Supplementary Information

Deciphering the Influence of Pd^{II} and Pd^{IV} Oxidation State on Non-Standard Chemical Bonds within Bis(*j*N-Heterocyclic Carbene) Complexes: Insights from DFT

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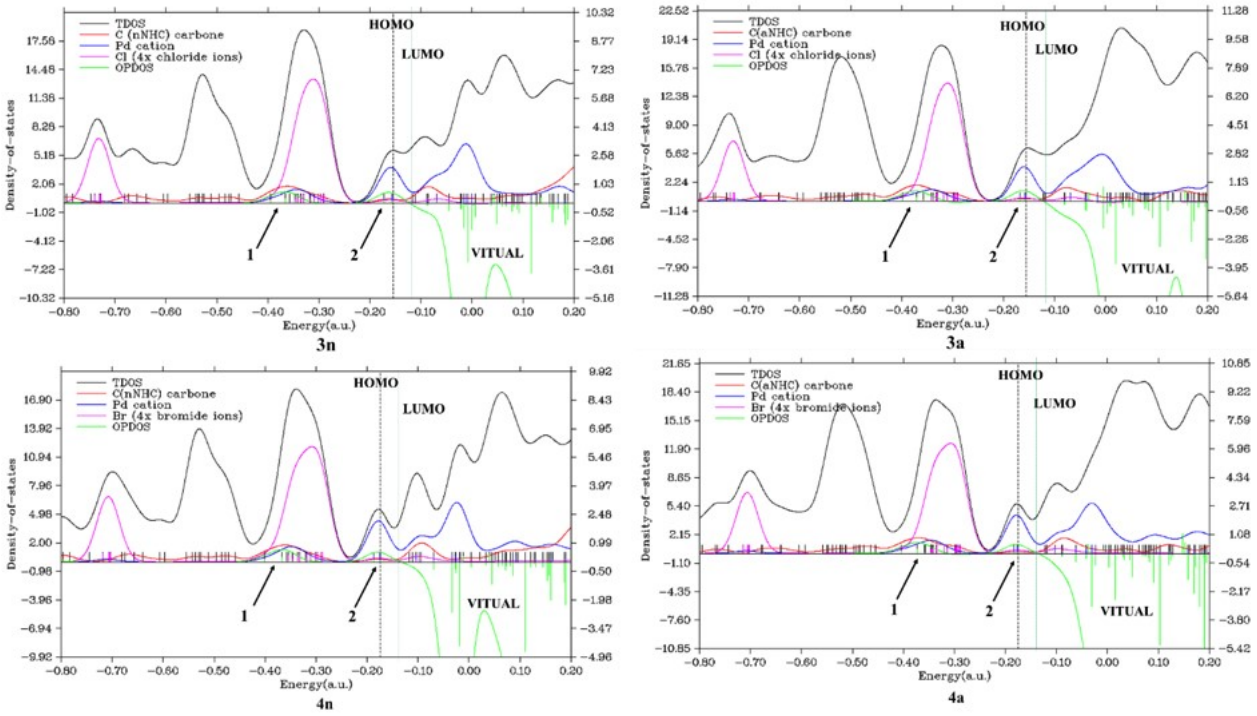
		in Complex		**in PdXi**		**in Bis(jNHC)**	
Complexes		Pd^{i+}	C_{jNHC}	Pd^{2+}	Pd^{4+}	C_{nNHC}	C_{aNHC}
$X = Cl$	**1n**	-0.01	0.32	0.53	-	0.14	-
	1a	0.04	0.02				
$X = Br$	**2n**	-0.18	0.32	0.44	-		
	2a	-0.16	0.02				
$X = Cl$	**3n**	-0.08	0.39	-	0.44	-	-0.18
	3a	-0.02	0.10				
$X = Br$	**4n**	-0.33	0.38	-	0.18		
	4a	-0.27	0.09				

Table 2S. Palladium Natural Electron Configuration in different complexes.

