Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Cyclic Six-membered Palladium Complexes Derived from Palladium Mediated C-N Coupling of Organonitrile and Formamidine

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

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**). In case of reaction of formamidinium salt containing non-coordinating anions, such as $(BF_4)^-$ (**2**) and $(PF_6)^-$ (**3**) with palladium acetate in acetonitrile or propanenitrile lead 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 converting to the cyclic six-membered palladium complexes (**4**, **5** and **10**) in presence of organonitriles.

Introduction

Metal mediated activation of C-N bond in organonitrile is of great interest as they can provide an easier and accessible route for 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 organonitriles in the presence of Lewis/Bronsted acidic or basic medium. Depending upon the nature of oxidation state of 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 on organonitrile is widely studied for the past two decades due to the simple way of preparation of compounds containing new C-C and C-X (X= N, O, P, S) bond. The extension of this work was also carried out by using multi-functional nitrile or the 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 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 are carried out by at least seven different synthetic methods. In almost all the 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 is 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 undergoes Michael-type addition with amines. Using this procedure a large number of CN coupled *β*-amino products were synthesized.[3] In addition the palladium catalyzed reactions of acrylonitrile either in 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 alkene group which is a key intermediate before the product formation.[4a,b] Among them 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 control over the product formation, the reaction of **1** with palladium acetate in various organonitriles were 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 is reported. Moreover, to the best of our knowledge, complex **10** is the first example of anionic palladacyle derived from acrylonitrile.

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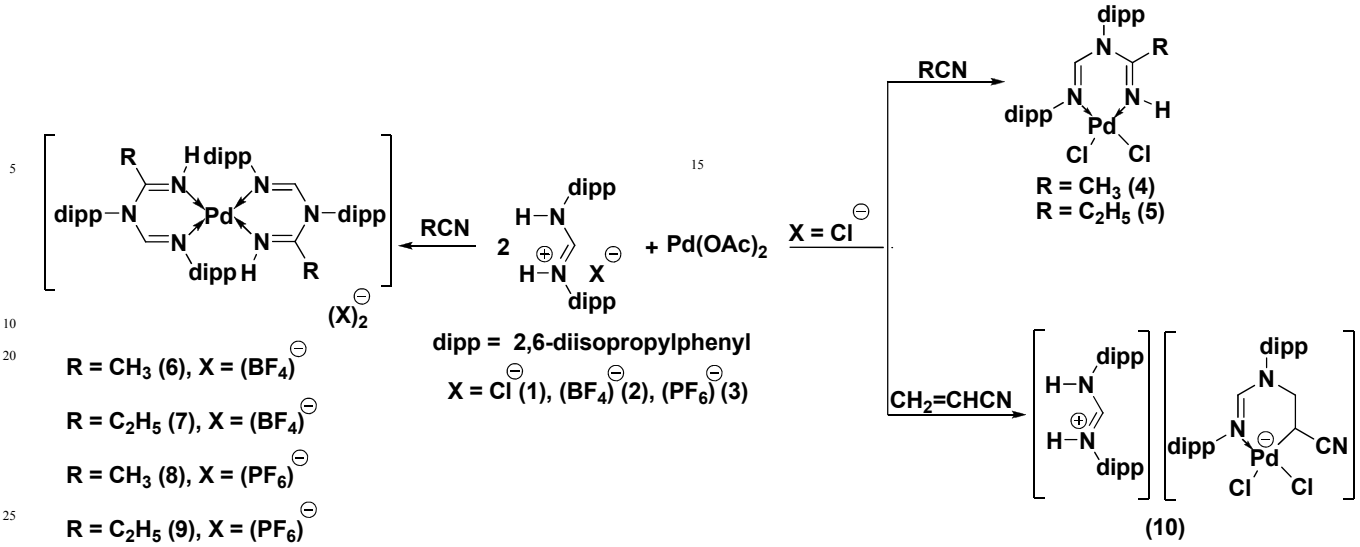
†Electronic Supplementary Information (ESI) available: Additional figures and X-ray crystallographic data in CIF format have been deposited with the Cambridge Structural Database. CCDC 1014314-1014318 for (**1**), (**4**), (**5**), (**10**) and (**11**) and 1020744-1020747 for (**6**), (**7**), (**8**) and (**9**).



