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Acyclic diaminocarbene complexes of palladium obtained by intermolecular hydroamination of a metal bound isonitrile moiety using secondary amines

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A series of palladium complexes supported over acyclic diaminocarbene (ADC) ligands were conveniently obtained by the hydroamination of a metal bound isonitrile moiety. In particular, the hydroamination reaction using various secondary amines namely, pyrrolidine, morpholine and piperidene on a palladium isonitrile derivative, *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2PdCl_2$, yielded the desired palladium acyclic diaminocarbene (ADC) complexes of the type, *cis*-[(R^1NH)(R^2)methylidene]$PdCl_2$(CNR^1) [R^1 = 2,6-*i*-$Pr_2C_6H_3$: R^2 = NC_4H_8 (**1**); NC_4H_8O (**2**); NC_5H_{10} (**3**)], under ambient reaction conditions in moderate to good yields (*ca*. 68–73%). The structural characterization of the palladium complexes (**1**-**3**) attested to the formation of the metal bound acyclic diaminocarbene ligand via an intermolecular hydroamination reaction on the metal bound isonitrile moiety in a palladium precursor complex.

Keywords: Palladium, acyclic diaminocarbene complexes (ADCs), isonitrile, hydroamination, secondary amines.

Introduction

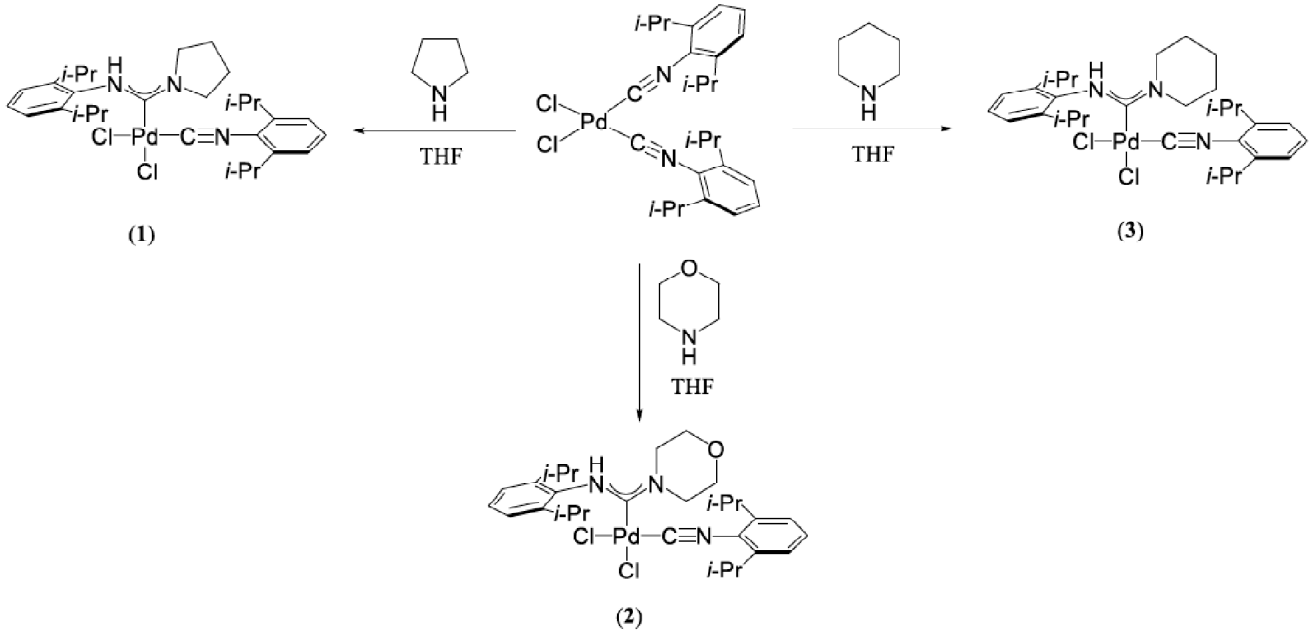
Altogether as a ligand, the acyclic diaminocarbenes (ADCs)[1–4], with greater conformational flexibility, offer a new perspective to the horizons of the N-heterocyclic carbene mediated homogeneous catalysis[5–7]. In this context a systematic comparison of the acyclic diaminocarbenes with the much renowned N-heterocyclic carbenes[8–12] with similar steric and electronic requirements arise interest[13]. For example, the N-heterocyclic carbene based catalyst, {*trans*-(1,3-Me_2-imidazolin-2-ylidene)Pd(PPh_3)$_2$Cl}PF_6, exhibited 84% yield for the amination reaction of bromobenzene with morpholine whereas the acyclic diaminocarbene counterpart, {*trans*-(Me_2N)methylidene(Me_2N)Pd(PPh_3)$_2$Cl}PF_6, showed slightly higher yield of 89% under analogues conditions at 1 mol% of the catalyst loading[13]. The conformational flexibility of the N-substituents of the acyclic diaminocarbenes (ADC) allow for suitable encapsulation of the active sites bearing metal center facilitating the catalysis[14–20]. Subscribing to this viewpoint, we decided to explore the chemistry of transition metal acyclic diaminocarbene complexes, particularly from the perspective of obtaining a comparison with the more successful imidazole derived N-heterocyclic carbene ligands in homogeneous catalysis.

