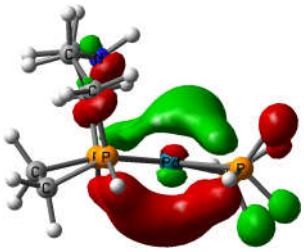
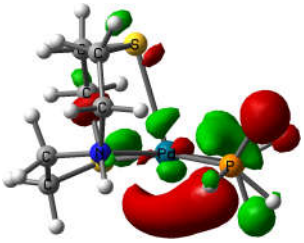
Supplementary Information

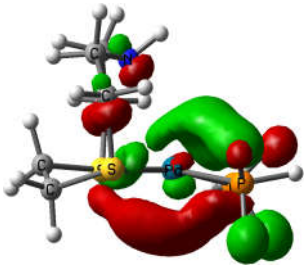
Figure S1. Geometric structures of Pd complexes [*endo*-Pd([9]ane**A**$_2$**B**)**L**$_2$, *endo*-Pd([9]ane**ABA**)**L**$_2$ {**A**=P, S; **B**=N; **L**=Cl$^-$, PH_3, $P(CH_3)_3$}] including the $3a_{1g}$(5s) and $2a_{1g}$ orbitals optimized at the B3P86//6-311+G(d,p)/(lanl2DZ for Pd) levels. The *endo*-[Pd([9]anePNP)$(PH_3)_2]^{2+}$ and *endo*-[Pd([9]anePNP)$\{P(CH_3)_3\}_2]^{2+}$ complexes could not be optimized.



endo-[Pd([9]aneP_2N)$(PH_3)_2]^{2+}$

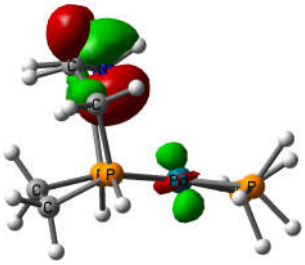


endo-[Pd([9]aneSNS)$(PH_3)_2]^{2+}$

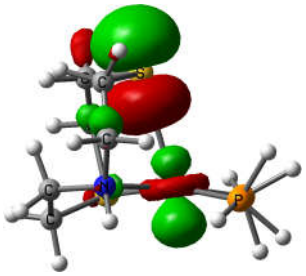


endo-[Pd([9]aneS_2N)$(PH_3)_2]^{2+}$

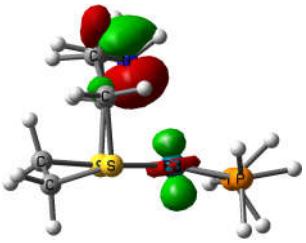
$3a_{1g}$ (5s)



endo-[Pd([9]aneP_2N)$(PH_3)_2]^{2+}$

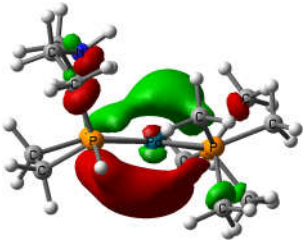


endo-[Pd([9]aneSNS)$(PH_3)_2]^{2+}$

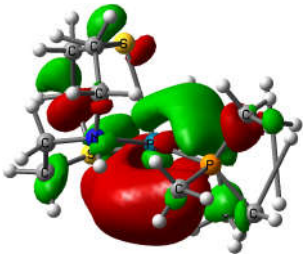


endo-[Pd([9]aneS_2N)$(PH_3)_2]^{2+}$

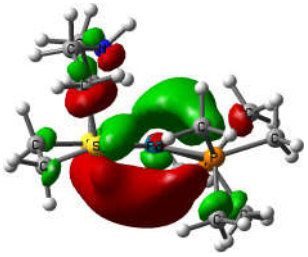
$2a_{1g}$



endo-[Pd([9]aneP_2N)$\{P(CH_3)_3\}_2]^{2+}$



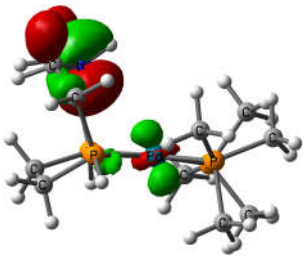
endo-[Pd([9]aneSNS)$\{P(CH_3)_3\}_2]^{2+}$



