Supporting information

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

Vivek Gupta, Vedhagiri Karthik, and Ganapathi Anantharaman*[a]

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur – 208016, India.

CORRESPONDING AUTHOR FOOTNOTE: * To whom correspondence should be addressed.

E-mail: garaman@iitk.ac.in, phone +91-512-2597517, fax +91-512-2597436

Table S1 Crystallographic data for **1**, **4-7**

Identification code	**1**	**4**	**5**	**6**	**7**
Formula	$C_{25}H_{37}ClN_2$	$C_{27}H_{39}Cl_2N_3Pd$	$C_{29}H_{42}Cl_5N_3Pd$	$C_{54}H_{78}B_2F_8N_6Pd$	$C_{56}H_{82}B_2F_8N_6Pd$
Fw	401.02	582.91	716.31	1091.24	1119.30
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P-1	$Pbca$	$P2_1/n$	$P2_1/n$
a, Å	11.682(7)	10.4915(7)	12.857(5)	11.3947(6)	11.417(5)
b, Å	17.097(10)	12.1600(8)	21.354(5)	12.3625(6)	12.755(5)
c, Å	12.553(7)	13.8790(9)	23.497(5)	19.4057(9)	19.529(5)
α, deg	90	68.813(10)	90.000(5)	90	90
β, deg	103.143(11)	68.158(10)	90.000(5)	98.3820(10)	97.614(1)
γ, deg	90	75.069(2)	90.000(5)	90	90
V, Å^3	2442(2)	1516.83(17)	6451(3)	2704.4(2)	2818.8(18)
Z	4	2	8	2	2
ρcalcd, g cm-3	1.091	1.276	1.475	1.340	1.319
μ, mm-1	0.168	0.806	1.013	0.412	0.397
F(000)	872	604	2944	1144	1176
Reflections collected	12698	10658	34159	20061	16405
Independent reflections, R(int)	4517, 0.0867	5622, 0.0279	6304, 0.0459	5301, 0.0310	5525, 0.0550
Completeness to θ (%)	99.5 %	99.5 %	99.5 %	99.9 %	99.9 %
Data / restraints / parameters	4517 / 0 / 261	5622 / 0 / 307	6304 / 0 / 352	5301 / 0 / 331	5525 / 0 / 340
GOF on F^2	1.032	1.045	1.169	1.049	1.046
Final R indices [I>2sigma(I)]	$R1$ = 0.0791, $wR2$ = 0.1945	$R1$ = 0.0342, $wR2$ = 0.0814	$R1$ = 0.0380, $wR2$ = 0.0971	$R1$ = 0.0297, $wR2$ = 0.0661	$R1$ = 0.0413, $wR2$ = 0.0830
R indices (all data)	$R1$ = 0.1199, $wR2$ = 0.2263	$R1$ = 0.0451, $wR2$ = 0.0845	$R1$ = 0.0480, $wR2$ = 0.1194	$R1$ = 0.0394, $wR2$ = 0.0702	$R1$ = 0.0777, $wR2$ = 0.1028
Largest diff. peak and hole/ e Å^{-3}	0.737 and -0.544	1.547 and -0.385	2.670 and -0.704	0.661 and -0.376	0.485 and -0.399
CCDC no.	1014314	1014315	1014316	1020744	1020745