With our interest primarily lying in biomedical applications[21–23] as well as in chemical catalyses[24–27] using transition metal N-heterocyclic carbene ligands of varying motifs namely, imidazole derived N-heterocyclic carbenes[28–36], triazole derived N-heterocyclic carbenes[37–41], abnormal N-heterocyclic carbenes[42–44], oxazolidine-fused N-heterocyclic carbenes[45], tricyclic triazolooxazine based N-heterocyclic carbenes[46], six-membered saturated N-heterocyclic carbenes[47] and acyclic diaminocarbene complexes[48], we set out to synthesize palladium complexes of acyclic diaminocarbenes (ADC) for their potential utility in homogeneous catalysis.

Results and discussion

A new series of acyclic diaminocarbene ligands namely, [(R^1NH)(R^2)methylidene] [R^1 = 2,6-*i*-$Pr_2C_6H_3$: R^2 = NC_4H_8; NC_4H_8O; NC_5H_{10}] were generated on metal platform by intermolecular hydroamination reaction using secondary amines on the C≡N bonds of a metal bound isonitrile precursor complex. Specifically, the reaction of secondary amines namely, pyrrolidine, morpholine and piperidine, with *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2PdCl_2$ gave the corresponding palladium acyclic diaminocarbene complexes of the formula *cis*-

[(R^1NH)(R^2)methylidene]$PdCl_2$(CNR^1) {R^1 = 2,6-*i*-$Pr_2C_6H_3$: R^2 = NC_4H_8 (**1**); NC_4H_8O (**2**); NC_5H_{10} (**3**)} in moderate to good yields (*ca*. 68–73%) as shown in Scheme 1.



Scheme 1. Strategy for the synthesis of the palladium (**1**-**3**) acyclic diaminocarbene complexes.

The ^{13}C NMR spectra of the palladium (**1**-**3**) complexes showed the metal bound Pd-C_{CNR} resonances at 122.8 ppm (**1**), 123.0 ppm (**2**) and 123.7 ppm (**3**) and the Pd-$C_{Carbene}$ resonances at 177.0 ppm (**1**), 178.6 ppm (**2**) and 176.6 ppm (**3**), in agreement with the formation of acyclic diaminocarbene ligands by the intermolecular N-H hydroamination of one of the two metal bound isonitrile moiety with the other one remaining coordinated to the metal center. Further corroboration came from the infrared spectrum that showed the presence of metal bound isonitrile moiety as observed by metal coordinated $\nu_{(C\equiv N)}$ stretching bands appearing at 2189 cm^{-1} (**1**), 2191 cm^{-1} (**2**) and 2189 cm^{-1} (**3**).

Quite interestingly the ^{1}H NMR spectra of the (**1**-**3**) complexes, showed that, while the compound (**1**) existed in two isomeric form in the solution (Fig. 1)[14], the compound (**2**) and (**3**) existed as single isomers. Additionally, the observation of six different sets of methyl resonances for the 2,6-*i*-$Pr_2C_6H_3$ group appearing as doublets suggested the inequivalency of the two isopropylphenyl moieties possibly due to restricted rotational freedom. The ^{13}C NMR signals too supported similar viewpoint as observed from the twelve sets of different aromatic resonances for the (**1**-**3**) complexes.

With the intent of gaining an insight on the pathway of

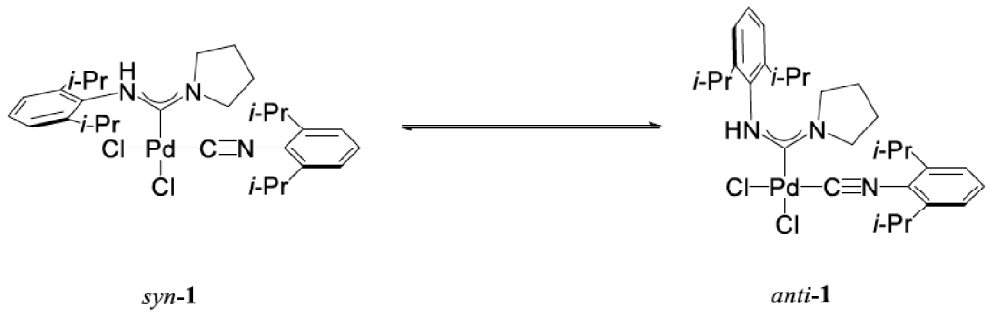


Fig. 1. Conformational *syn*-**1**/*anti*-**1** rotamers of complex **1**.