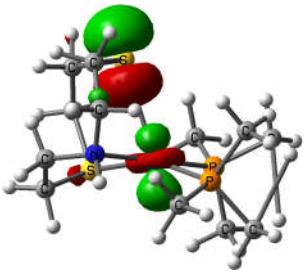
endo-[Pd([9]aneS_2N)$\{P(CH_3)_3\}_2]^{2+}$

$3a_{1g}$ (5s)

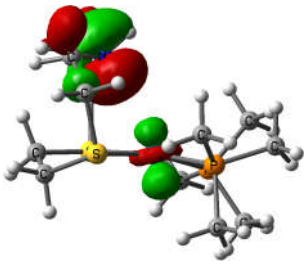
Figure S1. *Cont.*



endo-[Pd([9]aneP$_2$N){P(CH$_3$)$_3$}$_2$]$^{2+}$

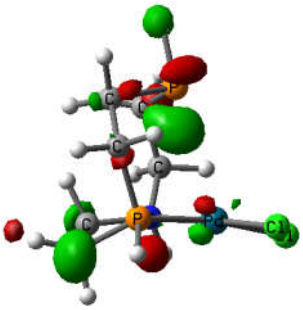


endo-[Pd([9]aneSNS){P(CH$_3$)$_3$}$_2$]$^{2+}$

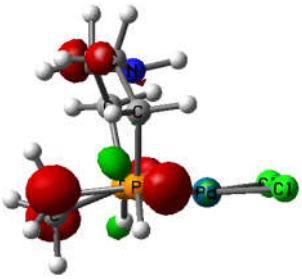


endo-[Pd([9]aneS$_2$N){P(CH$_3$)$_3$}$_2$]$^{2+}$

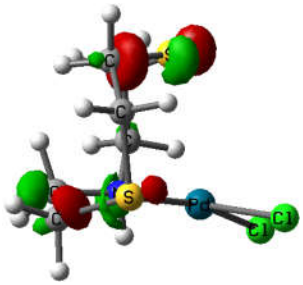
2a$_{1g}$



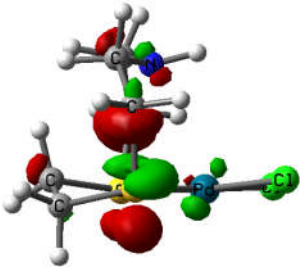
endo-Pd([9]anePNP)Cl$_2$



endo-Pd([9]aneP$_2$N)Cl$_2$

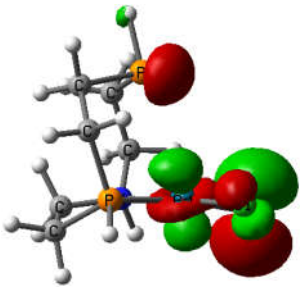


endo-Pd([9]aneSNS)Cl$_2$

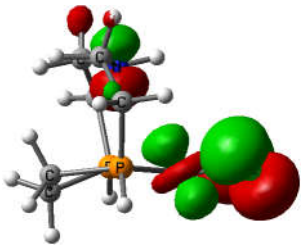


endo-Pd([9]aneS$_2$N)Cl$_2$

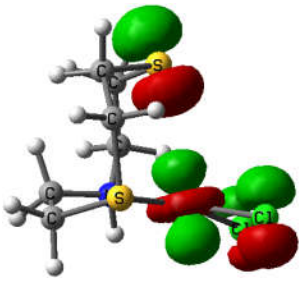
3a$_{1g}$ (5s)



