Electronic Supplementary Information for Dalton Transactions


# Supporting Information

# Fascinating Frontiers of *N*/*O*–functionalized N-Heterocyclic Carbene Chemistry: From Chemical Catalysis to Biomedical Applications

Alex John and Prasenjit Ghosh*

Department of Chemistry

Indian Institute of Technology Bombay,

Powai, Mumbai 400 076.

Email: pghosh@chem.iitb.ac.in

Tel.: +91-22-2576-7178; Fax: +91-22-2572-3480

The density functional theory calculations were performed on six PEPPSI type palladium complex namely, [1,3-*bis*(2,6-*di*-*i*-propylphenyl)-imidazolidine-2-ylidene]$PdCl_2(NC_5H_5)$ (**Pd-7**), [1,3-*bis*(2,6-*di*-ethylphenyl)-imidazolidine-2-ylidene]$PdCl_2(NC_5H_5)$ (**Pd-8**), [1,3-*bis*(2,4,6-*tri*-methylphenyl)-imidazolidine-2-ylidene]$PdCl_2(NC_5H_5)$ (**Pd-9**), [1,3-*bis*(2,6-*di*-methylphenyl)-imidazolidine-2-ylidene]$PdCl_2(NC_5H_5)$ (**Pd-10**), [1-(benzyl)-4-(*i*-propyl)-1,2,4-triazol-5-ylidene]$PdBr_2(NC_5H_5)$ (**Pd-11**), [1-(benzyl)-4-(N-*tert*-butylacetamide)-1,2,4-triazol-5-ylidine]$PdBr_2(NC_5H_5)$ (**Pd-12**) using GAUSSIAN 03[1] suite of quantum chemical programs.

**Table S1.** B3LYP/SDD, 6-31G* optimized coordinates of **Pd-7**

Ground state electronic energy = -2457.9886554 hartree/particle.

| | | | |
|---|---|---|---|
| Pd | -0.00192 | 1.170061 | -0.00076 |
| Cl | 0.94956 | 1.193028 | -2.15637 |
| Cl | -0.95319 | 1.193439 | 2.154954 |
| N | 1.095318 | -1.60569 | 0.124301 |
| N | -1.09065 | -1.60885 | -0.12108 |
| N | -0.00547 | 3.32082 | -0.00234 |
| C | 0.001343 | -0.82278 | 0.000708 |
| C | 0.72684 | -3.03351 | 0.249444 |
| H | 0.811608 | -3.34245 | 1.298706 |
| H | 1.387425 | -3.65921 | -0.35105 |
| C | -0.71843 | -3.03568 | -0.24476 |
| H | -0.80244 | -3.34613 | -1.29364 |
| H | -1.37728 | -3.66245 | 0.356527 |
| C | -1.0539 | 4.005385 | 0.491918 |
| H | -1.85673 | 3.406251 | 0.904482 |
| C | -1.09667 | 5.396779 | 0.498634 |
| H | -1.9685 | 5.90245 | 0.900718 |
| C | -0.00981 | 6.109126 | -0.00588 |
| H | -0.01156 | 7.195571 | -0.00737 |
| C | 1.079327 | 5.398898 | -0.50846 |
| H | 1.949584 | 5.90628 | -0.9118 |
| C | 1.040955 | 4.007406 | -0.49814 |
| H | 1.845738 | 3.409723 | -0.90895 |
| C | 2.47415 | -1.2092 | 0.304687 |