formation of the acyclic diaminocarbene ligand by an intermolecular N-H hydroamination reaction on a metal bound C≡N isonitrile precursor *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2$PdCl$_2$, we set out to structurally characterize the palladium isonitrile precursor, to see the geometric isomeric form it existed in[49]. It is worth noting that despite the synthesis of the *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2$PdCl$_2$ complex have been reported earlier[14,50], the structural characterization of the same has not been done. As expected of a d^8 configuration, the palladium center in the complex *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2$PdCl$_2$ exhibited square planar geometry as shown in Fig. 2. Indeed, the molecular structure of the *cis*-(2,6-*i*-$Pr_2C_6H_3$)NC]$_2$PdCl$_2$ complex showed the *cis*-disposition of the 2,6-*i*-$Pr_2C_6H_3$ moiety with the acyclic diaminocarbene ligand and also between the two chloride moieties around the palladium center.

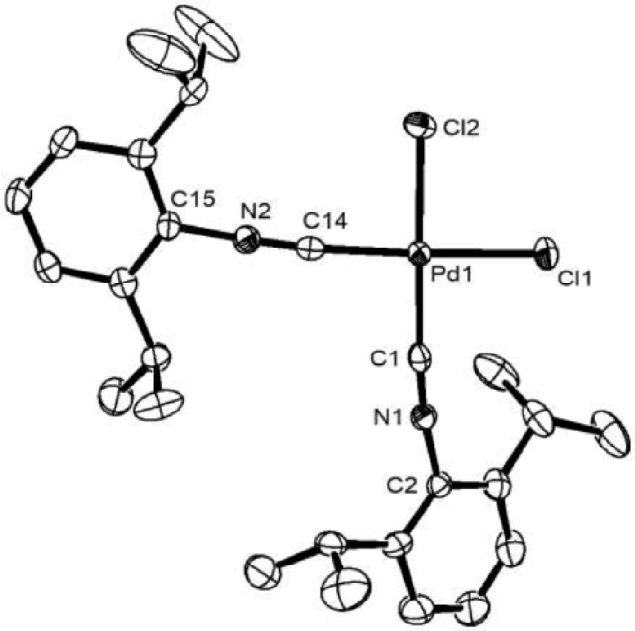


Fig. 2. ORTEP of *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2$PdCl$_2$, with thermal ellipsoids drawn at 50% probability level. Selected bond length (Å) and bond angle (°): Pd1-C1 1.955(3), Pd1-C14 1.940(3), Pd1-Cl2 2.3016(10), Pd1-Cl1 2.3130(10), C1-N1 1.139(4), C14-N2 1.144(4), Cl2-Pd1-Cl1 91.96(4), C1-Pd1-Cl2 178.48(9), C1-Pd1-Cl1 87.21(10), C14-Pd1-Cl2 86.37(9), C14-Pd1-Cl1 175.88(9), C14-Pd1-C1 94.37(13), N1-C1-Pd1 175.2(3), N2-C14-Pd1 173.1(3).

The Pd-C_{CNR} bond distances of 1.955(3) Å and 1.940(3) Å in the *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2$PdCl$_2$ complex are slightly shorter than the sum of individual radii of palladium and carbon (C_{sp}) (2.08 Å)[51] but compare well with the related complexes namely, *cis*-[(C_6H_5)NC]$_2$PdCl$_2$ [1.936(3) Å and 1.929(3) Å][52], *cis*-[(4-$CF_3C_6H_4$)NC]$_2$PdCl$_2$ [1.939(2) Å and 1.933(3) Å][52], *cis*-[(4-FC_6H_4)NC]$_2$PdCl$_2$ [1.941(9) Å and 1.932(9) Å][52], *cis*-[(4-$CH_3C_6H_4$)NC]$_2$PdCl$_2$ [1.938(4) Å and 1.934(5) Å][52], *cis*-[(4-$OMeC_6H_4$)NC]$_2$PdCl$_2$ [1.949(2) Å and 1.923(2) Å][52] and *cis*-[(2,6-$Me_2C_6H_3$)NC]$_2$PdCl$_2$ [1.9333(14) Å and 1.9307(13) Å][52]. Similarly, the Pd-Cl bond distances of 2.3130(10) Å and 2.3016(10) Å in the *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2$PdCl$_2$ complex compare well with its related analogues namely, *cis*-[(C_6H_5)NC]$_2$PdCl$_2$ [2.3086(7) Å and 2.2942(7) Å][52], *cis*-[(4-$CF_3C_6H_4$)NC]$_2$PdCl$_2$ [2.3091(6) Å and 2.3081(6) Å][52], *cis*-[(4-FC_6H_4)NC]$_2$PdCl$_2$ [2.312(2) Å and 2.303(2) Å][52], *cis*-[(4-$CH_3C_6H_4$)NC]$_2$PdCl$_2$ [2.3086(11) Å and 2.3016(11) Å][52], *cis*-[(4-$OMeC_6H_4$)NC]$_2$PdCl$_2$ [2.3131(5) Å and 2.3119(5) Å][52] and *cis*-[(2,6-$Me_2C_6H_3$)NC]$_2$PdCl$_2$ [2.3097(3) Å and 2.3063(3) Å][52].