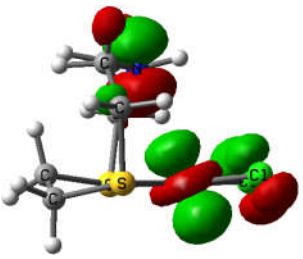
endo-Pd([9]anePNP)Cl$_2$



endo-Pd([9]aneP$_2$N)Cl$_2$



endo-Pd([9]aneSNS)Cl$_2$



endo-Pd([9]aneS$_2$N)Cl$_2$

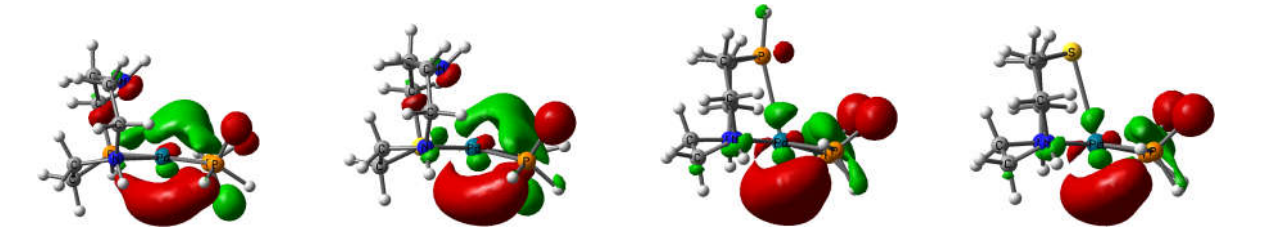
2a$_{1g}$

Table S1. Optimized average bond distances (Å), average atomic charges (CHelpG, au), and relative energies (eV) of the equilibrium structures {Pd([9]ane$\mathbf{A_2B}$)$\mathbf{L}_2$ and [Pd([9]ane**ABA**)$\mathbf{L}_2$} at the B3P86//6-311+G(d,p) (lanl2DZ for Pd) levels.

Compound	Average distance				Average atomic charge				Relative energy	
	$R^a_{Pd\text{-}P}$	$R^a_{Pd\text{-}N}$	$R^b_{Pd\cdots P}$	$R^b_{Pd\cdots N}$	Q^c_{Pd}	Q^c_{PH3}	Q^d_P	Q^d_N	$\Delta E^e_{H\text{-}L}$	$\Delta E^f_{BAB\text{-}B2A}$
endo- [Pd([9]aneP_2N) $(PH_3)_2$]$^{2+}$	2.342			3.217	0.448	0.343		−0.185	3.82	
	$R^a_{Pd\text{-}S}$	$R^a_{Pd\text{-}N}$	$R^b_{Pd\cdots S}$	$R^b_{Pd\cdots N}$	Q^c_{Pd}	Q^c_{PH3}	Q^d_S	Q^d_N		
endo-[Pd([9]aneSNS)$(PH_3)_2$]$^{2+}$	2.369	2.161	2.867		0.377	0.359	−0.322		2.96	0.01
endo-[Pd([9]aneS_2N) $(PH_3)_2$]$^{2+}$	2.373			2.895	0.396	0.363		−0.239	3.38	0.00
	$R^a_{Pd\text{-}P}$	$R^a_{Pd\text{-}N}$	$R^b_{Pd\cdots P}$	$R^b_{Pd\cdots N}$	Q^c_{Pd}	$Q^c_{P(CH3)3}$	Q^d_P	Q^d_N		
endo-[Pd([9]aneP_2N){$P(CH_3)_3$}$_2$]$^{2+}$	2.364			3.290	0.633	−0.461		0.180	4.31	
	$R^a_{Pd\text{-}S}$	$R^a_{Pd\text{-}N}$	$R^b_{Pd\cdots S}$	$R^b_{Pd\cdots N}$	Q^c_{Pd}	$Q^c_{P(CH3)3}$	Q^d_S	Q^d_N		
endo-[Pd([9]aneSNS){$P(CH_3)_3$}$_2$]$^{2+}$	2.424	2.193	2.916		0.456	0.398	-0.063		3.51	0.02
endo-[Pd([9]aneS_2N){$P(CH_3)_3$}$_2$]$^{2+}$	2.410			3.136	0.482	0.392		-0.133	3.84	0.00
	$R^a_{Pd\text{-}P}$	$R^a_{Pd\text{-}N}$	$R^b_{Pd\cdots P}$	$R^b_{Pd\cdots N}$	Q^c_{Pd}	Q^c_{Cl}	Q^d_P	Q^d_N	$\Delta E^e_{H\text{-}L}$	$\Delta E^f_{BAB\text{-}B2A}$
endo-Pd([9]anePNP)Cl_2	2.209	2.130	3.175		0.929	−0.795	−0.285		3.92	0.55
endo-Pd([9]aneP_2N)Cl_2	2.247			3.072	0.945	−0.820		−0.191	4.14	0.00
	$R^a_{Pd\text{-}S}$	$R^a_{Pd\text{-}N}$	$R^b_{Pd\cdots S}$	$R^b_{Pd\cdots N}$	Q^c_{Pd}	Q^c_{Cl}	Q^d_S	Q^d_N		
endo-Pd([9]aneSNS)Cl_2	2.282	2.132	3.093		0.788	−0.755	−0.246		3.38	0.23
exptl	2.263[g]	2.087[g]	2.928[g] 3.011[h]							
endo-Pd([9]aneS_2N)Cl_2	2.297			2.904	0.884	−0.770		−0.205	3.50	0.00
exptl[g]	2.269			2.722						

