Supporting Information

Palladium Complexes of Abnormal N-heterocyclic Carbenes as Precatalysts for the Much Preferred Cu-free and Amine-free Sonogashira Coupling in Air in a Mixed-aqueous Medium

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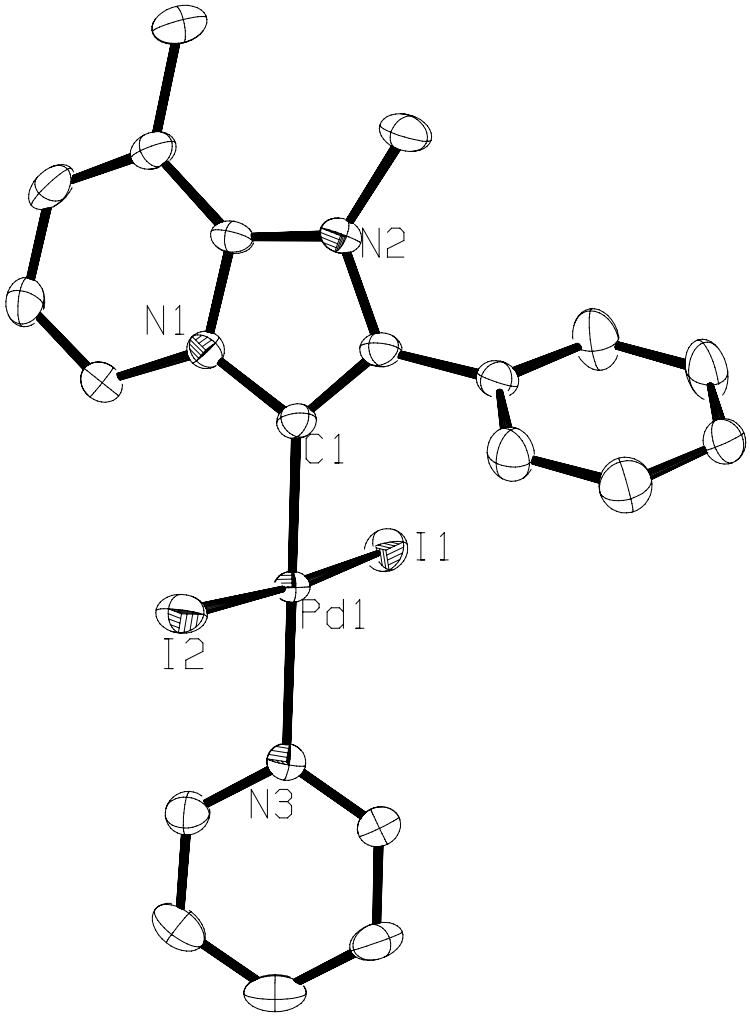


Figure S1. Ortep of **2b**. Selected bond lengths (Å) and angles (°): Pd1-C1 1.968(3), Pd1-N3 2.100(2), Pd1-I2 2.5986(3), Pd1-I1 2.6089(3), C1-Pd1-N3 178.87(10), C1-Pd1-I2 88.34(7), N3-Pd1-I2 90.56(6).

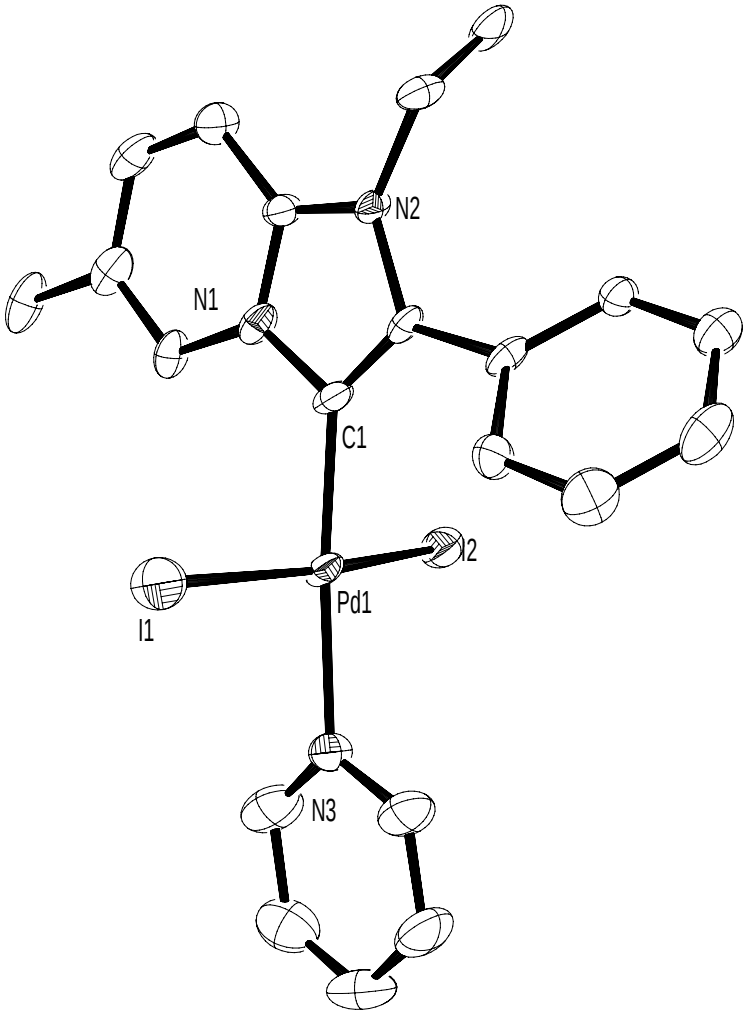


Figure S2. Ortep of **3b**. Selected bond lengths (Å) and angles (^{o}): Pd1-C1 1.984(8), Pd1-N3 2.100(7), Pd1-I2 2.5929(8), Pd1-I1 2.5887(9), C1-Pd1-N3 174.7(3), C1-Pd1-I2 88.6 (2), N3-Pd1-I2 91.27(19).

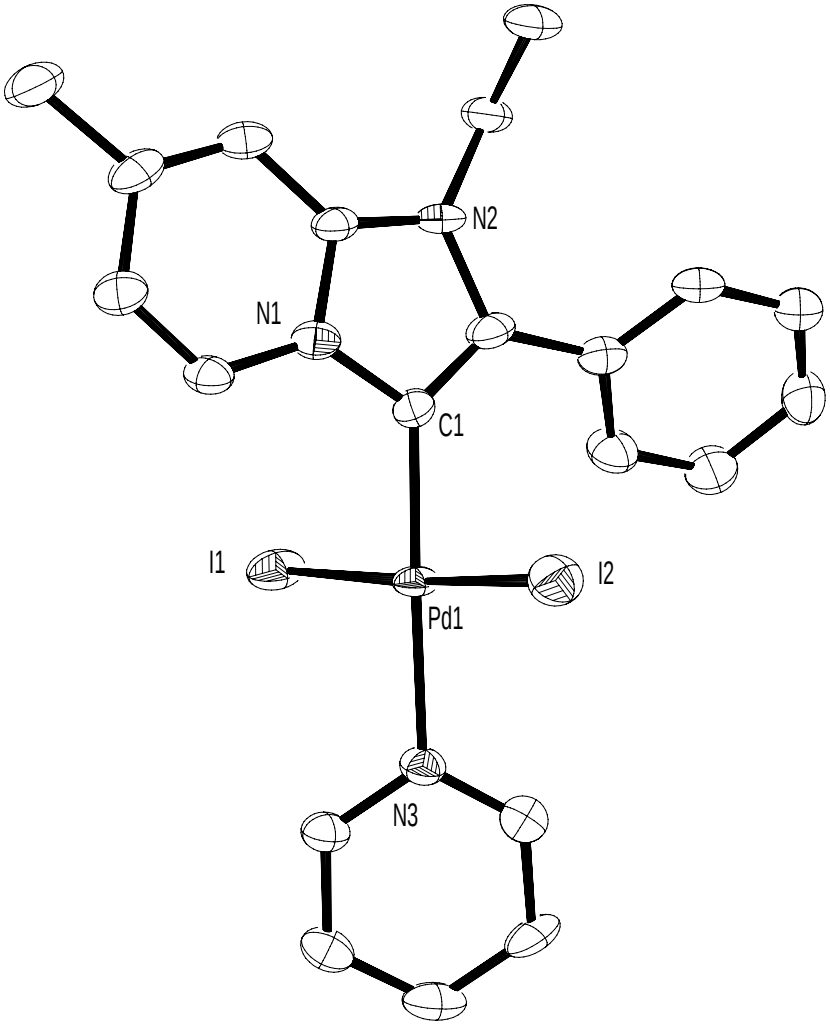


Figure S3. Ortep of **4b**. Selected bond lengths (Å) and angles (°): Pd1-C1 1.976(8), Pd1-N3 2.121(6), Pd1-I2 2.5993(8), Pd1-I1 2.5887(8), C1-Pd1-N3 174.7(3), C1-Pd1-I2 90.0 (2), N3-Pd1-I2 93.05(18).

