Electronic Supplementary Material (ESI) for RSC Advances

Electronic Supplementary Information

Directed synthesis of bis-benzaldehyde thiosemicarbazone complexes of palladium having *cis*-geometry: Structure determination and catalytic application for C–C coupling

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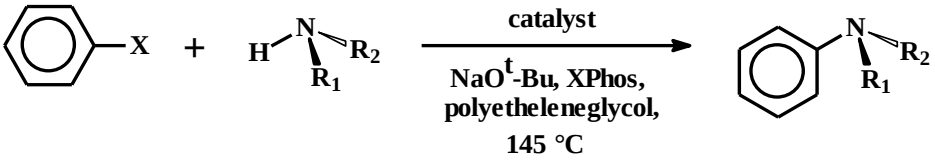
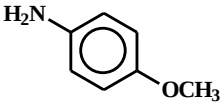
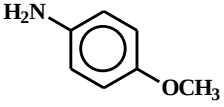
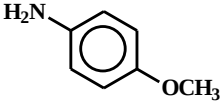
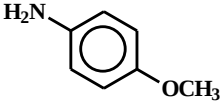
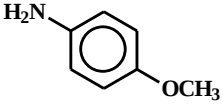
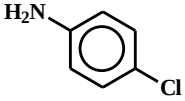
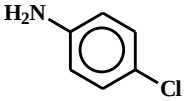
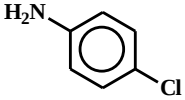
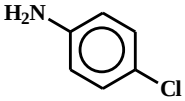
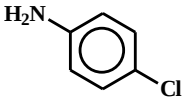
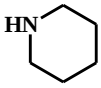
Table S1 Selected bond distances and bond angles for [Pd(NS-CH_3)$_2$], [Pd(NS-Cl)$_2$], [Pd(CNS-H)(PPh_3)] and [Pd(CNS-Cl)(PPh_3)]

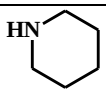
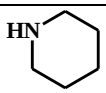
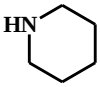
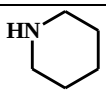
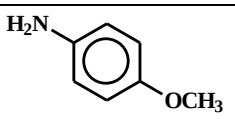
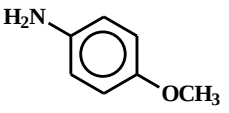
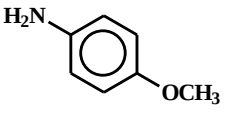
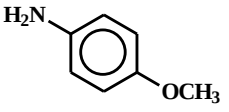
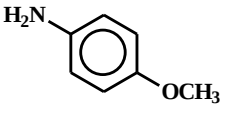
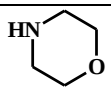
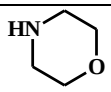
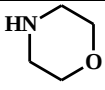
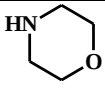
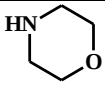
[Pd(NS-CH_3)$_2$]			
Bond distances (Å)			
Pd1-N1	2.069(4)	Pd1-N4	2.075(3)
Pd1-S1	2.2642(12)	Pd1-S2	2.2471(14)
N1-C8	1.269(6)	N4-C17	1.282(5)
N1-N2	1.410(5)	N4-N5	1.398(5)
N2-C9	1.300(6)	N5-C18	1.299(5)
C9-S1	1.735(5)	C18-S2	1.756(4)
C9-N3	1.370(5)	C18-N6	1.354(5)
Bond angles (°)			
N1-Pd1-S2	172.15(10)	N1-Pd1-S1	81.99(9)
N4-Pd1-S1	171.22(9)	N4-Pd1-S2	82.36(11)
[Pd(NS-Cl)$_2$]			
Bond distances (Å)			
Pd1-N1	2.08(3)	Pd1-N4	2.15(2)
Pd1-S1	2.275(9)	Pd1-S2	2.257(9)
N1-C7	1.44(4)	N4-C15	1.18(4)
N1-N2	1.39(4)	N4-N5	1.44(3)
N2-C8	1.25(5)	N5-C16	1.27(4)
C8-S1	1.71(4)	C16-S2	1.80(3)
C8-N3	1.34(5)	C16-N6	1.41(4)
Bond angles (°)			
N1-Pd1-S2	169.9(8)	N1-Pd1-S1	81.6(8)
N4-Pd1-S1	171.0(7)	N4-Pd1-S2	83.3(6)
[Pd(CNS-H)(PPh_3)]			
Bond distances (Å)			
Pd1-C2	2.08(3)	C7- N1	1.33(4)
Pd1-N1	2.06(2)	N1-N2	1.35(3)