The structural characterization of the subsequent palladium acyclic diaminocarbene complexes namely, *cis*-[(R^1NH)(R^2)methylidene]PdCl$_2$(CNR^1) {R^1 = 2,6-*i*-$Pr_2C_6H_3$: R^2 = NC_4H_8 (**1**); NC_4H_8O (**2**); NC_5H_{10} (**3**)} indeed showed their monomeric nature with the palladium center in a square planar geometry with one site occupied by an acyclic diaminocarbene moiety and the other sites by a metal based isonitrile moiety and two chloride moieties in a *cis*-disposition to each other as shown in Figs. (3-5). Of particular interest is the Pd-$C_{Carbene}$ distances of 1.9910(15) Å (**1**), 2.006(4) Å (**2**), 2.003(6) Å (**3**) are shorter than the sum of individual palladium and carbon (C_{sp2}) (2.12 Å)[51] but well compared with those of the related analogues namely, *cis*-[(R^1NH)(R^2)methylidene] PdCl$_2$(CNR^1) [R^1 = 2,6-$(CH_3)_2C_6H_3$: R^2 = 2,6-$(CH_3)_2C_6H_3$NH; 2.003 (7) Å[53]; R^1 = C_6H_{11}: R^2 = Ph_2C=N-NH; 1.966(3) Å[54]; R^1 = 2,6-$(CH_3)_2C_6H_3$: R^2 = 5-$(NH_2)C_6H_4$NH, 1.979(3) Å[18]; R^1 = *t*-Bu: R^2 = Ph_2CNH, 1.994(3) Å][19]. The Pd-Cl bond distances of 2.3747(4) Å and 2.3130(5) (**1**), 2.3798(10) Å and 2.2989(9) (**2**), 2.3865(16) Å and 2.3157(16) (**3**) are also in agreement with that observed in the related once reported in literature[18,19,53,54].

The observation of a longer Pd-Cl bond located *trans* to the acyclic diaminocarbene (ADC) ligand [(R^1NH)(R^2) methylidene] [R^1 = 2,6-*i*-$Pr_2C_6H_3$: R^2 = NC_4H_8; NC_4H_8O; NC_5H_{10}], as compared to the Pd-Cl bond located *trans* to the di-*i*-propylphenyl isonitrile ligand in the complexes **1** [2.3747(4) Å, 2.3130(5) Å], **2** [2.3798(10) Å, 2.2989(9) Å] and **3** [2.3865(16) Å, 2.3157(16) Å], indicated stronger *trans*

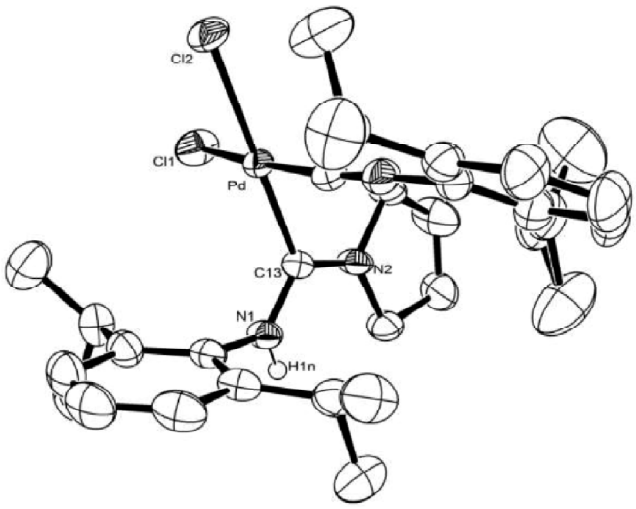


Fig. 3. ORTEP of **1** with thermal ellipsoids drawn at 50% probability level. Selected bond length (Å) and bond angle (°): Pd–C18 1.926(17), Pd-C13 1.991(15), Pd-Cl1 2.313(5), Pd-Cl2 2.374(4), N1-C13 1.332(2), N2-C13 1.322(2), N3-C18 1.147(2), C18-Pd-Cl3 90.82(6), C18-Pd-Cl1 172.12(5), C13-Pd-Cl1 86.73(5), C18-Pd-Cl2 90.02(5), C13-Pd-Cl2 178.90(5), N2-C13-N1 118.36(14), N2-C13-Pd 119.35(11), N1-C13-Pd 122.26(12).

