

Supporting Information For

A Palladacyclic N-Heterocyclic Carbene System Used to Probe the Donating Capabilities of Monoanionic Chelators

*Xuechao Yan,^a Rui Feng,^a Chunhui Yan,^a Peng Lei,^a Shuai Guo,^{*a} Han Vinh Huynh^{*b}*

^a Department of Chemistry, Capital Normal University, Beijing, People's Republic of China 100048.

^b Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543.

1. Figure SI-1. Molecular structures of complexes 6 and 7 showing 50% probability ellipsoids.	2
2. Figure SI-2. Molecular structure of complex 10 showing 50% probability ellipsoids.	2
3. Scheme SI-1. Syntheses of monocationic triazolium salts c and d	2
4. Table SI-1. Selected Interatomic Distances (Å) and Angles (°) for Complexes 5 , 6 , 7 , and 10	3
5. Table SI-2. Selected X-ray Crystallographic Data for Complexes 5 , 6 , 7 , and 10	4
6. Figure SI-3. The ¹ Pr ₂ -bimy ¹³ C _{carbene} signals on a ¹³ C NMR scale indicating the relative donor abilities of trz ligands.	5
7. Figure SI-4. 1D NOESY spectrum of palladacyclic complex 12 with signals (δ = 5.96 ppm) of isopropyl C–H protons (H _a) suppressed.	5

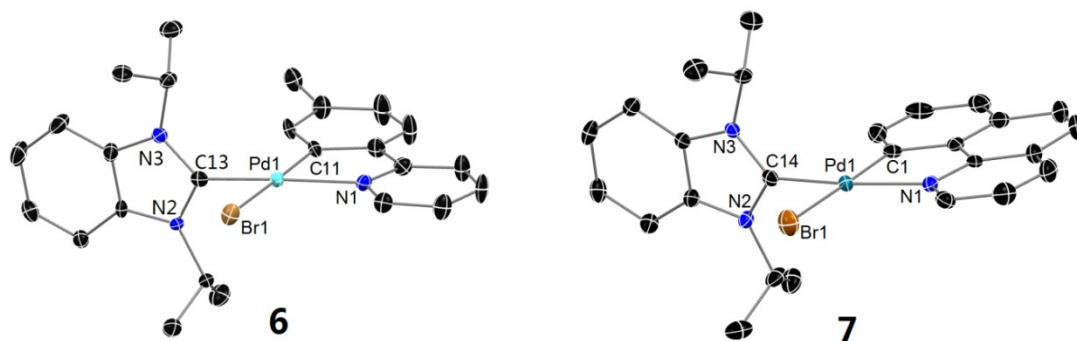


Figure SI-1. Molecular structures of complexes **6** and **7** showing 50% probability ellipsoids. Hydrogen atoms, solvent molecules, and another crystallographically independent molecule (for **6**) are omitted for clarity.

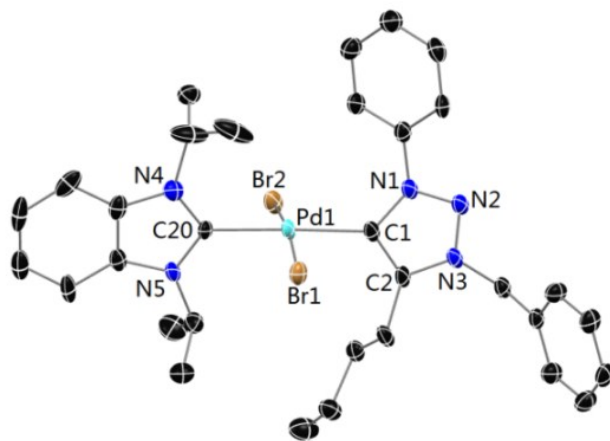
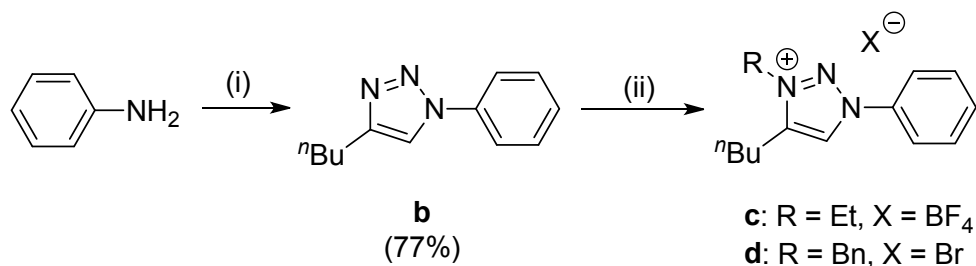


Figure SI-2. Molecular structure of complex **10** showing 50% probability ellipsoids. Hydrogen atoms and another crystallographically independent molecule are omitted for clarity.