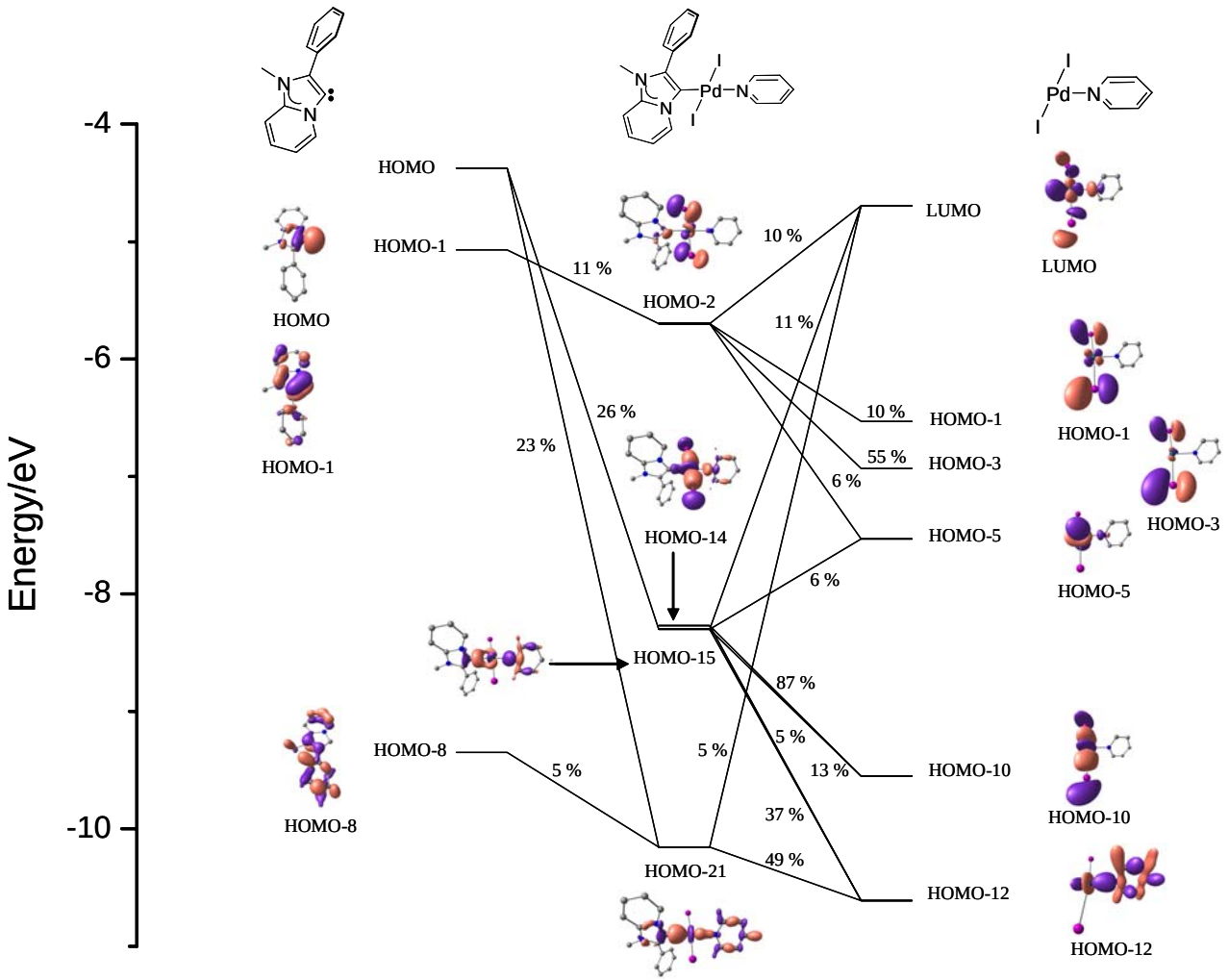


Figure S4. Detailed orbital interaction diagram showing major contributions to the NHC-palladium bond in **1b**.

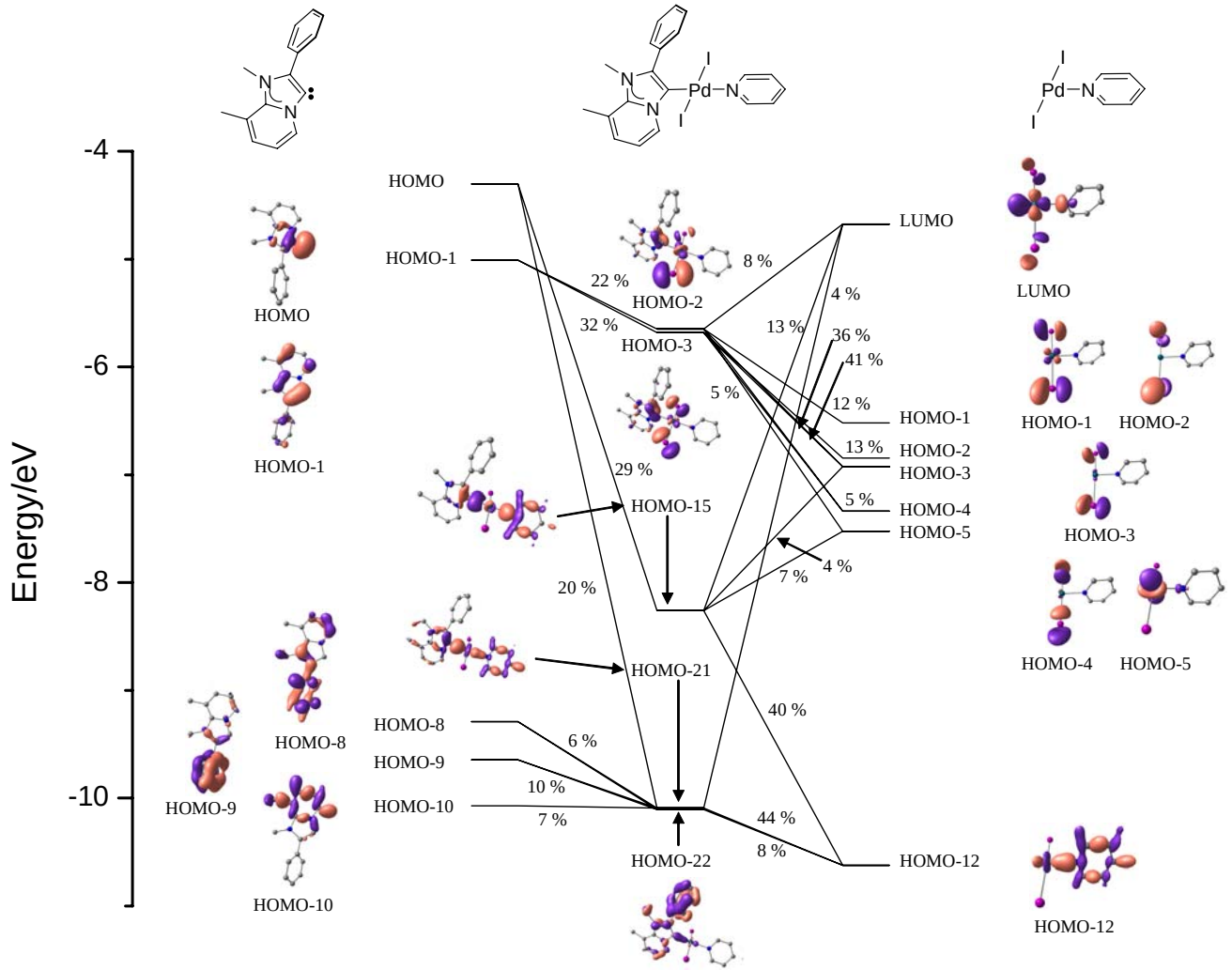
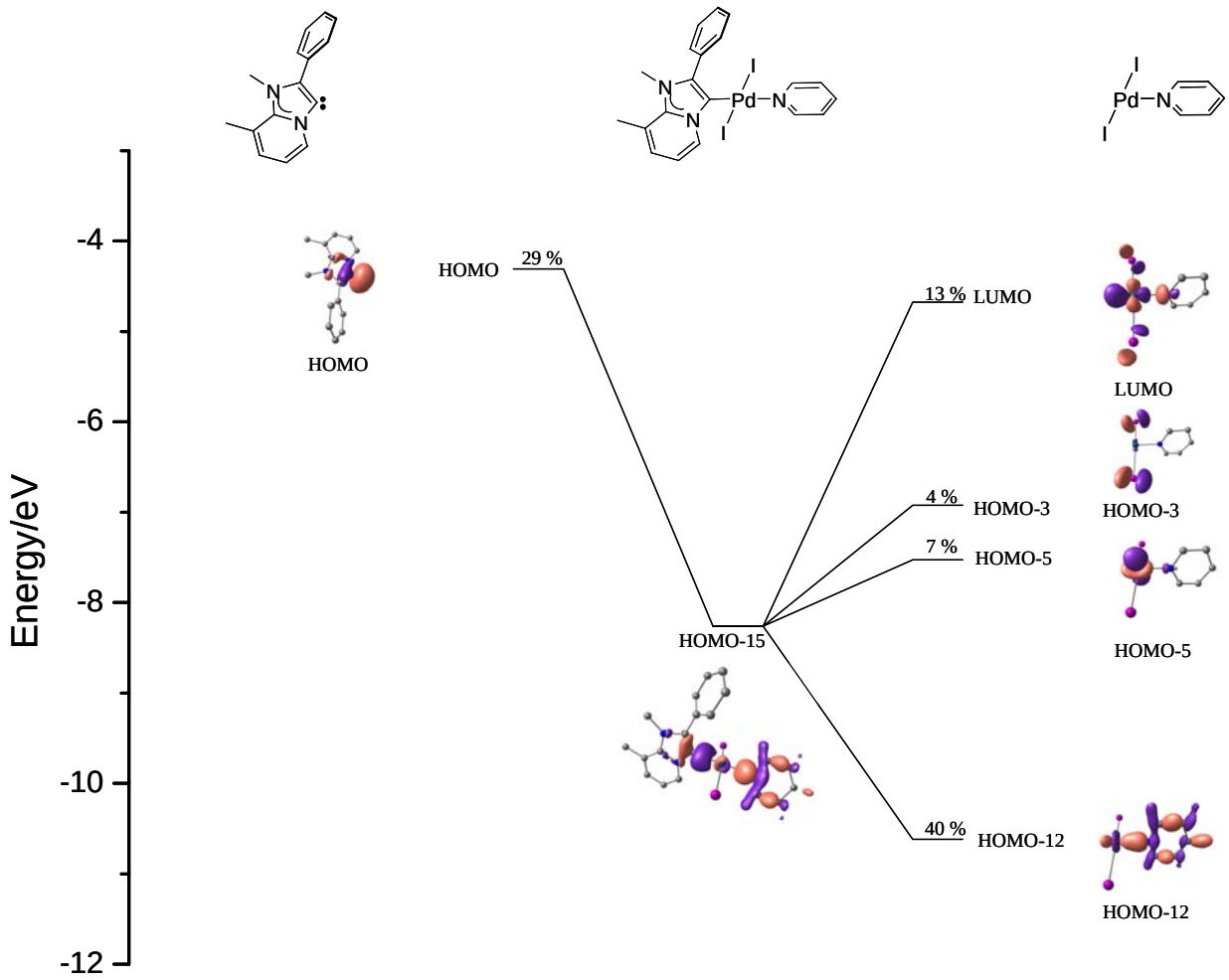


