Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

for

Mixed NHC-thiolato complexes of palladium: Understanding the formation of di- versus mononuclear complexes

Han Vinh Huynh,* Hong Lee Ong and Kausani Ghatak

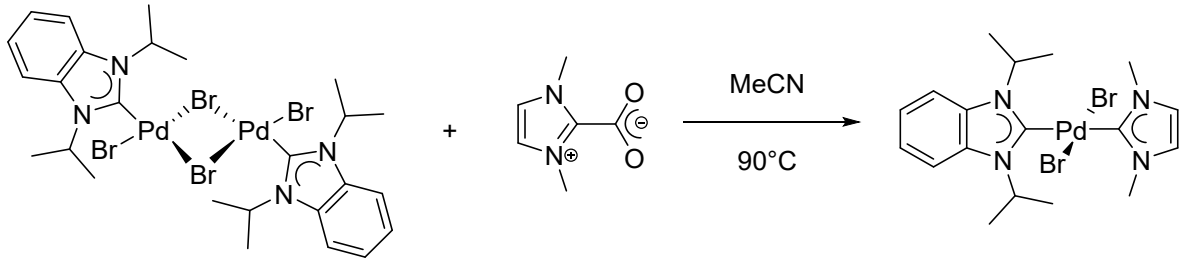
Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543 Singapore, Republic of Singapore

E-mail: chmhhv@nus.edu.sg

Donor strength evaluation of 1,3-dimethylimidazolin-2-ylidene (IMe), 1,3-dimethylbenzimidazolin-2-ylidene (Me_2-bimy) and 1,4-dimethyl-1,2,4-triazolin-5-ylidene (Me_2-tria) using the Huynh Electronic Parameter (HEP)

Preparation of *trans*-[$PdBr_2$($^i Pr_2$-bimy)(NHC)] complexes (14–16)

trans-Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(1,3-dimethylimidazolin-2-ylidene)palladium(II) (14)



A mixture 1,3-dimethylimidazolium-2-carboxylate (28 mg, 0.2 mmol) and Di-μ-bromido-bis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromidodipalladium(II) (93 mg, 0.1 mmol) in 10 mL acetonitrile was heated at 90 °C overnight. The resultant solution was dried in vacuo to give the crude product as a yellow solid. Slow evaporation at ambient temperature of a concentrated chloroform solution yielded crystals suitable for X-ray diffraction studies (79 mg, 0.14 mmol, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57–7.55 (m, 2 H, Ar-H), 7.20–7.18 (m, 20 H, Ar-H), 6.85 (s, 2 H, Ar-H), 6.21 (septet, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$), 4.09 (s, 3 H, C*H*$_3$), 1.81 (dd, ^3J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$): δ = 179.9$_0$ (HEP), 170.1 (IMe_{NCN}), 134.3, 122.8, 122.6, 113.2 (Ar-C), 54.5 (*C*H(CH_3)$_2$), 38.7 (CH_3), 21.8 (CH(*C*H$_3$)$_2$). Anal calcd. for $C_{18}H_{26}Br_2N_4Pd$: C, 38.29; H, 4.64; N, 9.92; found: C, 38.03; H, 4.45; N, 9.54. MS (ESI) *m/z* 483 [M – Br]$^+$. HRMS (ESI) *m/z* calcd. for $C_{18}H_{26}N_4BrPd$ [M – Br]$^+$ 483.0374; found, *m/z* 483.0372.