Table S2 Crystallographic data for **8-11**

Identification code	**8**	**9**	**10**	**11**
Formula	$C_{54}H_{78}F_{12}N_6P_2Pd$	$C_{56}H_{82}F_{12}N_6P_2Pd$	$C_{54}H_{77}Cl_4N_5Pd$	$C_{50}H_{72}Cl_2N_4Pd$
Fw	1207.56	1235.62	1044.41	906.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	P-1
a, Å	10.4943(18)	11.370(2)	10.2658(18)	10.132(5)
b, Å	21.691(4)	13.036(3)	14.678(3)	12.087(5)
c, Å	12.734(2)	19.856(4)	36.568(6)	12.675(5)
α, deg	90	90	90	98.951(5)
β, deg	90.428(3)	96.279(3)	97.918(3)	102.976(5)
γ, deg	90	90	90	102.750(5)
V, Å^3	2898.6(8)	2925.4	5457.5(17)	1440.5(11)
Z	2	2	4	1
ρcalcd, g cm-3	1.384	1.403	1.271	1.045
μ, mm-1	0.454	0.452	0.575	0.445
F(000)	1256	1288	2200	480
Reflections collected	15376	15379	29117	13618
Independent reflections, R(int)	5342, 0.0302	5409, 0.0399	10110, 0.0475	5336, 0.0392
Completeness to θ (%)	99.0 %	99.5 %	99.3 %	99.4 %
Data / restraints / parameters	5342 / 30 / 349	5409 / 0 / 358	10110 / 0 / 593	5336 / 0 / 267
GOF on F^2	1.090	1.089	1.058	1.052
Final R indices [I>2sigma(I)]	$R1$ = 0.0725, $wR2$ = 0.2024	$R1$ = 0.0661, $wR2$ = 0.1783	$R1$ = 0.0532, $wR2$ = 0.1376	$R1$ = 0.0513, $wR2$ = 0.1243
R indices (all data)	$R1$ = 0.0827, $wR2$ = 0.2164	$R1$ = 0.0833, $wR2$ = 0.1977	$R1$ = 0.0750, $wR2$ = 0.1849	$R1$ = 0.0662, $wR2$ = 0.1304
Largest diff. peak and hole/ e Å^{-3}	2.402 and -1.495	1.802 and -1.067	1.215 and -0.729	0.472 and -0.402
CCDC no.	1020746	1020747	1014317	1014318

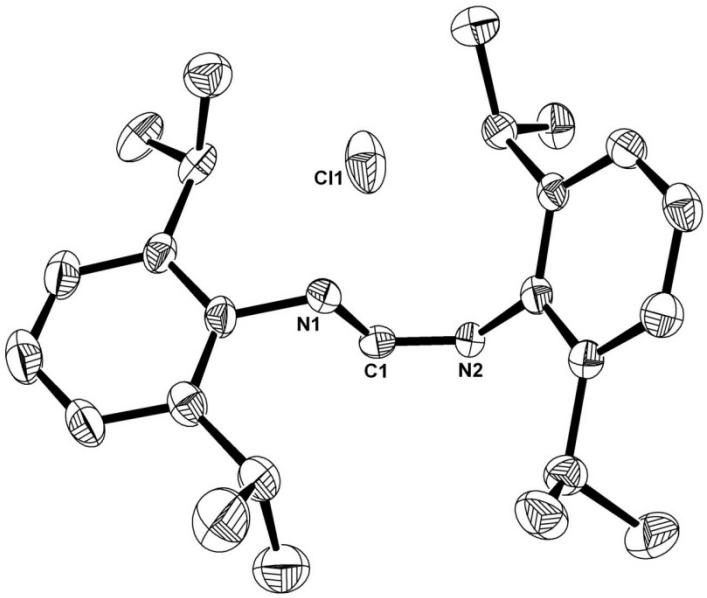
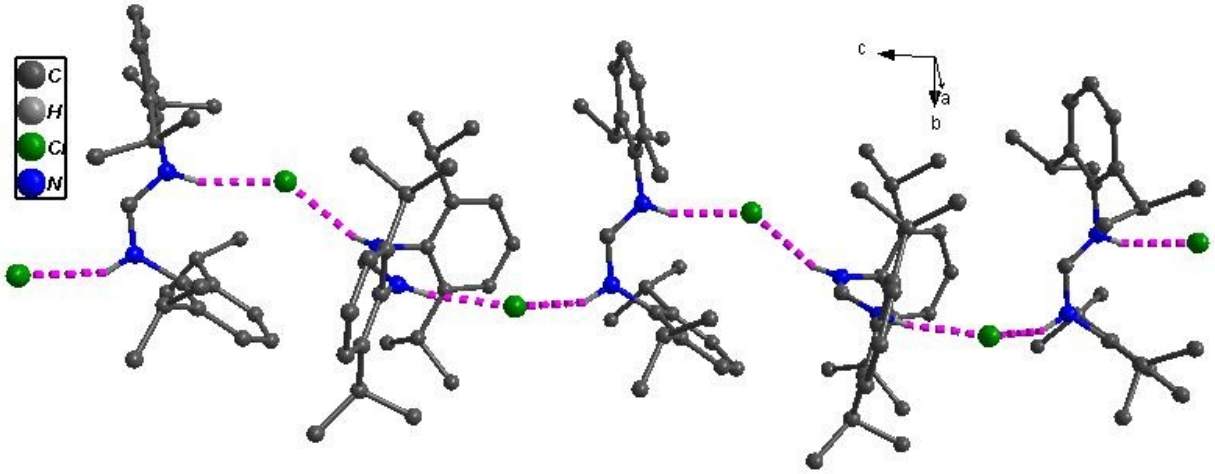


Figure S1: ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for compound **1.** Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-N(1) 1.293(4), C(1)-N(2) 1.314(4), N(1)-C(1)-N(2) 126.1(3).