Scheme SI-1. Syntheses of monocationic triazolium salts **c** and **d**. Condition for step (i): a) NaNO₂, HCl; b) NaN₃; c) 1 mol% [CuCl(IPr)], 1-butyne, CH₃OH/H₂O. Condition for step (ii): for **c**, (CH₃CH₂)₃OBF₄, 1,2-dichloroethane; for **d**, benzyl bromide, neat.

Table SI-1. Selected Interatomic Distances (Å) and Angles (°) for Complexes **5**, **6**, **7**, and **10**.

Complex	5		6	
Bond Distances (Å)	Pd1–C11	1.969(4)	Pd1–C11	2.002(4)
	Pd1–N1	2.087(3)	Pd1–N1	2.095(3)
	Pd1–Br1	2.5134(5)	Pd1–Br1	2.5236(5)
	Pd1–C12	1.973(4)	Pd1–C13	1.972(4)
	H19···Pd1	2.756	H23···Pd1	2.778
	H22···Pd1	2.687	H14···Pd1	2.666
Bond Angles (°)	C11–Pd1–C12	92.72(15)	C11–Pd1–C13	92.01(15)
	C12–Pd1–Br1	88.25(10)	C13–Pd1–Br1	89.10(11)
	N1–Pd1–Br1	97.60(9)	N1–Pd1–Br1	97.75(9)
	C11–Pd1–N1	81.42(14)	C11–Pd1–N1	81.28(14)
	C19–H19···Pd1	120.66	C23–H23···Pd1	121.08
	C22–H22···Pd1	121.44	C14–H14···Pd1	122.70
Complex	7		10	
Bond Distances (Å)	Pd1–C14	1.965(4)	Pd1–Br1	2.4483(6)
	Pd1–N1	2.091(3)	Pd1–Br2	2.4627(6)
	Pd1–Br1	2.5020(5)	Pd1–C1	2.044(5)
	Pd1–C1	1.975(4)	Pd1–C20	2.037(5)
	H21···Pd1	2.750		
	H24···Pd1	2.657		
Bond Angles (°)	C14–Pd1–C1	90.91(17)	Br1–Pd1–Br2	169.62(2)
	C14–Pd1–Br1	90.26(11)	Br1–Pd1–C1	92.62(13)
	N1–Pd1–Br1	95.73(10)	Br2–Pd1–C1	89.65(13)
	C1–Pd1–N1	83.05(16)	Br1–Pd1–C20	88.24(13)
	C21–H21···Pd1	120.56	Br2–Pd1–C20	89.10(13)
	C24–H24···Pd1	122.10	C1–Pd1–C20	177.6(2)

Table SI-2. Selected X-ray Crystallographic Data for Complexes **5**, **6**, **7**, and **10**.

Comp.	5	6	7	10
Formula	C ₂₄ H ₂₆ BrN ₃ Pd	C ₂₅ H ₂₈ BrN ₃ Pd	C ₂₆ H ₂₆ BrN ₃ Pd	C ₃₂ H ₃₉ Br ₂ N ₅ Pd
Formula weight	542.79	556.81	566.81	759.90
Crystal size [mm]	0.45 × 0.45 × 0.40	0.3 × 0.25 × 0.15	0.40 × 0.36 × 0.12	0.20 × 0.15 × 0.10
Temperature [K]	101.8	99.9(2)	113.8	100.00(10)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c	P2(1)/n	P2(1)/c
<i>a</i> [Å]	12.7217(3)	10.9330(5)	12.6065(6)	32.3500(3)
<i>b</i> [Å]	10.2318(3)	23.8367(10)	10.0844(4)	8.65960(10)
<i>c</i> [Å]	17.5246(4)	18.1370(7)	18.4740(9)	25.0145(2)
α [°]	90.00	90	90.00	90
β [°]	102.488(2)	98.263(4)	98.288(5)	94.5210(10)
γ [°]	90.00	90	90.00	90
<i>V</i> [Å ³]	2227.13(9)	4677.6(3)	2324.05(18)	6985.71(12)
<i>Z</i>	4	8	4	8
<i>D_c</i> [g·cm ⁻³]	1.619	1.581	1.620	1.445
μ [mm ⁻¹]	2.642	2.518	2.536	7.165
θ range [°]	5.98-52	6.57-50.998	6.02-52	7.09-147.816
no. of unique data	12213	28266	12320	41137
Final R indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0344, <i>wR</i> ₂ = 0.0725	<i>R</i> ₁ = 0.0414, <i>wR</i> ₂ = 0.0725	<i>R</i> ₁ = 0.0405, <i>wR</i> ₂ = 0.0884	<i>R</i> ₁ = 0.0656, <i>wR</i> ₂ = 0.1747
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0412, <i>wR</i> ₂ = 0.0752	<i>R</i> ₁ = 0.0594, <i>wR</i> ₂ = 0.0796	<i>R</i> ₁ = 0.0511, <i>wR</i> ₂ = 0.0941	<i>R</i> ₁ = 0.0714, <i>wR</i> ₂ = 0.1791
goodness of fit on <i>F</i> ²	1.042	1.045	1.023	1.063
Peak/hole [e·Å ⁻³]	2.580 / -0.475	0.86 / -0.85	1.385 / -1.092	2.38 / -2.29