Figure S5. Detailed orbital interaction diagram showing major contributions to the NHC-palladium bond in **2b**.



FigureS6. Simplified orbital interaction diagram showing major contributions to the NHC-palladium bonding orbital HOMO-15 in **2b**.

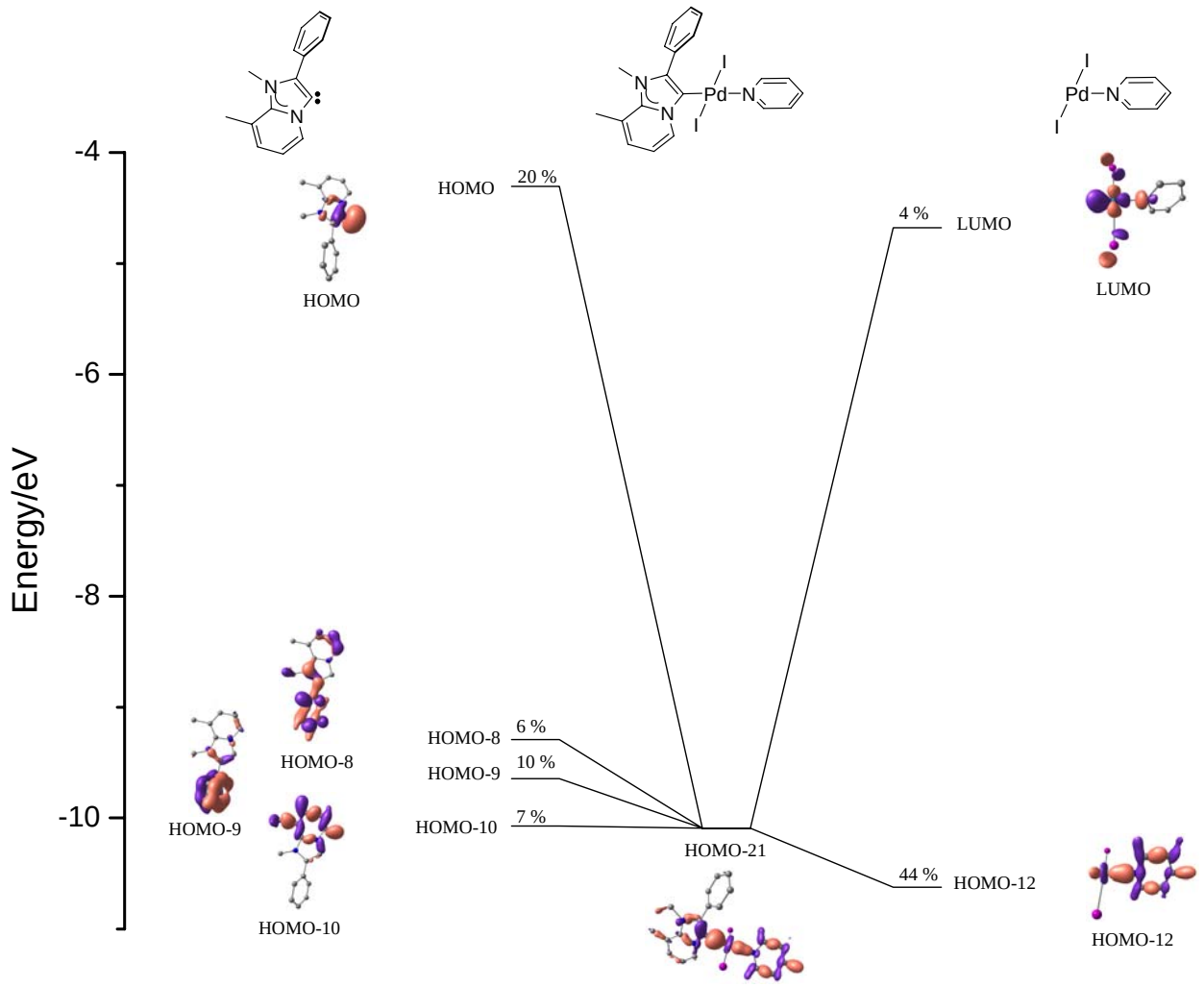


Figure S7. Simplified orbital interaction diagram showing major contributions to the NHC-palladium bonding orbital HOMO-21 in **2b**.

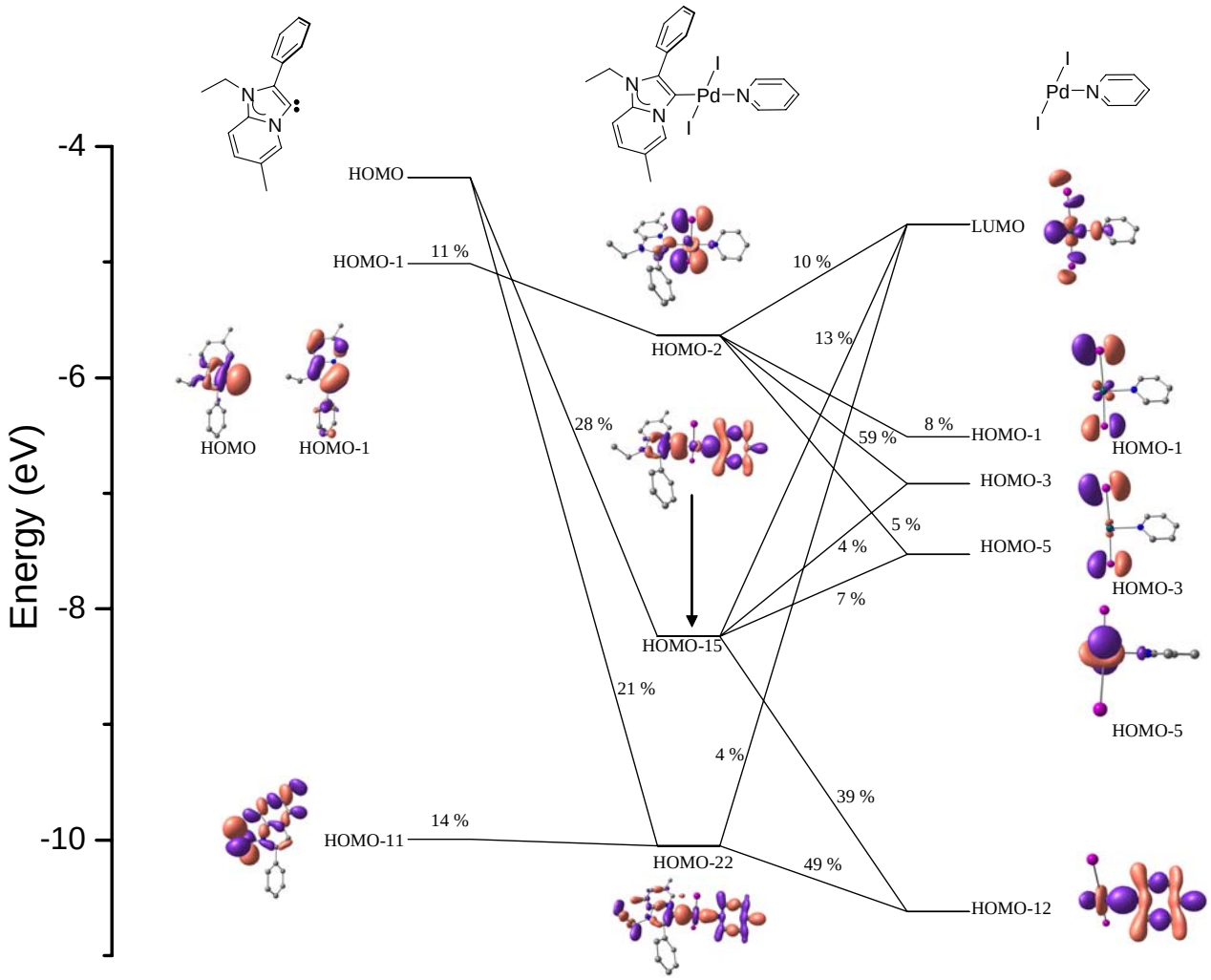


Figure S8. Detailed orbital interaction diagram showing major contributions to the NHC-palladium bond in **3b**.