Scheme 1 Synthesis of compounds **4**-**10**

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] **1** was confirmed by spectroscopic, spectrometric and analytical methods. Compared to the formamidine,[6] the ^{1}HNMR shows a single doublet (1.26 ppm) and a septet (3.29 ppm) for the isopropyl groups of dipp indicating the symmetry of **1**. Further **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 (figure 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 bond between N-C-N in **1**. Earlier it has been proposed and demonstrated that *C*-bound metal formamidinium complex undergoes isomerization to give the *N*-bound metal formamidine complex which is similar to that of an metal-imidazole isomerisation between *C*-bound and *N*-bound metal centre.[7] Keeping this in view, 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 yellow coloured product (**4** or **5**) (scheme 1).[9] The ^{1}H NMR spectrum of **4** and **5** shows two different doublets and septets for isopropyl CH_3 and CH groups respectively, indicating 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 spectrum for **4** or **5** recorded in positive ion mode corresponds to the formamidinium cation. Further, 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 figure 1 (**5** in figure S3) and crystallographic parameters are given in table S1 (ESI). Surprisingly, molecular structure of **4** or **5** consists 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 in *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 were observed in ^{1}H and ^{13}C NMR spectra.

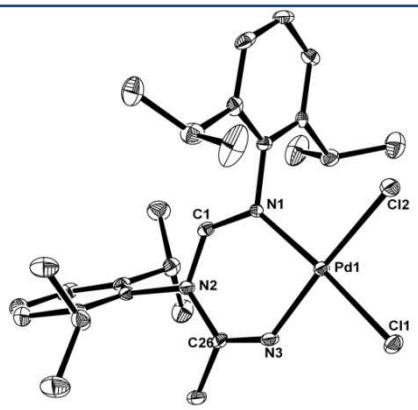


Fig. 1 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **4.** Hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths [Å] and angles (deg) 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)

During the course of investigation of 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, a 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 addition of amidine derivatives to the organonitrile.[1c] Based on these literatures, we propose that the complex **4** or **5** must have been formed through multistep synthesis which is shown in scheme 2. Accordingly, the deprotonation of formamidinium salt results in formamidine bound palladium chloride complex (either *trans* or *cis*). The *cis*-complex of the latter in the presence of acetonitrile losses one of the formamidine unit which is replaced by an acetonitrile molecule to afford formamidine(acetonitrile)-palladium dichloride complex. Subsequently, a C-N coupled product, tap-palladium dichloride was obtained due to the nucleophilic addition of 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 spectrum shows the presence of molecular ion peak $[(M\text{-}Cl^-)+CH_3CN]^+$ for **4** or **5**. Further, 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 IR spectrum of **4** and **5** which supports the proposed mechanism (scheme 2).

It has been shown earlier that the reactions of bis-substituted tap-platinum complexes were synthesized starting from the nitrile adduct of platinum chloride with formamidine derivative.[10] In a similar manner it may be possible to prepare the bis-tap complexes of palladium if the counter anion exchanged formamidine is used as precursors. 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 lead 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** is similar to that of **4** and **5** except that the proton of N-CH-N is slightly deshielded as compared to the latter one. Also the monocationic molecular ions $[M\text{-}(BF_4)^-]^+$ for **6** and **7** or $[M\text{-}(PF_6)^-]^+$ for **8** and **9** were observed in ESI-MS. Further the structures of **6-9** were confirmed by single crystal X-ray diffraction studies.

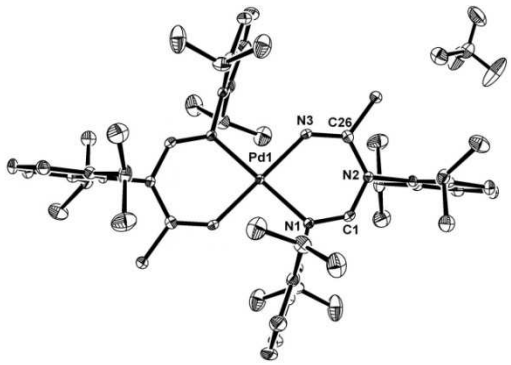


Figure 2 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **6.** Hydrogen atoms have been omitted for clarity.