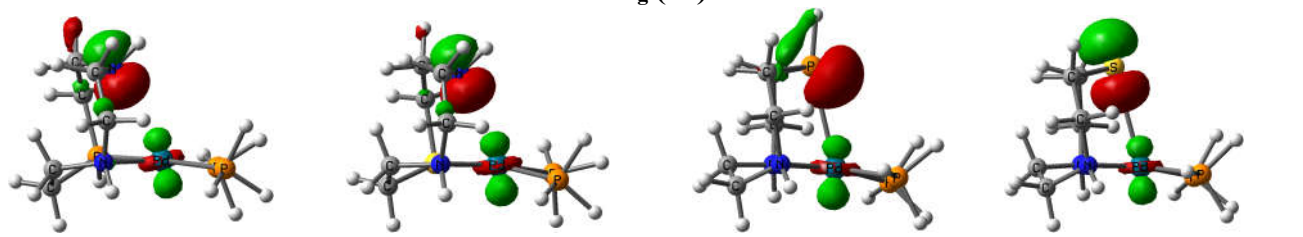
[a]Bond length between the Pd^{II} center and equatorial binding site of the tridentate ligand. [b]Bond length between the Pd^{II} center and axial binding site of the tridentate ligand. [c]Atomic charges of the Pd^{II} center and the binding atom of *trans* **L**-ligand. [d]Atomic charge of an apical binding atom. [e]Energy gap between HOMO and LUMO. [f]Relative energy gap between Pd([9]ane$\mathbf{A_2B}$)$\mathbf{L}_2$ and Pd([9]ane**ABA**)$\mathbf{L}_2$. [g]Ref. [39]. [h]Cited from Ref. [39].

Figure S2. The $3a_{1g}$(5s) and $2a_{1g}$ orbitals of *endo*-Pd([9]ane**B**$_2$**A**)**L**$_2$ and *endo*-Pd([9]ane**BAB**)**L**$_2$ (**A**=P, S; **B**=N; **L**=PH_3, Cl^-) calculated at the CAM-B3LYP/6-311+G(d,p) (lanl2DZ for Pd) level.



