Accessing Chelating Extended Linker Bis(NHC) Palladium(II) Complexes: Sterically Triggered Divergent Reaction Pathways

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Supporting Information

Table of Contents

I. NMR Spectra for Compound VII

MesIm)(1,2-Me$_2$Im-4H)C$_2$H$_4$][PdBr$_4$] (VII)
^{1}H NMR (DMSO-d_6, 400 MHz)

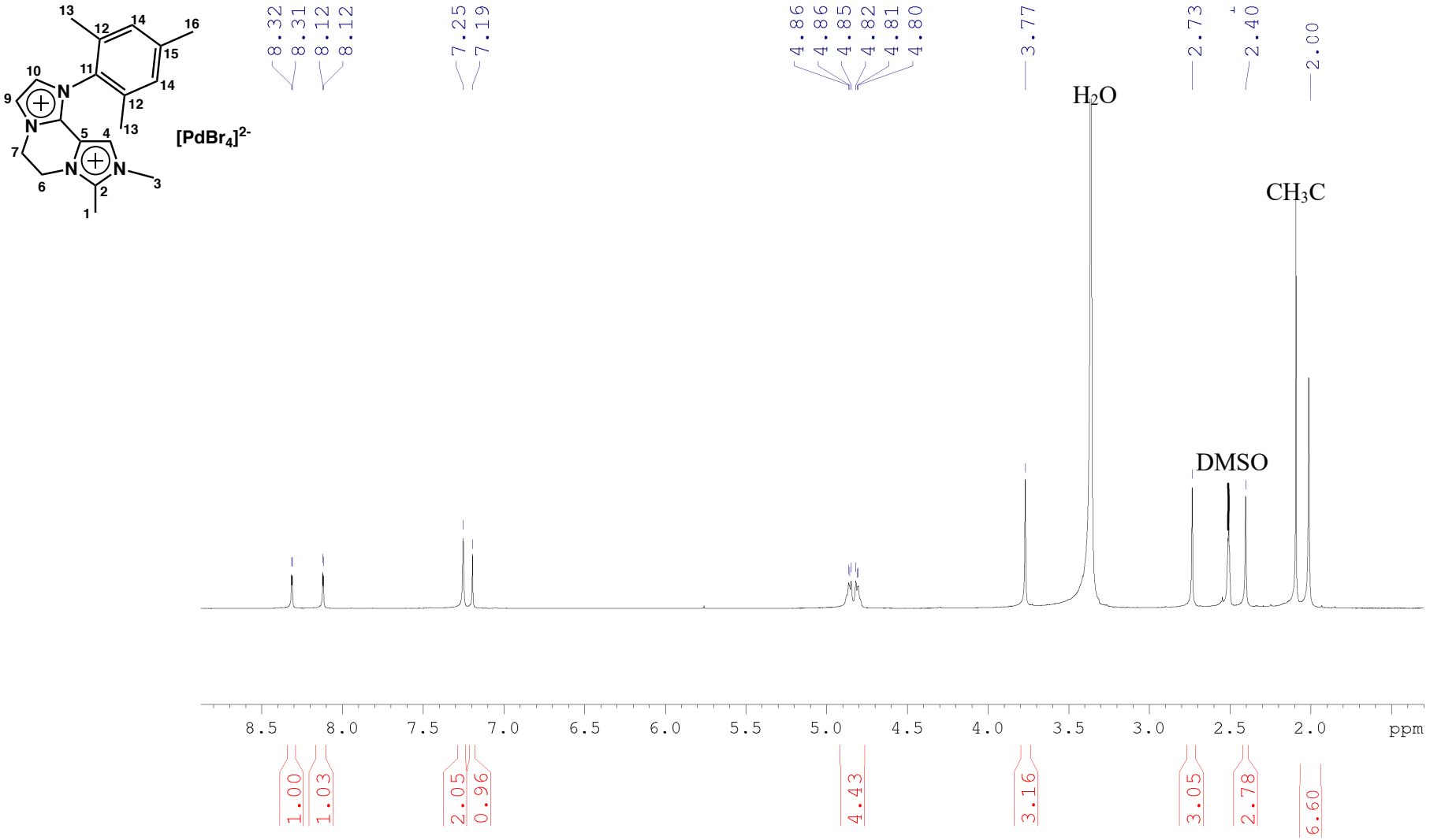

Figure S1 ^{1}H NMR spectrum of compound **VII** in DMSO-d_6

^{13}C NMR (DMSO-*d6,* 400 MHz)