| | | | |
|---|---|---|---|
| C | 2.927563 | -0.80313 | 1.581407 |
| C | 2.042248 | -0.79844 | 2.824719 |
| H | 0.996776 | -0.84782 | 2.512218 |
| C | 2.342433 | -2.03745 | 3.697058 |
| H | 2.219085 | -2.97301 | 3.138688 |
| H | 1.669828 | -2.06738 | 4.562649 |
| H | 3.372977 | -2.0146 | 4.071954 |
| C | 2.185736 | 0.486694 | 3.659904 |
| H | 3.182421 | 0.575291 | 4.108974 |
| H | 1.454006 | 0.48086 | 4.474553 |
| H | 1.993149 | 1.37438 | 3.05191 |
| C | 4.281698 | -0.46776 | 1.717632 |
| H | 4.652068 | -0.14615 | 2.685973 |
| C | 5.162762 | -0.55628 | 0.646186 |
| H | 6.20896 | -0.29173 | 0.7772 |
| C | 4.706036 | -1.00477 | -0.58872 |
| H | 5.404941 | -1.09345 | -1.41476 |
| C | 3.363585 | -1.34623 | -0.78931 |
| C | 2.944944 | -1.91079 | -2.14585 |
| H | 1.851485 | -1.91114 | -2.18767 |
| C | 3.444874 | -3.36434 | -2.30864 |
| H | 4.540806 | -3.39802 | -2.32259 |
| H | 3.085737 | -3.78901 | -3.25382 |
| H | 3.113623 | -4.01969 | -1.49484 |
| C | 3.439501 | -1.06274 | -3.33267 |
| H | 3.119128 | -0.0242 | -3.23009 |
| H | 3.026031 | -1.45942 | -4.26768 |
| H | 4.531872 | -1.08948 | -3.42432 |
| C | -2.47043 | -1.21628 | -0.30263 |
| C | -2.92438 | -0.81476 | -1.5806 |
| C | -2.03872 | -0.81099 | -2.82367 |
| H | -0.99325 | -0.85628 | -2.51058 |
| C | -2.18555 | 0.471499 | -3.66241 |
| H | -1.4518 | 0.466675 | -4.47522 |
| H | -1.99809 | 1.36139 | -3.05605 |
| H | -3.18151 | 0.554791 | -4.11419 |
| C | -2.33491 | -2.05328 | -3.69271 |
| H | -3.36552 | -2.03463 | -4.06766 |
| H | -2.2087 | -2.98704 | -3.13198 |
| H | -1.66226 | -2.08339 | -4.55826 |
| C | -4.27921 | -0.48268 | -1.71806 |
| H | -4.65004 | -0.16433 | -2.6873 |
| C | -5.1603 | -0.57022 | -0.64657 |
| H | -6.20704 | -0.30828 | -0.77855 |
| C | -4.70289 | -1.01417 | 0.589708 |
| H | -5.40181 | -1.10195 | 1.415802 |

| | | | |
|---|---|---|---|
| C | -3.35973 | -1.35221 | 0.791591 |
| C | -2.93976 | -1.91213 | 2.14962 |
| H | -1.84632 | -1.90881 | 2.191901 |
| C | -3.43508 | -3.36685 | 2.316008 |
| H | -3.07619 | -3.78739 | 3.263144 |
| H | -3.10007 | -4.02364 | 1.50494 |
| H | -4.53094 | -3.40425 | 2.328063 |
| C | -3.43739 | -1.06287 | 3.334336 |
| H | -4.52936 | -1.0966 | 3.428543 |
| H | -3.12401 | -0.02265 | 3.227387 |
| H | -3.0192 | -1.45337 | 4.269838 |

**Table S2.** B3LYP/SDD, 6-31G* optimized coordinates of **Pd-8**

Ground state electronic energy = -2300.7458207 hartree/particle.

| | | | |
|---|---|---|---|
| Pd | 0.000032 | 1.088253 | -0.00023 |
| Cl | 0.591851 | 1.103489 | 2.287826 |
| Cl | -0.59192 | 1.10375 | -2.28825 |
| N | -1.09531 | -1.68417 | 0.071383 |
| N | 1.095513 | -1.68415 | -0.07174 |
| N | -0.00004 | 3.234697 | -5.2E-05 |
| C | 0.000083 | -0.90376 | -0.00026 |
| C | -0.75784 | -3.12211 | 0.129482 |
| H | -1.31961 | -3.67659 | -0.62679 |
| H | -1.01908 | -3.5242 | 1.115034 |
| C | 0.758095 | -3.12214 | -0.1292 |
| H | 1.319886 | -3.67626 | 0.627316 |
| H | 1.019322 | -3.52467 | -1.11457 |
| C | -2.46668 | -1.24966 | 0.16671 |
| C | -3.24894 | -1.20876 | -1.00716 |
| C | -2.73642 | -1.64559 | -2.3655 |
| H | -1.64752 | -1.72218 | -2.35541 |
| H | -2.96391 | -0.85947 | -3.09404 |
| C | -3.3584 | -2.97209 | -2.84158 |
| H | -3.13584 | -3.7962 | -2.15237 |
| H | -2.9719 | -3.24531 | -3.83022 |
| H | -4.44929 | -2.89904 | -2.91617 |
| C | -4.57375 | -0.76933 | -0.89917 |
| H | -5.18178 | -0.70921 | -1.79875 |
| C | -5.11466 | -0.40046 | 0.329482 |
| H | -6.14146 | -0.04897 | 0.389884 |
| C | -4.33788 | -0.49005 | 1.480942 |
| H | -4.76194 | -0.21722 | 2.444489 |
| C | -3.00791 | -0.9269 | 1.429066 |