(A···H-D)	*d* (A···H-D) (Å)	*d* (A···D) (Å)	< (A···H-D)(°)
Cl1···H1A-N1	2.24(3)	3.05(8)	154.08(1)
Cl1···H2-N2	2.32(1)	3.01(2)	135.49(1)

Figure S2

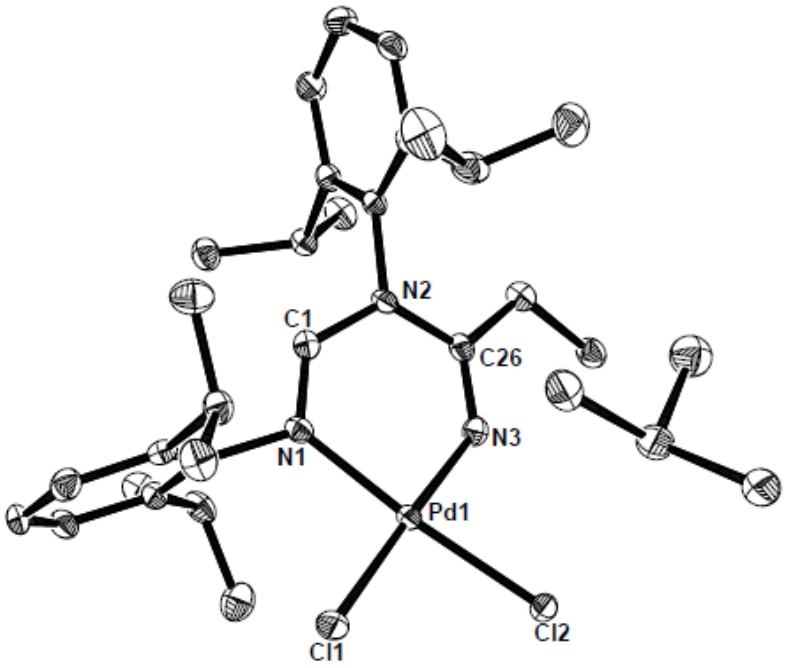


Figure S3: ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **5.** Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg):C(1)-N(1) 1.284(4), C(1)-N(2) 1.385(4), C(26)-N(3) 1.282(4), N(1)-Pd(1) 2.019(3), N(3)-Pd(1) 1.978(3), N(3)-Pd(1)-N(1) 87.27(9), N(1)-Pd(1)-Cl(1) 94.51(7), N(3)-Pd(1)-Cl(2) 87.23(7), Cl(1)-Pd(1)-Cl(2) 90.98(3).