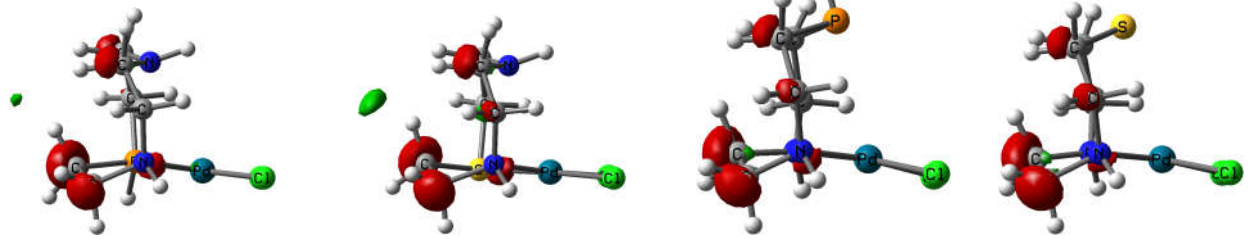
endo-[Pd([9]aneNPN)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneNSN)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneN_2P)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneN_2S)$(PH_3)_2$]$^{2+}$

$3a_{1g}$ (5s)



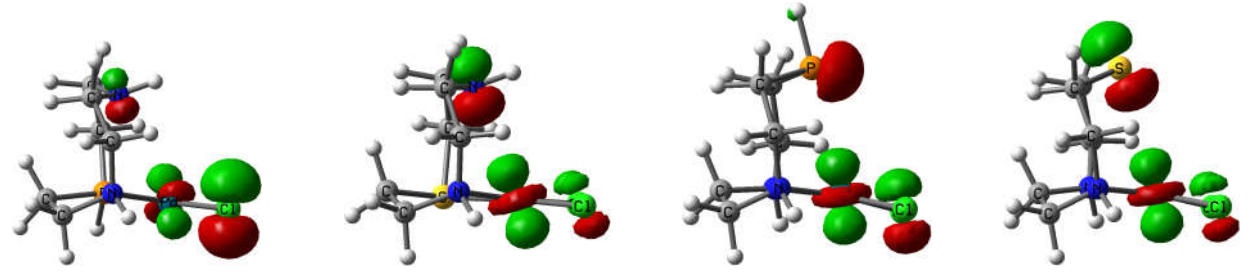
endo-[Pd([9]aneNPN)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneNSN)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneN_2P)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneN_2S)$(PH_3)_2$]$^{2+}$

$2a_{1g}$



endo-Pd([9]aneNPN)Cl_2 *endo*-Pd([9]aneNSN)Cl_2 *endo*-Pd([9]aneN_2P)Cl_2 *endo*-Pd([9]aneN_2S)Cl_2

$3a_{1g}$ (5s)



endo-Pd([9]aneNPN)Cl_2 *endo*-Pd([9]aneNSN)Cl_2 *endo*-Pd([9]aneN_2P)Cl_2 *endo*-Pd([9]aneN_2S)Cl_2

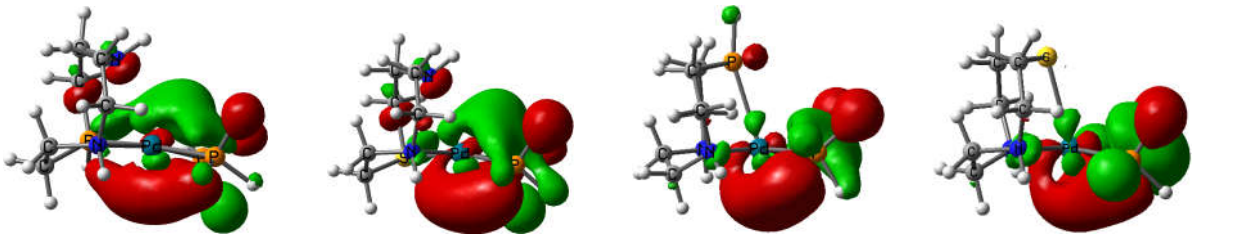
$2a_{1g}$

Table S2. Optimized average bond distances (Å), average atomic charges (NBO, au), and relative energies (eV) of the equilibrium structures {Pd([9]ane$\mathbf{B_2A}$)$\mathbf{L_2}$ and [Pd([9]ane**BAB**)$\mathbf{L_2}$} at the CAM-B3LYP/6-311+G(d,p) (lanl2DZ for Pd) levels.