Pd1-S1	2.332(8)	N2-C8	1.28(4)
Pd1-P1	2.243(8)	C8-S1	1.76(3)
		C8-N3	1.36(4)
Bond angles (°)			
N1-Pd1-P1	177.4(6)	N1-Pd1-S1	80.4(6)
C2-Pd1- S1	164.1(8)	N1-Pd1-C2	84.1(9)
[Pd(CNS-Cl)(PPh_3)]			
Bond distances (Å)			
Pd1-C2	2.046(2)	C7- N1	1.280(4)
Pd1-N1	2.0297(19)	N1-N2	1.375(3)
Pd1-S1	2.3479(9)	N2-C8	1.299(4)
Pd1-P1	2.2503(5)	C8-S1	1.753(2)
		C8-N3	1.351(4)
Bond angles (°)			
N1-Pd1-P1	176.91(6)	N1-Pd1-S1	81.79(6)
C2-Pd1- S1	163.08(6)	N1-Pd1-C2	81.33(8)

Table S2 Effect of variation of reaction time on C-N cross-coupling reaction of aryl halides with amines[a]



Entry	X	amine	Catalyst	Amt of cat., mol%	Time, h	Yield[b], %	TON
1	I		[Pd(NS-H)$_2$]	0.01	24	100	10 000
2	I		[Pd(NS-H)$_2$]	0.01	22	95	9500
3	I		[Pd(NS-H)$_2$]	0.01	20	76	7600
4	I		[Pd(NS-H)$_2$]	0.01	18	56	5600
5	I		[Pd(NS-H)$_2$]	0.01	16	29	2900
6	I		[Pd(NS-H)$_2$]	0.01	24	100	10 000
7	I		[Pd(NS-H)$_2$]	0.01	22	97	9700
8	I		[Pd(NS-H)$_2$]	0.01	20	80	8000
9	I		[Pd(NS-H)$_2$]	0.01	18	46	4600
10	I		[Pd(NS-H)$_2$]	0.01	16	32	3200
11	I		[Pd(NS-H)$_2$]	0.01	24	100	10 000

12	I		[Pd(NS-H)$_2$]	0.01	22	96	10 000
13	I		[Pd(NS-H)$_2$]	0.01	20	72	10 000
14	I		[Pd(NS-H)$_2$]	0.01	18	58	10 000
15	I		[Pd(NS-H)$_2$]	0.01	16	30	10 000
16	Br		[Pd(NS-H)$_2$]	0.1	24	100	1000
17	Br		[Pd(NS-H)$_2$]	0.1	22	89	890
18	Br		[Pd(NS-H)$_2$]	0.1	20	67	670
19	Br		[Pd(NS-H)$_2$]	0.1	18	35	350
20	Br		[Pd(NS-H)$_2$]	0.1	16	19	190
21	Br		[Pd(NS-H)$_2$]	0.1	24	100	1000
22	Br		[Pd(NS-H)$_2$]	0.1	22	88	880
23	Br		[Pd(NS-H)$_2$]	0.1	20	63	630
24	Br		[Pd(NS-H)$_2$]	0.1	18	37	370
25	Br		[Pd(NS-H)$_2$]	0.1	16	23	230

[a] Reaction conditions: aryl halide (1.0 mmol), amines (1.0 mmol), NaO^t-Bu (1.7 mmol), Pd catalyst, polyetheleneglycol (2 mL).
[b] Determined by GCMS.