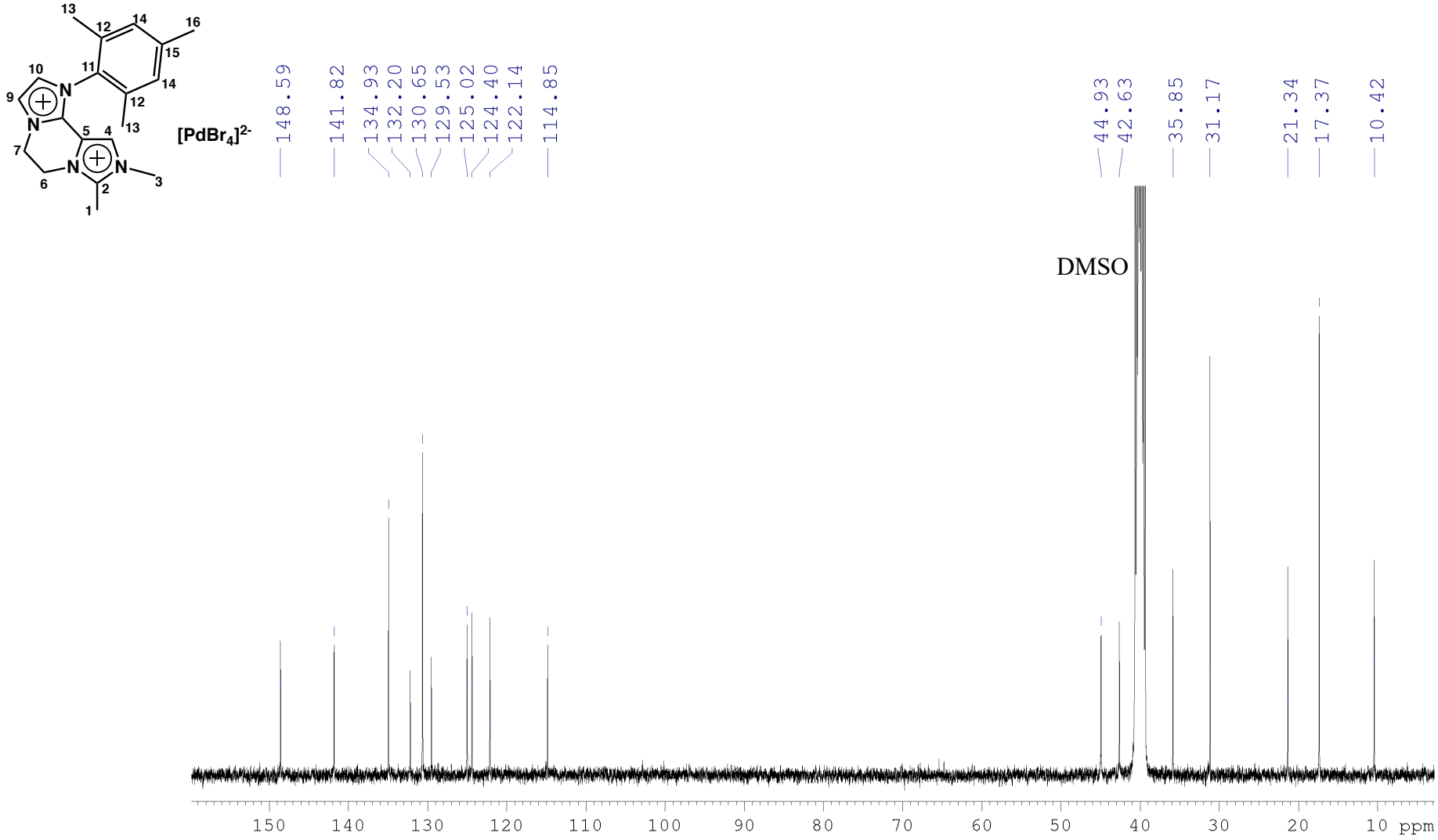

Figure S2 ^{13}C NMR spectrum of compound **VII** in DMSO-d_6

II. X-Ray Crystallographic Data

Crystallographic data for compounds **Ia, Ic, IIa, IIb, IIIb, IVc, V, VI** and **VII**.

Crystal data for compound **Ia**: $C_{24}H_{28}N_4Br_2$, M = 532.32, orthorhombic, a = 17.472(4), b = 6.4620(13) c = 21.226(4) Å, U = 2396.5(8) Å^{3,} T = 100 K, space group $Pna2_1$ (no. 33), Z = 4, 46094 reflections measured, 6990 unique (R_{int} = 0.0662), 5971 > 4σ(F), R = 0.0522 (observed), R_w = 0.1461 (all data). CCDC Number: 1915454

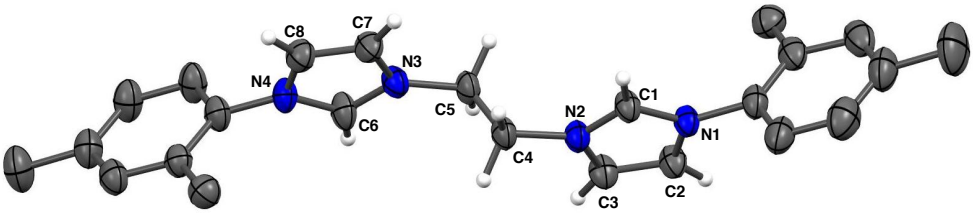

Figure S3. Structural representation of compound **Ia**. Thermal ellipsoids are shown at 50% probability level. Br$^-$ counteranions and *N*-substituent hydrogen atoms have been omitted for clarity