Compound	Average distance				Average atomic charge				Relative energy	
	$R^a_{Pd\text{-}N}$	$R^a_{Pd\text{-}P}$	$R^b_{Pd\cdots N}$	$R^b_{Pd\cdots P}$	Q^c_{Pd}	Q^c_{PH3}	Q^d_N	Q^d_P	$\Delta E^e_{H\text{-}L}$	$\Delta E^f_{BAB\text{-}B2A}$
endo-[Pd([9]aneNPN)$(PH_3)_2$]$^{2+}$	2.191	2.296	2.898		0.186	0.301	−0.691		6.37	0.35
endo-[Pd([9]aneN_2P)$(PH_3)_2$]$^{2+}$	2.137			2.879	0.044	0.340		0.608	5.68	0.00
	$R^a_{Pd\text{-}N}$	$R^a_{Pd\text{-}S}$	$R^b_{Pd\cdots N}$	$R^b_{Pd\cdots S}$	Q^c_{Pd}	Q^c_{PH3}	Q^d_N	Q^d_S		
endo-[Pd([9]aneNSN)$(PH_3)_2$]$^{2+}$	2.156	2.364	2.771		0.115	0.337	−0.686		6.13	0.11
endo-[Pd([9]aneN_2S)$(PH_3)_2$]$^{2+}$	2.136			2.931	0.019	0.339		0.314	5.67	0.00
	$R^a_{Pd\text{-}N}$	$R^a_{Pd\text{-}P}$	$R^b_{Pd\cdots N}$	$R^b_{Pd\cdots P}$	Q^c_{Pd}	Q^c_{Cl}	Q^d_N	Q^d_P		
endo-Pd([9]aneNPN)Cl_2	2.119	2.241	3.065		0.101	−0.480	−0.710		6.81	−0.22
endo-Pd([9]aneN_2P)Cl_2	2.094			3.162	0.299	−0.451		0.627	6.80	0.00
	$R^a_{Pd\text{-}N}$	$R^a_{Pd\text{-}S}$	$R^b_{Pd\cdots N}$	$R^b_{Pd\cdots S}$	Q^c_{Pd}	Q^c_{Cl}	Q^d_N	Q^d_S		
endo-Pd([9]aneNSN)Cl_2	2.102	2.348	2.935		0.177	−0.450	−0.702		6.48	−0.16
endo-Pd([9]aneN_2S)Cl_2	2.097			3.238	0.309	−0.458		0.269	6.68	0.00

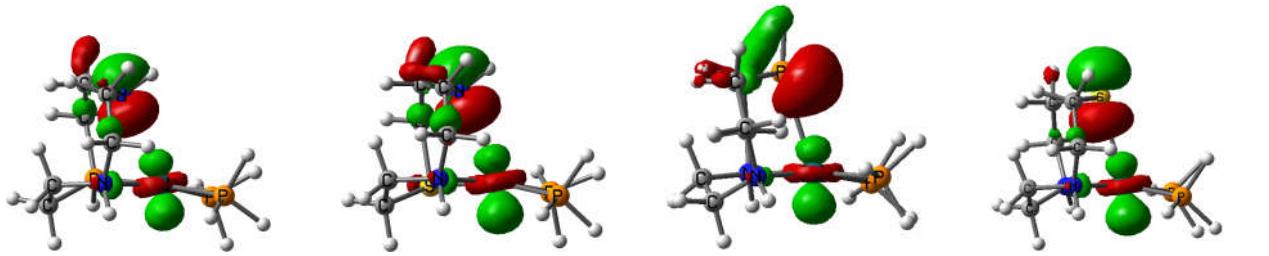
[a]Bond length between the Pd^{II} center and equatorial binding atom of the tridentate ligand. [b]Bond length between the Pd^{II} center and axial binding site of the tridentate ligand. [c]Atomic charges of the Pd^{II} center and the binding atom of *trans* **L**-ligand. [d]Atomic charge of an apical binding atom. [e]Relative energy gap between HOMO and LUMO. [f]Energy gap between Pd([9]ane$\mathbf{B_2A}$)$\mathbf{L_2}$ and Pd([9]ane**BAB**)$\mathbf{L_2}$ types. [g]Energy gap between *exo*- and *endo*-type structures.