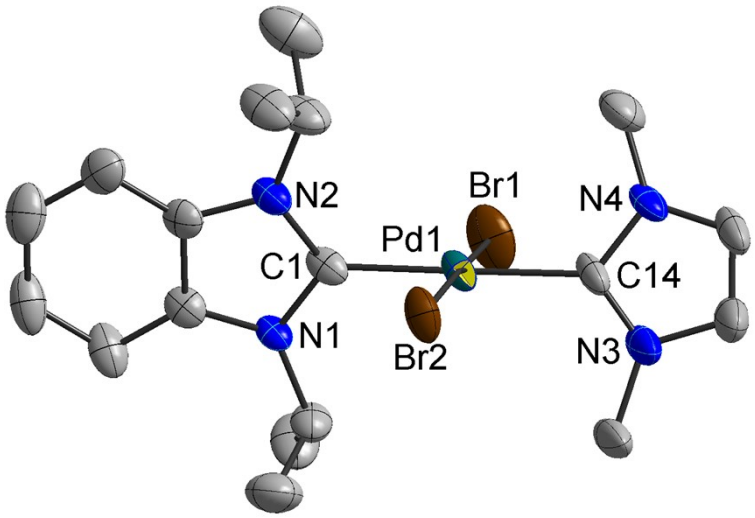
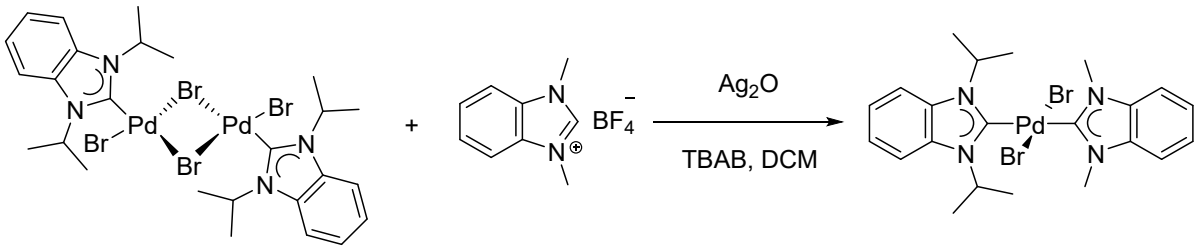


Figure S1. Molecular structure of complex **14** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd1−C1 2.005(9), Pd1−C14 2.047(8), Pd1−Br2 2.4432(1), Pd1−Br1 2.4189(1); C14−Pd1−C1 178.3(3), C1−Pd1−Br1 90.4(2), Br1−Pd1−Br2 178.58(5), Br2−Pd1−C14 90.5(3), C14−Pd1−Br1 91.0(3), C1−Pd1−Br2 88.1(2).

trans-Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(1,3-dimethylbenzimidazolin-2-ylidene)palladium(II) (15)



A mixture 1,3-dimethylbenzimidazolium tetrafluoroborate (47 mg, 0.2 mmol), Di-μ-bromido-bis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromidodipalladium(II) (93 mg, 0.1 mmol), silver oxide (28 mg, 0.12 mmol) and tetrabutylammonium bromide (TBAB) (130 mg, 0.4 mmol) was suspended in 10 mL acetonitrile and stirred at ambient temperature overnight shielded from light. The resultant suspension was filtered over celite, and the filtrate was dried and redissolved in DCM. This was then subjected to silica gel filtration, and the filtrate was collected and dried in vacuo to yield the product as a yellow (87 mg, 0.142 mmol, 71%). ^{1}H NMR (500MHz, $CDCl_3$): δ 7.60–7.58 (m, 2 H, Ar-H), 7.39–7.37 (m, 2 H, Ar-H), 7.30–7.28 (m, 2 H, Ar-H), 7.23–7.21 (m, 2 H, Ar-H), 6.26 (septet, ^{3}J(H,H) = 7 Hz, 2 H, C*H*$(CH_3)_2$), 4.32 (s, 6 H, NCH_3), 1.86 (d, ^{3}J(H,H) = 7 Hz, 12 H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):

δ 182.5 (Me_2-$Bimy_{NCN}$), 179.4$_0$ (HEP), 135.7, 134.2, 123.5, 122.7, 113.3, 110.6 (Ar-C), 54.5 (*C*H(CH_3)$_2$), 35.4 (CH_3), 21.8 (CH(*C*H_3)$_2$). Anal calcd. for $C_{22}H_{28}Br_2N_4Pd$: C, 42.99; H, 4.59; N, 9.11; found: C, 42.62; H, 4.45; N, 9.54. MS (ESI) *m/z* 535 $[M - Br]^+$. HRMS (ESI) *m/z* calcd for $C_{22}H_{28}BrN_4Pd$ $[M - Br]^+$ 533.0527; found, *m/z* 533.0529.

