(6)	1.391(6)
C(26)–N(3)	1.278(2)	1.282(4)	1.282(7)	1.278(6)
N(3)–Pd(1)–N(1)	86.92(6)	86.56(10)	86.18(17)	86.05(16)
N(3)–C(26)–N(2)	120.56(17)	119.9(3)	121.3(5)	120.2(4)
C(1)–N(2)–C(26)	124.65(16)	124.9(3)	124.8(4)	124.3(4)
N(1)–C(1)–N(2)	127.99(18)	127.9(3)	126.5(5)	128.6(4)
C(1)–N(1)–Pd(1)	125.53(14)	125.6(2)	127.9(3)	125.4(3)

Table 3 Selected bond lengths (Å) and bond angles (°) for compound **10**

Bond lengths		Bond angles	
Pd(1)–N(1)	2.062(4)	C(27)–Pd(1)–N(1)	88.87(16)
C(27)–Pd(1)	2.033(5)	C(1)–N(1)–Pd(1)	125.2(3)
C(1)–N(1)	1.306(6)	N(1)–C(1)–N(2)	127.7(4)
C(1)–N(2)	1.331(6)	C(1)–N(2)–C(26)	124.7(4)
C(26)–N(2)	1.475(5)	N(2)–C(26)–C(27)	113.7(4)
C(26)–C(27)	1.511(6)	C(26)–C(27)–Pd(1)	113.2(3)
C(28)–N(3)	1.133(6)	C(27)–Pd(1)–Cl(2)	87.18(13)
Pd(1)–Cl(1)	2.4265(12)	N(1)–Pd(1)–Cl(2)	176.05(11)
Pd(1)–Cl(2)	2.3152(12)	C(27)–Pd(1)–Cl(1)	176.62(13)
		N(1)–Pd(1)–Cl(1)	94.31(11)
		Cl(2)–Pd(1)–Cl(1)	89.64(4)

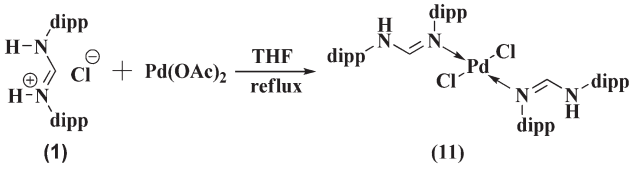
remains uncoordinated as was observed in the IR spectrum. The Pd–C bond distance in **10** is 2.033(5) Å, which is slightly shorter than the known Pd–C bond length 2.058(6) Å of the acrylonitrile derivative of palladium complexes.[4c] Due to the *trans* influence of carbon (C27), the Pd–Cl(1) bond is elongated 2.426(1) Å as compared to the other Pd–Cl(2) bond with a length of 2.315(1) Å (Fig. 3, Tables 3 and S2†).

The formation of **10** can be understood by studying the mechanism for the formations of **4** and **5**, as well as the known binding modes of acrylonitrile with a palladium center and also by Michael type reactions (Scheme 2).[4b,c] Once the formamidine complex of palladium dichloride is formed, the dissociation of formamidine occurs from the *cis* isomer and subsequently the acrylonitrile is bound to the palladium center. Even though both the N-bound or π-bound complexation of the C=C of acrylonitrile to the palladium center is possible, it was shown that the latter mode of binding is known to give the 2,1-inserted product involving Pd–C bond formation.[4a,b] Based on this information, we assume that the first step is correlated to the nucleophilic addition of the amine from the formamidine unit at the methylene electrophilic center of acrylonitrile, as in a Michael type reaction, followed by the palladium carbon σ-bond formation to give cyclic and anionic six-membered palladacycle, **10** in addition to *N*-(2-cyanoethyl)-*N*,*N*′-bis(2,6diisopropylphenyl)-formimidamide.

As mentioned in the mechanism above (Scheme 2), the six-membered rings **4**, **5** and **10** are formed through the acyclic formamidine complex of palladium dichloride. Thus a reaction between **1** and palladium acetate in THF was carried out in the anticipation of isolation of the latter complex (Scheme 3). A yellow coloured formamidine palladium dichloride complex (**11**) was formed in good yield, and was thoroughly characterized by spectroscopic and analytical methods as well as by single crystal X-ray crystallography.

