Electronic Supplementary Information for Dalton Transactions

Supporting Information

A Comparison Between Nickel and Palladium Precatalysts of 1,2,4-triazole Based N-heterocyclic Carbenes in Hydroamination of Activated Olefins

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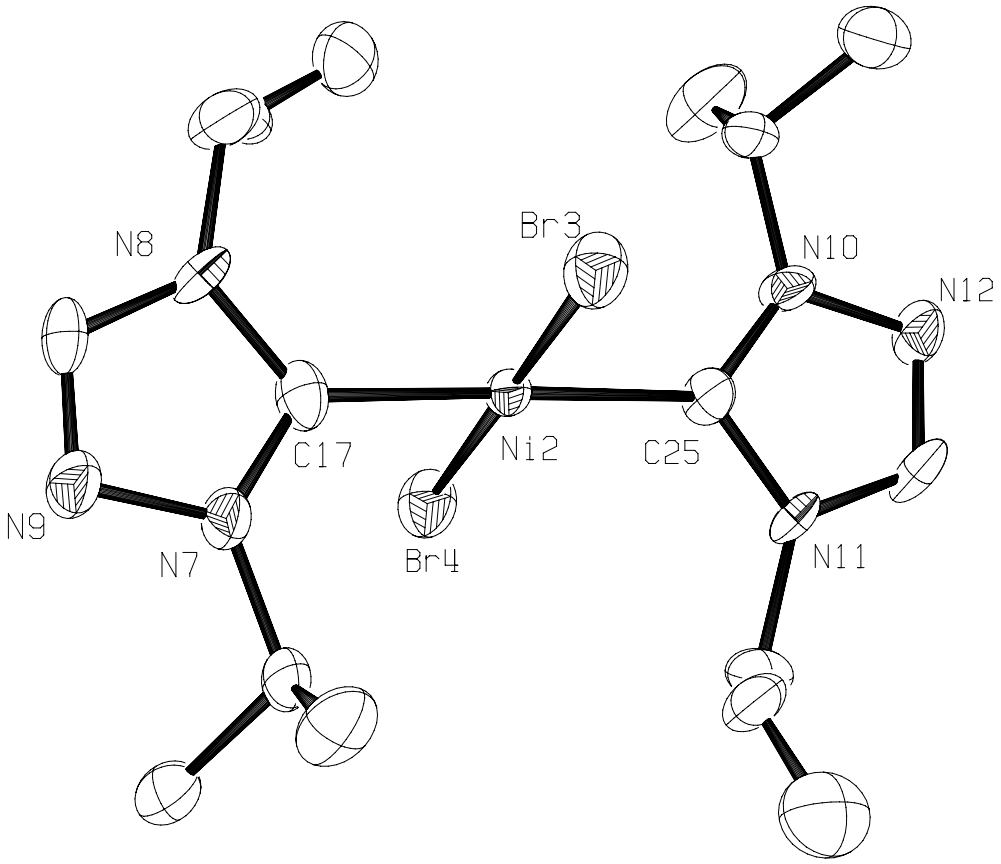


Figure S1. ORTEP drawing of **2b** with thermal ellipsoids shown at the 50 % probability level. Selected bond lengths (Å) and angles (^{o}): Ni(2)-C(17) 1.925(8), Ni(2)-C(25) 1.931(7), Ni(2)-Br(3) 2.3037(14), Ni(2)-Br(4) 2.3059(14), C(17)-Ni(2)-Br(3) 88.8(2), C(25)-Ni(2)-Br(3) 90.5(2), C(17)-Ni(2)-Br(4) 90.3(2), C(25)-Ni(2)-Br(4) 90.3(2).

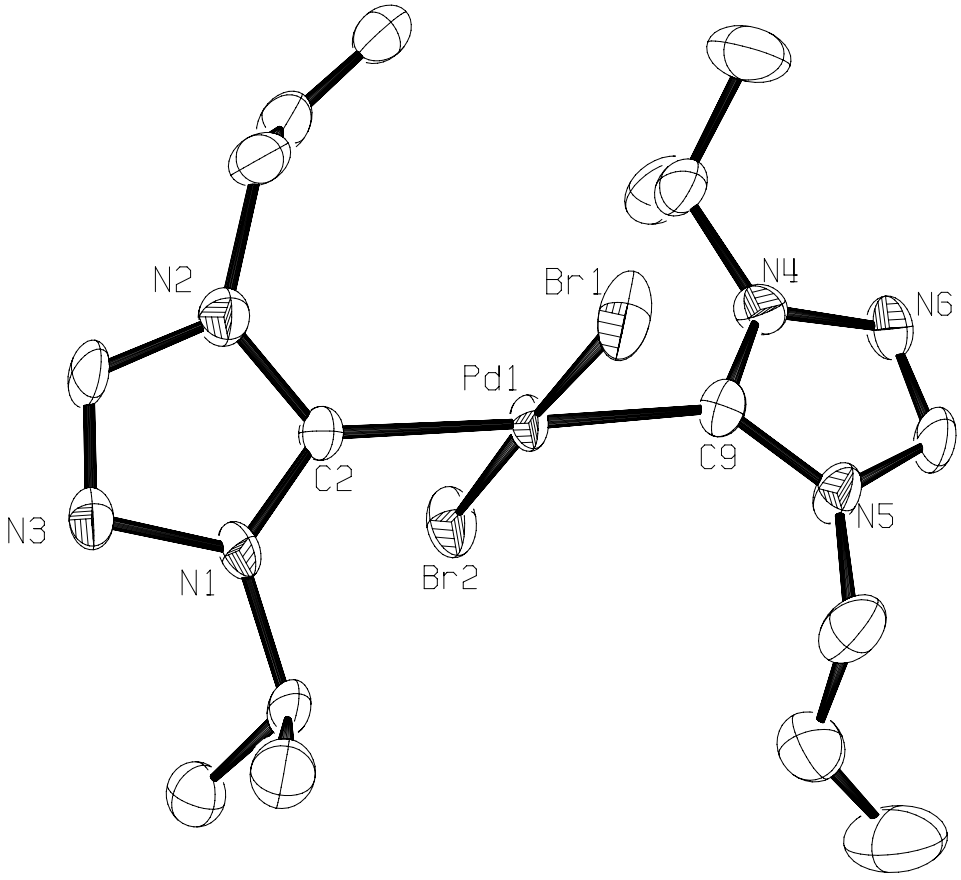


Figure S2. ORTEP drawing of **2c** with thermal ellipsoids shown at the 50 % probability level. Selected bond lengths (Å) and angles (°): Pd(1)-C(2) 2.030(8), Pd(1)-C(9) 2.010(8), Pd(1)-Br(1) 2.4349(10), Pd(1)-Br(2) 2.4392(10), C(2)-Pd(1)-Br(1) 91.8(2), C(9)-Pd(1)-Br(1) 90.1(2), C(2)-Pd(1)-Br(2) 90.3(2), C(9)-Pd(1)-Br(2) 87.8(2).