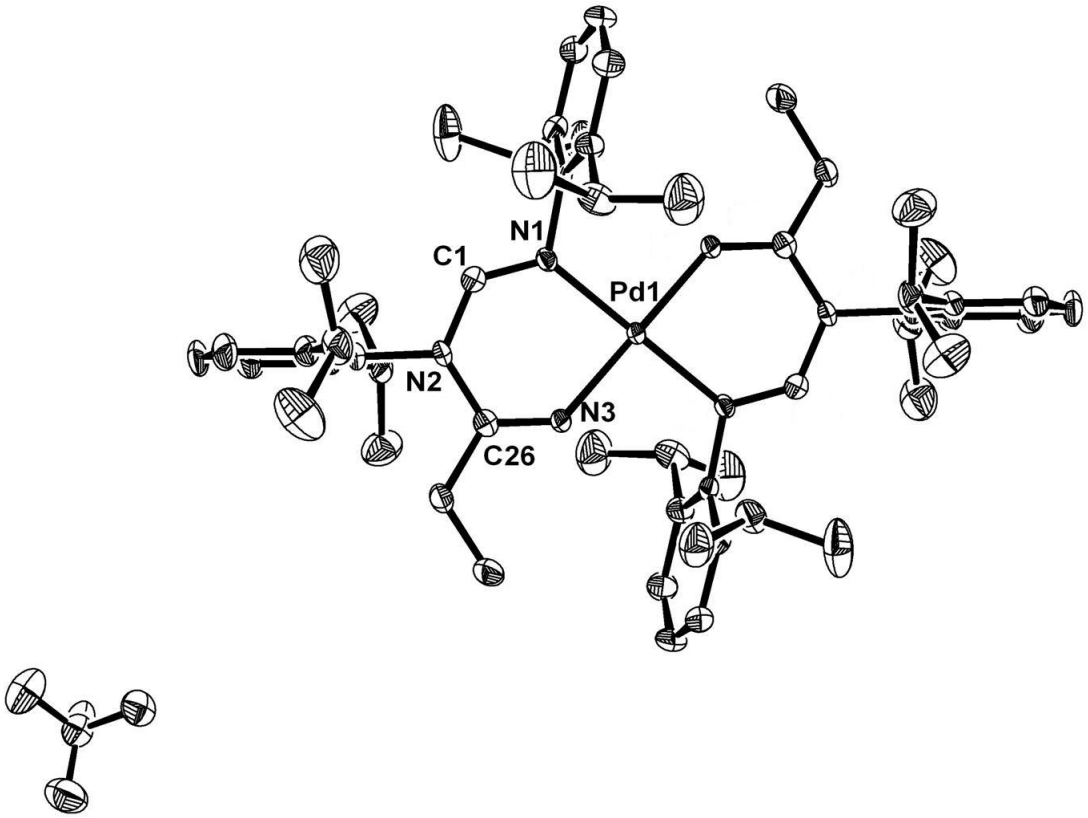


Figure S4: ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **7.** Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg):C(1)-N(1) 1.284(4), C(1)-N(2) 1.360(4), C(26)-N(3) 1.282(4), N(1)-Pd(1) 2.009(3), N(3)-Pd(1) 1.985(2), N(3)-Pd(1)-N(1) 86.56(10).

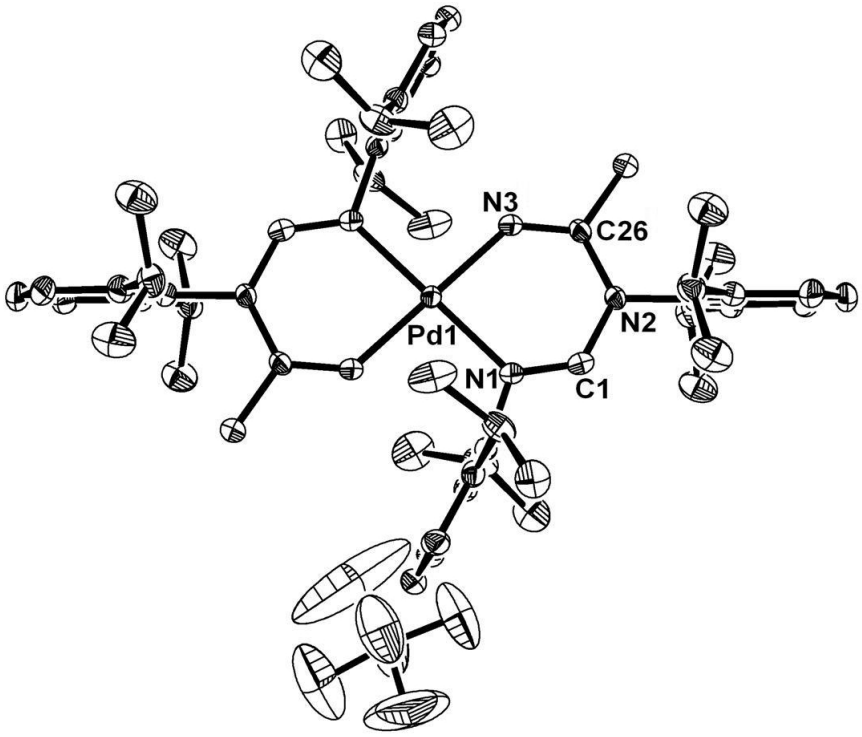


Figure S5: ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **8.** Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg):C(1)-N(1) 1.275(7), C(1)-N(2) 1.374(6), C(26)-N(3) 1.282(7), N(1)-Pd(1) 2.021(4), N(3)-Pd(1) 1.975(4), N(3)-Pd(1)-N(1))#1 86.18(17).