The ESI-MS recorded in positive ion mode shows the presence of a molecular ion $[M - Cl^-]^+$ peak corresponding to its formation. Additionally, strong bands at 1639 cm^{-1} and 3369 cm^{-1} were observed in the IR spectrum, which could be assigned to ν(C=N) and ν(N–H) respectively. To understand further the formation of **11**, the product was crystallized by slow evaporation using a dichloromethane–toluene–dimethylsulphoxide mixture to afford yellow coloured crystals (**11** in Fig. 4).

The molecular structure of **11** and important bond distances and angles (as legend) are given in Fig. 4. It consists of



Scheme 3 Synthesis of compound **11**.

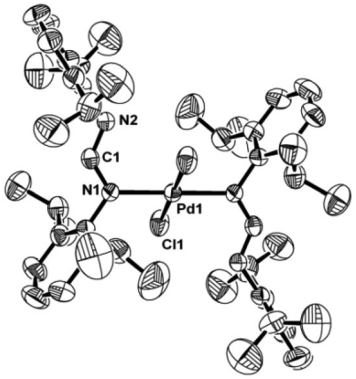


Fig. 4 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **11**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): N(1)–Pd(1) 2.056(3), Pd(1)–Cl(1) 2.2913 (13), N(1)–Pd(1)–Cl(1) 88.79(8).

a square-planar palladium center which is surrounded by two formamidine ligands coordinated through the imine nitrogen atom and two chloride atoms in *trans* mode. The Pd–N bond distance is slightly longer than the reported formamidine complex of palladium dichloride, whereas the Pd–Cl bond distance is of the same value as reported in the literature.[11]

When the reaction was carried out between **11** and organonitriles (acetonitrile, propanenitrile and acrylonitrile), it resulted in the formation of **4**, **5** and **10** respectively, which was confirmed through spectroscopic and spectrometric methods; although in the case of **10**, additional peaks in the ^{1}H NMR spectrum were observed along with those expected, plausibly because of formation of unidentifiable side products. These results suggest that **11** could be a possible intermediate, if the reaction was carried out in a step-wise manner using two different solvents (THF followed by organonitriles).

Conclusions

In this report, a palladium mediated C–N coupling between organonitrile and formamidine is described. Cyclic six-membered neutral (in the cases of acetonitrile and propanenitrile) or anionic (in the case of acrylonitrile) palladium complexes were successfully isolated. The neutral tap–palladium dichloride complexes (**4** and **5**) consist of a cyclic six-membered PdC_2N_3 unit in which a chelating *N*,*N*, coordination to palladium was observed, whereas exchanging the counteranion from Cl^- to non-coordinating anions such as $(BF_4)^-$ and $(PF_6)^-$ in **2** and **3** led to the formation of cationic bis tap–palladium complexes (**6–9**). The anionic palladacycle (**10**) has a *N*,*C* coordination in which the carbon is σ-bonded to the palladium centre. Complex **10** is the first example of a palladacycle derived from acrylonitrile through C–N coupling in the presence of a formamidine unit.[12]

Experimental section

General procedures

All of the reactions and manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk line techniques unless otherwise mentioned. Solvents were dried according to the standard literature procedures and they were freshly distilled prior to use. All other reagents were used as received. Glassware was dried in an oven at 140 °C overnight. Chemicals such as 2,6-diisopropylaniline, acrylonitrile and palladium acetate were purchased from Aldrich Chemicals and used as received. Compound *N*,*N*′-bis(2,6-diisopropylphenyl)-formamidine[6] was prepared according to literature procedures.

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL-DELTA 500 spectrometer. The spectra were recorded in $CDCl_3$ and CD_3CN as the solvent. Chemical shifts were referenced with respect to tetramethylsilane (TMS). Infrared spectra were recorded as KBr pellets on a FT-IR Bruker Vector model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Waters-Q-Tof Premier-HAB213 spectrometer. Elemental analyses were performed with an EAI Exeter analytical, INC CE-440 Elemental analyzer. Melting points reported are uncorrected.