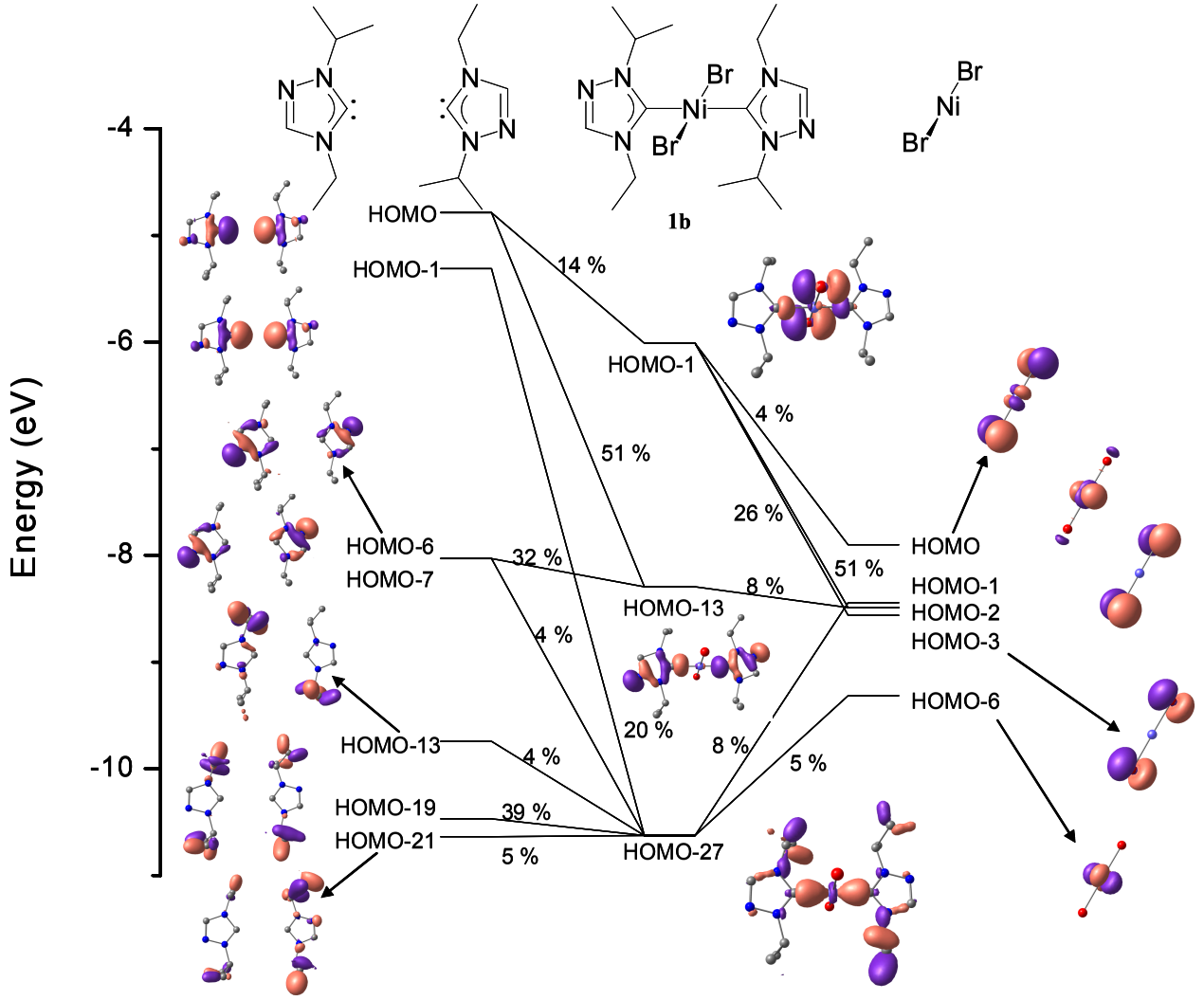


Figure S3. Orbital interaction diagram showing the major contributions of the NHC-nickel bond in **1b.**

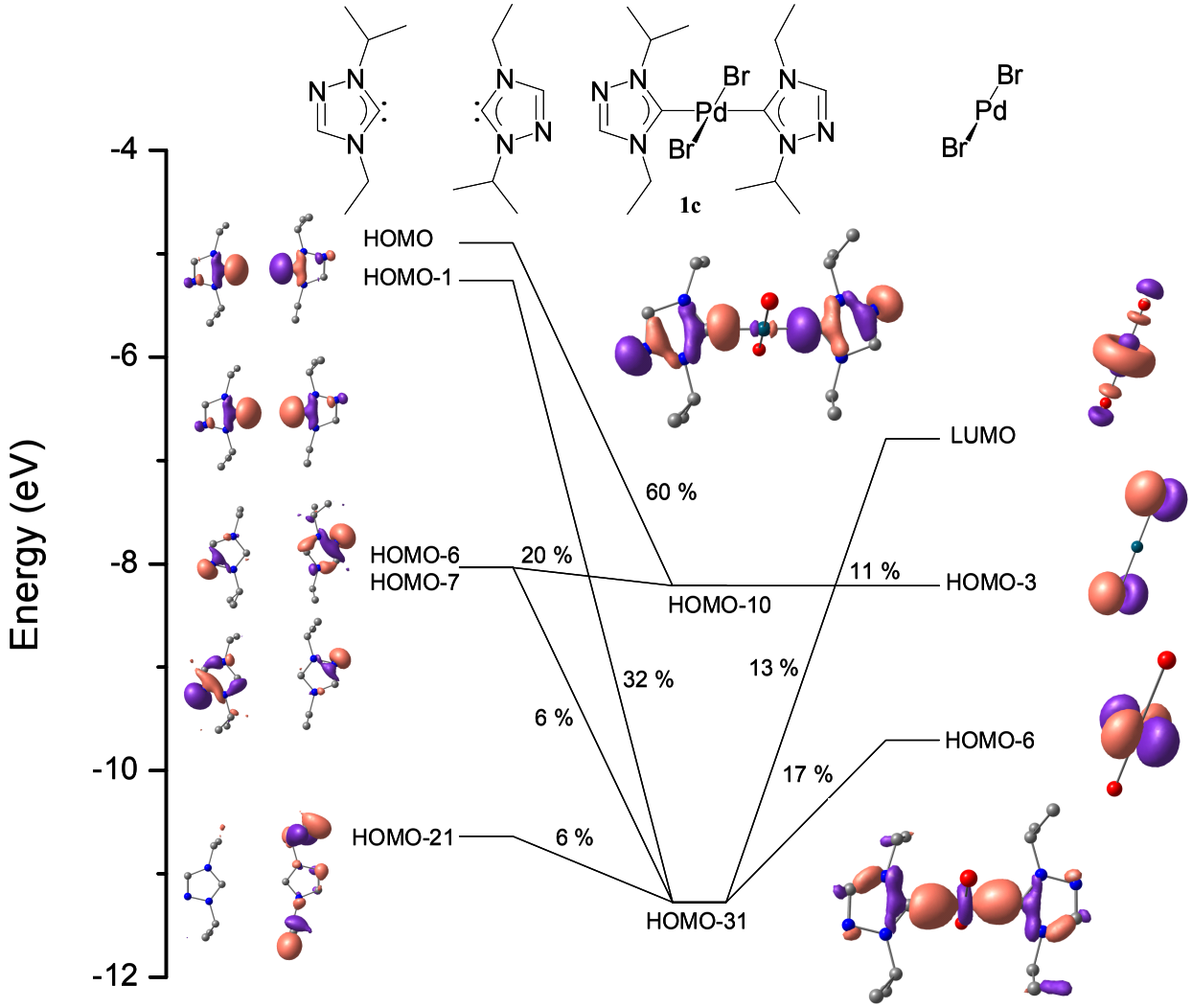


Figure S4. Orbital interaction diagram showing the major contributions of the NHC-palladium bond in **1c.**