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

Table 2. Selected bond lengths [Å] and bond angles (deg) for compound **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)

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 in **4** and **5**, the IR spectra of **10** shows a peak at 2199 cm^{-1} corresponding to the presence of unreacted CN of acrylonitrile. The ^{1}H-NMR spectrum of **10** gave multiple peaks for the CH_3 and CH protons of 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, like AB type pattern at ~ 1.9 ppm corresponding to CH_2 proton and a multiplet for CH proton merged with septets of isopropyl CH of dipp, which gave an indication that C=C activated acrylonitrile derivative is formed in **10**. However, the ESI-MS spectrum, recorded in positive ion mode showed only the presence of formamidinium moiety. Further yellow crystals of **10** were obtained in dichloromethane solution by slow evaporation method and were subjected to single crystal X-ray diffraction analysis.

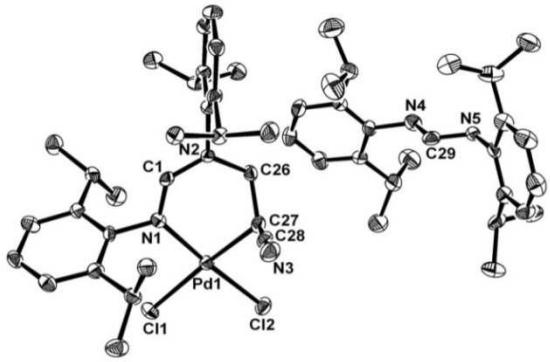
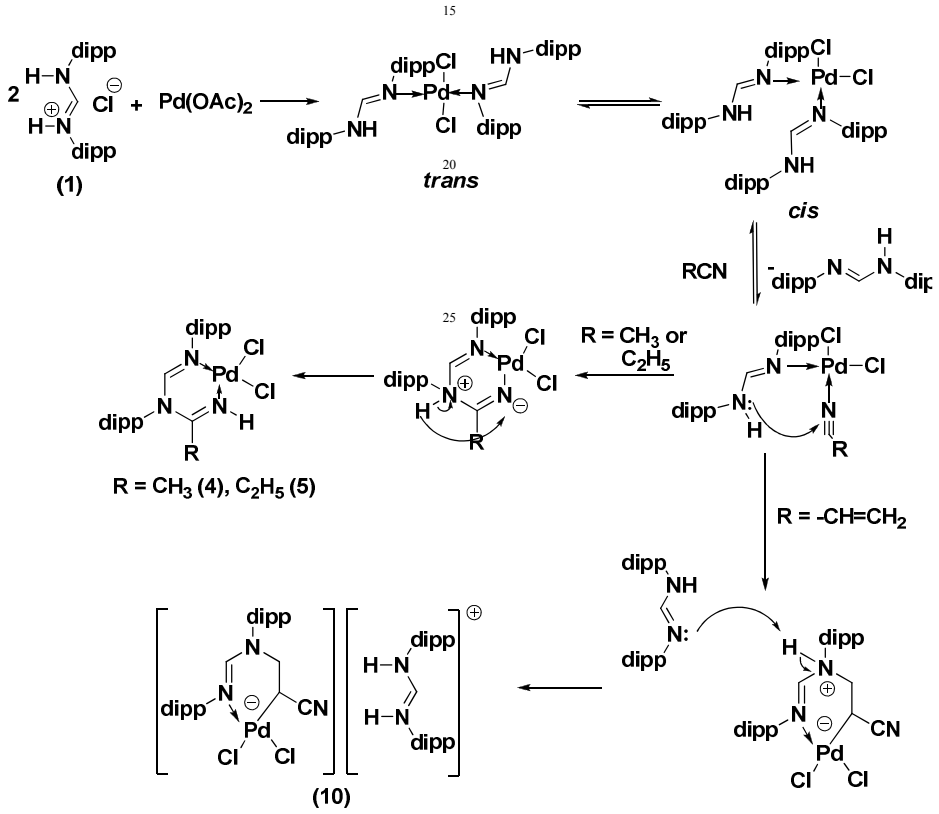


Fig. 3 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **10.** Hydrogen atoms and one solvent DCM molecule have been omitted for clarity.