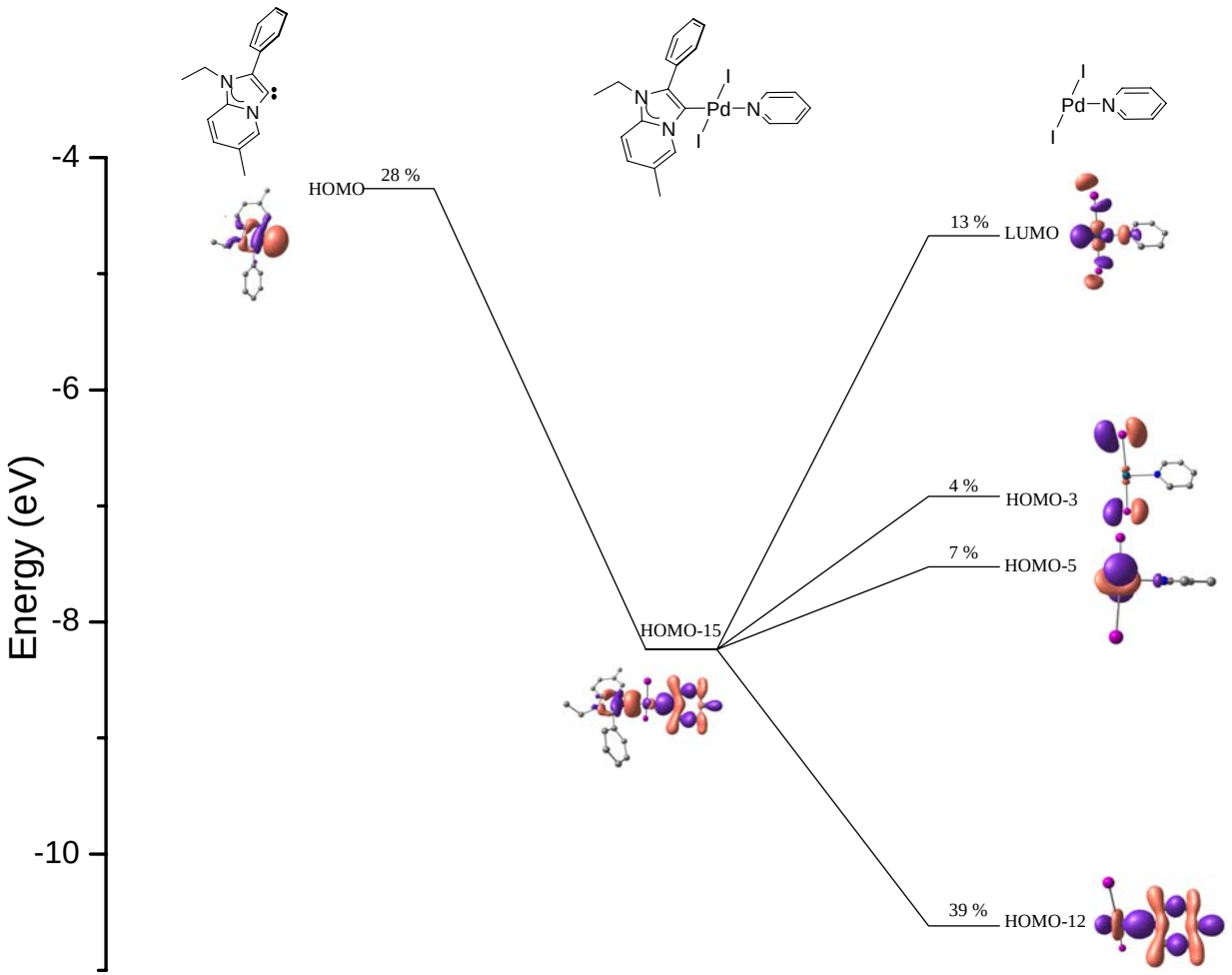


Figure S9. Simplified orbital interaction diagram showing major contributions to the NHC-palladium bonding orbital HOMO-15 in **3b**.

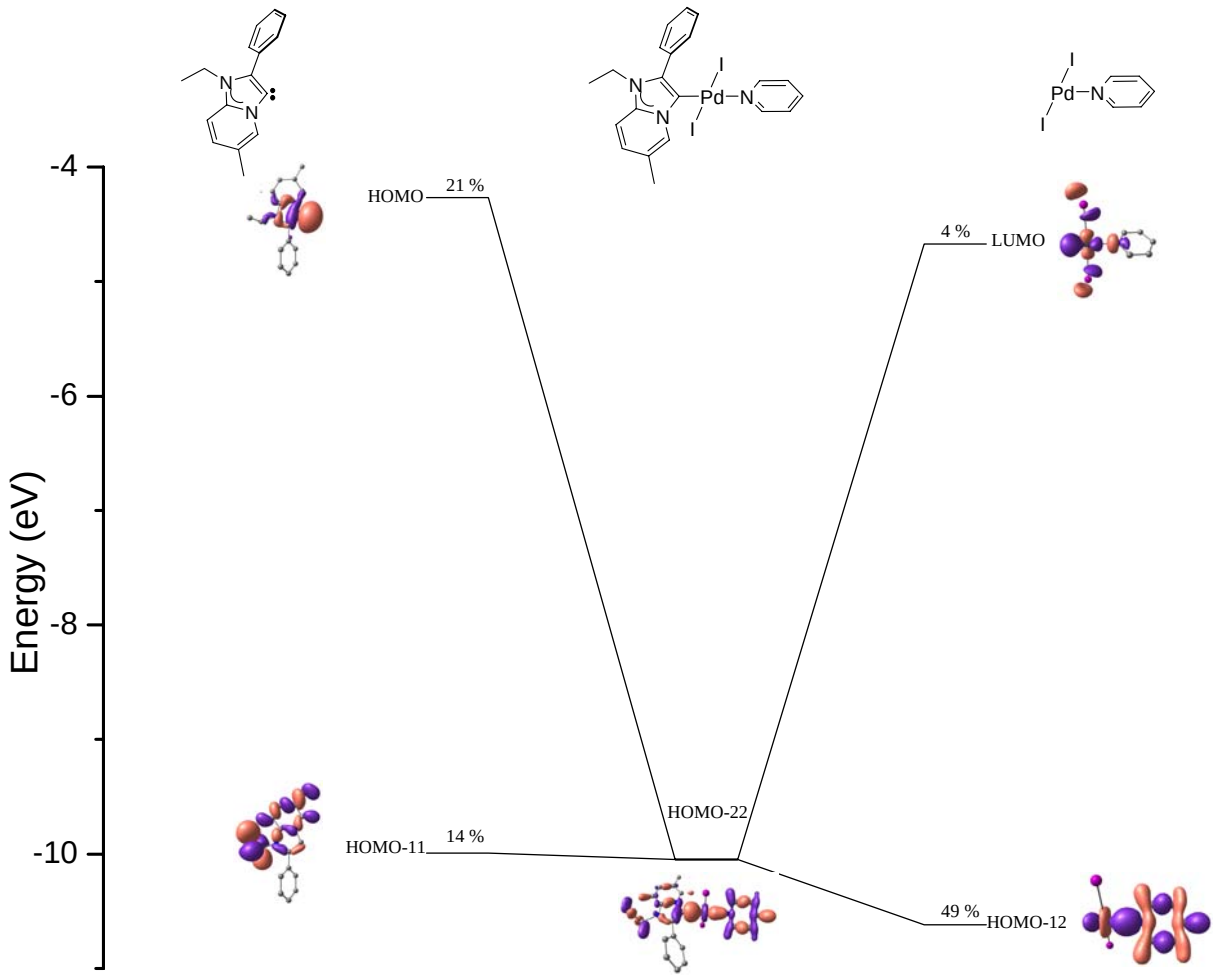


Figure S10. Simplified orbital interaction diagram showing major contributions to the NHC-palladium bonding orbital HOMO-22 in **3b**.