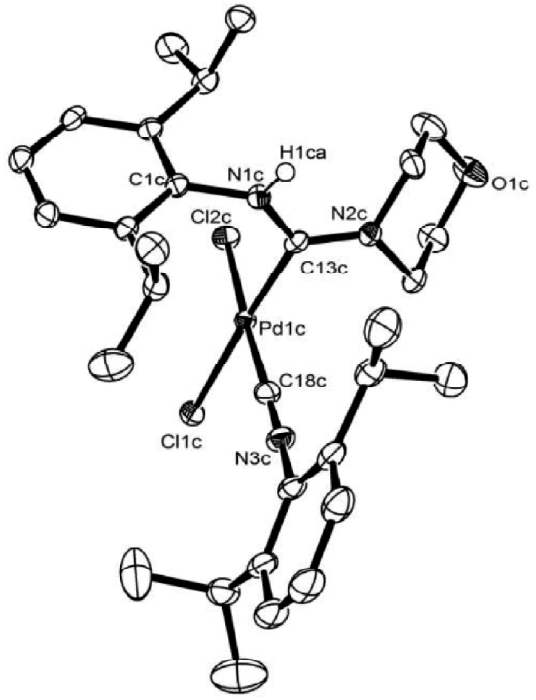


Fig. 4. ORTEP of **2** with thermal ellipsoids drawn at 50% probability level. Selected bond length (Å) and bond angle (°): Pd1C-C13C 2.005(4), Pd1C-Cl1C 2.3800(10), Pd1C-Cl2C 2.3080(9), N1C-C13C 1.337(4), N2C-C13C 1.320(5), N1C-H1CA 0.8800, N2C-C13C-N1C 118.2(3), C13C-Pd1C-Cl1C 176.89(10), C15C-O1C-C16C 110.6(3).

effect of the acyclic diaminocarbene (ADC) ligand, similar to what has been observed in other related complexes namely, *cis*-[(R^1NH)(R^2)methylidene]$PdCl_2$(CNR^1) [R^1 = 2,6-$(CH_3)_2C_6H_3$: R^2 = 2,6-$(CH_3)_2C_6H_3$NH, 2.3838(18) Å, 2.316(2) Å[53]; R^1 = C_6H_{11}: R^2 = Ph_2C=N-NH, 2.3671(17) Å, 2.3232(7) Å[54]; R^1 = 2,6-$(CH_3)_2C_6H_3$: R^2 = 5-$(NH_2)C_6H_4$NH, 2.3843(7) Å, 2.3289(8) Å[18]; R^1 = *t*-Bu: R^2 = Ph_2CNH, 2.3698(8) Å, 2.3241(8) Å][19].

A careful scrutiny of the molecular structure of (**1**-**3**) complexes reveal near equal C=N bond lengths [(**1** N2-C13 1.332(2) Å, N1-C13 1.322(2) Å); **2** (N1c-C13c 1.337(4) Å, N2c-C13c 1.320(5) Å); **3** (N1a-Ca 1.323(7) Å, N2a-C13a 1.320(7) Å)] which falls between a C-N single bond (1.469 Å) in amine[55] and the C=N double bond length (1.279 Å) in imines[55].

In summary, a series of palladium complexes of acyclic diaminocarbene ligands have been conveniently synthesized by intermolecular N-H hydroamination reaction of metal bound C≡N isonitrile species under ambient condition in moderate to good yields. The structural characterization of the palladium (**1**-**3**) complexes reveal their discrete monomeric nature displaying the palladium center in a square planar environment.

Experimental

General procedures:

All manipulations were carried out using of a glovebox and standard Schlenk techniques. $PdCl_2$ was purchased from SD-fine Chemicals (India), pyrrolidine, piperidine, and morpholine were purchased from Spectrochem Pvt. Ltd. (India) and used without any further purification. *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2PdCl_2$[14,50], was synthesized by known literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 400 MHz and 500 MHz NMR spectrometer. ^{1}H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), quartet of doublet (qd) and septet (sept). Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer and Bruker Maxis impact. Elemental analysis was carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer. The X-ray diffraction data were collected on Rigaku Hg 724+ diffractometer and refined by fullmatrix least-squares procedures on F^2 with