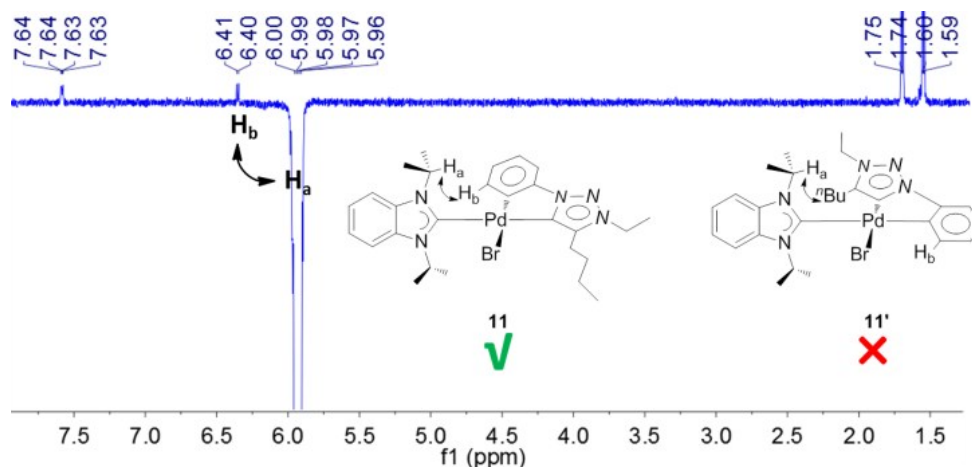


Figure SI-3. 1D NOESY spectrum of palladacycle **11** with the isopropyl C–H_a signals at $\delta = 5.98$ ppm suppressed.

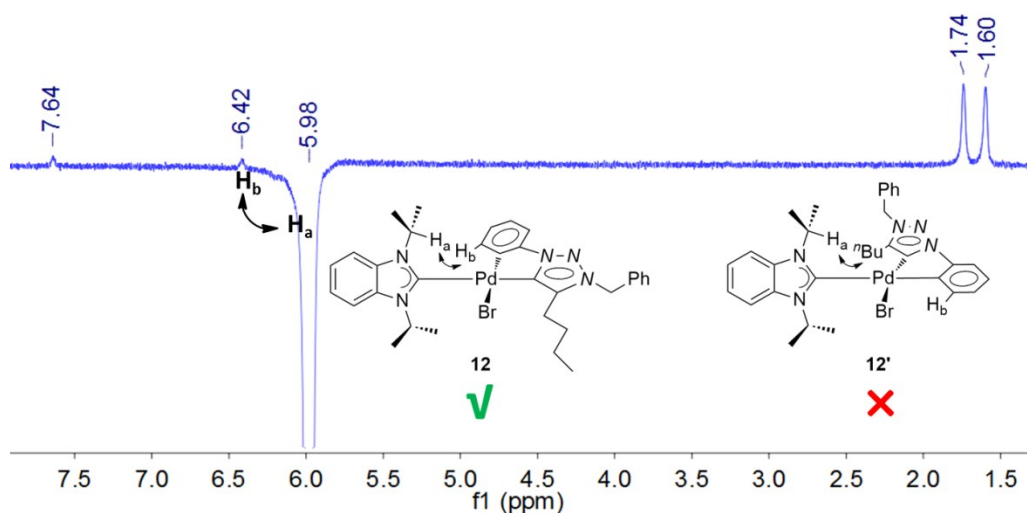


Figure SI-4. 1D NOESY spectrum of palladacyclic complex **12** with signals ($\delta = 5.96$ ppm) of isopropyl C–H protons (H_a) suppressed.

In a 1D NOESY spectrum, a pre-selected nucleus gives a negative peak while the spatially close nuclei show positive resonances. For example, in the case of **11**, upon selective inversion of the signal at 5.98 ppm for isopropyl C–H protons (H_a), NOE peaks of the physically neighboring nuclei including H_b were observed. No through-space correlation between H_a and the *n*-butyl group was found. All these observations unambiguously confirm the presence of **11** instead of **11'** as the single isomer.