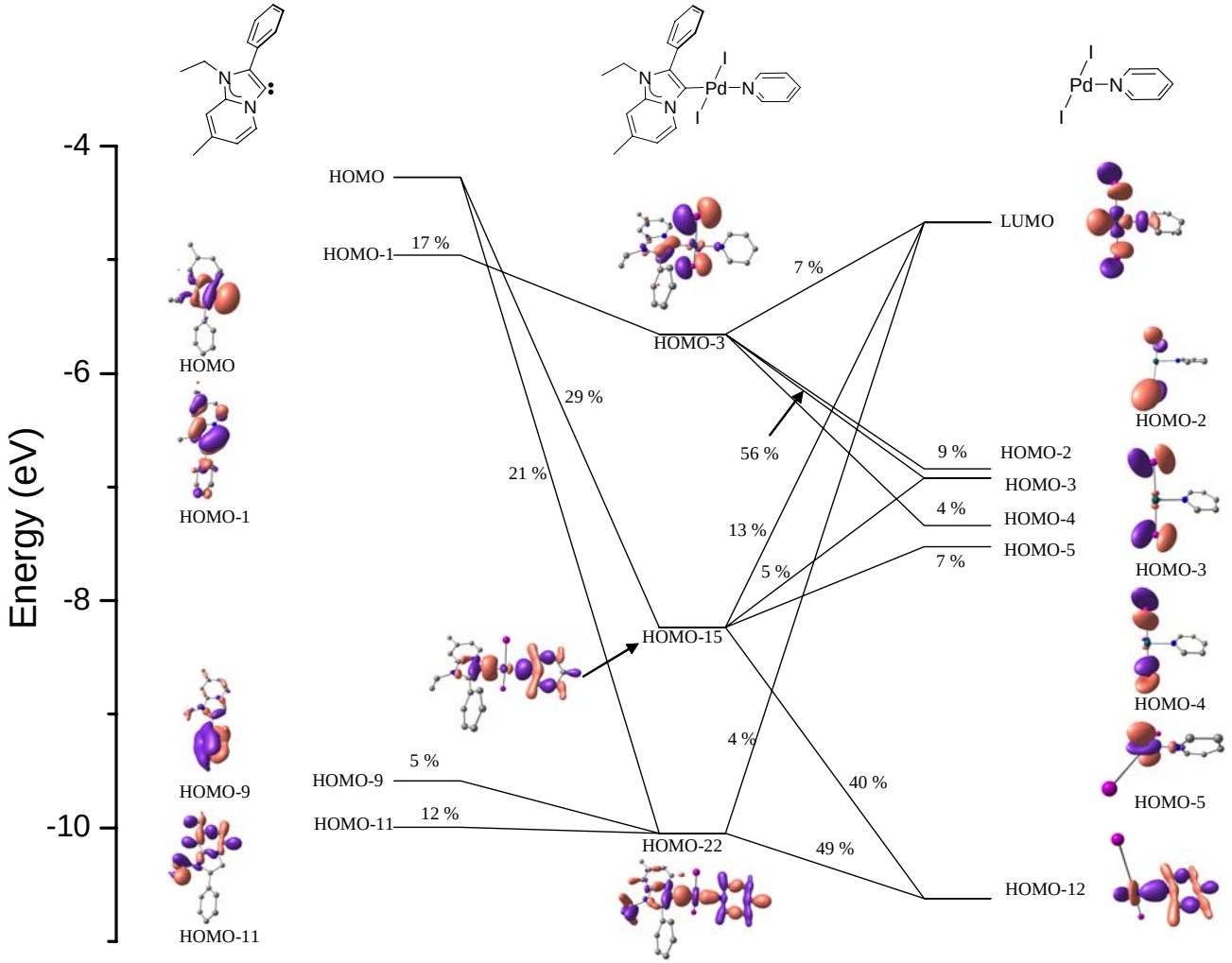


Figure S11. Detailed orbital interaction diagram showing major contributions to the NHC-palladium bond in **4b**.

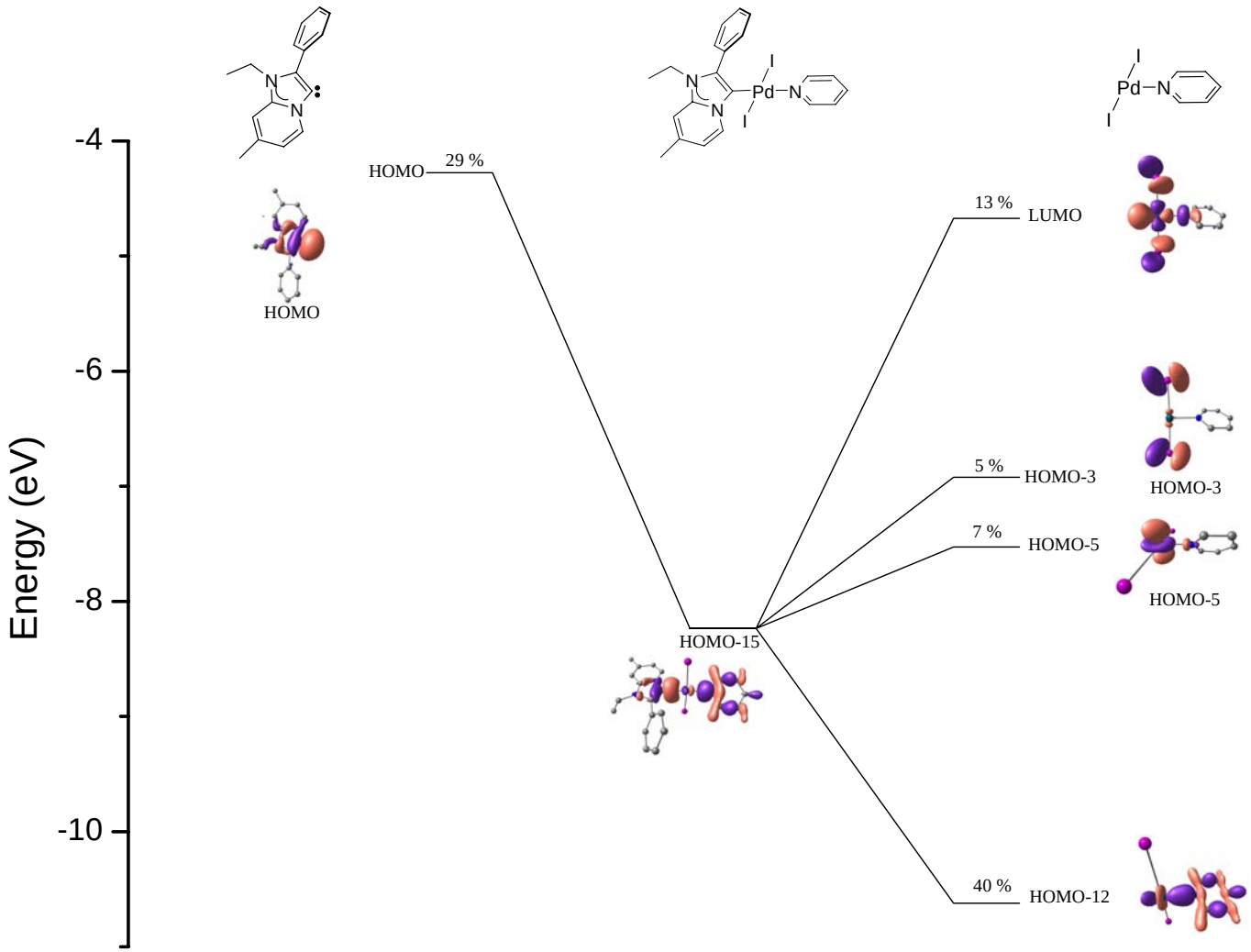


Figure S12. Simplified orbital interaction diagram showing major contributions to the NHC-palladium bonding orbital HOMO-15 in **4b**.