Species	Natural Electron Configuration	Isoleted state
1n	[core]5S(0.41)4d(9.02)5p(0.29)5d(0.01)6p(0.21)	[core]4d(8.00)
1a	[core]5S(0.40)4d(9.01)5p(0.28)5d(0.01)6p(0.19)	
2n	[core]5S(0.42)4d(9.07)5p(0.31)5d(0.01)6p(0.23)	
2a	[core]5S(0.41)4d(9.06)5p(0.29)5d(0.01)6p(0.21)	
3n	[core]5S(0.38)4d(8.73)5p(0.32)5d(0.01)6p(0.64)	
3a	[core]5S(0.36)4d(8.71)5p(0.32)5d(0.01)6p(0.62)	
4n	[core]5S(0.42)4d(8.85)5p(0.70)5d(0.01)6p(0.36)	
4a	[core]5S(0.40)4d(8.83)5p(0.68)5d(0.01)6p(0.35)	

Table 3S. Natural Hybrid Orbital (NHO) Analysis of Pd-X bond in different complexes.

Compl.	Occu.	Polarizability		Hybridation	
		Pd	X/X'X^{eq}/X$^{eq'}$	Pd	X/X^{eq}/X$^{eq'}$
1n	1.90 1.90 - -	18.34% 18.34% - -	81.66% 81.66% - -	s(23.44%),p(52.83%),d(23.73%) s(23.44%),p(52.83%),d(23.73%) - -	s(15.35%),p(84.65%) s(15.35%),p(84.65%) - -
2n	1.89 1.89 - -	21.04% 21.04% - -	78.96% 78.96% - -	s(23.23%),p(53.33%),d(23.44%) s(23.23%),p(53.33%),d(23.44%) - -	s(14.26%),p(85.74%) s(14.26%),p(85.74%) - -
3n	1.86 1.86 1.83 1.83	27.13% 27.13% 29.12% 28.46%	72.87% 72.87% 70.88% 71.54%	s(15.19%),p(52.71%),d(32.10%) s(15.19%),p(52.71%),d(32.10%) s(16.23%),p(49.61%),d(34.16%) s(15.89%),p(50.24%),d(33.88%)	s(10.71%),p(89.29%) s(10.71%),p(89.29%) s(9.00%),p(91.00%) s(9.40%),p(90.60%)
4n	1.84 1.84 1.81 1.81	31.82% 31.82% 32.99% 31.94%	68.18% 68.18% 67.01% 68.06%	s(14.40%),p(53.15%),d(32.45%) s(14.40%),p(53.15%),d(32.45%) s(16.84%),p(49.79%),d(33.36%) s(16.79%),p(50.19%),d(33.03%)	s(9.28%),p(90.72%) s(9.28%),p(90.72%) s(7.98%),p(92.02%) s(8.34%),p(91.66%)
1a	1.91 1.91 - -	17.26% 17.26% - -	82.74% 82.74% - -	s(23.41%),p(53.70%),d(22.89%) s(23.41%),p(53.70%),d(22.89%) - -	s(16.25%),p(83.75%) s(16.25%),p(83.75%) - -
2a	1.90 1.90 - -	19.61% 19.61% - -	80.39% 80.39% - -	s(23.22%),p(54.12%),d(22.67%) s(23.22%),p(54.12%),d(22.67%) - -	s(15.15%),p(84.85%) s(15.15%),p(84.85%) - -
3a	1.87 1.87 1.84 1.82	24.93% 24.93% 26.73% 29.18%	75.07% 75.07% 73.27% 70.82%	s(15.46%),p(54.22%),d(30.32%) s(15.46%),p(54.22%),d(30.32%) s(15.99%),p(50.66%),d(33.36%) s(16.09%),p(49.10%),d(34.81%)	s(12.19%),p(87.81%) s(12.19%),p(87.81%) s(10.02%),p(89.98%) s(9.08%),p(90.92%)
4a	1.86 1.86 1.82 1.80	29.14% 29.14% 30.38% 32.76%	70.86% 70.86% 69.62% 67.24%	s(14.81%),p(54.64%),d(30.55%) s(14.81%),p(54.64%),d(30.55%) s(16.86%),p(50.55%),d(32.58%) s(16.91%),p(49.27%),d(33.83%)	s(10.80%),p(89.20%) s(10.80%),p(89.20%) s(8.97%),p(91.03%) s(8.21%,)p(91.79%)