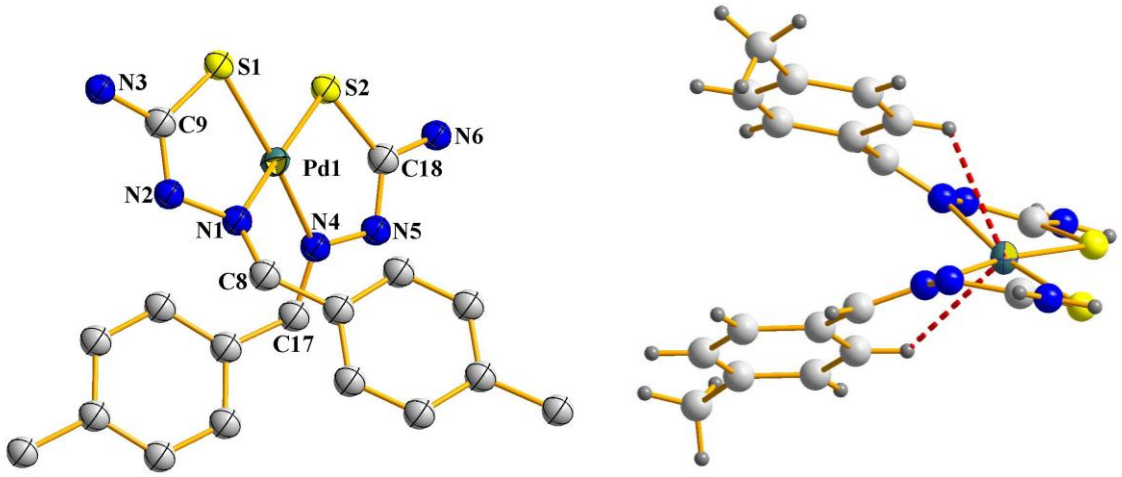
Table S3 Crystallographic data for $[Pd(NS\text{-}CH_3)_2]$, $[Pd(NS\text{-}Cl)_2]$, $[Pd(CNS\text{-}H)(PPh_3)]$ and $[Pd(CNS\text{-}Cl)(PPh_3)]$

Complex	$[Pd(NS\text{-}CH_3)_2]$	$[Pd(NS\text{-}Cl)_2]$	$[Pd(CNS\text{-}H)(PPh_3)]$	$[Pd(CNS\text{-}Cl)(PPh_3)]$
Empirical formula	$C_{18}H_{20}N_6S_2Pd$	$C_{16}H_{14}N_6S_2Cl_2Pd$	$C_{26}H_{22}N_3OPSPd$	$C_{26}H_{21}N_3PSClPd$
Formula weight	490.96	531.79	561.93	580.37
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1$	$P\bar{1}$	$P\bar{1}$
a/Å	17.3130(7)	7.908(4)	9.9825(10)	9.9226(3)
b/Å	13.4192(6)	26.302(14)	10.0841(10)	10.9475(3)
c/Å	19.7406(9)	9.794(5)	26.259(3)	12.4090(3)
α/°	90	90	100.477(5)	91.136(1)
β/°	115.153(2)	90.686(7)	93.419(6)	107.096(1)
γ/°	90	90	96.826(5)	109.299(1)
V/Å^3	4151.4(3)	2037.0(18)	2571.9(5)	1205.73(6)
Z	8	4	4	2
D_{calcd} /mg m^{-3}	1.571	1.734	1.451	1.599
F(000)	1984	1056	1136	584
λ/Å	0.71073	0.71073	0.71073	0.71073
crystal size /mm^3	0.23 × 0.24 × 0.25	0.14 × 0.15 × 0.18	0.24 × 0.24 × 0.25	0.21 × 0.23 × 0.25
Temp./K	273	273	296	273
μ/mm^{-1}	1.110	1.392	0.887	1.053
Collected reflections	25456	9566	28006	19534
R_{int}	0.049	0.094	0.069	0.019
Independent reflections	6277	4042	7388	5492
$R1$[a]	0.0335	0.1218	0.2018	0.0246
$wR2$[b]	0.1231	0.3127	0.4961	0.0744
GOF[c]	0.85	1.97	1.32	0.82

[a] $R1 = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$.

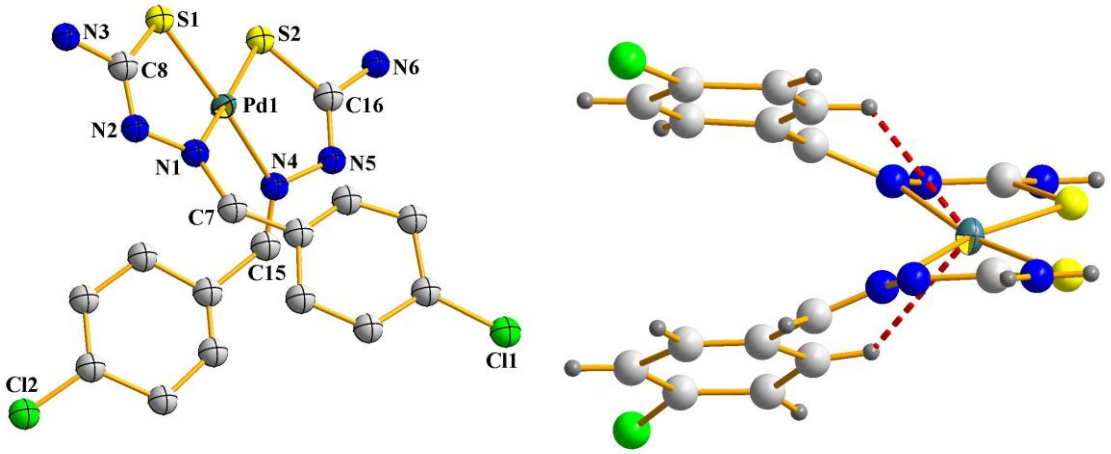
[b] $wR2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$.