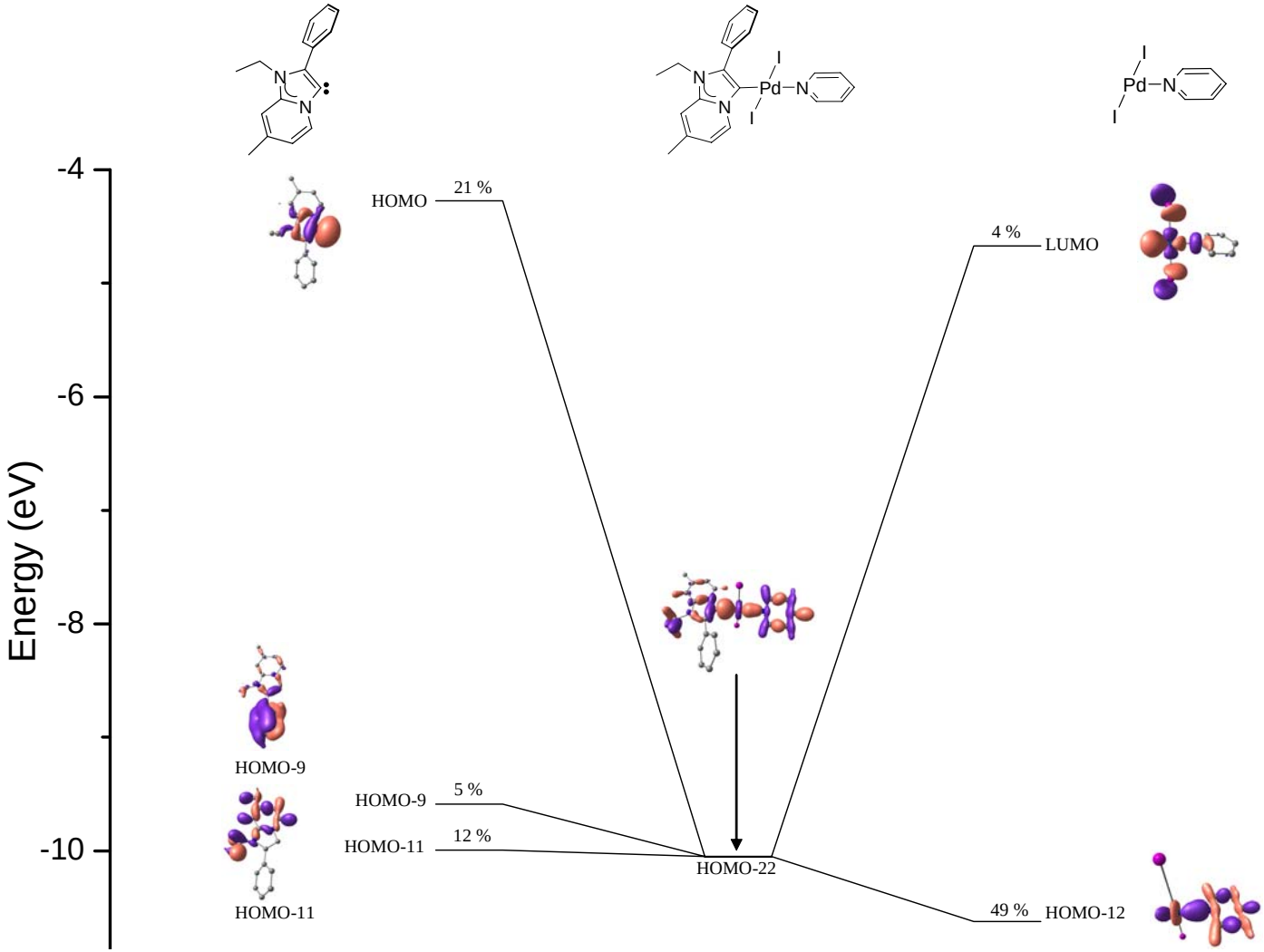


Figure S13. Simplified orbital interaction diagram showing major contributions to the NHC-palladium bonding orbital HOMO-22 in **4b**.

The density functional theory calculations were performed for the palladium **1b–4b** complexes by using the GAUSSIAN 03[1] suite of quantum chemical programs.

Table S1. B3LYP/SDD, 6-31G(d) optimized coordinates of **1b**.

Ground State electronic energy = -1049.3915773 hartree/particle.

Pd	3.767044	13.29196	2.20024
I	2.558052	12.24299	0.013335
I	4.832019	14.07036	4.586982
N	-0.11086	14.25704	3.60274
N	1.298225	12.58273	3.752596
N	5.716568	13.08389	1.304893
C	1.957162	13.55038	2.983844
C	1.061534	14.59444	2.89628
C	0.041832	13.01994	4.12268
C	-0.80389	12.21704	4.902634
H	-1.78927	12.57364	5.179276
C	-0.34179	10.97432	5.28673
H	-0.97116	10.32695	5.888513
C	0.948037	10.53688	4.893673
H	1.314717	9.560745	5.189042
C	1.749527	11.34479	4.131892
H	2.744268	11.09488	3.788485
C	-1.2709	15.10185	3.855474
H	-2.12373	14.79606	3.239974
H	-1.01091	16.13174	3.614314
H	-1.54656	15.04321	4.912295
C	1.213253	15.87781	2.190419
C	2.346725	16.67425	2.426103
H	3.090688	16.34098	3.143015
C	2.51053	17.88094	1.745671
H	3.390112	18.48863	1.939839
C	1.550183	18.30949	0.826535
H	1.680769	19.25049	0.298952
C	0.423253	17.52118	0.582389
H	-0.31964	17.83961	-0.14379
C	0.256002	16.31215	1.256803
H	-0.60227	15.68414	1.032986
C	5.975946	13.67909	0.125532
H	5.154063	14.22519	-0.32243
C	7.215896	13.58916	-0.50058
H	7.374167	14.09299	-1.44843

C	8.224479	12.84057	0.104308
H	9.200539	12.74542	-0.36303
C	7.954285	12.21648	1.32115
H	8.705082	11.6239	1.8335
C	6.693612	12.36874	1.891574
H	6.448425	11.928	2.850586

Table S2. B3LYP/SDD, 6-31G(d) optimized coordinates of **2b**.

Ground State electronic energy = -1088.70508 hartree/particle.

Pd	4.897061	2.735011	6.862727
I	6.011878	1.444183	8.969616
I	3.894221	3.78342	4.556194
N	7.332584	2.00244	5.26314
N	8.84593	3.557816	5.573549
N	2.935047	2.575301	7.732266
C	6.729502	2.936504	6.112092
C	7.688541	3.903261	6.300195
C	10.01688	4.417622	5.416812
H	10.8649	4.049152	6.001647
H	9.753864	5.412372	5.773566
H	10.29825	4.486486	4.365698
C	8.625872	2.376704	4.938044
C	10.85719	1.889841	3.735337
H	11.31141	1.03318	3.230137
H	11.47096	2.117389	4.612668
H	10.92312	2.743052	3.050425
C	9.429266	1.558314	4.104303
C	8.839378	0.395882	3.637955
H	9.42279	-0.26367	3.002342
C	7.512339	0.035926	3.971444
H	7.075988	-0.88086	3.592576
C	6.773975	0.844322	4.786893
H	5.757875	0.661789	5.108514
C	7.607018	5.115624	7.134052
C	8.55404	5.370899	8.141259
H	9.355158	4.658386	8.319342
C	8.447323	6.508007	8.941166
H	9.180854	6.68732	9.722468
C	7.390997	7.402032	8.750437
H	7.307002	8.286572	9.376111
C	6.44085	7.151534	7.758018
H	5.615975	7.842085	7.604875
C	6.545449	6.017692	6.951715

H	5.808178	5.821082	6.179548
C	2.689781	3.131965	8.932962
H	3.529646	3.624323	9.409201
C	1.441049	3.069467	9.544727
H	1.294922	3.539643	10.51164
C	0.407348	2.391084	8.900683
H	-0.57651	2.318929	9.355583
C	0.662518	1.807202	7.660872
H	-0.10798	1.269853	7.117758
C	1.934288	1.928374	7.107897
H	2.169277	1.516483	6.133548

Table S3. B3LYP/SDD, 6-31G(d) optimized coordinates of **3b**.

Ground State electronic energy = -1128.0244896 hartree/particle.

C	2.56381	2.545195	3.131437
C	1.75577	1.537761	3.610906
C	0.584029	3.429926	3.859875
C	2.153357	4.999365	2.960703
H	3.135661	5.102328	2.518338
C	1.278967	6.03497	3.174384
C	1.654371	7.450076	2.810583
H	1.702296	8.087685	3.701794
H	0.916501	7.891624	2.130479
H	2.629957	7.488314	2.317935
C	0.007856	5.741575	3.746598
H	-0.69569	6.551962	3.914694
C	-0.63183	1.381036	4.577897
H	-0.5016	0.331103	4.310434
H	-1.51098	1.74906	4.036873
C	-0.82363	1.533246	6.089112
H	0.038684	1.143193	6.637148
H	-1.71221	0.975418	6.40388
H	-0.95994	2.580435	6.377229
C	2.031124	0.088981	3.659525
C	2.011714	-0.62366	4.870244
H	1.816666	-0.09931	5.801181
C	2.287134	-1.99078	4.891762
H	2.277894	-2.52661	5.837
C	2.591994	-2.66305	3.706285
H	2.809554	-3.72761	3.724568
C	-0.34694	4.454864	4.090124
H	-1.31303	4.227306	4.525074
C	2.623282	-1.96084	2.499511

H	2.861659	-2.47708	1.573452
C	2.344057	-0.59426	2.472294
H	2.368777	-0.0452	1.535885
C	6.819191	1.409748	0.88676
H	6.062412	0.660916	0.684111
C	8.108439	1.297828	0.374388
H	8.37258	0.433686	-0.22632
C	9.02991	2.309556	0.640092
H	10.042	2.254272	0.249298
C	8.625665	3.393206	1.417973
H	9.304947	4.205305	1.655641
C	7.322571	3.423225	1.906758
H	6.973977	4.229876	2.540914
Pd	4.417858	2.530101	2.408978
I	3.390355	2.567667	-0.11286
I	5.304478	2.780544	4.959138
N	1.808762	3.713674	3.296103
N	0.541667	2.093604	4.063811
N	6.42991	2.45176	1.644008

Table S4. B3LYP/SDD, 6-31G(d) optimized coordinates of **4b**.

Ground State electronic energy = -1128.0258816 hartree/particle.