Crystal data for compound **Ic**: $C_{34}H_{48}N_4Br_2Cl_4$, M = 775.24, triclinic, a = 8.8660(18), b = 9.4750(19) c = 12.860(3) Å, α = 99.02(3), β = 99.32(3), γ = 113.93(3) ° U = 944.3(4) Å^{3,} T = 100 K, space group P-1 (no. 2), Z = 1, 15531 reflections measured, 4064 unique (R_{int} = 0.0737), 3440 > 4σ(F), R = 0.0751 (observed), R_w = 0.2208 (all data). CCDC Number: 1915452

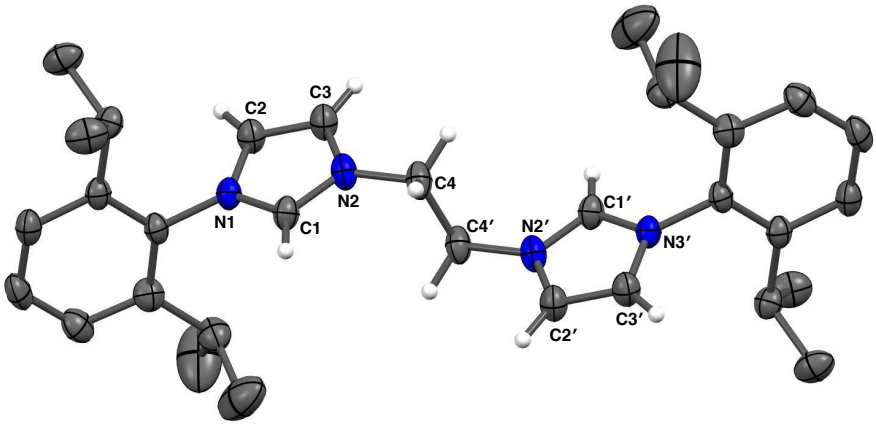

Figure S4. Structural representation of compound **Ic** (' denotes symmetry operator: -*x*, -*y*, -*z*). Thermal ellipsoids are shown at 50% probability level. Br$^-$ counteranions, lattice CH_2Cl_2 solvent molecules and *N*-substituent hydrogen atoms have been omitted for clarity.