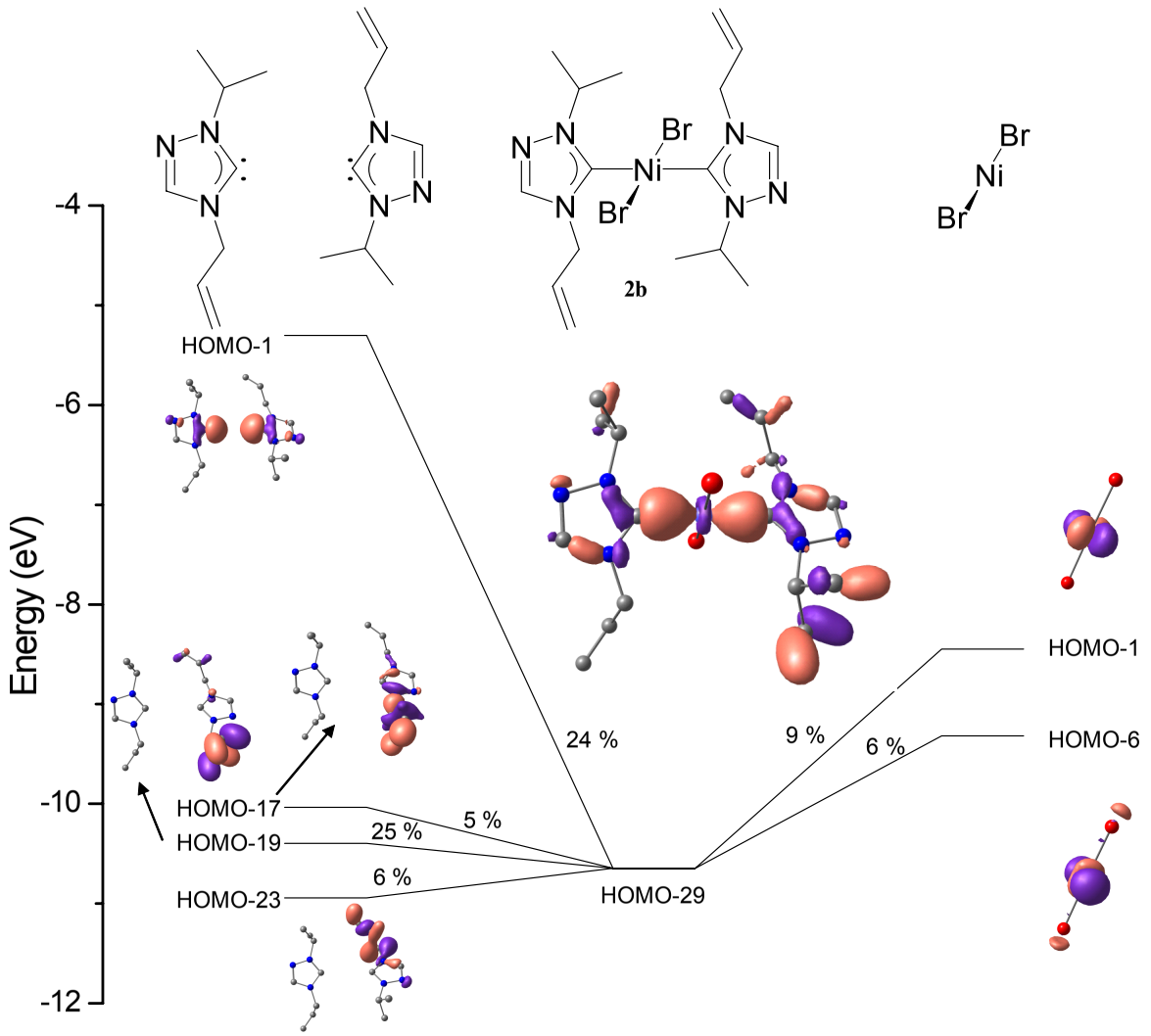


Figure S5. Simplified orbital interaction diagram showing the major contributions of the NHC-nickel bond in **2b.**

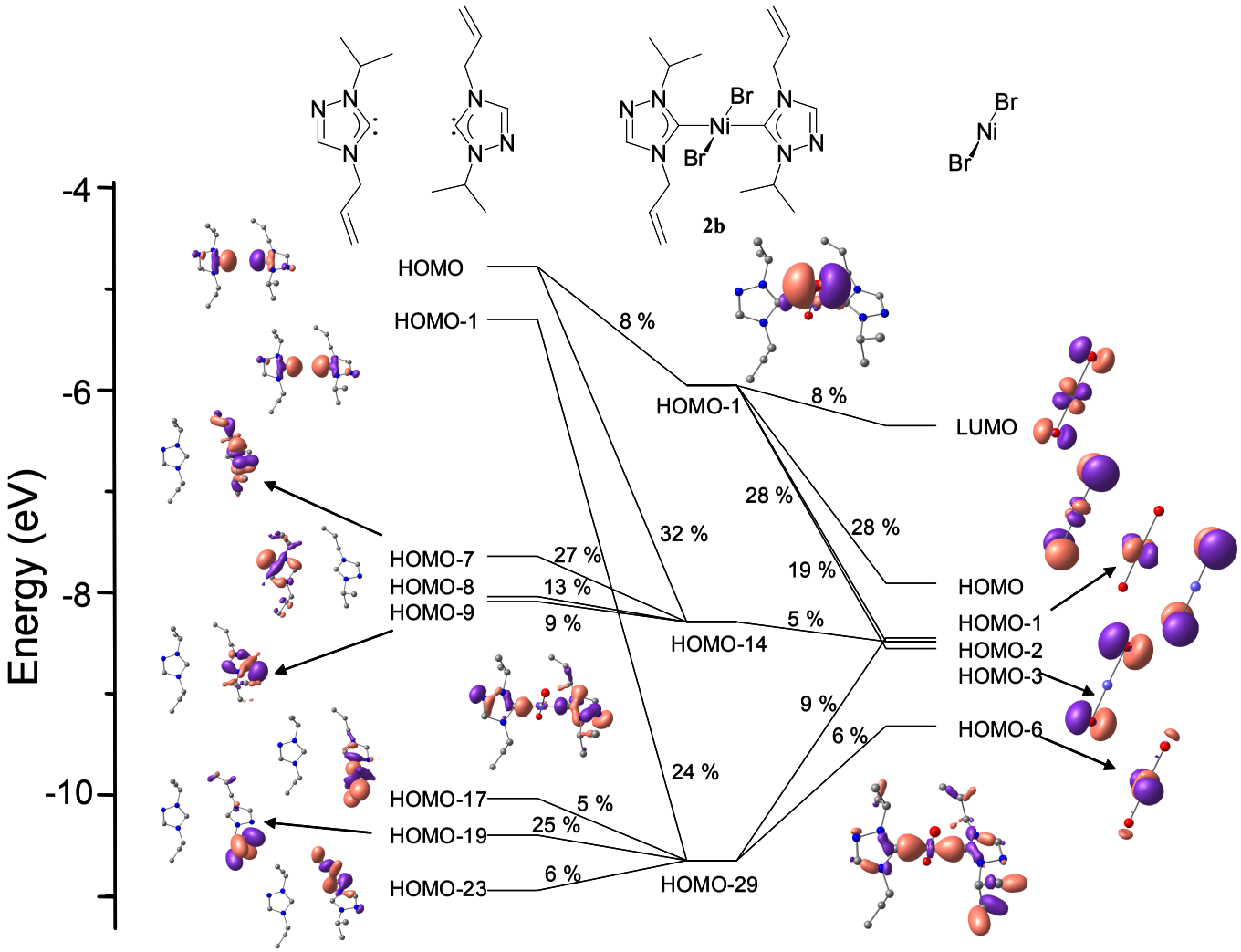


Figure S6. Orbital interaction diagram showing the major contributions of the NHC-nickel bond in **2b.**