Pd	0.22292	0.854063	-0.45744
I	-2.25388	1.89912	-0.00997
I	2.542081	-0.3777	-1.1257
N	-1.16413	-1.80267	-0.60795
N	-0.95054	-2.80482	1.331511
N	0.992286	2.760102	-1.09322
C	-0.44579	-0.90368	0.192002
C	-1.47223	-2.94888	0.092882
C	-0.31967	-1.54272	1.405021
C	-1.56345	-1.65616	-1.91114
H	-1.27082	-0.72538	-2.37819
C	-2.28627	-2.64741	-2.51323
H	-2.59643	-2.51373	-3.54412
C	-2.63947	-3.83651	-1.81075
C	-3.44626	-4.90587	-2.50062
H	-3.66006	-5.74467	-1.83191
H	-2.91229	-5.2969	-3.37561
H	-4.40211	-4.50542	-2.85997
C	-2.22275	-3.97769	-0.49923
H	-2.46542	-4.8656	0.073573
C	-1.15077	-3.76942	2.417646

H	-2.21275	-4.03995	2.433062
H	-0.93695	-3.24151	3.34836
C	-0.27643	-5.02019	2.294281
H	-0.47546	-5.56486	1.365944
H	-0.48044	-5.6932	3.134135
H	0.786495	-4.76298	2.311483
C	0.340143	-1.0518	2.628749
C	1.35391	-1.78812	3.265366
H	1.68275	-2.7313	2.839244
C	1.977233	-1.29365	4.410808
H	2.76604	-1.87084	4.885562
C	1.602665	-0.05358	4.932703
H	2.091065	0.332485	5.823418
C	0.603841	0.690461	4.300838
H	0.30809	1.657175	4.699306
C	-0.02638	0.197597	3.157999
H	-0.80401	0.77447	2.667331
C	2.085376	3.269832	-0.49591
H	2.531902	2.658141	0.279445
C	2.629708	4.499127	-0.85663
H	3.509874	4.866956	-0.33959
C	2.032714	5.225144	-1.88621
H	2.437847	6.184504	-2.19544
C	0.905054	4.694475	-2.51072
H	0.402354	5.220631	-3.31562
C	0.412194	3.465635	-2.08083
H	-0.47832	3.029209	-2.51778

Table S5. Bond distance & bond energy of Pd-$C_{carbene}$ and Pd-$N_{pyridine}$ in **1b**–**4b**.

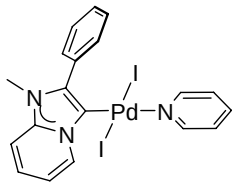
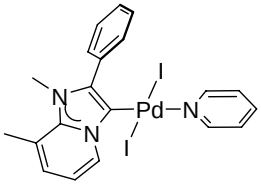
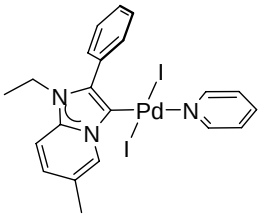
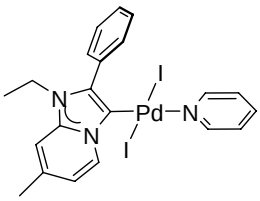
compound	d(Pd-$C_{carbene}$) (Å)	D_e(Pd-$C_{carbene}$) (kcal/mol)	d(Pd-$N_{pyridine}$) (Å)	D_e(Pd-$N_{pyridine}$) (kcal/mol)
 **1b**	1.99	83.89	2.15	29.17
 **2b**	1.99	83.94	2.15	28.91
 **3b**	1.99	75.19	2.15	28.49
 **4b**	1.99	75.05	2.15	28.72

Table S6. Mulliken and natural charge analyses of the normal carbene, 1,3-dimethylimidazol-2-ylidene and the abnormal carbene, 1,3-dimethylimidazol-4-ylidene.

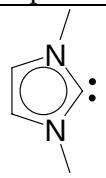
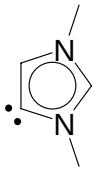
specie	Mulliken charge	natural charge
 normal carbene	0.071	0.102
 abnormal carbene	-0.103	-0.185

Table S7. B3LYP/ 6-31G(d) optimized coordinates of the normal carbene, 1,3-dimethylimidazol-2-ylidene.

Ground State electronic energy = -304.7924681 hartree/particle.

N	-1.17656	-0.63763	-2.61735
C	-1.19333	0.527962	-1.89241
C	-1.18265	-1.7793	-1.82158
C	-1.20526	-1.34118	-0.53789
N	-1.21125	0.048951	-0.60632
H	-1.21688	-1.88822	0.39382
H	-1.17178	-2.78194	-2.22419
C	-1.23358	0.924473	0.552096
H	-2.13345	0.756128	1.155018
H	-0.35133	0.764658	1.182748
H	-1.23272	1.950373	0.18278
C	-1.15383	-0.65253	-4.06932
H	-0.2535	-1.15359	-4.44349
H	-2.03548	-1.16511	-4.47133
H	-1.15529	0.385252	-4.40371

Table S8. B3LYP/ 6-31G(d) optimized coordinates of the abnormal carbene, 1,3-dimethylimidazol-4-ylidene.

Ground State electronic energy = -304.76113 hartree/particle.

N	-1.21147	-0.65493	-2.6226
C	-1.17471	0.456293	-1.8663
C	-1.25465	-1.85469	-1.8719
C	-1.24322	-1.33726	-0.58636
N	-1.19407	0.06289	-0.58701
H	-1.13887	1.483572	-2.1998
H	-1.27067	-1.84969	0.366584
C	-1.201	0.941881	0.572444
H	-2.14645	0.84769	1.116072
H	-0.37886	0.676803	1.24384
H	-1.07605	1.97921	0.254236
C	-1.16198	-0.64629	-4.07743
H	-0.15423	-0.89367	-4.42656
H	-1.85255	-1.40649	-4.44534
H	-1.44809	0.336113	-4.4664

Table S9. Charge decomposition analysis (CDA) results showing the $NHC \xrightarrow{\sigma} PdI_2(NC_5H_5)$ donation (*d*), the $NHC \xleftarrow{\pi} PdI_2(NC_5H_5)$ donation (*b*), *d*/*b* ratio and the $NHC \leftrightarrow PdI_2(NC_5H_5)$ repulsive polarization (*r*) for the Pd-NHC complexes.

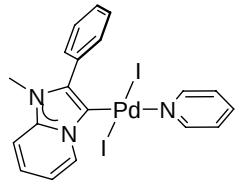
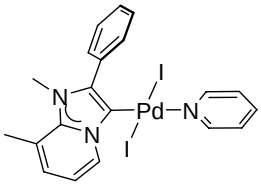
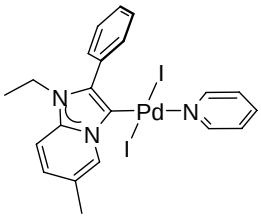
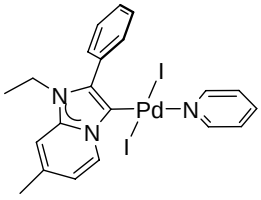
compound	$NHC \xrightarrow{\sigma} PdI_2(NC_5H_5)$ (*d*)	$NHC \xleftarrow{\pi} PdI_2(NC_5H_5)$ (*b*)	*d*/*b* ratio	Repulsive polarization (*r*)
 **1b**	0.541	0.121	4.47	-0.161
 **2b**	0.545	0.118	4.62	-0.162
 **3b**	0.548	0.119	4.61	-0.158
 **4b**	0.549	0.118	4.65	-0.159

Table S10. Natural charge analyses of the palladium **1b** and **2b** complexes.

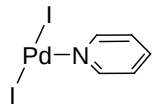
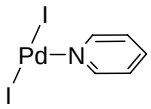
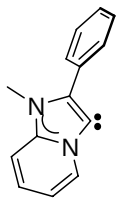
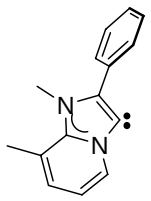
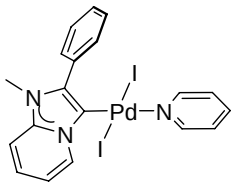
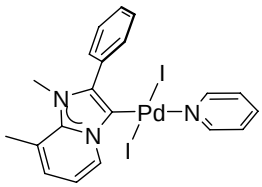
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		0.580			0.579
	-0.159			-0.159	
	0.004	0.405		0.005	0.404
1b			**2b**		

Table S11. Natural charge analyses of the palladium **3b** and **4b** complexes.

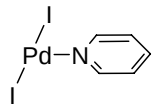
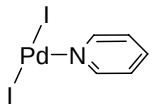
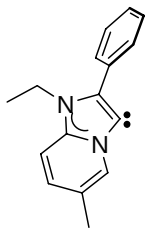
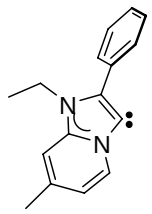
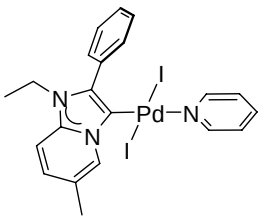
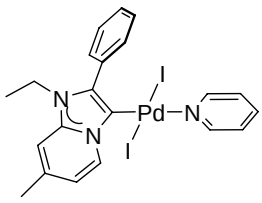
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		0.578			0.578
	-0.155			-0.155	
 **3b**	0.004	0.405	 **4b**	0.003	0.404

Table S12. Mulliken charge analyses of the palladium **1b** and **2b** complexes.