Crystal data for compound **IIa**: $C_{24}H_{26}Br_2N_4Pd$, M = 636.71, triclinic, a = 7.9690(16), b = 15.138(3), c = 19.963(4) Å, α = 89.51(3), β = 89.98(3), γ = 83.31(3) °, U = 2391.8(8) Å^3, T = 100 K, space group P-1 (no 2), Z = 4, 50914 reflections measured, 13311 unique (R_{int} = 0.1154), 10264 > 4$\sigma(F)$, R = 0.0566 (observed), R_w = 0.1546 (all data). CCDC Number: 1915457

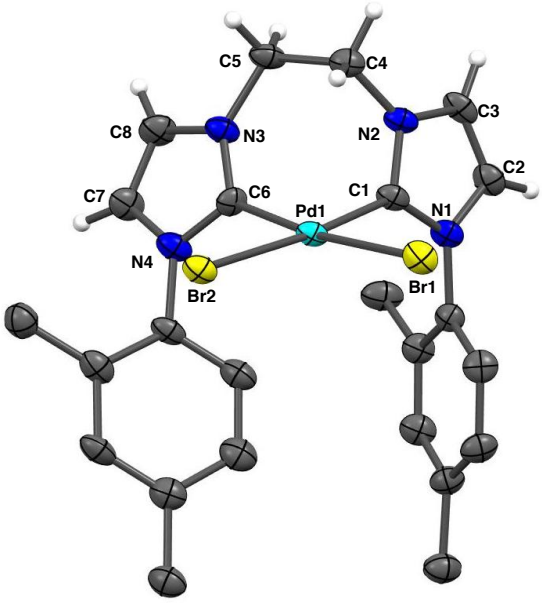

Figure S5. Structural representation of compound **IIa**. Thermal ellipsoids are shown at 50% probability level. *N*-substituent hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-C1,C6 1.973(6), 1.977(5), Pd1-Br1,Br2 2.477(1), 2.504(1), C1-Pd1-C6 85.5(2), Br1-Pd1-Br2 94.91(2), Pd1-C1-N2 120.6(4), Pd1-C6-N3 127.6(4) .

Crystal data for complex **IIb**: $C_{27}H_{32}Br_2Cl_2N_4Pd$, M = 749.68, monoclinic, a = 11.631(3), b = 14.050(9) c = 17.964(2) Å, α = 90, β = 99.88(7), γ = 90 °, U = 2982.1(10) Å^3, T = 100 K, space group $P2_1/n$ (no. 14), Z = 4, 43671 reflections measured, 6345 unique (R_{int} = 0.0347), 6204 > 4$\sigma(F)$, R = 0.0795 (observed), R_w = 0.2145 (all data). CCDC Number: 1915459