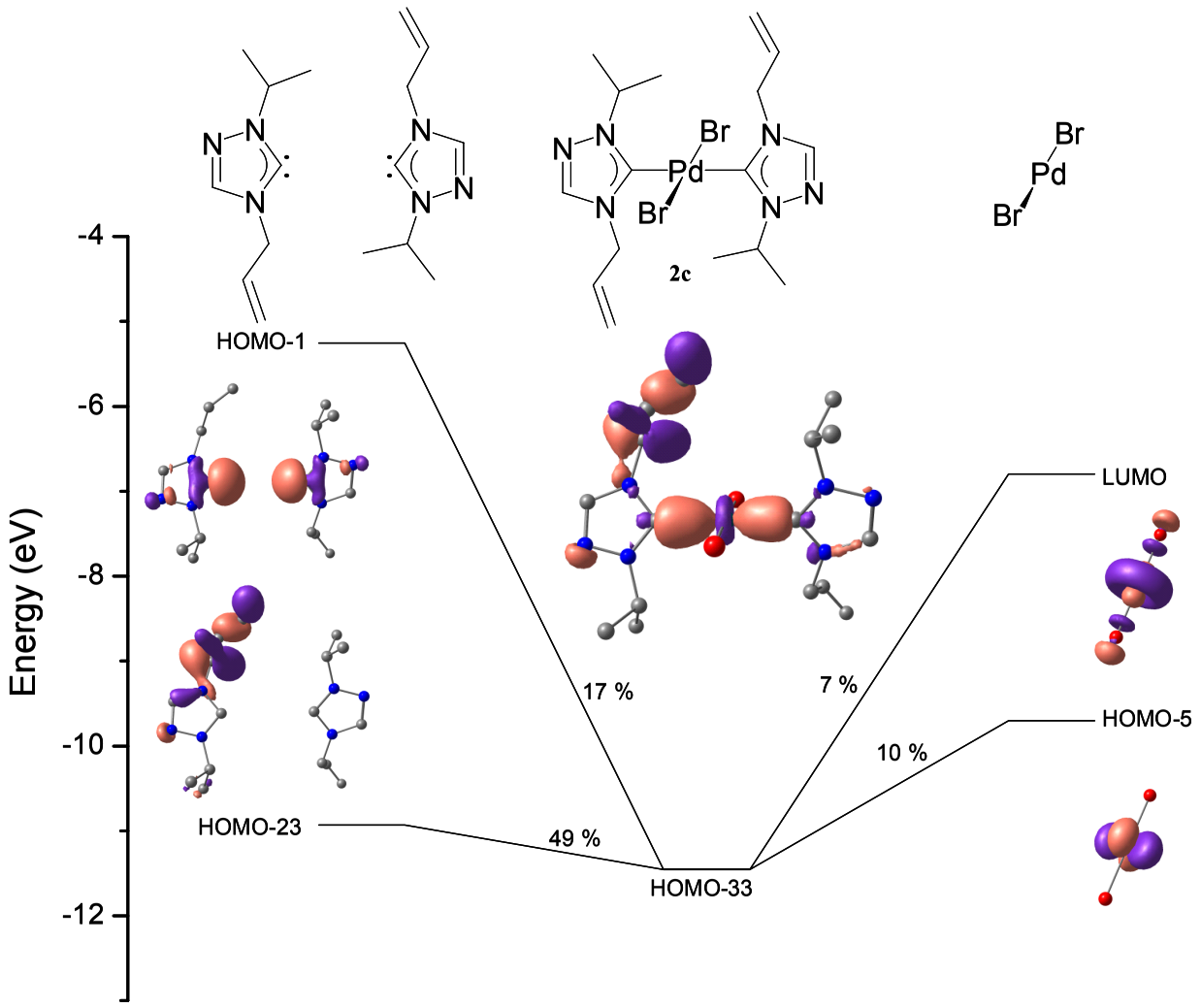


Figure S7. Simplified orbital interaction diagram showing the major contributions of the NHC-palladium bond in **2c.**

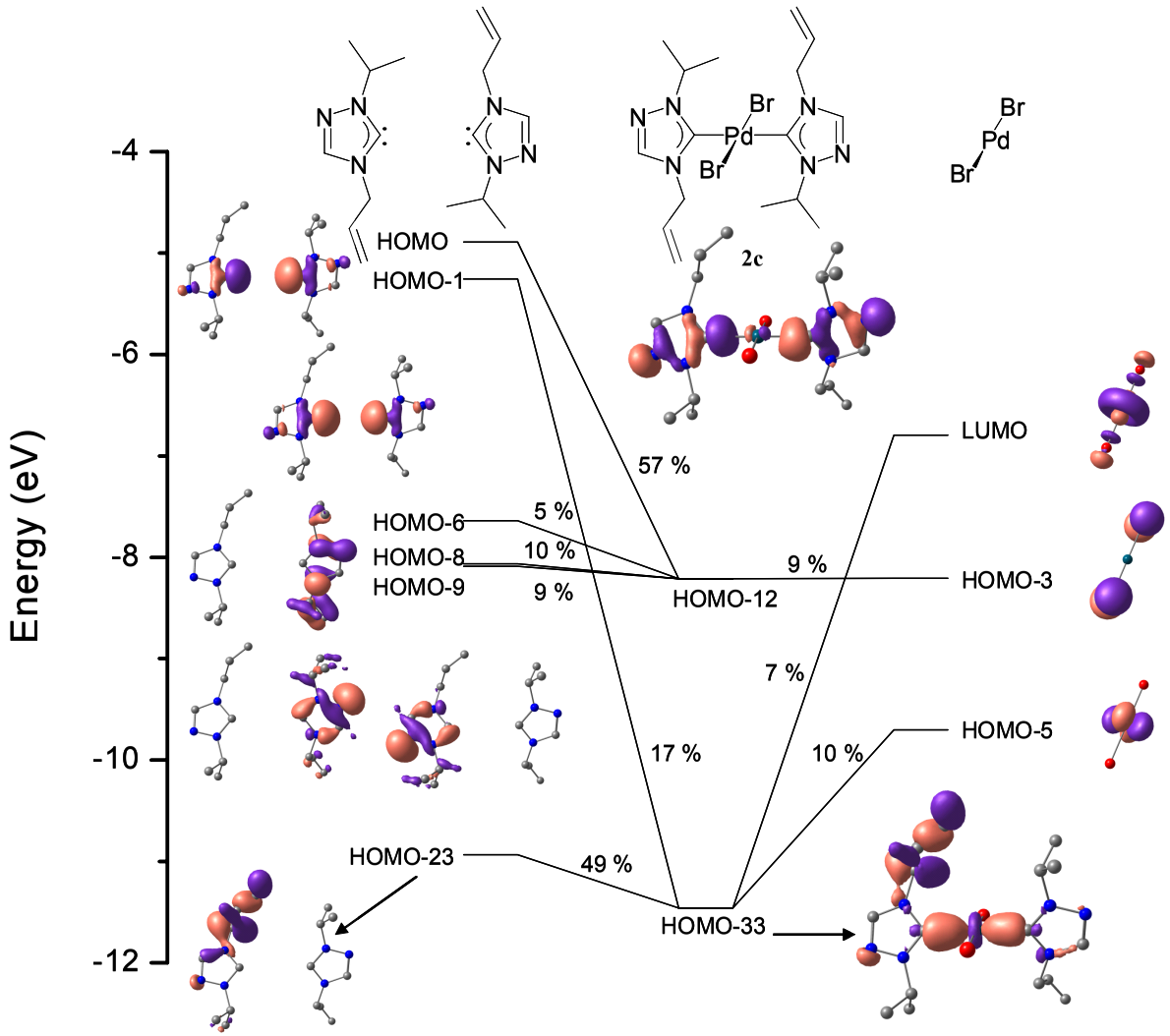


Figure S8. Orbital interaction diagram showing the major contributions of the NHC-palladium bond in **2c.**