| | | | |
|---|---|---|---|
| C | -2.24203 | -1.07344 | 2.728639 |
| H | -1.16788 | -1.12054 | 2.544481 |
| H | -2.39046 | -0.16811 | 3.328704 |
| C | -2.69389 | -2.29792 | 3.547087 |
| H | -3.75973 | -2.24245 | 3.796536 |
| H | -2.13045 | -2.36144 | 4.484976 |
| H | -2.53764 | -3.23299 | 2.994947 |
| C | 2.466872 | -1.24953 | -0.16687 |
| C | 3.008143 | -0.92634 | -1.4291 |
| C | 2.242557 | -1.07309 | -2.72881 |
| H | 2.392961 | -0.16877 | -3.32989 |
| H | 1.16824 | -1.1181 | -2.54512 |
| C | 2.692828 | -2.29925 | -3.54564 |
| H | 3.758722 | -2.24537 | -3.79522 |
| H | 2.129251 | -2.36334 | -4.48341 |
| H | 2.535517 | -3.23341 | -2.99227 |
| C | 4.338 | -0.48913 | -1.48074 |
| H | 4.762077 | -0.21598 | -2.4442 |
| C | 5.114678 | -0.39968 | -0.3292 |
| H | 6.141406 | -0.04795 | -0.38942 |
| C | 4.573754 | -0.76902 | 0.899301 |
| H | 5.181687 | -0.70898 | 1.798953 |
| C | 3.249015 | -1.20872 | 1.007077 |
| C | 2.73644 | -1.64579 | 2.365324 |
| H | 2.963453 | -0.85958 | 3.093902 |
| H | 1.647562 | -1.72282 | 2.355054 |
| C | 3.358876 | -2.97204 | 2.841506 |
| H | 3.136771 | -3.79623 | 2.15225 |
| H | 2.972307 | -3.24543 | 3.830074 |
| H | 4.44972 | -2.89855 | 2.916294 |
| C | -0.96021 | 3.919714 | -0.64836 |
| H | -1.69217 | 3.320492 | -1.17632 |
| C | -0.999 | 5.311188 | -0.66305 |
| H | -1.79862 | 5.817981 | -1.19345 |
| C | -0.00033 | 6.02235 | 0.000384 |
| H | -0.00045 | 7.108847 | 0.000562 |
| C | 0.998494 | 5.311189 | 0.663588 |
| H | 1.798002 | 5.817982 | 1.194142 |
| C | 0.959991 | 3.919712 | 0.648463 |
| H | 1.692079 | 3.320482 | 1.176236 |

**Table S3.** B3LYP/SDD, 6-31G* optimized coordinates of **Pd-9**

Ground state electronic energy = -2222.1363043 hartree/particle.