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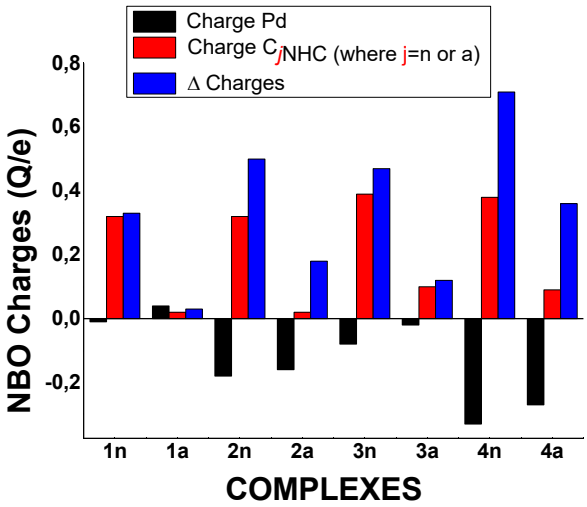

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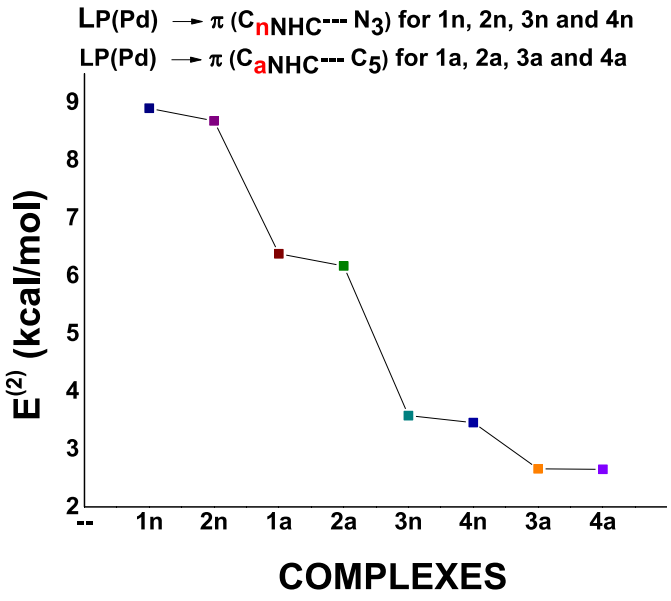

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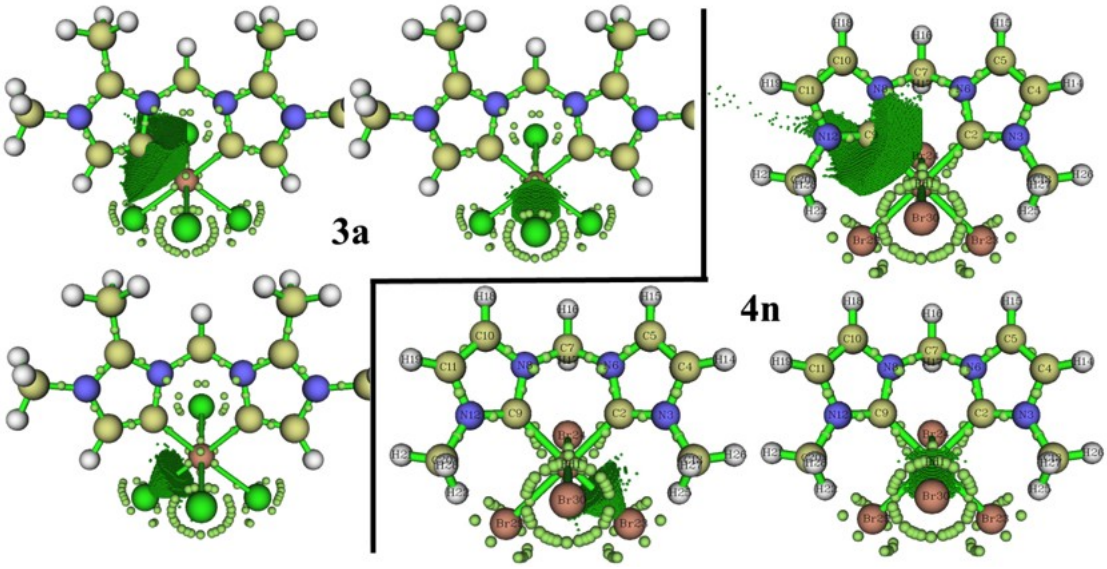

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