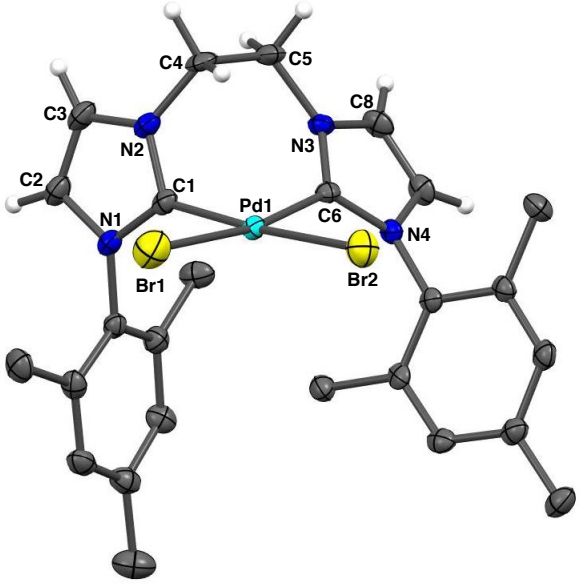

Figure S6. Structural representation of complex **IIb**. Thermal ellipsoids are shown at 50% probability level. Lattice CH_2Cl_2 solvent molecules and *N*-substituent hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-C1,C6 2.002(7), 1.992(7), Pd1-Br1,Br2 2.4996(13), 2.4907(12), C1-Pd1-C6 87.5(3), Br1-Pd1-Br2 90.66(4)

Crystal data for complex **IIIb**: $C_{26}H_{29}Br_3N_4Pd$, M = 743.67, monoclinic, a = 16.659(3), b = 11.386(2), c = 17.142(3) Å, β = 104.31(3) °, U = 3150.7(12) Å^{3,} T = 100 K, space group $P2_1/n$ (no. 14), Z = 4, 48236 reflections measured, 6952 unique (R_{int} = 0.0496), 5715 > 4σ(F), R = 0.0395 (observed), R_w = 0.1003 (all data). CCDC Number: 1915458

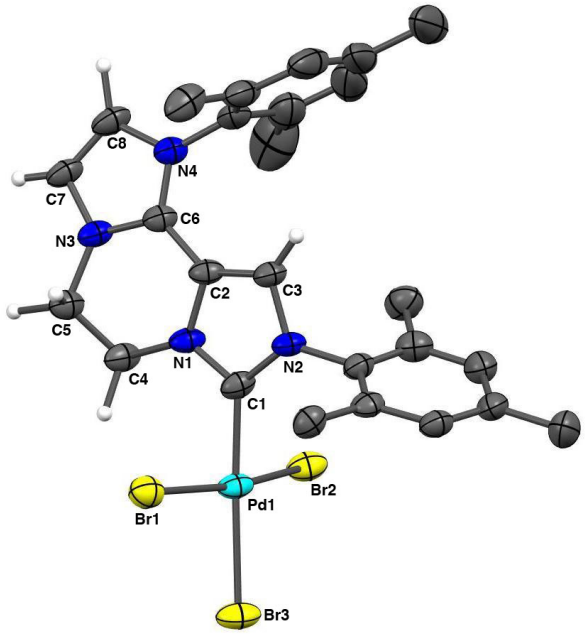

Figure S7. Structural representation of complex **IIIb**. Thermal ellipsoids are shown at 50% probability level. *N*-substituent hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-C1 1.954(4), Pd1-Br1,Br2,Br3 2.4497(8), 2.4914(8), 2.4451(8), C1-Pd1-Br1,Br3 89.19(14), 85.57(14), Br1-Pd1-Br2 90.59(3), Br2-Pd1-Br3 95.35(3).

Crystal data for complex **IVc**: $C_{33.79}H_{45.6825}Br_3N_{4.895}Pd$, M = 866.57, triclinic, a = 10.417(2), b = 13.912(3), c = 27.084(5) Å, α = 83.16(3), β = 79.93(3), γ = 74.26(3) ° U = 3709.1(15) Å^{3,} T = 100 K, space group P-1 (no. 2), Z = 4, 62580 reflections measured, 16270 unique (R_{int} = 0.1123), 10207 > 4σ(F), R = 0.0701 (observed), R_w = 0.2004 (all data). CCDC Number: 1915453