X-ray crystallography

The crystal data were collected on a Bruker SMART APEX CCD diffractometer. Data were collected using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 100 K. All the structures were solved by direct methods using SHELXTL-97[13] and refined by full matrix least-squares on F^2. All of the hydrogen atoms were included in idealized positions and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. In compound **4**, the disordered solvent molecule was treated by squeeze refinement using PLATON.[13c]

General procedure for synthesis of 1, 2 and 3. A schlenk flask was charged with *N*,*N*′-bis(2,6-diisopropylphenyl)formamidine (1.82 g, 5 mmol) and dissolved in dichloromethane (40 mL). To this acid (5.5 mmol) [HCl for **1**, HBF_4 for **2**, HPF_6 for **3**] was added at 0 °C and stirred for 2 h. Volatiles were removed under vacuum and washed with hot hexane (in case of **1** and **3**) or with diethylether (in case of **2**) which gave a colourless residue.

Synthesis of *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinium chloride (1). Crystals were obtained by slow evaporation of acetone–toluene solution of **1** at room temperature. Yield: 1.56 g (78%). Mp: 228–232 °C. Anal. calcd for $C_{25}H_{37}ClN_2$: C, 74.87; H, 9.30; N, 6.99. Found: C, 73.46; H, 9.33; N, 7.01. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.26 (d, 24H, CH_3), 3.29 (sept. 4H, CH(CH_3)$_2$), 7.21 (d, 4H, C_6H_{5meta}), 7.37 (m, 3H, C_6H_{5para} +C_2–H), 12.43 (d, 2H, NH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.8 (*C*H_3), 28.7 (*C*H), 124.3(*meta*-C_6H_3), 130.0(*para*-C_6H_3), 131.1 (*ortho*-C_6H_3), 145.3(*ipso*-C_6H_3), 158.9(N*C*N). IR (KBr, cm^{-1}): 3079 (w), 3033 (w), 2962 (vs), 2928 (s), 2869 (s), 2663 (m), 1679 (vs), 1590 (w), 1536 (m), 1466 (m), 1412 (w), 1384 (w), 1363 (m), 1325 (s), 1279 (w), 1257 (w), 1181 (w), 1098 (w), 1060 (w), 1044 (w), 938 (w), 802 (m), 752 (w), 716 (w), 503(w), 428 (w) cm^{-1}. ESI-MS: calcd for (M − Cl$^-$)$^+$: 365.2956, found: 365.2950.

Synthesis of *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinium tetrafluoroborate (2). Yield: 1.74 g (78%). Mp: 206–208 °C. Anal. Calcd for $C_{25}H_{37}BF_4N_2$: C, 66.38; H, 8.24; N, 6.19. Found: C, 66.15; H, 8.12; N, 6.18. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.18 (m, 18H, CH_3), 1.33 (d, 6H, CH_3), 2.85 (br, 2H, CH(CH_3)$_2$), 3.06 (br, 2H, CH(CH_3)$_2$), 7.18 (d, 2H, C_6H_{5meta}), 7.34 (d, 2H, C_6H_{5meta}), 7.48 (m, 2H, C_6H_{5para}), 8.24 (br, 1H, C_2–H), 10.21 (d, 2H, NH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 22.3, 23.6, 25.2, 25.3, 28.7, 29.0, 124.5, 125.2, 125.6, 129.5, 130.2, 130.7, 130.9, 131.8, 145.2, 145.6, 145.8, 157.7, 158.3. IR (KBr, cm^{-1}): 3231 (w), 3049 (w), 2967 (s), 2932 (m), 2872 (w), 1676 (vs), 1590 (w), 1536 (m), 1466 (w), 1365 (w), 1334 (w), 1083 (s), 1036 (s), 801 (m), 768 (w), 718 (w), 522 (w), 434 (w) cm^{-1}. ESI-MS: calcd 365.2956, found: 365.2950 (M − $(BF_4)^-$)$^+$.

Synthesis of *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinium hexafluorophosphate (3). Yield: 1.83 g (72%). Mp: 138–142 °C. Anal. Calcd for $C_{25}H_{37}F_6N_2P$: C, 58.81; H, 7.30; N, 5.49. Found: C, 58.33; H, 7.04; N, 5.27. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.18 (d, 24H, CH_3), 3.21 (sept., 4H, CH(CH_3)$_2$), 7.17 (d, 4H, C_6H_{5meta}), 7.32 (m, 3H, C_6H_{5para} +C_2–H), 11.10 (br., 2H, NH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.7, 28.4, 124.2, 130.1, 131.2, 145.8, 157.8. IR (KBr, cm^{-1}): 3184 (m), 2965 (vs), 2871 (m), 1677 (vs), 1589 (w), 1466 (m), 1386 (w), 1365 (w), 1334 (w), 1183 (w), 1083 (m), 1061 (m), 937 (w), 846 (w), 802 (m), 755 (m), 481 (w), 435 (w) cm^{-1}. ESI-MS: calcd 365.2956, found: 365.2950 (M − $(PF_6)^-$)$^+$.