| | | | |
|---|---|---|---|
| Pd | 0.003033 | 0.822643 | 0.005539 |
| Cl | -0.01863 | 0.886019 | -2.35716 |
| Cl | 0.025965 | 0.919444 | 2.36809 |
| N | 1.092209 | -1.96633 | 0.065791 |
| N | -1.10347 | -1.9605 | 0.092562 |
| N | 0.012349 | 2.967537 | -0.01125 |
| C | -0.00399 | -1.18271 | 0.045269 |
| C | 0.760333 | -3.4055 | 0.147152 |
| H | 1.185595 | -3.83739 | 1.058545 |
| H | 1.182656 | -3.9377 | -0.71082 |
| C | -0.77733 | -3.40216 | 0.151209 |
| H | -1.20599 | -3.91917 | -0.71322 |
| H | -1.20015 | -3.8463 | 1.05755 |
| C | 2.475884 | -1.56488 | -0.00649 |
| C | 3.206129 | -1.38361 | 1.184368 |
| C | 2.587381 | -1.59454 | 2.545244 |
| H | 1.712323 | -0.95563 | 2.694905 |
| H | 3.313444 | -1.36822 | 3.332101 |
| H | 2.270346 | -2.63663 | 2.686858 |
| C | 4.555067 | -1.02723 | 1.080767 |
| H | 5.124081 | -0.87501 | 1.995511 |
| C | 5.191042 | -0.87447 | -0.15442 |
| C | 6.638684 | -0.44923 | -0.23584 |
| H | 7.206484 | -0.78614 | 0.638232 |
| H | 6.726392 | 0.644618 | -0.27871 |
| H | 7.124684 | -0.84852 | -1.13254 |
| C | 4.450291 | -1.12613 | -1.31233 |
| H | 4.935836 | -1.05071 | -2.2829 |
| C | 3.098576 | -1.48328 | -1.26733 |
| C | 2.360348 | -1.78897 | -2.54815 |
| H | 1.916275 | -2.79276 | -2.53368 |
| H | 3.045318 | -1.7474 | -3.40048 |
| H | 1.552976 | -1.07159 | -2.72402 |
| C | -2.48664 | -1.55216 | 0.059792 |
| C | -3.14319 | -1.45784 | -1.18251 |
| C | -2.44119 | -1.75466 | -2.48565 |
| H | -3.14992 | -1.70842 | -3.31818 |
| H | -1.996 | -2.75796 | -2.49039 |
| H | -1.63864 | -1.03613 | -2.67928 |
| C | -4.49483 | -1.09594 | -1.18735 |
| H | -5.0071 | -1.01244 | -2.14347 |
| C | -5.20246 | -0.85159 | -0.0076 |
| C | -6.65086 | -0.42262 | -0.04343 |
| H | -6.73946 | 0.670994 | 0.002644 |
| H | -7.21127 | -0.82799 | 0.806267 |
| H | -7.14418 | -0.7508 | -0.96443 |

| | | | |
|---|---|---|---|
| C | -4.53294 | -1.01611 | 1.208486 |
| H | -5.07548 | -0.86829 | 2.139832 |
| C | -3.1833 | -1.37749 | 1.271883 |
| C | -2.52726 | -1.59875 | 2.613362 |
| H | -3.23382 | -1.38665 | 3.421499 |
| H | -1.65407 | -0.95383 | 2.74648 |
| H | -2.19759 | -2.63941 | 2.734678 |
| C | 0.852397 | 3.653862 | 0.78497 |
| H | 1.485815 | 3.057729 | 1.430482 |
| C | 0.892481 | 5.045165 | 0.799576 |
| H | 1.59393 | 5.552608 | 1.453714 |
| C | 0.020333 | 5.755069 | -0.02412 |
| H | 0.023182 | 6.841477 | -0.02886 |
| C | -0.8555 | 5.042524 | -0.8416 |
| H | -1.55405 | 5.54796 | -1.50037 |
| C | -0.82336 | 3.651149 | -0.81426 |
| H | -1.45999 | 3.052613 | -1.45438 |

**Table S4.** B3LYP/SDD, 6-31G* optimized coordinates of **Pd-10**

Ground state electronic energy =-2143.5012997 hartree/particle.

| | | | |
|---|---|---|---|
| Pd | -0.02601 | 0.794409 | 0.00259 |
| Cl | 0.533657 | 0.894307 | 2.295629 |
| Cl | -0.58262 | 0.831325 | -2.2924 |
| N | 1.168961 | -1.95417 | -0.01445 |
| N | -1.0218 | -2.02479 | 0.110855 |
| N | -0.10907 | 2.936589 | -0.01719 |
| C | 0.047101 | -1.20747 | 0.022859 |
| C | -0.63344 | -3.44768 | 0.229109 |
| H | -1.17541 | -4.05488 | -0.50007 |
| H | -0.87845 | -3.81464 | 1.232252 |
| C | 0.879214 | -3.40466 | -0.03111 |
| H | 1.458662 | -3.91883 | 0.739522 |
| H | 1.15347 | -3.82598 | -1.00526 |
| C | 2.533306 | -1.50321 | -0.14321 |
| C | 3.051389 | -1.22995 | -1.42425 |
| C | 2.228131 | -1.39128 | -2.67916 |
| H | 1.467746 | -0.60854 | -2.76958 |
| H | 1.701344 | -2.3524 | -2.70224 |
| H | 2.87337 | -1.34755 | -3.56197 |
| C | 4.385835 | -0.8132 | -1.51674 |
| H | 4.798426 | -0.58805 | -2.49671 |
| C | 5.1848 | -0.70113 | -0.38208 |
| H | 6.21723 | -0.37421 | -0.4739 |