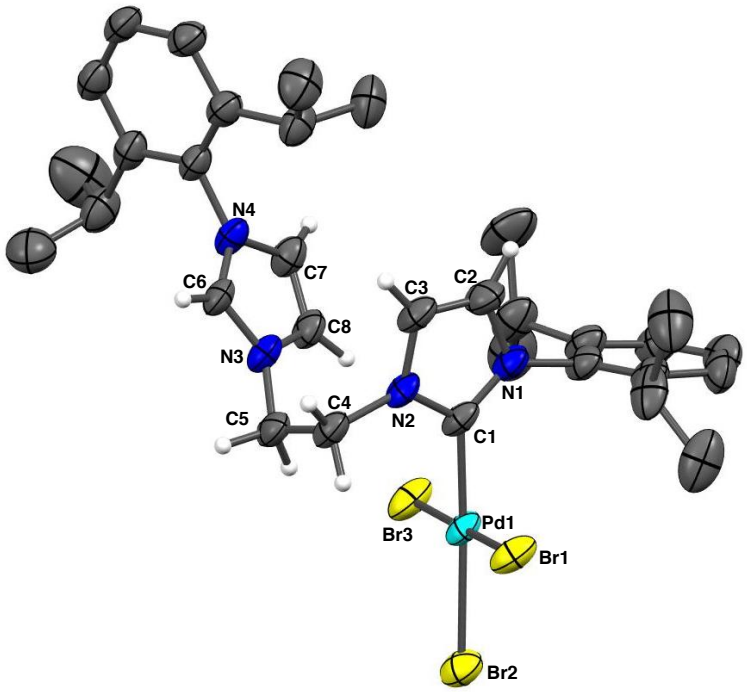

Figure S8. Structural representation of complex **IVc**. Thermal ellipsoids are shown at 50% probability level. *N*-substituent hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-C1 1.993(1), Pd1-Br1,Br2,Br3 2.429(1), 2.518(1), 2.424(1), C1-Pd1-Br1,Br3 86.1(2), 92.4(2), Br1-Pd1-Br1,Br3 92.63(3), 88.82(4).

Crystal data for compound **VI**: $C_{19}H_{26}Br_2N_4$, M = 470.26, monoclinic, a = 10.451(2), b = 8.0570(16), c = 24.629(5) Å, β = 101.11(3) ° , U = 2035.0(7) Å^3, T = 100 K, space group $P12_1/c_1$ (no. 14), Z = 4, 33377 reflections measured, 4567 unique (R_{int} = 0.0384), 3924 > 4σ(F), R = 0.0427 (observed), R_w = 0.1124 (all data). CCDC Number: 1915455

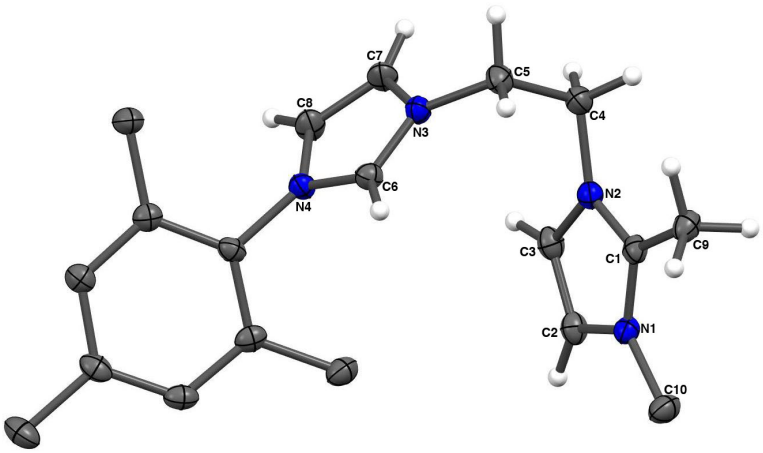

Figure S9. Structural representation of compound **VI**. Thermal ellipsoids are shown at 50% probability level. Br^- counteranions and *N*-substituent hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1-C9 1.479(5), N1-C1-C9 125.3(3), N2-C1-C9 125.3(3).