Synthesis of compound 4. A schlenk flask was charged with compound **1** (0.20 g, 0.5 mmol) and palladium acetate (0.056 g, 0.25 mmol). To this acetonitrile (30 mL) was added and heated at 80 °C for 20 h. The yellow coloured solution was filtered through celite and volatiles were removed under vacuum. The resultant solid was washed with diethyl ether and dried under vacuum to afford a yellow residue. Crystals were obtained by slow evaporation of acetonitrile solution of **4** at room temperature. Yield: 0.132 g (91%). Mp: 196–200 °C (decomp.). Anal. calcd for $C_{27}H_{39}Cl_2N_3Pd$: C, 56.23; H, 6.74; N, 7.21. Found: C, 56.53; H, 6.95; N, 7.44. ^{1}H NMR (CD_3CN, 500 MHz): δ 1.12–1.59 (m, 12H, CH_3) 1.22 (d, 6H, CH_3), 1.45 (d, 6H, CH_3), 1.93 (s, 3H, CH_3–C═NH), 2.87 (sept., 2H, CH(CH_3)$_2$), 3.31 (sept., 2H, CH(CH_3)$_2$), 7.08 (d, 2H, C_6H_{3meta}), 7.15 (t, 1H, C_6H_{3para}), 7.34 (d, 2H, C_6H_{3meta}), 7.49 (t, 1H, C_6H_{3para}), 7.59 (s, 1H, C_2–H). ^{13}C NMR (CD_3CN, 125 MHz): δ 23.0(CH-(*C*H_3)$_2$), 23.7(CH(*C*H_3)$_2$), 24.1(N═C–*C*H_3), 28.2(*C*H(CH_3)$_2$), 28.3 (*C*H(CH_3)$_2$), 123.1, 125.5, 127.5, 131.6, 134.2, 141.8, 142.9, 146.2, 151.3(N–H*C*═N), 158.4(H_3C–*C*═NH). IR (KBr, cm^{-1}): 3326 (m), 2962 (vs), 2927 (m), 2866 (m), 1663 (vs), 1601 (m), 1461 (m), 1443 (m), 1397 (m), 1361 (m), 1271 (m), 1256 (m), 1215 (m), 1169 (m), 1098 (m), 1056 (m), 933 (w), 818 (m), 804 (m), 753 (m), 730 (m), 617 (w), 589 (w) 565 (w), 531 (w), 481 (w), 443 (w) cm^{-1}. ESI-MS calcd for [(M − Cl$^-$ + CH_3CN)]$^+$: 587.2154, found: 587.2098.

Synthesis of compound 5. Compound **1** (0.200 g, 0.5 mmol) and palladium acetate (0.056 g, 0.25 mmol) were taken in a schlenk flask and propanenitrile (20 mL) was added to it. The solution was heated at 80 °C for 20 h. A yellow coloured precipitate was formed and it was filtered. The volatiles were removed under vacuum and washed with diethyl ether and dried under vacuum to give a yellow coloured residue. Crystals were obtained by slow evaporation of chloroform–ethyl acetate solution of **5** at room temperature. Yield: 0.10 g (68%). Mp: 208–212 °C (decomp.). Anal. calcd for $C_{28}H_{41}Cl_2N_3Pd$: C, 56.33; H, 6.92; N, 7.04. Found: C, 55.80; H, 7.10; N, 7.23. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.14–1.29 (m, 21H, CH_3 + CH_3CH$_2$), 1.54 (d, 6H, CH_3), 1.98 (quartet, 2H, CH$_3$–CH_2–C═NH), 2.83 (sept., 2H, CH(CH$_3$)$_2$), 3.32 (sept., 2H, CH(CH$_3$)$_2$), 7.10 (d, 2H, C$_6H_{3meta}$), 7.20 (t, 1H, C$_6H_{3para}$), 7.27 (s, 1H, C$_2$–H), 7.31 (d, 2H, C$_6H_{3meta}$), 7.51 (t, 1H, C$_6H_{3para}$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.9, 24.0, 24.7, 25.1, 27.4, 28.7, 123.7, 126.0, 128.3, 132.1, 133.2, 141.6, 142.6, 146.1, 150.3 (N–HC═N), 160.9 (H$_2$C–C═NH). IR (KBr, cm^{-1}): 3335 (m), 2964 (vs), 2928 (m), 2870 (w), 1663 (vs), 1595 (w), 1464 (m), 1443 (w), 1408 (w), 1387 (w), 1364 (w), 1313 (w), 1255 (m), 1214 (w), 1169 (w), 1117 (w), 1059 (w), 814 (m), 803 (m), 785 (w), 758 (m), 612 (w), 560 (w), 529 (w), 449 (w) cm^{-1}. ESI-MS calcd for [(M − Cl$^-$) + CH$_3$CN]$^+$: 601.2289, found: 601.2287.