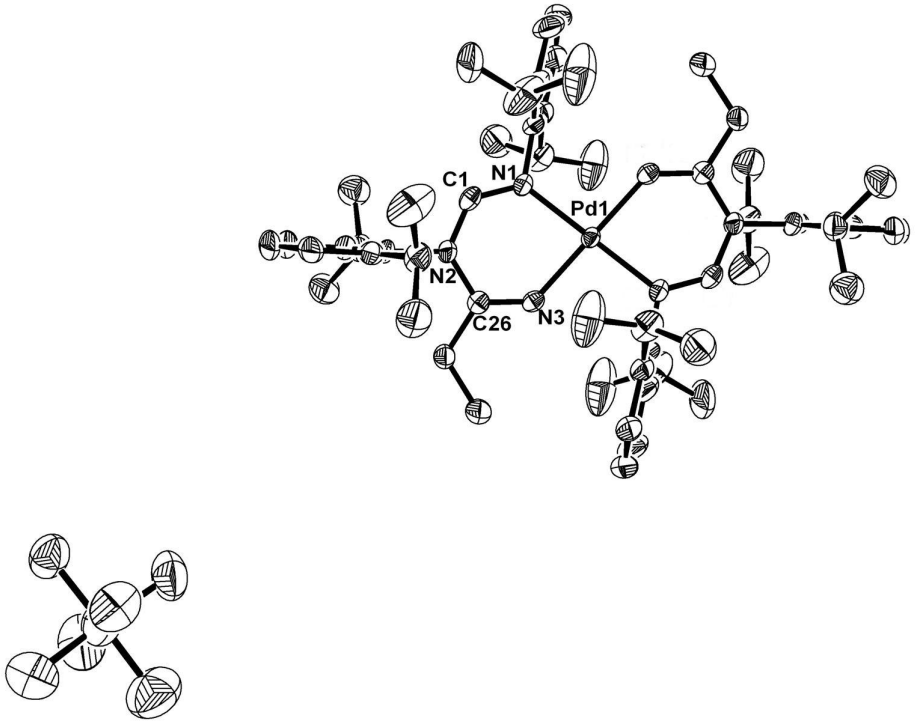


Figure S6: ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **9.** Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg):C(1)-N(1) 1.282(6), C(1)-N(2) 1.359(6), C(26)-N(3) 1.278(6), N(1)-Pd(1) 2.017(4), N(3)-Pd(1) 2.000(4), N(3)-Pd(1)-N(1) 86.05(16).

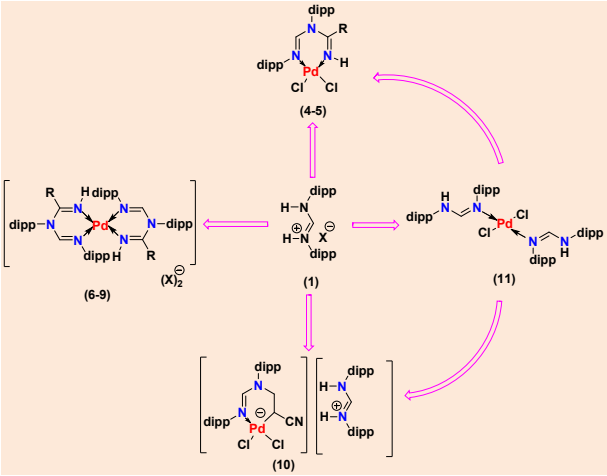
Graphical Abstract

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

Vivek Gupta, Vedhagiri Karthik, and Ganapathi Anantharaman*[a]

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur – 208016, India.

Synthesis and structural characterization of neutral, cationic and anionic six-membered palladium complexes via Pd mediated C-N bond coupling between organonitrile and formamidinium salt.



CORRESPONDING AUTHOR FOOTNOTE: * To whom correspondence should be addressed.

E-mail: garaman@iitk.ac.in, phone +91-512-2597517, fax +91-512-2597436