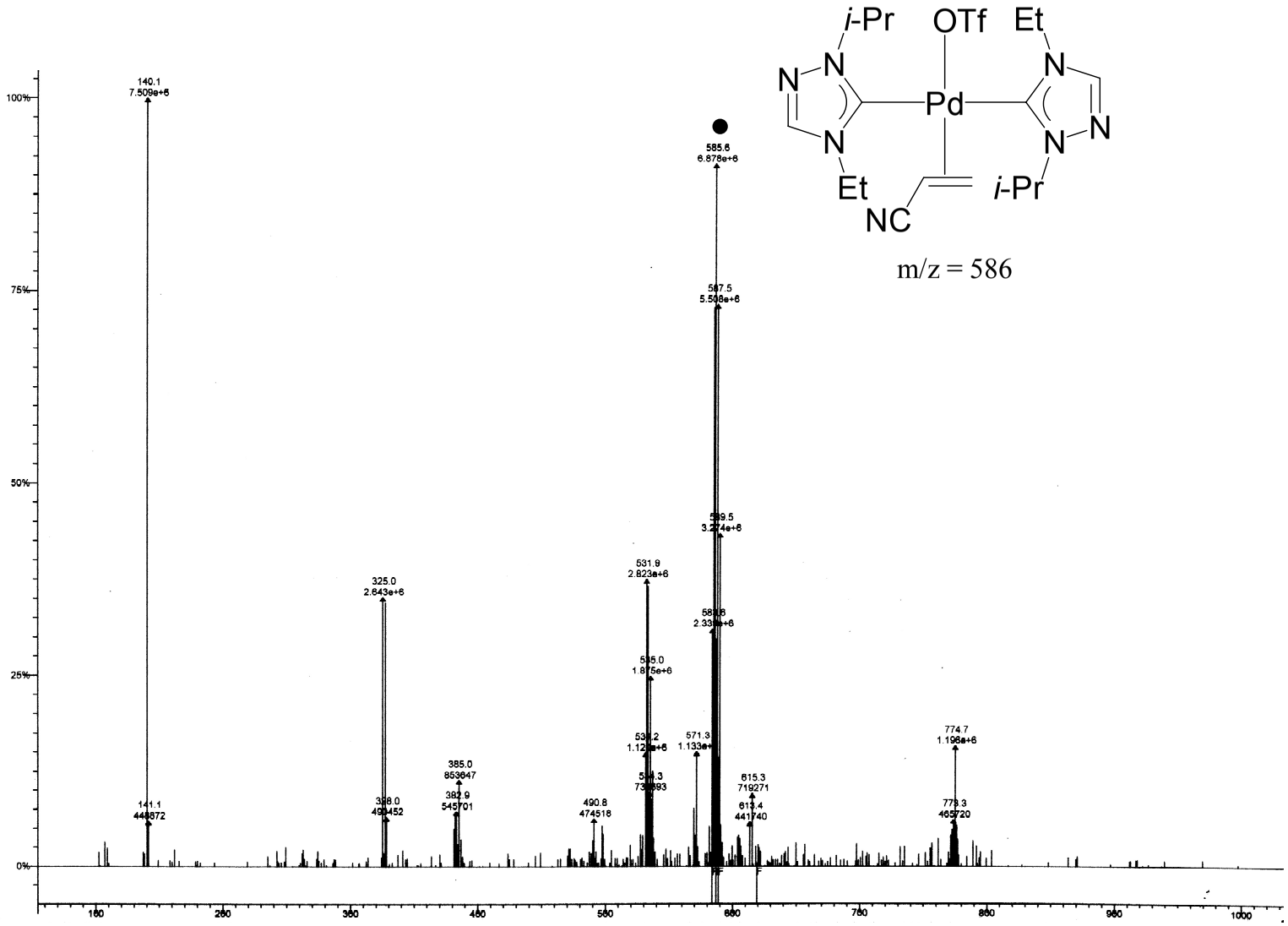


Figure S9. LCMS–ESI mass spectrum (in positive ion mode) of olefin adduct of **1c** in $CHCl_3$.

The density functional theory calculations were performed on **1b**, **2b**, **1c** and **2c** using GAUSSIAN 03[1] suite of quantum chemical programs.

Table S1. B3LYP/LANL2DZ, 6-31G* optimized coordinates of **1b**.

Ground state electronic energy = -6189.8867185 hartree/particle.

Ni	0.077871	0.075937	8.282736
Br	0.113026	0.168181	10.656394
Br	0.020148	0.005255	5.910527
N	-0.483943	2.977783	8.280916
N	1.592267	2.623105	8.024727
N	0.077932	4.227405	8.169213
N	-1.433072	-2.457151	8.643456
N	0.601156	-2.83983	8.175426
N	0.029448	-4.082094	8.315766
C	0.403192	1.97432	8.198449
C	1.345641	3.973139	8.017557
H	2.11265	4.723826	7.893304
C	-1.942439	2.853103	8.450664
H	-2.107361	1.774208	8.514445
C	-2.377097	3.510777	9.762761
H	-1.861366	3.048792	10.610125
H	-3.456464	3.383011	9.899365
H	-2.154523	4.582385	9.751572
C	-2.661291	3.408843	7.218229
H	-2.459319	4.478299	7.102358
H	-3.742431	3.270634	7.327266
H	-2.332759	2.887932	6.313246
C	2.903527	1.978136	7.897886
H	2.734359	1.040045	7.364263
H	3.517603	2.616479	7.254133
C	3.573193	1.745456	9.252613
H	3.773672	2.694401	9.762381
H	4.527989	1.227456	9.108527
H	2.931902	1.136759	9.89722
C	-0.254957	-1.823372	8.366221
C	-1.212057	-3.81039	8.598301
H	-1.976693	-4.550897	8.783438

C	-2.713256	-1.792337	8.910791
H	-2.481141	-0.904095	9.503359
H	-3.300964	-2.466871	9.541916
C	-3.46388	-1.440457	7.625955
H	-2.849904	-0.800731	6.984384
H	-4.391648	-0.911931	7.872382
H	-3.724299	-2.342199	7.060789
C	2.032087	-2.739673	7.836981
H	2.217422	-1.663209	7.798118
C	2.878232	-3.370363	8.946163
H	2.67256	-2.893746	9.910092
H	3.941714	-3.245205	8.715685
H	2.667109	-4.440729	9.032807
C	2.28672	-3.344452	6.453883
H	2.031456	-4.40881	6.443901
H	3.345939	-3.239538	6.194926
H	1.690051	-2.824587	5.698386

Table S2. B3LYP/LANL2DZ, 6-31G* optimized coordinates of **2b**.

Ground state electronic energy = -6266.0339022 hartree/particle.

Ni	-0.1124	-0.0287	-0.0101
Br	0.16331	0.64457	-2.2809
Br	-0.363	-0.655	2.26864
N	-2.9775	0.67266	0.19846
N	-2.7343	-1.0535	-1.0122
N	-4.2497	0.33341	-0.1962
N	2.72778	-0.8101	0.37576
N	2.50539	1.30034	0.37486
N	3.99924	-0.3168	0.55552
C	-2.0227	-0.1447	-0.2769
C	-4.0641	-0.7234	-0.9315
H	-4.8506	-1.2772	-1.4235
C	-2.7902	1.86184	1.05216
H	-1.7189	1.86855	1.26532
C	-3.5566	1.69183	2.36585
H	-4.6317	1.60172	2.18192
H	-3.3849	2.56514	3.00425
H	-3.2047	0.80191	2.89532

C	-3.1811	3.12462	0.27868
H	-2.5944	3.21743	-0.6413
H	-2.997	4.00843	0.89901
H	-4.2432	3.10415	0.01425
C	-2.1768	-2.1573	-1.8044
H	-2.9785	-2.4742	-2.4835
H	-1.3625	-1.7498	-2.4094
C	-1.7128	-3.3188	-0.965
H	-2.3745	-3.6217	-0.1544
C	-0.5875	-3.9919	-1.2046
H	0.09038	-3.7061	-2.006
H	-0.3084	-4.858	-0.6112
C	1.78904	0.14238	0.26021
C	3.82748	0.97323	0.54727
H	4.61693	1.70223	0.65301
C	2.52024	-2.2696	0.34764
H	1.44499	-2.3841	0.18996
C	2.89683	-2.8781	1.70104
H	3.95622	-2.7121	1.92135
H	2.71126	-3.9576	1.68268
H	2.28907	-2.4349	2.49509
C	3.28731	-2.8827	-0.8275
H	2.9762	-2.4325	-1.7761
H	3.09244	-3.9596	-0.8728
H	4.3649	-2.7323	-0.7085
C	1.96097	2.66399	0.30169
H	0.88488	2.54403	0.1541
H	2.12524	3.1613	1.26403
C	2.56656	3.4491	-0.8297
H	2.41044	3.02461	-1.8199
C	3.22853	4.59443	-0.6633
H	3.38355	5.03052	0.32202
H	3.62959	5.14817	-1.5075

Table S3. B3LYP/SDD, 6-31G* optimized coordinates of **1c**.