Synthesis of compound 6. Compound **2** (0.226 g, 0.5 mmol) and palladium acetate (0.056 g, 0.25 mmol) were taken in a schlenk flask and acetonitrile (30 mL) was added to it. The solution was heated at 80 °C for 20 h. The yellow coloured solution was filtered through celite and volatiles were removed under vacuum and washed with diethyl ether and dried under vacuum to give a yellow coloured residue. Crystals were obtained by slow evaporation of acetonitrile solution of **6** at room temperature. Yield: 0.195 g (72%). Mp: 202–206 °C. Anal. Calcd for $C_{54}H_{78}B_2F_8N_6Pd$: C, 59.38; H, 7.29; N, 7.69. Found: C, 59.41; H, 7.39; N, 7.74. ^{1}H NMR (CD_3CN, 500 MHz): δ 1.20 (m, 18H, CH_3) 1.43 (d, 6H, CH_3), 1.65 (s, 3H, CH_3–C═NH), 2.72 (sept., 2H, CH(CH$_3$)$_2$), 3.18 (sept., 2H, CH(CH$_3$)$_2$), 7.40 (d, 2H, C$_6H_{3meta}$), 7.48 (d, 2H, C$_6H_{3meta}$), 7.58 (m, 2H, C$_6H_{3para}$), 8.08 (s, 1H, C$_2$–H). ^{13}C NMR (CD_3CN, 125 MHz): δ 22.9, 23.5, 24.0, 28.3, 28.5, 125.7, 126.1, 130.8, 132.5, 133.0, 136.4, 142.6, 145.6, 154.0, 163.0. IR (KBr, cm^{-1}): 3300 (m), 2966 (s), 2929 (w), 2871 (w), 1662 (vs), 1597 (w), 1463 (w), 1389 (w), 1364 (w), 1329 (w), 1300 (s), 1217 (w), 1165 (w), 1076 (s), 1051 (vs), 1036 (s), 932 (w), 812 (w), 764 (w), 731 (w), 626 (w), 568 (w), 521 (w), 463 (w) cm^{-1}. ESI-MS: calcd 1003.5409, found: 1003.5414 (M − (BF$_4$)$^-$)$^+$.

Synthesis of compound 7. Compound **2** (0.226 g, 0.5 mmol) and palladium acetate (0.056 g, 0.25 mmol) were taken in a schlenk flask and propanenitrile (20 mL) was added to it. The solution was heated at 80 °C for 2 h. The yellow coloured solution was filtered through celite and volatiles were removed under vacuum and washed with the mixture of 1 mL THF and 15 mL ether and dried under vacuum gave yellow residue. Crystals were obtained by slow evaporation of mixture of chloroform–ethyl acetate solution of **7** at room temperature. Yield: 0.113 g (41%). Mp: 158–162 °C. Anal. Calcd for $C_{56}H_{82}B_2F_8N_6Pd$: C, 60.09; H, 7.38; N, 7.51. Found: C, 59.79; H, 7.27; N, 7.54. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.16 (m, 18H, CH_3), 1.30 (t, 3H, CH_2CH$_3$), 1.49 (d, 6H, CH_3), 2.04 (quartet, 2H, CH$_3$–CH_2–C═NH), 2.88 (sept., 2H, CH(CH$_3$)$_2$), 3.53 (sept., 2H, CH(CH$_3$)$_2$), 7.28 (d, 2H, C$_6H_{3meta}$), 7.38 (d, 2H, C$_6H_{3meta}$), 7.44 ((m, 3H, C$_6H_{3para}$ + C$_2$–H)). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.6, 23.9, 24.9, 25.0, 28.3, 28.4, 126.1, 130.8, 132.4, 132.5, 137.2, 143.8, 145.9, 146.4, 152.8, 166.3. IR (KBr, cm^{-1}): 3303 (m), 2966 (s), 2929 (m), 2873 (m), 1659 (vs), 1596 (w), 1464 (m), 1418 (w), 1388 (w), 1365 (w), 1329 (w), 1299 (m), 1215 (w), 1170 (w), 1133 (m), 1045 (vs), 1032 (vs), 932 (w), 812 (m), 764 (w), 615 (w), 565 (w), 520 (w) cm^{-1}. ESI-MS: calcd 1031.5670, found: 1031.5746 (M − (BF$_4$)$^-$)$^+$.