Crystal data for compound **VII**: $C_{21}H_{27}Br_4N_5Pd$, M = 775.51, monoclinic, a = 19.980(4), b = 8.0800(16), c = 16.845(3) Å, β = 103.24(3) °, U = 2647.2(10) Å^3, T = 100 K, space group $C121$ (no. 5), Z = 4, 22260 reflections measured, 6256 unique (R_{int} = 0.1044), 4454 > 4σ(F), R = 0.0684 (observed), R_w = 0.1815 (all data). CCDC Number: 1915456

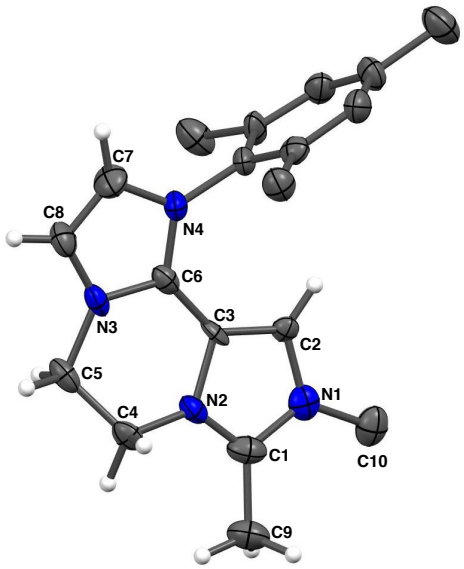

Figure S10. Structural representation of compound **VII**. Thermal ellipsoids are shown at 50% probability level. $[PdBr_4]^{2-}$ counteranion, lattice acetonitrile solvent molecules and *N*-substituent hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1-C9 1.501(3), C3-C6 1.417(2), N1-C1-C9 124.92(1), N2-C1-C9 126.29(1), N2-C3-C6 117.08(1) N4-C6-C3 130.30(1), C2-C3-C6 135.98(1).

II. Density Functional Theory Computational Data

Table S1. Total energies for all of the calculated structures

1
E (B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6726.643269 au
H(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6726.024656 au
G(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6726.144782 au
E(B3LYP/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6733.782326 au
E(M06/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6732.420723 au

2
E (B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6726.629585 au
H(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6726.011068 au
G(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6726.130683 au
E(B3LYP/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6733.769807 au
E(M06/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -6732.411312 au

3
E (B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4155.037211 au
H(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4154.421327 au
G(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4154.536051 au
E(B3LYP/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4159.430358 au
E(M06/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4158.195471 au

Br^-
E (B3LYP/BS1, Solvent = DiMethylSulfoxide) = -2571.574251 au
H(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -2571.57189 au
G(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -2571.590426 au
E(B3LYP/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -2574.334887 au
E(M06/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -2574.192852 au

$TS_{3\text{-}4}$
E (B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4154.998951 au
H(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4154.387613 au
G(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4154.497913 au
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HOAc
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E(M06/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -229.0428887 au

IIb
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TS_{IIb-5}
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5
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TS_{3-6}
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H(B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4154.390321 au
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E(M06/BS2//B3LYP/BS1, Solvent = DiMethylSulfoxide) = -4158.165245 au