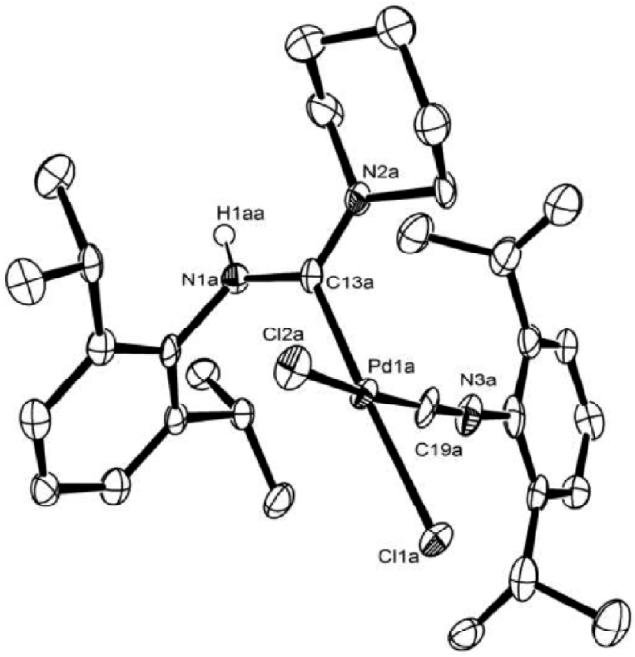


Fig. 5. ORTEP of **3** with thermal ellipsoids drawn at 50% probability level. Selected bond length (Å) and bond angle (°): Pd1A-C13A 2.022(6), Pd1A-Cl1A 2.3878(18), Pd1A-Cl2A 2.3112(17), N1A-C13A 1.323(7), N2A-C13A 1.320(7), N1A-H1AA 0.8800, N2A-C13A-N1A 119.8(6), C13A-N1A-H1AA 118.0, C13A-Pd1A-Cl1A 174.75(16), Cl2A-Pd1A-Cl1A 94.46(6).

SHELXTL (Version 6.10). CCDC 1435625 {*cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2$$PdCl_2$}, 918897 (**1**), 939566 (**2**) and 942019 (**3**), contain the supplementary crystallographic data for this paper (Supporting information). These data can be obtained free of charge from the Cambridge Crystallographic Data center via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of cis-[((2,6-di-i-propylphenylamino)(pyrrolidin-1-yl)methylidene)]$PdCl_2$(2,6-di-i-propylphenylisonitrile) (1)

To a solution of *cis*-[$PdCl_2$(2,6-di-*i*-propylphenyl isonitrile)$_2$] (0.311 g, 0.563 mmol) in THF (*ca.* 10 mL), pyrrolidine (0.040 g, 0.563 mmol) was added at 0ºC. The reaction mixture was stirred overnight at room temperature, after which the solvent was removed under vacuum. The residue was purified by column chromatography using silica gel as a stationary phase and by eluting with a mixed medium, CH_2Cl_2/CH_3OH (99/1 v/v) to give pure product as a yellow solid (0.238 g, 68%). Isomer (*major*). ^{1}H NMR ($CDCl_3$, 400 MHz, 25ºC): δ 7.81 (s, 1H, N*H*), 7.44 (t, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 7.33 (t, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 7.24 (d, 2H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 7.13 (d, 2H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 4.41 (br, 2H, NC_4H_8), 3.35 (sept, 4H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[C*H*(CH_3)$_2$]), 2.69–2.66 (m, 2H, NC_4H_8), 1.90–1.87 (m, 2H, NC_4H_8), 1.79–1.76 (m, 2H, NC_4H_8), 1.31 (d, 12H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 1.15 (d, 6H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 1.09 (d, 6H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2$]). Isomer (*minor*); ^{1}H NMR ($CDCl_3$, 400 MHz, 25ºC): 7.37 (t, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 7.33 (t, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 7.25 (d, 2H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3 [$CH(CH_3)_2$]), 7.18 (d, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 6.66 (s, 1H, N*H*), 4.81–4.75 (m, 2H, NC_4H_8), 4.29–4.25 (m, 2H, NC_4H_8), 3.79–3.61 (m, 2H, NC_4H_8), 3.12 (sept, 4H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[C*H*(CH_3)$_2$]), 2.31–2.02 (m, 2H, NC_4H_8), 1.31 (d, 12H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 1.24 (d, 6H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2$]), 1.22 (d, 6H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2$]). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25ºC): δ 177.0 (NH*C*N), 148.6 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 145.9 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 145.7 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 133.9 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 131.1 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 130.8 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 129.8 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 129.4 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 123.8 {2×(2,6-C_6H_3[$CH(CH_3)_2$]$_2$)}, 123.7 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 123.5 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 122.8 (*C*N–2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 58.6 (NC_4H_8), 50.7 (NC_4H_8), 30.0 (2,6-C_6H_3[*C*H(CH_3)$_2$]$_2$), 29.7 (2,6-C_6H_3 [$CH(CH_3)_2$]$_2$), 29.0 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 28.8 (2,6-C_6H_3[*C*H(CH_3)$_2$]$_2$), 28.5 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 26.7 (NC_4H_8), 25.8 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 25.5 (2,6-C_6H_3 [$CH(CH_3)_2$]$_2$), 24.8 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 24.6 (NC_4H_8), 23.9 (2,6-C_6H_3 [$CH(CH_3)_2$]$_2$), 22.9 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 22.7 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 22.1 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$). IR data (KBr pellet): 3198 (w), 2964 (s), 2874 (w), 2189 (s), 1551 (s), 1463 (m), 801 (m), 750 (m) cm^{-1}. HRMS Calcd. for $[C_{30}H_{43}N_3Cl_2Pd\text{-}Cl]^+$ 586.2180, Found *m/z* 586.2181. Anal. Calcd. for $C_{30}H_{43}Cl_2N_3Pd$: C, 57.84; H, 6.96; N, 6.74. Found: C, 57.83; H, 6.85; N, 6.70%.