Synthesis of compound 8. A schlenk flask was charged with compound **3** (0.255 g, 0.5 mmol) and palladium acetate (0.056 g, 0.25 mmol) in 30 mL acetonitrile and was heated at 80 °C for 20 hours to give yellow coloured solution. The solution was filtered through celite and removal of volatiles under vacuum and washing with ether and dried under vacuum gave yellow residue. Crystals were obtained by slow evaporation of acetonitrile solution of **8** at room temperature. Yield: 0.241 g (80%). Mp: 176–180 °C. Anal. Calcd for $C_{54}H_{78}F_{12}N_6P_2Pd$: C, 53.71; H, 6.51; N, 6.96. Found: C, 53.13; H, 6.39; N, 6.59. ^{1}H NMR (CD_3CN, 500 MHz): δ 1.17 (m, 18H, CH_3) 1.42 (d, 6H, CH_3), 1.93 (s, 3H, CH_3–C═NH), 2.64 (sept., 2H, CH(CH$_3$)$_2$), 3.19 (sept., 2H, CH(CH$_3$)$_2$), 7.40 (d, 2H, C$_6H_{3meta}$), 7.48 (d, 2H, C$_6H_{3meta}$), 7.58 (m, 2H, C$_6H_{3para}$), 8.08 (s, 1H, C$_2$–H). ^{13}C NMR (CD_3CN, 125 MHz): δ 22.9, 23.5, 24.0, 28.3, 28.5, 122.9, 124.0, 125.6, 126.0, 130.7, 132.4, 142.6, 145.6, 153.9, 162.9. IR (KBr, cm^{-1}): 3276 (w), 2967 (m), 2930 (w), 2873 (w), 1661 (vs), 1595 (w), 1462 (m), 1439 (w), 1406 (w), 1389 (w), 1367 (w), 1328 (w), 1290 (s), 1218 (w), 1165 (w), 1099 (w), 1060 (w), 1043 (w), 935 (w), 842 (vs), 810 (m), 762 (w), 739 (w), 684 (w), 618 (w), 594 (w), 557 (m), 530 (w), 464 (w), 440 (w) cm^{-1}. ESI-MS: calcd 1061.4985, found: 1061.4971 (M − (PF$_6$)$^-$)$^+$.

Synthesis of compound 9. A schlenk flask was charged with compound **3** (0.255 g, 0.5 mmol) and palladium acetate (0.056 g, 0.25 mmol) in 20 mL propanenitrile and was heated at 80 °C for 2 h to give yellow coloured solution. The solution was filtered through celite and removal of volatiles under vacuum and washed with mixture of 1 mL THF and 15 mL ether and dried under vacuum to give yellow residue. Crystals were obtained by slow evaporation of methanol solution of **9** at room temperature. Yield: 0.119 g (40%). Mp: 108–112 °C. Anal. Calcd for $C_{56}H_{82}F_{12}N_6P_2Pd$: C, 54.43; H, 6.69; N, 6.80. Found: C, 53.93; H, 6.48; N, 6.62. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.11 (m, 18H, CH_3), 1.26 (t, 3H, CH_2CH$_3$), 1.46 (d, 6H, CH_3), 1.82 (quartet, 2H, CH$_3$–CH_2–C═NH), 2.80 (sept., 2H, CH(CH$_3$)$_2$), 3.29 (sept., 2H, CH(CH$_3$)$_2$), 7.29 (d, 2H, C$_6H_{3meta}$), 7.39 (d, 2H, C$_6H_{3meta}$), 7.45 (m, 3H, C$_6H_{3para}$ + C$_2$–H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.5, 23.9, 24.9, 25.0, 28.4, 28.5, 124.1, 126.2, 126.2, 130.9, 132.5, 137.1, 143.7, 146.4, 152.8, 166.5. IR (KBr, cm^{-1}): 3298 (m), 2966 (s), 2930 (m), 2873 (m), 1658 (vs), 1598 (w), 1465 (m), 1388 (w), 1366 (w), 1291 (m), 1215 (w), 1171 (w), 1132 (w), 1059 (m), 879 (vw), 843 (s), 808 (m), 760 (m), 558 (w),