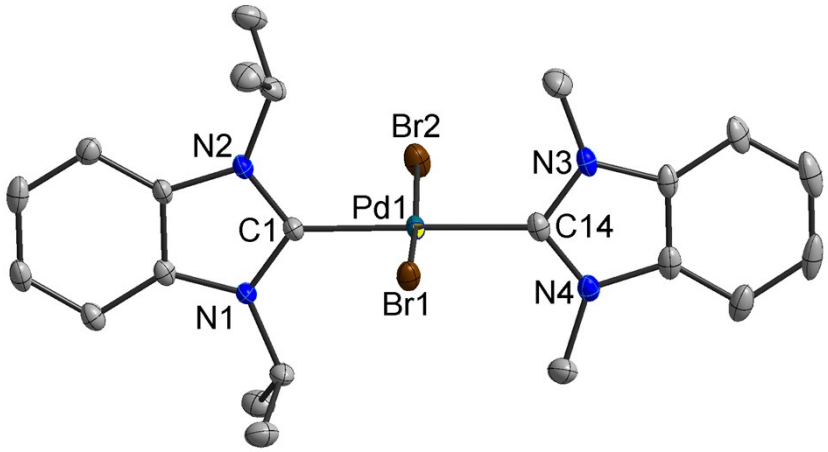
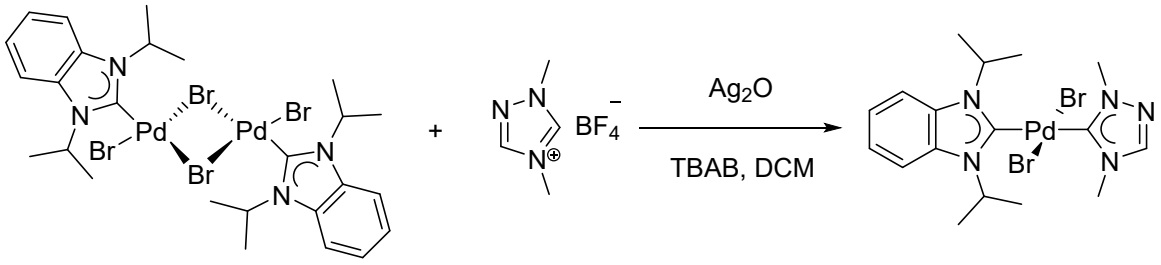


Figure S2. Molecular structure of complex **15**·CH_3Cl showing 50% probability ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd1−C1 2.012(4), Pd1−C14 2.025(4), Pd1−Br2 2.4372(6), Pd1−Br1 2.4462(6); C14−Pd1−C1 177.88(2), C1−Pd1−Br1 88.57(1), Br1−Pd1−Br2 172.00(2), Br2−Pd1−C14 88.90(1), C14−Pd1−Br1 93.20(1), C1−Pd1−Br2 89.56(1)

trans-Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(1,4-dimethyl-1,2,4-triazolidin-5-ylidene)palladium(II) (16)



A mixture 1,4-dimethyl-1,2,4-triazolium tetrafluoroborate (37 mg, 0.2 mmol), Di-μ-bromido-bis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromidodipalladium(II) (93 mg, 0.1 mmol), silver oxide (28 mg, 0.12 mmol) and tetrabutylammonium bromide (TBAB) (130 mg, 0.4 mmol) was suspended in 10 mL acetonitrile and stirred at ambient temperature overnight

shielded from light. The resultant suspension was filtered over celite, and the filtrate was dried and redissolved in DCM. This was then subjected to silica gel filtration, and the filtrate was collected and dried in vacuo to yield the product as a yellow solid (74 mg, 0.13 mmol, 65%). ^{1}H NMR (500MHz, $CDCl_3$): δ 7.96 (s, 1 H, NCHN), 7.59–7.57 (m, 2 H, Ar-H), 7.23–7.21 (m, 2 H, Ar-H), 6.16 (septet, ^{3}J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$), 4.29 (s, 3 H, NCH_3), 4.11 (s, 3 H, NCH_3), 1.83 (d, ^{3}J(H,H) = 7 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 177.2$_1$ (HEP), 174.4 (Me_2-tria$_{NCN}$), 143.3, 134.1, 122.7, 113.2 (Ar-C), 68.3, 54.5 (*C*H(CH_3)$_2$), 40.7, 36.0 (CH_3), 21.7 (CH(*C*H_3)$_2$). Anal calcd. for $C_{17}H_{25}Br_2N_5Pd$: C, 36.10 ; H, 4.46; N, 12.38; found: C, 36.03; H, 4.45; N, 12.02. MS (ESI) *m/z* 486 [M – Br]$^+$. HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}BrN_5Pd$ [M – Br]$^+$ 484.0325; found, *m/z* 484.0323.