Synthesis of cis-[((2,6-di-i-propylphenylamino)(morpholino)methylidene)]$PdCl_2$(2,6-di-i-propylphenylisonitrile) (2)

To a solution of *cis*-$PdCl_2$(2,6-di-*i*-propylphenyl isonitrile)$_2$] (0.202 g, 0.366 mmol) in THF (*ca.* 20 mL), morpholine (0.032 g, 0.366 mmol) was added at 0ºC. The reaction mixture was stirred overnight at room temperature, after which the solvent was removed under vacuum. The residue was purified by column chromatography using silica gel as a stationary

Table 1. X-Ray crystallographic data for complexes *cis*-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2PdCl_2$, **1**, **2** and **3**

	cis-[(2,6-*i*-$Pr_2C_6H_3$)NC]$_2PdCl_2$	**1**	**2**	**3**
Lattice	monoclinic	monoclinic	monoclinic	monoclinic
Formula	$C_{26}H_{34}Cl_2N_2Pd$	$C_{30}H_{43}Cl_2N_3Pd$	$C_{30}H_{43}Cl_2N_3O_1Pd$	$C_{31}H_{45}Cl_2N_3Pd$
Formula weight	551.85	622.97	638.97	637.00
Space group	P 1 21/n 1	P21/c	P21/n	P21/n
a (Å)	12.339(4)	11.3366(2)	16.831(3)	16.667(6)
b (Å)	13.369(4)	16.6592(3)	24.229(3)	23.321(8)
c (Å)	15.926(5)	16.4658(3)	16.994(3)	18.126(5)
α (°)	90.00	90.00	90.00	90.00
β (°)	91.247(6)	97.887(2)	117.404(2)	117.28(2)
γ (°)	90.00	90.00	90.00	90.00
V (Å^3)	2626.5(14)	3080.29(10)	6152.4(17)	6262(4)
Z	4	4	8	8
Temperature (K)	150(2)	296(2)	100(2)	100(2)
Radiation (λ, Å)	0.7107	0.71073	0.71073	0.71075
ρ (calcd.) (g cm^{-3})	1.396	1.343	1.380	1.351
μ (Mo Kα) mm^{-1}	0.925	0.798	0.803	0.787
θ max (deg.)	25.00	32.7436	25.25	25.00
No. of parameters	278	362	583	659
R_1	0.0363	0.0403	0.0470	0.0719
wR_2	0.0820	0.0795	0.1246	0.1644
GOF	1.058	1.166	1.138	1.259

phase and by eluting with a mixed medium, CH_2Cl_2/CH_3OH (99/1 v/v) to give pure product as a yellow solid (0.172 g, 73%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25ºC): δ 8.09 (s, 1H, N*H*), 7.45 (t, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 7.34 (t, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 7.24 (d, 2H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 7.18–7.16 (m, 2H, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 5.00–4.67 (m, 2H, NC_4H_8O), 4.14–3.87 (m, 4H, NC_4H_8O), 3.38–3.34 (m, 4H, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 3.12–2.96 (m, 2H, NC_5H_{10}), 1.32 (d, 12H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 1.29 (d, 3H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 1.23–1.21 (m, 6H, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 1.09–1.07 (m, 3H, 2,6-C_6H_3[$CH(CH_3)_2$]$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25ºC): δ 178.6 (NH*C*N), 146.0 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 145.9 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 134.3 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 131.5 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 131.3 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 131.2 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 130.9 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 130.1 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 124.3 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 124.1 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 123.9 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 123.8 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 123.0 (*C*N-2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 67.1 (NC_4H_8O), 66.1 (NC_4H_8O), 57.4 (NC_4H_8O), 49.7 (NC_4H_8O), 30.1 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 29.9 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 29.8 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 29.1 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 28.5 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 26.0 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 25.7 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 24.8 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 23.1 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 22.9 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 22.8 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$), 22.4 (2,6-C_6H_3[$CH(CH_3)_2$]$_2$). IR data (KBr pellet): 3119 (m), 2965 (s), 2869 (w), 2191 (s), 1589 (w), 1550 (s), 1462 (m), 1113 (m), 1025 (w), 800 (m), 750 (m) cm^{-1}. HRMS Calcd. for $[C_{30}H_{43}N_3Cl_2OPd\text{-}Cl]^+$ 602.2132, Found *m/z* 602.2131. Anal. Calcd. for $C_{30}H_{43}Cl_2N_3OPd$: C, 56.39; H, 6.78; N, 6.58. Found: C, 56.88; H, 7.10; N, 6.58%.