| | | | |
|---|---|---|---|
| C | 4.667001 | -1.0324 | 0.868228 |
| H | 5.298482 | -0.97404 | 1.750797 |
| C | 3.33886 | -1.44933 | 1.01307 |
| C | 2.81549 | -1.83825 | 2.374809 |
| H | 1.928806 | -1.25544 | 2.637735 |
| H | 3.578598 | -1.6618 | 3.138697 |
| H | 2.550909 | -2.90329 | 2.420657 |
| C | -2.41662 | -1.66045 | 0.163402 |
| C | -3.00878 | -1.36374 | 1.40733 |
| C | -2.23142 | -1.40521 | 2.700757 |
| H | -2.90757 | -1.28045 | 3.552023 |
| H | -1.47303 | -0.61753 | 2.748179 |
| H | -1.71073 | -2.36206 | 2.831456 |
| C | -4.37262 | -1.0438 | 1.423563 |
| H | -4.84352 | -0.80315 | 2.37308 |
| C | -5.12673 | -1.04533 | 0.252845 |
| H | -6.18336 | -0.79306 | 0.286259 |
| C | -4.53123 | -1.39439 | -0.95721 |
| H | -5.12452 | -1.4215 | -1.86733 |
| C | -3.17155 | -1.71939 | -1.02577 |
| C | -2.56071 | -2.13229 | -2.34352 |
| H | -3.31428 | -2.10274 | -3.13621 |
| H | -2.16571 | -3.15618 | -2.30869 |
| H | -1.74364 | -1.46239 | -2.62583 |
| C | -1.12944 | 3.579082 | -0.61451 |
| H | -1.86546 | 2.950591 | -1.10075 |
| C | -1.22561 | 4.967778 | -0.62928 |
| H | -2.07215 | 5.439386 | -1.11733 |
| C | -0.22283 | 5.721513 | -0.02098 |
| H | -0.26852 | 6.806906 | -0.02053 |
| C | 0.839117 | 5.054096 | 0.587631 |
| H | 1.645037 | 5.594446 | 1.073174 |
| C | 0.856355 | 3.662159 | 0.576316 |
| H | 1.642591 | 3.096491 | 1.061368 |

**Table S5.** B3LYP/SDD, 6-31G* optimized coordinates of **Pd-11**

Ground state electronic energy = -6149.724186 hartree/particle.

| | | | |
|---|---|---|---|
| Pd | 7.610954 | 3.285082 | 8.480642 |
| Br | 6.341827 | 5.238522 | 9.344956 |
| Br | 9.045916 | 1.375228 | 7.779311 |
| N | 10.10141 | 4.672081 | 9.417105 |
| N | 9.29291 | 3.456565 | 10.96985 |

| | | | |
|---|---|---|---|
| N | 10.94864 | 4.839383 | 10.48474 |
| N | 6.007843 | 2.691516 | 7.175454 |
| C | 9.083955 | 3.839124 | 9.678046 |
| C | 10.42928 | 4.086225 | 11.41159 |
| H | 10.84032 | 3.954142 | 12.40103 |
| C | 10.36762 | 5.391625 | 8.154803 |
| H | 9.572126 | 5.052362 | 7.485772 |
| C | 11.72642 | 4.970005 | 7.590291 |
| H | 12.53485 | 5.245201 | 8.274889 |
| H | 11.8959 | 5.474972 | 6.633421 |
| H | 11.75754 | 3.888938 | 7.422446 |
| C | 10.23854 | 6.900253 | 8.379676 |
| H | 9.241967 | 7.149488 | 8.756927 |
| H | 10.39249 | 7.425828 | 7.431238 |
| H | 10.98861 | 7.25151 | 9.095617 |
| C | 8.434552 | 2.552771 | 11.7571 |
| H | 7.699569 | 2.160757 | 11.05027 |
| H | 7.896282 | 3.15373 | 12.49698 |
| C | 9.218957 | 1.443262 | 12.42467 |
| C | 9.849027 | 0.456885 | 11.6505 |
| H | 9.772235 | 0.494034 | 10.56585 |
| C | 10.56643 | -0.56476 | 12.27101 |
| H | 11.04989 | -1.32586 | 11.66467 |
| C | 10.65964 | -0.61622 | 13.66538 |
| H | 11.21815 | -1.41576 | 14.14467 |
| C | 10.03149 | 0.359313 | 14.43973 |
| H | 10.09718 | 0.324005 | 15.52379 |
| C | 9.315163 | 1.386359 | 13.81946 |
| H | 8.822082 | 2.1442 | 14.42487 |
| C | 6.267233 | 2.229417 | 5.93725 |
| H | 7.31478 | 2.151213 | 5.67185 |
| C | 5.258208 | 1.849525 | 5.0571 |
| H | 5.520248 | 1.491005 | 4.067064 |
| C | 3.930633 | 1.931032 | 5.474393 |
| H | 3.12197 | 1.63513 | 4.812065 |
| C | 3.662606 | 2.400307 | 6.759283 |
| H | 2.647004 | 2.4832 | 7.132212 |
| C | 4.72479 | 2.77868 | 7.575397 |
| H | 4.56578 | 3.183724 | 8.567644 |