Ground state electronic energy = -6148.5188855 hartree/particle.

Pd	-0.03511	-0.23441	0.020966
Br	-0.08352	2.256082	0.085031

Br	0.009741	-2.7229	-0.05231
N	-0.39051	-0.56894	3.058237
N	1.598374	0.030813	2.612836
N	0.233989	-0.47305	4.277518
N	-1.68353	-0.42376	-2.56742
N	0.337317	0.055539	-3.01574
N	-0.29371	-0.00367	-4.2347
C	-0.47408	-0.19432	-1.97472
C	-1.52433	-0.29465	-3.92343
H	-2.32372	-0.42719	-4.63788
C	-2.93873	-0.71604	-1.86389
H	-3.55022	-1.32382	-2.53863
H	-2.67467	-1.33564	-1.00401
C	-3.67592	0.55401	-1.43848
H	-3.04595	1.164441	-0.78429
H	-4.59019	0.284963	-0.89776
H	-3.95838	1.158288	-2.30769
C	1.779246	0.365171	-2.96682
H	2.017724	0.337918	-1.90065
C	2.572327	-0.71987	-3.70062
H	2.37581	-1.70617	-3.26793
H	3.644316	-0.51132	-3.61646
H	2.307466	-0.74379	-4.76232
C	2.031277	1.775065	-3.5076
H	1.724828	1.849093	-4.55578
H	3.099866	2.007001	-3.44239
H	1.479184	2.514663	-2.91977
C	0.405021	-0.26899	2.018039
C	1.445427	-0.10887	3.968451
H	2.234836	0.069843	4.683929
C	2.833562	0.406906	1.913416
H	3.421615	1.013402	2.609782
H	2.536591	1.048833	1.080868
C	3.625504	-0.81038	1.435601
H	3.943437	-1.43309	2.279158
H	4.521242	-0.47867	0.898646
H	3.020051	-1.42579	0.763153
C	-1.81297	-0.95969	3.008858
H	-2.0428	-0.98027	1.940747
C	-1.99263	-2.36403	3.590752
H	-1.3974	-3.08987	3.028721

H	-3.04652	-2.65496	3.524001
H	-1.69238	-2.39075	4.642945
C	-2.6693	0.102271	3.704615
H	-3.72791	-0.16609	3.62141
H	-2.52288	1.084703	3.24404
H	-2.4134	0.171975	4.766566

Table S4. B3LYP/SDD, 6-31G* optimized coordinates of **2c**.

Ground state electronic energy = -6224.6661602 hartree/particle.

Pd	0.09908	0.00145	4.4E-05
Br	-0.2484	0.60874	-2.401
Br	0.38815	-0.5814	2.40447
N	3.09591	0.66533	0.17836
N	2.8079	-1.0289	-1.0709
N	4.356	0.31212	-0.2398
N	-2.8308	-0.8263	0.41431
N	-2.6519	1.29028	0.43863
N	-4.1099	-0.3611	0.60786
C	2.12148	-0.1246	-0.3055
C	4.14336	-0.7244	-0.997
H	4.91463	-1.2796	-1.5111
C	2.94339	1.8472	1.05162
H	1.87576	1.87255	1.27957
C	3.34788	3.1113	0.28707
H	4.40614	3.07579	0.00924
H	3.18656	3.99054	0.91999
H	2.75115	3.22594	-0.624
C	3.72778	1.64626	2.3502
H	3.36537	0.76049	2.87967
H	3.58582	2.51738	2.99873
H	4.79762	1.53464	2.14802
C	2.22703	-2.1224	-1.8647
H	2.99894	-2.4061	-2.5913
H	1.37674	-1.714	-2.4165
C	1.82512	-3.312	-1.0328
H	2.54667	-3.6453	-0.2874
C	0.67983	-3.9715	-1.2055
H	-0.0558	-3.6529	-1.9408

H	0.44108	-4.8557	-0.6215
C	-1.9138	0.14829	0.30559
C	-3.9652	0.93267	0.61246
H	-4.7699	1.64296	0.73157
C	-2.5933	-2.2819	0.35989
H	-1.5214	-2.3684	0.16383
C	-2.9144	-2.9155	1.71607
H	-2.2906	-2.4745	2.49907
H	-2.7111	-3.9911	1.67531
H	-3.9692	-2.7721	1.97196
C	-3.3839	-2.8955	-0.7992
H	-4.4603	-2.7745	-0.6432
H	-3.1636	-3.9664	-0.8665
H	-3.1143	-2.4248	-1.7505
C	-2.1381	2.66721	0.37062
H	-1.0491	2.5724	0.3486
H	-2.42	3.18896	1.29158
C	-2.6402	3.39445	-0.8472
H	-2.3758	2.93577	-1.7986
C	-3.3354	4.53075	-0.7928
H	-3.5968	5.00043	0.15404
H	-3.6589	5.04362	-1.6941

Table S5. Natural charge analyses of **1b** and **2b**.

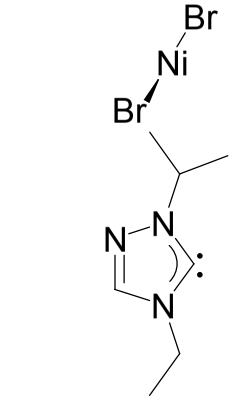
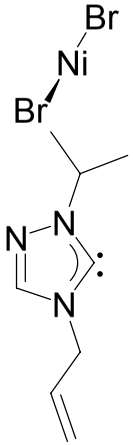
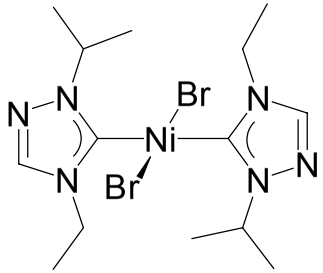
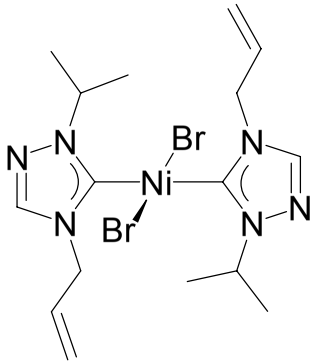
specie/compound	$C_{carbene}$	Ni	specie/compound	$C_{carbene}$	Ni
	0.130 0.130	0.806		0.138 0.132	0.808
 **1b**	0.180 0.177	0.598	 **2b**	0.181 0.177	0.607

Table S6. Mulliken charge analyses of **1b** and **2b**.