481 (w), 448 (w) cm^{-1}. ESI-MS: calcd 1089.5283, found: 1089.5286 $(M - (PF_6)^-)^+$.

Synthesis of compound 10. A schlenk flask was charged with compound **1** (0.20 g, 0.5 mmol) and palladium acetate (0.056 g, 0.25 mmol). To this acrylonitrile (10 mL) was added and heated at 80 °C for 20 h. A yellow coloured solution was formed. The volatiles were removed from solution under vacuum and extracted with hexane and dried under vacuum to afford yellow coloured residue. Crystals were obtained by slow evaporation of dichloromethane solution of **10** at room temperature. Yield: 0.162 g (68%). Mp: 118–122 °C (decomp.). Anal. calcd for $C_{53}H_{74}Cl_2N_5Pd$: C, 66.41; H, 7.78; N, 7.40. Found: C, 66.15; H, 7.72; N, 7.34. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.07–1.38 (m, 48H, CH_3) 1.85 (d, 1H, PdCH(CN)CH_2), 1.92 (d, 1H, PdCH(CN)CH_2), 2.91(m, 2H, C$H(CH_3)_2$), 3.14 (m, 2H, C$H(CH_3)_2$), 3.26 (m, 3H, C$H(CH_3)_2$ + PdCH(CN)CH_2), 3.48 (m, 2H, CH-$(CH_3)_2$), 6.88 (d, 1H, C_2–H), 7.12–7.36 (m, 13H, $C_6H_{3meta+para}$ +C_2–H), 12.34 (br., 2H, NH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.6, 23.9, 25.5, 26.3, 27.6, 28.7, 49.5, 52.5, 122.5, 123.3, 123.4, 124.3, 124.5, 125.2, 125.6, 127.1, 130.0, 131.2, 137.5, 145.6, 147.2, 152.4, 156.2 (N–HC═N). IR (KBr, cm^{-1}): 3070 (w), 2963 (vs), 2928 (s), 2869 (m), 2199 (w), 1686 (vs), 1629 (vs), 1585 (w), 1521 (vw), 1464 (s), 1385 (w), 1366 (w), 1323 (m), 1269 (w), 1256 (w), 1210 (w), 1178 (w), 1099 (w), 1058 (w), 1042 (w), 806 (m), 765 (m), 604 (w), 529 (w), 456 (w), 410 (w) cm^{-1}. ESI-MS calcd for (M^+): 365.2956, found: 365.2951. ***N*-(2-cyanoethyl)-*N*,*N*′-bis(2,6diisopropylphenyl)formimidamide**. The volatiles were removed from the filtrate (hexane) under vacuum and purified by column chromatography using 5% ethyl acetate in hexane as eluent to give pale yellow compound. Yield: 0.017 g (8%). Anal. calcd for $C_{28}H_{39}N_3$: C, 80.53; H, 9.41; N, 10.06. Found: C, 80.37; H, 9.52; N, 10.12. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.12–1.32 (m, 24H, CH_3) 2.95 (t, 2H, CNCH_2CH_2), 3.10 (sept., 4H, C$H(CH_3)_2$), 4.04 (t, 2H, CNCH_2CH$_2$), 7.01 (t, 1H, C_6H_{3para}), 7.08 (d, 2H, C_6H_{3meta}), 7.17 (d, 2H, C_6H_{3meta}), 7.21 (s, 1H, N–CH–N), 7.34 (t, 1H, C_6H_{3para}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.5, 24.2, 25.3, 28.1, 28.6, 46.4, 118.0, 122.8, 124.7, 129.3, 138.0, 139.6, 146.4, 147.7, 151.0. IR (KBr, cm^{-1}): 3401 (w), 2924 (vs), 2960 (vs), 2854 (m), 2248 (w), 1643 (vs), 1588 (w), 1463 (w), 1398 (w), 1378 (w), 1326 (m), 1296 (m), 1259 (m), 1238 (m), 1178 (w), 1100 (m), 1057 (m), 1041 (w), 990 (w), 933 (w), 894 (w), 815 (s), 804 (s), 761 (s), 596 (w), 556 (w), 435 (w) cm^{-1}. ESI-MS cacld for $(M + H^+)^+$: 418.3217, found: 418.3221.