**Table S6.** B3LYP/SDD, 6-31G* optimized coordinates of **Pd-12**

Ground state electronic energy = -6397.0418969 hartree/particle.

| | | | |
|---|---|---|---|
| Pd | 0.090957 | 1.044647 | 0.04902 |
| Br | 1.628027 | 1.369384 | 1.967635 |
| Br | -1.36464 | 0.486718 | -1.896 |
| O | -3.53161 | -2.35677 | 2.491756 |
| N | -0.31254 | -1.7588 | 1.044432 |
| N | 1.293835 | -1.6848 | -0.35382 |
| N | 0.139369 | -3.0537 | 0.94646 |
| N | -3.10304 | -1.94974 | 0.270217 |
| N | -0.22561 | 3.156177 | -0.18173 |
| C | 0.371938 | -0.90073 | 0.26865 |
| C | 1.115151 | -2.97303 | 0.08904 |
| H | 1.726076 | -3.80453 | -0.22844 |
| C | 2.299821 | -1.23235 | -1.33324 |
| H | 2.203119 | -0.14466 | -1.36711 |
| H | 2.015707 | -1.62214 | -2.31561 |
| C | 3.702593 | -1.66216 | -0.96045 |
| C | 4.311107 | -1.16238 | 0.201042 |
| H | 3.769361 | -0.46515 | 0.836984 |
| C | 5.604906 | -1.55869 | 0.536114 |
| H | 6.070128 | -1.16687 | 1.436402 |
| C | 6.304362 | -2.45093 | -0.28256 |
| H | 7.313369 | -2.75556 | -0.01822 |
| C | 5.705267 | -2.94729 | -1.44038 |
| H | 6.24385 | -3.63916 | -2.08212 |
| C | 4.406945 | -2.55465 | -1.77599 |
| H | 3.941839 | -2.93957 | -2.68126 |
| C | -1.39176 | -1.45694 | 1.977802 |
| H | -1.4194 | -0.36985 | 2.0892 |
| H | -1.14658 | -1.90371 | 2.941742 |
| C | -2.79101 | -1.98126 | 1.588321 |
| C | -4.42924 | -2.32148 | -0.28915 |
| C | -4.31248 | -2.19076 | -1.81573 |
| H | -4.04323 | -1.1702 | -2.10972 |
| H | -5.27015 | -2.44134 | -2.28371 |
| H | -3.55122 | -2.8732 | -2.21167 |
| C | -4.76312 | -3.7778 | 0.082234 |
| H | -3.98955 | -4.45647 | -0.29438 |
| H | -5.72005 | -4.06356 | -0.36966 |
| H | -4.83477 | -3.89705 | 1.164786 |
| C | -5.51081 | -1.36192 | 0.24365 |
| H | -5.56857 | -1.41971 | 1.333245 |
| H | -6.49022 | -1.62505 | -0.17285 |

| | | | |
|---|---|---|---|
| H | -5.28337 | -0.32885 | -0.04391 |
| C | -0.38433 | 3.946393 | 0.897557 |
| H | -0.30787 | 3.454921 | 1.859982 |
| C | -0.60798 | 5.315902 | 0.790956 |
| H | -0.73758 | 5.90707 | 1.691456 |
| C | -0.65184 | 5.897602 | -0.47503 |
| H | -0.81818 | 6.964967 | -0.58927 |
| C | -0.47761 | 5.081269 | -1.59158 |
| H | -0.50261 | 5.484768 | -2.59847 |
| C | -0.27597 | 3.71707 | -1.40531 |
| H | -0.16912 | 3.037761 | -2.24251 |
| H | -2.4807 | -1.44526 | -0.35575 |