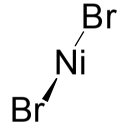
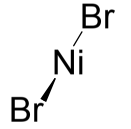
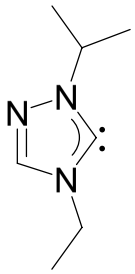
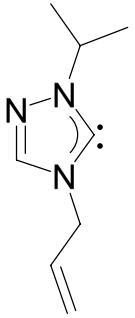
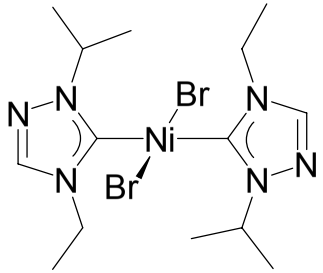
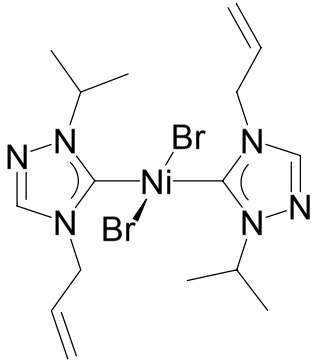
specie/compound	$C_{carbene}$	Ni	specie/compound	$C_{carbene}$	Ni
		0.375			0.374
	0.084 0.084			0.090 0.084	
	0.330 0.329	-0.184		0.324 0.323	-0.148
1b			**2b**		

Table S7. Natural charge analyses of **1c** and **2c**.

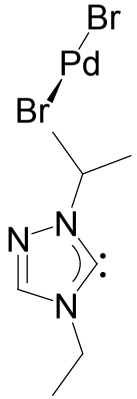
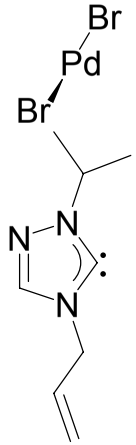
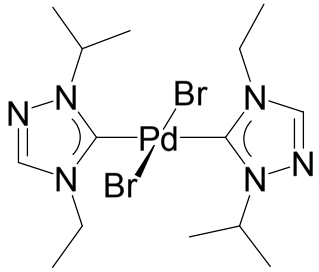
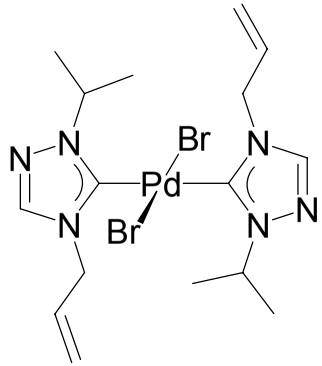
specie/compound	$C_{carbene}$	Pd	specie/compound	$C_{carbene}$	Pd
	0.126 0.126	0.885		0.135 0.128	0.884
 **1c**	0.226 0.224	0.411	 **2c**	0.222 0.230	0.421

Table S8. Mulliken charge analyses of **1c** and **2c**.

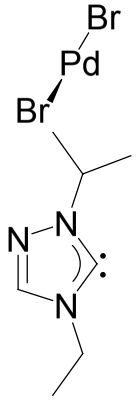
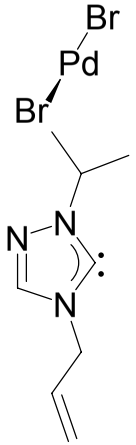
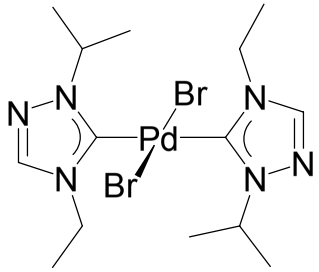
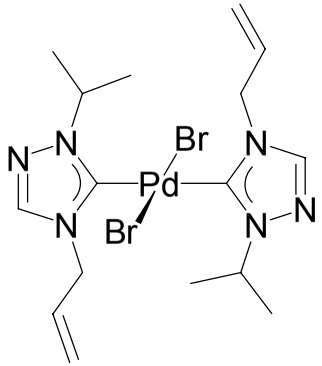
specie/compound	$C_{carbene}$	Pd	specie/compound	$C_{carbene}$	Pd
	0.081 0.080	0.365		0.088 0.081	0.365
 **1c**	0.429 0.429	-0.527	 **2c**	0.430 0.428	-0.465

Table S9. Electronic configuration of **1b** and **2b**.

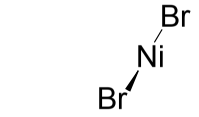
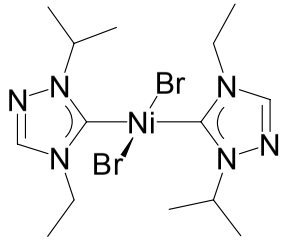
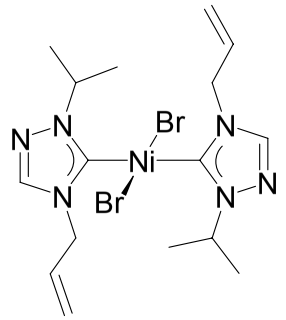
specie/compound	*4s*	*3d*	*4p*	*4d*	*5p*
Ni^{2+}		8.00			
	0.46	8.69	0.03		
 **1b**	0.43	8.95	0.01	0.01	0.01
 **2b**	0.43	8.95	0.01	0.01	0.01

Table S10. Electronic configuration of **1c** and **2c**.

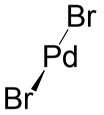
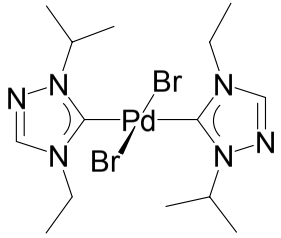
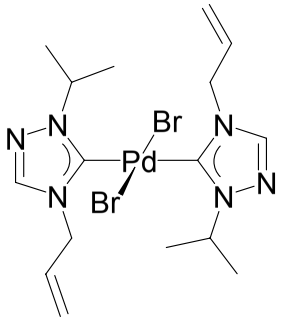
specie/compound	*5s*	*4d*	*5p*	*5d*	*6p*	*6d*	*7p*
Pd^{2+}		8.00					
	0.08	8.97	0.05	0.01			
 **1c**	0.50	9.07		0.01	0.01	0.01	0.01
 **2c**	0.49	9.06	0.01	0.01	0.01	0.01	0.01

Table S11. Hybrid orbitals of the $C_{carbene}$–Ni and $C_{carbene}$–Pd bond in **1b**, **2b**, **1c** and **2c**.

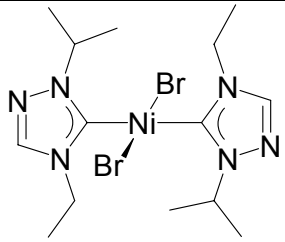
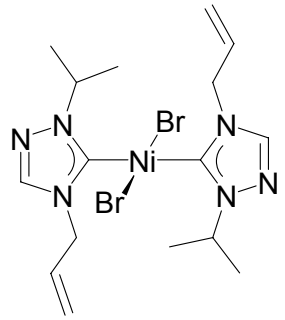
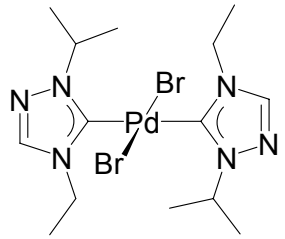
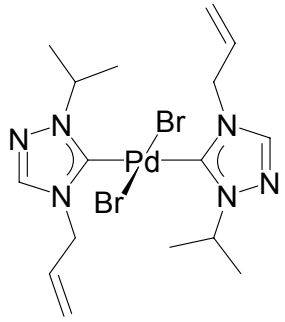
compound	hybrid orbitals of $C_{carbene}$–M bond (M = Ni, Pd)	$C_{carbene}$		M (M = Ni, Pd)	
		s (%)	*p* (%)	*s* (%)	*d* (%)
 **1b**	[C($sp^{1.69}$)–Ni($sd^{1.04}$)]	37.18	62.81	49.05	50.85
 **2b**	[C($sp^{1.70}$)–Ni($sd^{1.03}$)]	37.08	62.92	49.24	50.68
 **1c**	[C($sp^{1.64}$)–Pd($sd^{1.18}$)]	37.85	62.15	45.65	54.07
 **2c**	[C($sp^{1.65}$)–Pd($sd^{1.20}$)]	37.70	62.30	45.26	54.46

Table S12. Charge decomposition analysis (CDA) results showing the $NHC \xrightarrow{\sigma} MBr_2$ (M = Ni, Pd) donation (*d*), the $NHC \xleftarrow{\pi} MBr_2$ (M = Ni, Pd) donation (*b*), *d*/*b* ratio and the NHC↔MBr_2 (M = Ni, Pd) repulsive polarization (*r*) for **1b**, **2b**, **1c** and **2c**.