Comparison of donor strengths on the HEP scale

According to HEP, the donating ability of the three NHCs increases in the order Me2-tria (177.2$_1$ ppm) < Me_2-bimy (179.4$_0$ ppm) < IMe (179.9$_0$ ppm).

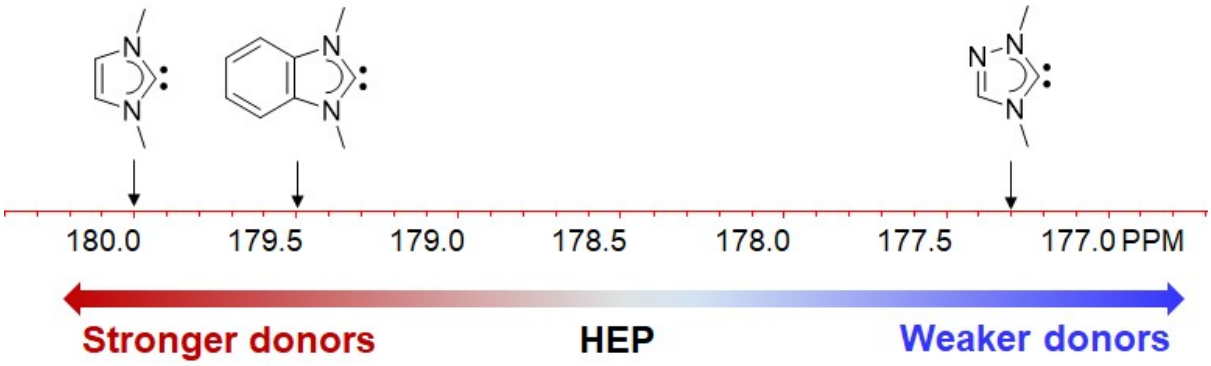


Figure S3. Donor strength comparison of three NHCs on the HEP scale.

Table S1. Selected X-ray crystallographic data for complexes **2**·2H_2O, *trans*-**4**·2CH_3CN, [**7**]I_2·4$CHCl_3$ and [**11**]$Cl_{1.5}I_{0.5}$·$H_2O_{1.75}$.