[c] $GOF = [\Sigma(w(F_o^2-F_c^2)^2)/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.



(a) **(b)**

Fig. S1(a) Structure of [Pd(NS-CH_3)$_2$] with atom numbering scheme and, (b) another view of the same structure showing agostic interaction between the ortho C-H and palladium.



(a) **(b)**

Fig. S2(a) Structure of [Pd(NS-Cl)$_2$] with atom numbering scheme and, (b) another view of the same structure showing agostic interaction between the ortho C-H and palladium.

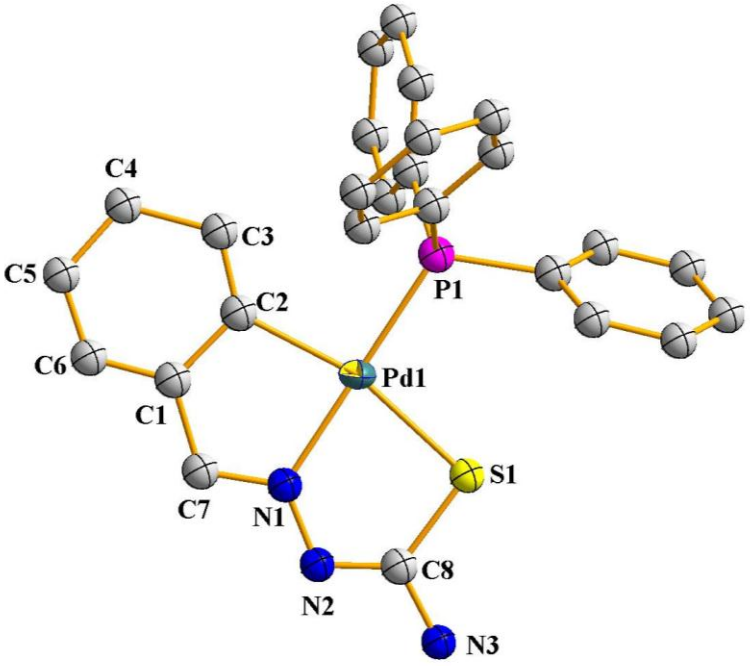


Fig. S3 Structure of [Pd(CNS-H)(PPh_3)] with atom numbering scheme.

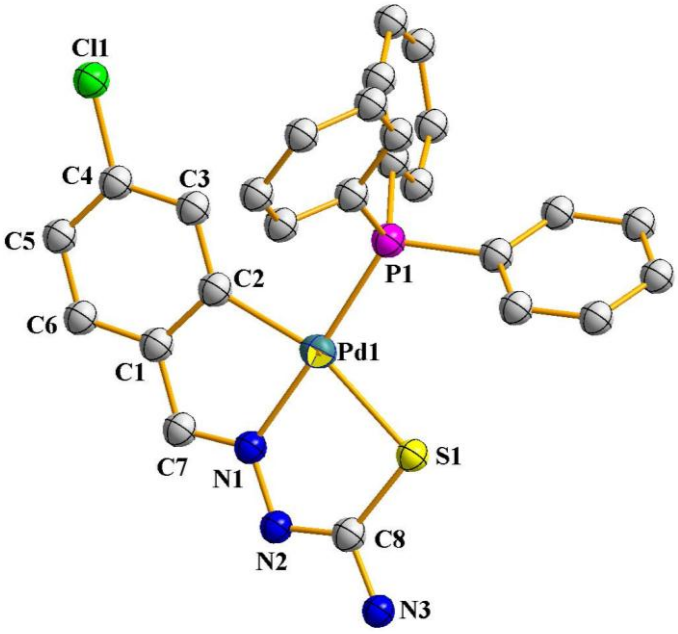


Fig. S4 Structure of [Pd(CNS-Cl)(PPh_3)] with atom numbering scheme.