Synthesis of compound 11. Compound **1** (0.200 g, 0.5 mmol) and palladium acetate (0.056 g, 0.25 mmol) were taken in a schlenk flask and it was charged with THF (30 mL). The solution was refluxed for 20 h to give a yellowish-orange coloured solution. The solution was filtered, and volatiles were removed under vacuum to afford yellow coloured residue. The residue was washed with diethyl ether and dried under vacuum. Crystals were obtained by slow evaporation using a mixture of dichloromethane–toluene–dimethyl sulfoxide solution of **11** at room temperature. Yield: 0.182 g (81%). Mp: 198–202 °C (decomp.). Anal. calcd for $C_{50}H_{72}Cl_2N_4Pd$: C, 66.25; H, 8.01; N, 6.18. Found: C, 66.01; H, 8.0; N, 6.02. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.03–1.25 (m, 36H, CH_3 major + minor isomer) 1.60–1.77 (m, 12H, CH_3 major + minor isomer), 2.90 (sept., 2H, C$H(CH_3)_2$ minor isomer), 3.44 (sept., 2H, CH-$(CH_3)_2$ major isomer), 3.78 (sept., 4H, C$H(CH_3)_2$ major + minor isomer), 5.92 (d, 2H, NH minor isomer), 6.59 (d, 2H, NH major isomer), 7.06–7.24 (m, 12H, $C_6H_{3ortho+para}$), 7.94 (d, 1H, C_2H minor isomer), 8.74 (d, 1H, C_2H major isomer). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.0, 24.1, 24.4, 25.0, 25.3, 26.0, 28.1, 28.2, 123.7, 123.8, 124.1, 124.4, 126.6, 126.8, 127.7, 128.5, 128.9, 132.6, 143.9, 144.5, 144.6, 144.9, 147.4, 147.5, 158.1 (N–HC═N), 159.8 (N–HC═N). IR (KBr, cm^{-1}): 3369 (w), 3243 (w), 2962 (s), 2869 (w), 1639 (vs), 1585 (w), 1464 (w), 1382 (w), 1361 (w), 1323 (w), 1260 (w), 1178 (w), 1098 (w), 1057 (w), 935 (w), 802 (m), 756 (w), 637 (w), 574 (w) cm^{-1}. ESI-MS: calcd 869.4480, found: 869.4489 $(M - Cl^-)^+$.

Synthesis of compound 4 from 11. A schlenk flask was charged with compound **11** (0.091 g, 0.1 mmol) in acetonitrile (10 mL) and heated at 80 °C for 20 h to give a yellow coloured solution. The volatiles were removed under vacuum and washed with diethyl ether and dried under vacuum to afford a yellow residue. Yield: 0.052 g (90%). The ^{1}H, ^{13}C NMR, IR and ESI-MS analysis were found to be similar to those reported for compound **4** as mentioned above.

Synthesis of compound 5 from 11. The same procedure is used as described above except that propanenitrile (20 mL) is used and heated at 80 °C for 2 h. Yield: 0.046 g (78%). The ^{1}H, ^{13}C NMR, IR and ESI-MS analysis were found to be similar to those reported for compound **5** as mentioned above.

Synthesis of compound 10 from 11. The same procedure was used as described above except that acrylonitrile (5 mL) was used and heated at 80 °C for 5 h. Yield: 0.032 g (33%). ^{1}H NMR of this residue shows resonances for **6** as well as some additional peaks for the presence of other by-products.

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