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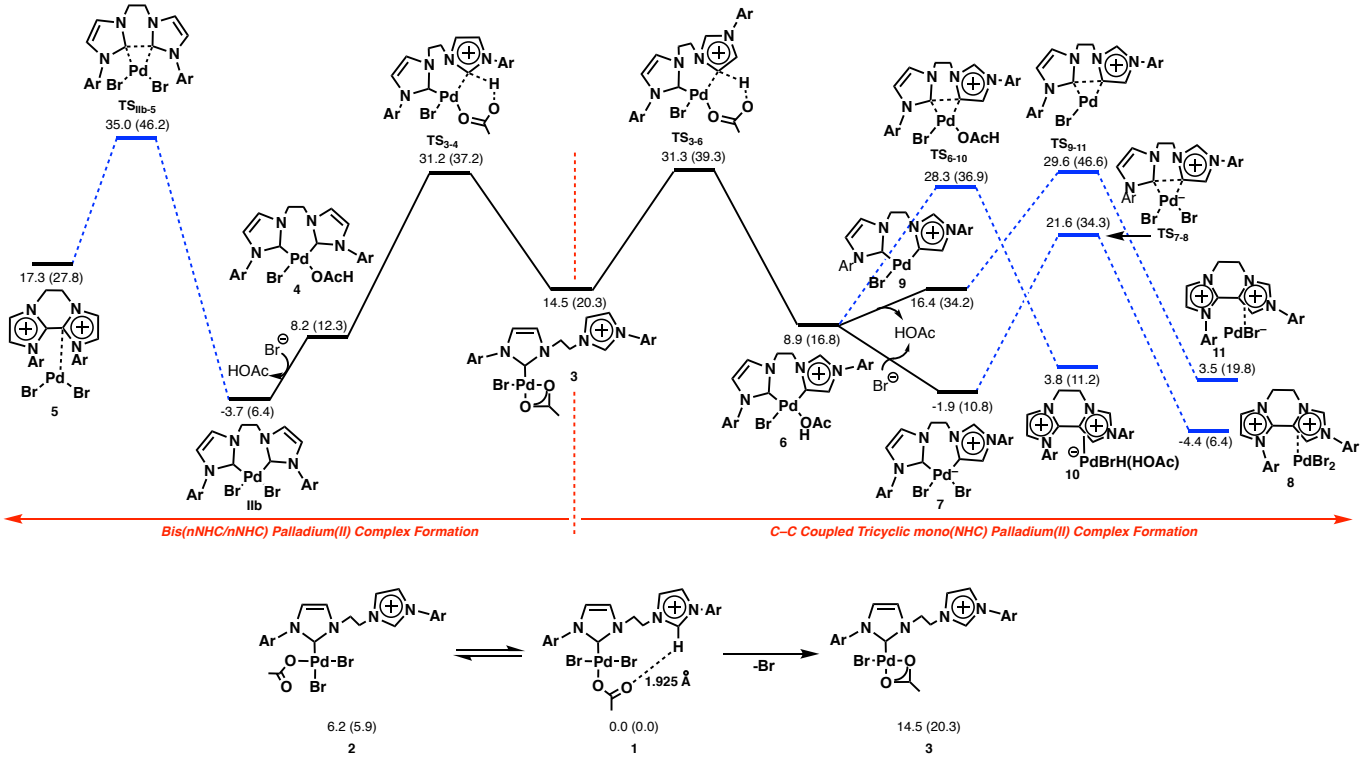

Figure S11. Energy profile calculated for the formation of abnormal and normal carbenes promoted by Pd^{II}. The relative Gibbs and electronic energies (in parentheses) obtained from the M06/BS2//B3LYP/BS1 calculations in dimethylsulfoxide are given in kcal/mol.

Computational details: Gaussian 09[1] was used to fully optimize all the structures reported in this paper at the B3LYP level of density functional theory (DFT) in dimethylsulfoxide using the CPCM solvation model.[2,3] The effective-core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ)[4] was chosen to describe Pd. The 6-31G(d) basis set was used for other atoms.[5] A Polarization function of ξ_f = 1.472 were also added for Pd.[6] This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as those for the structural optimization. Transition states were located using the Berny algorithm. Intrinsic reaction coordinate (IRC)[7] calculations were used to confirm the connectivity between transition structures and minima. To further refine the energies obtained from the B3LYP/BS1 calculations, we carried out single-point energy calculations for all of the structures with a larger basis set (BS2) at the B3LYP and M06[8] levels with inclusion of the solvent effect. BS2 utilizes the quadruple-ζ valence def2-QZVP[9] basis set on Pd and the 6-311+G(2d,p) basis set on other atoms. We have used the potential and Gibbs free energies obtained from the M06/BS2//B3LYP/BS1 calculations in dimethylsulfoxide throughout the paper unless otherwise stated. The atomic orbital populations were calculated on the basis of natural bond orbital (NBO) analyses.[10]

IV. References

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