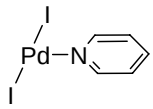
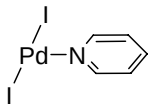
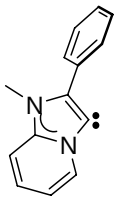
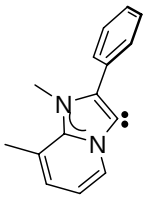
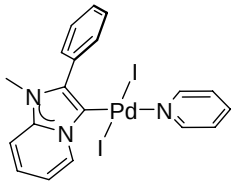
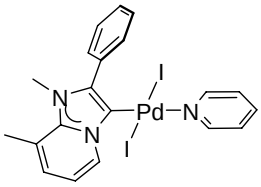
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		0.151			0.146
	-0.118			-0.121	
	0.189	-0.127		0.192	-0.130
1b			**2b**		

Table S13. Mulliken charge analyses of the palladium **3b** and **4b** complexes.

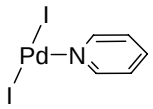
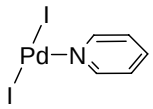
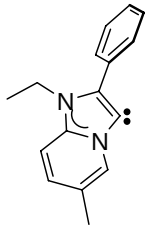
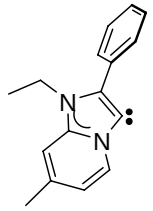
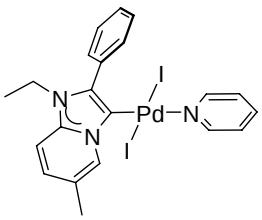
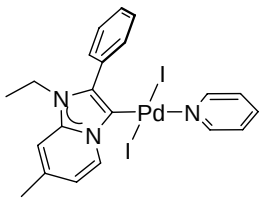
compound/specie	$C_{carbene}$	Pd	compound/specie	$C_{carbene}$	Pd
		0.145			0.145
	-0.112			-0.113	
	0.191	-0.129		0.191	-0.129
3b			**4b**		

Table S14. Electronic configuration of Pd in the palladium **1b** and **2b** complexes.

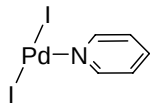
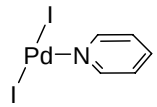
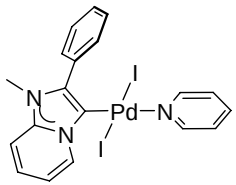
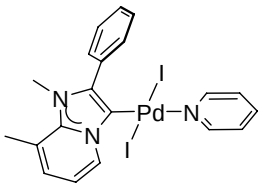
compound/specie	*5s*	*4d*	*5p*	*5d*	*6p*	*6d*	compound/specie	*5s*	*4d*	*5p*	*5d*	*6p*	*6d*
Pd^{2+}		8.00					Pd^{2+}		8.00				
	0.33	9.06	0.01		0.02	0.01		0.33	9.06	0.01		0.02	0.01
 **1b**	0.46	9.10		0.01	0.02	0.01	 **2b**	0.47	9.10		0.01	0.02	0.01

Table S15. Electronic configuration of Pd in the palladium **3b** and **4b** complexes.

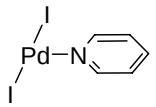
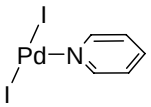
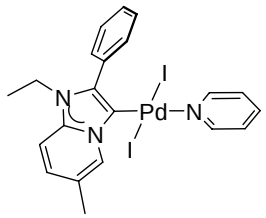
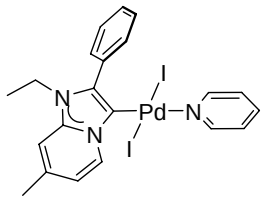
compound/specie	*5s*	*4d*	*5p*	*5d*	*6p*	*6d*	compound/specie	*5s*	*4d*	*5p*	*5d*	*6p*	*6d*
Pd^{2+}		8.00					Pd^{2+}		8.00				
	0.33	9.06	0.01		0.02	0.01		0.33	9.06	0.01		0.02	0.01
 **3b**	0.46	9.10		0.01	0.02	0.01	 **4b**	0.47	9.10			0.02	0.01

Table S16. Hybrid orbitals of the $C_{carbene}$–Pd bond in **1b**–**4b**.

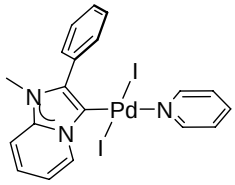
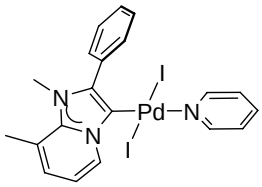
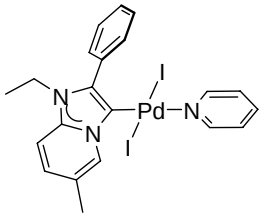
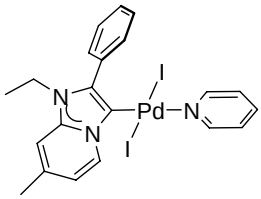
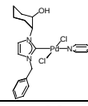
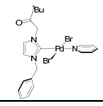
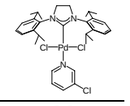
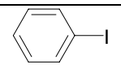
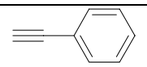
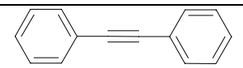
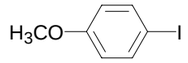
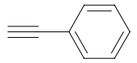
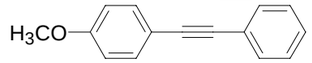
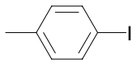
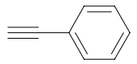
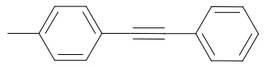
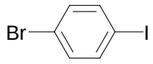
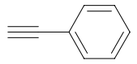
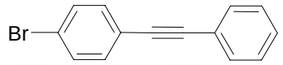
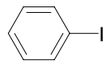
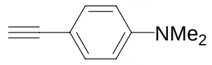
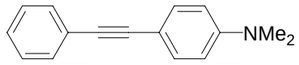
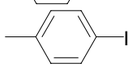
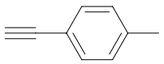
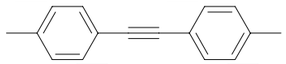
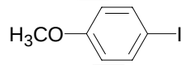
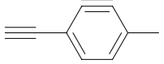
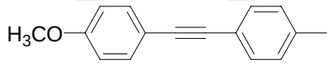
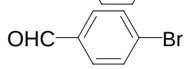
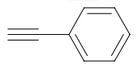
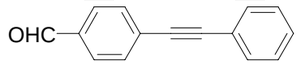
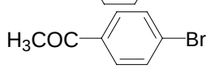
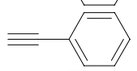
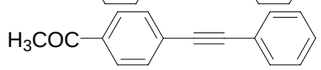
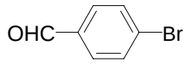
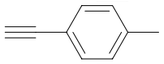
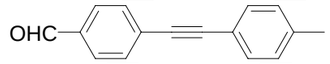
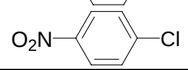
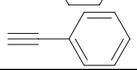
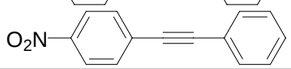
compound	hybrid orbitals of $C_{carbene}$–Pd bond	$C_{carbene}$		Pd	
		s (%)	*p* (%)	*s* (%)	*d* (%)
 **1b**	[C($sp^{1.98}$)–Pd($s^{0.07}d$)]	33.51	66.49	6.66	93.22
 **2b**	[C($sp^{1.98}$)–Pd($s^{0.07}d$)]	33.53	66.47	6.62	93.26
 **3b**	[C($sp^{1.99}$)–Pd($s^{0.07}d$)]	33.44	66.56	6.69	93.19
 **4b**	[C($sp^{1.99}$)–Pd($s^{0.07}d$)]	3.46	66.54	6.68	93.20

Table S17. Selected results for Sonogashira cross-coupling reaction of aryl halides (ArX; X = I, Br, Cl) by $PdCl_2$ and PEPPSI themed complexes of normal carbenes (See references [b], [c] and [d]).

entry	reagent	reagent	cross-coupled product	time (h)	Yield[a] $PdCl_2$	[b] 	[c] 	[d] 
1[e]				1	57	68	82	98
2[e]				1	74	75	58	78
3[e]				1	73	47	60	94
4[e]				1	47	49	53	75
5[e]				1	28	52	35	22
6[e]				1	62	73	76	98
7[e]				1	65	46	59	50
8[f]				3	58	66	67	>99
9[f]				3	64	74	30	>99
10[f]				3	61	97	77	>99
11[f]				3	0	0	0	5

[a] The yields (%) were determined by GC using diethyleneglycol-di-n-butylether as an internal standard. [b] L. Ray, M. M. Shaikh and P. Ghosh, *Dalton Trans.* 2007, 4546–4555. [c] L. Ray, S. Barman, M. M. Shaikh and P. Ghosh, *Chem. Eur. J.* 2008, **14**, 6646–6655. [d] M. G. Organ, M. Abdel–Hadi, S. Avola, N. Hadei, J. Nasielski, C. J. O'Brien and C. Valente, *Chem. Eur. J.* 2007, **13**, 150-157. [e] 1.00 mmol of aryl iodide, 2.00 mmol of acetylene, 2.00 mmol of Cs_2CO_3 and 2 mol % of $PdCl_2$ or Pd complex in 10 mL of DMF:H_2O (7:3 v/v) at 90 °C for 1 hour. [f] 1.00 mmol of aryl bromide or chloride, 2.00 mmol of acetylene, 2.00 mmol of Cs_2CO_3 and 4 mol % of $PdCl_2$ or Pd complex in 10 mL of DMF:H_2O (7:3 v/v) at 90 °C for 3 hours.

References

[1]. GAUSSIAN 03: Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.