**Table S7**. Charge decomposition analysis (CDA) results showing the $NHC \xrightarrow{\sigma} Pd(pyridine)X_2$ donation (*d*), the $NHC \xleftarrow{\pi} Pd(pyridine)X_2$ donation (*b*), *d*/*b* ratio and the NHC↔Pd(pyridine)$X_2$ (X = Cl, Br) repulsive polarization (*r*) for the Pd-NHC complexes.

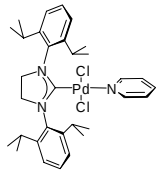
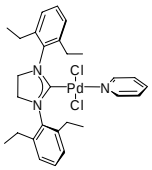
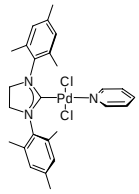
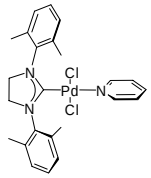
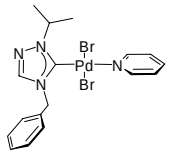
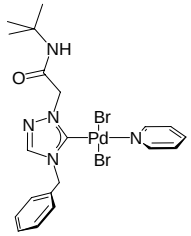
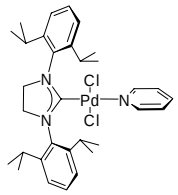
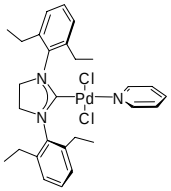
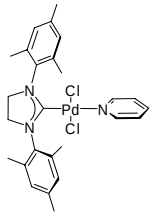
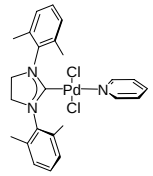
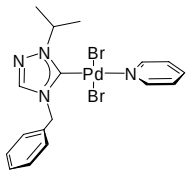
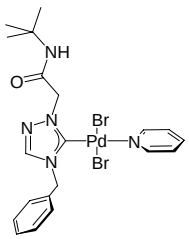
| Complex | $NHC \xrightarrow{\sigma} PdCl_2(NC_5H_5)$ (*d*) | $NHC \xleftarrow{\pi} PdCl_2(NC_5H_5)$ (*b*) | *d*/*b* ratio | Repulsive polarization (*r*) |
|---|---|---|---|---|
|  **Pd-7** | 0.317 | 0.114 | 2.78 | -0.184 |
|  **Pd-8** | 0.286 | 0.092 | 3.11 | -0.160 |
|  **Pd-9** | 0.318 | 0.140 | 2.27 | -0.177 |
|  **Pd-10** | 0.317 | 0.133 | 2.38 | -0.179 |
|  **Pd-11** | 0.261 | 0.084 | 3.11 | -0.170 |
|  **Pd-12** | 0.267 | 0.113 | 2.36 | -0.181 |

**Table S8**. Bond distance & bond energy of Pd–$C_{carbene}$ and Pd–$N_{pyridine}$.

| Complex | d(Pd-$C_{carbene}$) (Å) | $D_e$(Pd-$C_{carbene}$) (kcal/mol) | d(Pd-$N_{pyridine}$) (Å) | $D_e$(Pd-$N_{pyridine}$) (kcal/mol) |
|---|---|---|---|---|
|  **Pd-7** | 1.993 | 74.21 | 2.15 | 31.42 |
|  **Pd-8** | 1.992 | 74.83 | 2.15 | 31.36 |
|  **Pd-9** | 2.006 | 76.77 | 2.14 | 30.99 |
|  **Pd-10** | 2.003 | 76.26 | 2.14 | 31.53 |
|  **Pd-11** | 1.977 | 75.82 | 2.15 | 33.32 |
|  **Pd-12** | 1.978 | 76.63 | 2.15 | 34.44 |

## 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.