The molecular structure of **10** and crystallographic parameters are given in Figure 3 and Table 3 (Table S2) respectively. Unlike in **4** and **5**, compound **10** consists of a cyclic and anionic six membered palladacycle containing PdC_3N_2 unit in



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

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 *cis* position to complete the four coordination around palladium centre and thus adopt 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 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 remain uncoordinated as it was observed in 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 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 2.315(1) Å (Figure 3, Table 3 and Table S2).

The formation of **10** can be understood by studying the mechanism for the formations of **4** or **5** as well as known binding modes of acrylonitrile with palladium center as well as 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 *N*-bound or π bound C=C of acrylonitrile to the palladium center is possible, it was shown that the latter mode of binding is known to give 2,1-inserted product containing Pd-C bond formation.[4a,b] Based on the above literatures, we assume that the first step is correlated to the nucleophilic addition of amine from formamidine unit at the methylene electrophilic center of acrylonitrile, like in 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.

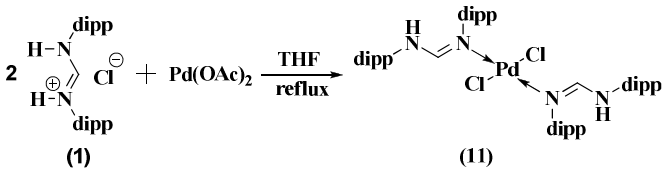
Table 3. Selected bond lengths [Å] and bond angles (deg) for compound **10**.

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)

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 which 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 molecular ion $[M–Cl^-]^+$ peak corresponding to its formation. Further a strong band at 1639 cm^{-1} and 3369 cm^{-1} was observed which could be assigned for ν(C=N) and ν(N-H) respectively in IR spectra. To understand further the formation of

11, the product was crystallized by slow evaporation using dichloromethane/toluene/dimethylsulphoxide mixture to afford yellow coloured crystals (**11** in Figure 4).



Scheme 3 Synthesis of compound **11**

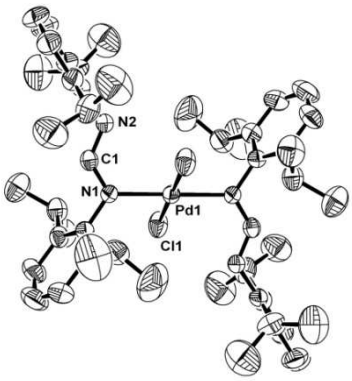


Fig. 4 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **11.** Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): N(1)-Pd(1) 2.056(3), Pd(1)-Cl(1) 2.2913(13), N(1)-Pd(1)-Cl(1) 88.79(8).

The molecular structure of **11**, important bond distances and angles (as legend) are given in Figure 4. It consists of square-planar palladium center which is surrounded by two formamidine ligands coordinated through 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 spectromertric methods, although in case of **10**, additional peaks in ^{1}HNMR 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 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. A cyclic six-membered neutral (in case of acetonitrile and propanenitrile) or anionic (in case of acrylonitrile) palladium complexes were successfully isolated. The neutral tap-palladium dichloride complexes (**4** and **5**) consists of a cyclic six-membered PdC_2N_3 unit of 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** lead 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 palladium centre. Complex **10** depicts the first example of palladacycle derived from acrylonitrile through C-N coupling in the presence of formamidine unit.[12]

Experimental Section

General procedures

All the reactions and manipulations were carried out under 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. Glasswares were 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 by 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 masspectrometry (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 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, N*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.8 (CH_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 $(M\text{-}Cl^-)^+$: 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, C*H*$_3$), 1.33 (d, 6H, C*H*$_3$), 2.85 (br, 2H, C*H*$(CH_3)_2$), 3.06 (br, 2H, C*H*$(CH_3)_2$), 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, N*H*). ^{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 $(M\text{-}(BF_4)^-)^+$.

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, C*H*$_3$), 3.21 (sept., 4H, C*H*$(CH_3)_2$), 7.17 (d, 4H, C_6H_{5meta}), 7.32 (m, 3H, C_6H_{5para} +C_2-*H*), 11.10 (br., 2H, N*H*). ^{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 $(M\text{-}(PF_6)^-)^+$.