	2·2H_2O	*trans*-**4**·2CH_3CN	[**7**]I_2·4$CHCl_3$	[**10**]$Cl_{1.5}I_{0.5}$·$H_2O_{1.75}$
formula	$C_{32}H_{50}Br_2N_4O_2Pd_2S_2$	$C_{36}H_{56}N_6PdS_2$	$C_{46}H_{58}Cl_{12}I_2N_8Pd_2S_2$	$C_{26}H_{46}Cl_{1.5}I_{0.5}N_8O_{1.75}Pd_2S_2$
formula wt, Fw	959.50	743.39	1679.12	892.25
color, habit	yellow, block	yellow, block	colorless, rod	yellow, block
cryst size [mm]	0.60 × 0.50 × 0.40	0.56 × 0.36 × 0.26	0.30 × 0.08 × 0.08	0.222 × 0.219 × 0.207
temp [K]	223(2)	100(2)	223(2)	100(2)
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	12.0247(9)	10.7132(4)	11.1677(11)	23.4302(5)
b [Å]	20.8936(15)	16.3123(6)	14.0905(14)	17.5754(5)
c [Å]	8.5817(6)	11.7957(5)	20.730(2)	9.5225(2)
α [deg]	90	90	90	90
β [deg]	90	115.4020(10)	92.045(2)	97.8600(10)
γ [deg]	90	90	90	90
V [Å^3]	2156.1(3)	1862.09(13)	3260.0(6)	3884.48(16)
Z	2	2	2	4
D_c [g cm^{-3}]	1.478	1.326	1.711	1.526
radiation used	Mo K*α*	Mo K*α*	Mo K*α*	Mo K*α*
μ [mm^{-1}]	2.813	0.643	2.092	1.566
θ range [deg]	1.949–27.495	2.15–27.50	1.75–27.50	2.501–29.627
no. of unique data	4936	4267	7468	10825
final R indices [$I>2\sigma(I)$]]	R_1 = 0.0300, wR_2 = 0.0852	R_1 = 0.0257, wR_2 = 0.0643	R_1 = 0.0753, wR_2 = 0.1611	R_1 = 0.0338, wR_2 = 0.0933
R indices (all data)	R_1 = 0.0316, wR_2 = 0.0860	R_1 = 0.0281, wR_2 = 0.0657	R_1 = 0.0932, wR_2 = 0.1683	R_1 = 0.0408, wR_2 = 0.0992
goodness-of-fit on F^2	1.095	1.044	1.144	1.042
peak/hole [e Å^{-3}]	1.134/–0.330	0.544/–0.295	1.377/–1.351	1.404/–1.178

Table S2. Selected X-ray crystallographic data for complexes *trans-anti*-**12**·H_2O, [**13**]Cl_2·$6H_2O$, **14** and **15**·$CHCl_3$.

	trans-anti-**12**·H_2O	[**13**]Cl_2·$6H_2O$	**14**	**15**·$CHCl_3$
formula	$C_{14}H_{30}N_6OPdS_2$	$C_{22}H_{42}Cl_2N_{12}O_6Pd_2S_2$	$C_{18}H_{26}Br_2N_4Pd$	$C_{23}H_{29}Br_2Cl_3N_4Pd$
formula wt, Fw	468.96	918.49	564.65	734.07
color, habit	yellow, block	orange, thin plate	pale-yellow, plate	yellow, block
cryst size [mm]	0.305 × 0.167 × 0.124	0.249 × 0.142 × 0.056	0.102 × 0.194 × 0.274	0.112 × 0.102 × 0.072
temp [K]	100(2)	100(2)	100(2)	100(2)
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic
space group	C2/c	*P-1*	Pbca	$P2_1$
a [Å]	19.2127(5)	9.1475(3)	9.0107(6)	10.6178(3)
b [Å]	8.3951(3)	10.4335(4)	16.9043(11)	11.6652(2)
c [Å]	14.5503(5)	11.9175(4)	29.042(2)	11.9931(3)
α [deg]	90	83.3350(10)	90	90
β [deg]	120.6380(10)	80.5710(10)	90	112.9471(1)
γ [deg]	90	64.6560(10)	90	90
V [Å^3]	2019.24(11)	1012.71(6)	4423.7(5)	1367.90(6)
Z	4	1	8	2
D_c [g cm^{-3}]	1.543	1.506	1.696	1.782
radiation used	Mo K*α*	Mo K*α*	Mo K*α*	Mo K*α*
μ [mm^{-1}]	1.140	1.170	4.460	3.912
θ range [deg]	2.721–28.276	3.206–29.613	2.66–28.29	3.46–29.59
no. of unique data	2566	5674	5487	7341
final R indices [$I>2\sigma(I)$]]	R_1 = 0.0373, wR_2 = 0.0892	R_1 = 0.0340, wR_2 = 0.1054	R_1 = 0.0775, wR_2 = 0.2051	R_1 = 0.0248, wR_2 = 0.0658
R indices (all data)	R_1 = 0.0425, wR_2 = 0.0919	R_1 = 0.0373, wR_2 = 0.1091	R_1 = 0.0957, wR_2 = 0.2204	R_1 = 0.0259, wR_2 = 0.0661
goodness-of-fit on F^2	1.128	1.050	1.088	1.135
peak/hole [e Å^{-3}]	1.875/–0.581	1.889/–0.648	3.738/–2.182	0.661/–0.751