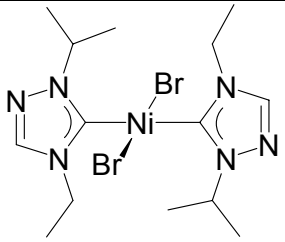
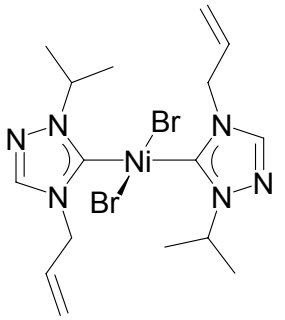
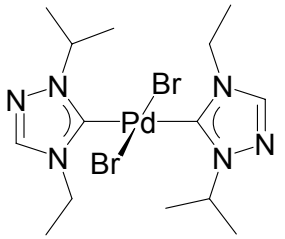
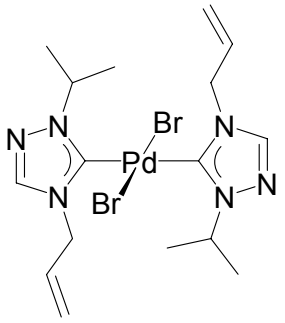
compound	$NHC \xrightarrow{\sigma} MBr_2$ (*d*)	$NHC \xleftarrow{\pi} MBr_2$ (*b*)	*d*/*b* ratio	repulsive polarization (*r*)
 **1b**	0.260	0.140	1.86	-0.023
 **2b**	0.249	0.145	1.72	-0.028
 **1c**	0.481	0.132	3.64	-0.175
 **2c**	0.453	0.139	3.26	-0.182

Table S13. Bond distance and bond energy of $C_{carbene}$–Ni or $C_{carbene}$–Pd bonds in **1b**, **2b**, **1c** and **2c**.

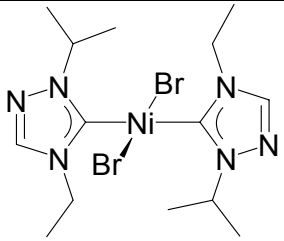
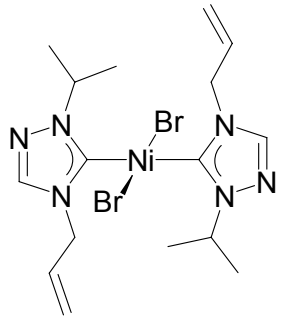
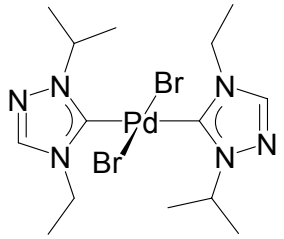
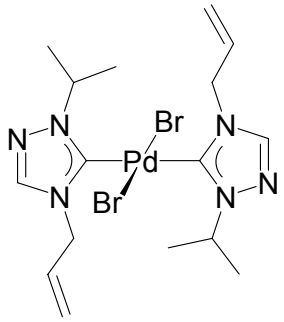
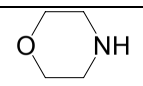
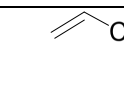
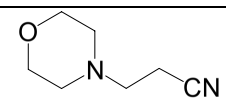
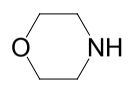
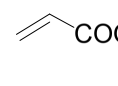
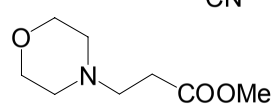
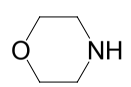
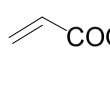
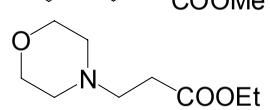
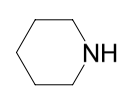
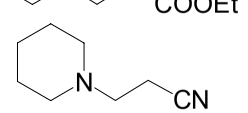
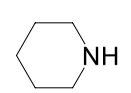
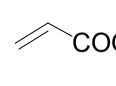
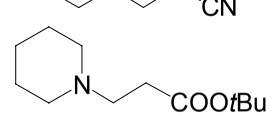
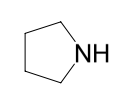
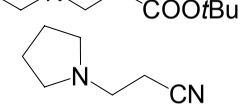
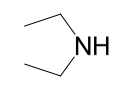
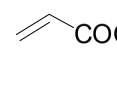
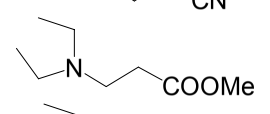
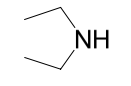
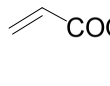
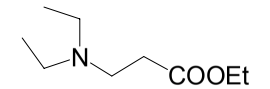
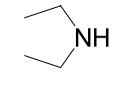
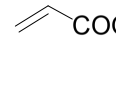
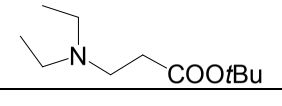
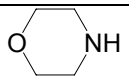
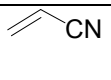
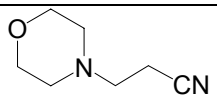
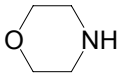
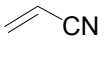
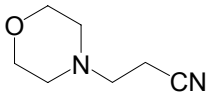
compound	d/($C_{carbene}$–Ni) or d/($C_{carbene}$–Pd) (Å)	D_e ($C_{carbene}$–Ni) or D_e ($C_{carbene}$–Pd) (kcal/mol)
 **1b**	1.93	68.8
 **2b**	1.93	68.9
 **1c**	2.05	74.7
 **2c**	2.05	74.8

Table S14. Selected results of control and blank experiments of hydroamination reaction with aliphatic amines catalyzed by $NiBr_2$/AgOTf, $NiCl_2$/AgOTf, $PdBr_2$/AgOTf and $PdCl_2$/AgOTf, AgOTf and blank.[a]

entry	reagent	reagent	product	$NiBr_2$/AgOTf Yield[b]	$NiCl_2$/AgOTf Yield[b]	$PdBr_2$/AgOTf Yield[b]	$PdCl_2$/AgOTf Yield[b]	AgOTf Yield[b]	blank Yield[b]
1				8	16	43	49	3	1
2				21	30	15	37	15	14
3				20	28	11	20	24	15
4				55	67	45	58	56	40
5				72	61	45	51	62	39
6				49	56	47	53	46	46
7				18	43	7	16	3	5
8				14	15	6	12	7	7
9				4	6	1	8	1	1

[a] Reaction conditions: 0.50 mmol of aliphatic amines, 1.00 mmol of activated olefin, 5 mol % of $NiCl_2$ or $NiBr_2$ or $PdBr_2$ or $PdCl_2$/ 10 mol % AgOTf , 10 mol% AgOTf and blank and 5 mL of dry CH_3CN at room temperature under inert conditions (1 hour). [b] The yields (%) were determined by GC using diethylene glycol-di-*n*-butyl ether as an internal standard.

Table S15. Selected results of control experiments of hydroamination reaction with aliphatic amines catalyzed by NHC ligand precursors **1a** and **2a**.

NHC ligand precursor	reagent[a]	reagent[a]	product	ligand/KO^{t}Bu Yield[b]	ligand/Et_3N Yield[b]
1a				4	1
2a				8	5

[a] Reaction conditions: 0.50 mmol of aliphatic amines, 1.00 mmol of activated olefin, 10 mol % of **1a** or **2a**, 12 mol % base and 5 mL of dry CH_3CN at room temperature under inert conditions (1 hour). [b] The yields (%) were determined by GC using diethylene glycol-di-*n*-butyl ether as an internal standard.

References

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