Synthesis of cis-[((2,6-di-i-propylphenylamino)(piperidin-1-yl)methylidene)]PdCl$_2$(2,6-di-i-propylphenylisonitrile) (3)

To a solution of *cis*-[$PdCl_2$(2,6-di-*i*-propylphenyl isonitrile)$_2$]

(0.203 g, 0.368 mmol) in THF (*ca.* 20 mL), piperidine (0.031 g, 0.368 mmol) was added at 0ºC. The reaction mixture was stirred overnight at room temperature, after which the solvent was removed under vacuum. The residue was purified by column chromatography using silica gel as a stationary phase and by eluting with a mixed medium, CH_2Cl_2/CH_3OH (99/1 v/v) to give pure product as a yellow solid (0.164 g, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25ºC): δ 7.69 (s, 1H, N*H*), 7.44 (t, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2]_2$), 7.32 (t, 1H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2]_2$), 7.24 (d, 2H, $^3J_{HH}$ = 8Hz, 2,6-C_6H_3[$CH(CH_3)_2]_2$), 7.16 (br, 2H, 2,6-C_6H_3 [$CH(CH_3)_2]_2$), 4.72–4.31 (m, 4H, NC_5H_{10}), 3.39 (sept, 4H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2]_2$), 3.12–3.01 (m, 4H, NC_5H_{10}), 1.87–1.83 (m, 1H, NC_5H_{10}), 1.48 (br, 1H, NC_5H_{10}), 1.32 (d, 12H, $^3J_{HH}$ = 7Hz, 2,6-C_6H_3[$CH(CH_3)_2]_2$), 1.25 (br, 6H, 2,6-C_6H_3 [$CH(CH_3)_2]_2$), 1.17 (br, 6H, 2,6-C_6H_3 [$CH(CH_3)_2]_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25ºC): ´ 176.6 (NH*C*N), 146.9 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 146.5 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 146.0 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 134.8 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 131.9 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 131.5 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 131.1 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 131.0 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 129.6 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 124.1 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 123.9 {2×(2,6-C_6H_3[$CH(CH_3)_2]_2$)}, 123.7 (*C*N-2,6-C_6H_3 [$CH(CH_3)_2]_2$), 59.0 (NC_5H_{10}), 49.9 (NC_5H_{10}), 49.8 (NC_5H_{10}), 44.9 (NC_5H_{10}), 31.7 (NC_5H_{10}), 30.1 (2,6-C_6H_3[*C*$H(CH_3)_2]_2$), 30.0 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 29.9 (2,6-C_6H_3[*C*$H(CH_3)_2]_2$), 29.8 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 27.4 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 26.4 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 26.0 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 23.9 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 23.1 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 23.0 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 22.8 (2,6-C_6H_3[$CH(CH_3)_2]_2$), 22.4 (2,6-C_6H_3[$CH(CH_3)_2]_2$). IR data (KBr pellet): 3219 (s), 2964 (s), 2867 (w), 2189 (s), 1551 (s), 1464 (m), 1329 (m), 1242 (m), 1022 (w), 801 (m), 750 (m) cm^{-1}. HRMS Calcd. for $[C_{31}H_{45}N_3Cl_2Pd\text{-}Cl]^+$ 600.2340, Found *m/z* 600.2369. Anal. Calcd. for $C_{31}H_{45}Cl_2N_3Pd$: C, 58.45; H, 7.12; N, 6.60. Found: C, 57.90; H, 6.84; N, 7.54%.

Supporting information

The ^{1}H NMR, ^{13}C{^{1}H} NMR, IR, HRMS, and the CHN data of the ADC palladium complexes (**1**-**3**); CIF file giving X-ray crystallographic data associated with this article can be found in the journal webpage. This material is available free of charge via the journal webpage.

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