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 diethylether 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, C*H*$_3$) 1.22 (d, 6H, CH_3), 1.45 (d, 6H, CH_3), 1.93 (s, 3H, C*H*$_3$-C=NH), 2.87 (sept., 2H, C*H*$(CH_3)_2$), 3.31 (sept., 2H, C*H*$(CH_3)_2$), 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 $[(M\text{-}Cl^-+CH_3CN)]^+$: 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 diethylether 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, C*H*$_3$ + C*H*$_3$CH$_2$), 1.54 (d, 6H, C*H*$_3$), 1.98 (quartet, 2H, CH_3-C*H*$_2$-C=NH), 2.83 (sept., 2H, C*H*$(CH_3)_2$), 3.32 (sept., 2H, C*H*$(CH_3)_2$), 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-H*C*=N), 160.9 (H_2C-*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 $[(M\text{-}Cl^-)+CH_3CN]^+$: 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 diethylether 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, C*H*$_3$) 1.43 (d, 6H, C*H*$_3$), 1.65 (s, 3H, C*H*$_3$-C=NH), 2.72 (sept., 2H, C*H*$(CH_3)_2$), 3.18 (sept., 2H, C*H*$(CH_3)_2$), 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 $(M\text{-}(BF_4)^-)^+$.

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 1mL THF and 15 mL ether and dried under vacuum gave yellow residue. Crystals were obtained by slow evaporation of mixture of chloroform/ethylacetate 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, C*H*$_3$), 1.30 (t, 3H, C*H*$_2$CH$_3$), 1.49 (d, 6H, C*H*$_3$), 2.04 (quartet, 2H, CH$_3$-C*H*$_2$-C=NH), 2.88 (sept., 2H, C*H*$(CH_3)_2$), 3.53 (sept., 2H, C*H*$(CH_3)_2$), 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 $(M\text{-}(BF_4)^-)^+$.

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$_3$CN, 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 1mL 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, CH(CH$_3$)$_2$), 3.14 (m, 2H, CH(CH$_3$)$_2$), 3.26 (m, 3H, CH(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$_6H_{3\ meta\ +para}$ +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 cacld 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% ethylacetate 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$_2$CH_2), 3.10 (sept., 4H, CH(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 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 diethylether 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, CH(CH$_3$)$_2$ minor isomer), 3.44 (sept., 2H, CH(CH$_3$)$_2$ major isomer), 3.78 (sept., 4H, CH(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 diethylether 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 is used as described above except that acrylonitrile (5 mL) is 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.

Acknowledgment

This work was supported by the Department of Science and Technology (DST) and the Council of Scientific and Industrial Research (CSIR), Government of India. V. G. and V. K. thank the University Grants Commission (UGC) and CSIR for their fellowships.

Notes and references

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Graphical Abstract

Cyclic Six-membered Palladium Complexes Derived from Palladium Mediated C-N Coupling of Organonitrile and Formamidine

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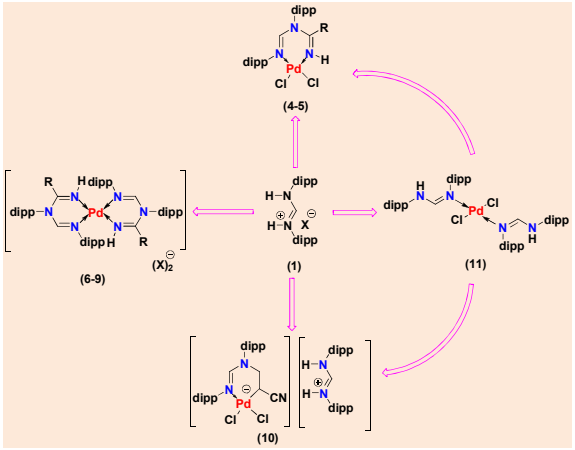
Synthesis and structural characterizations of neutral, cationic and anionic six-membered palladium complexes obtained through palladium mediated C-N bond coupling between organonitrile and formamidinium salt are reported.



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