Figure S3. The $3a_{1g}$(5s) and $2a_{1g}$ orbitals of *endo*-Pd([9]ane**B**$_2$**A**)**L**$_2$ and *endo*-Pd([9]ane**BAB**)**L**$_2$ (**A**=P, S; **B**=N; **L**= PH_3, Cl^-) calculated at the B3P86/6-311+G(d,p) (3-21G(d) for Pd) level.



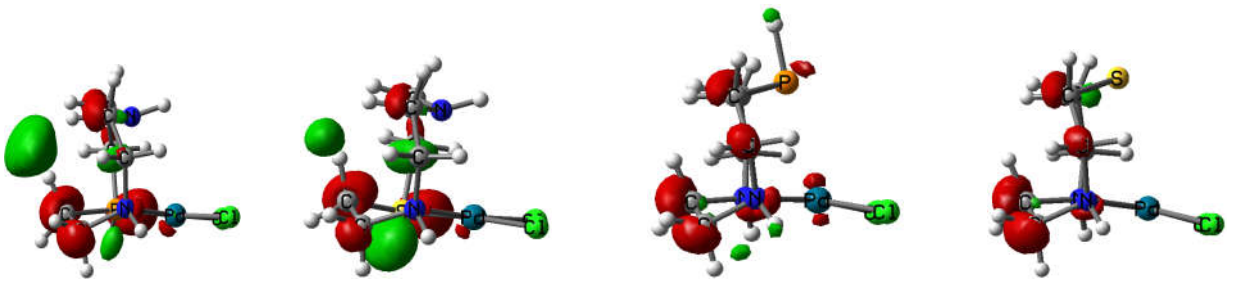
endo-[Pd([9]aneNPN)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneNSN)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneN_2P)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneN_2S)$(PH_3)_2$]$^{2+}$

$3a_{1g}$ (5s)



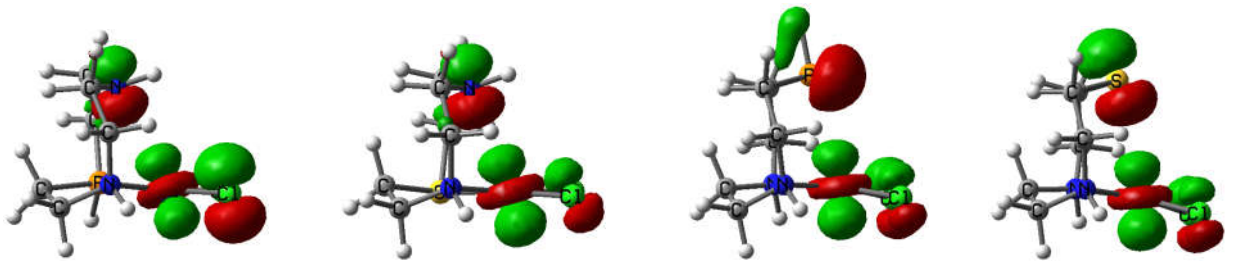
endo-[Pd([9]aneNPN)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneNSN)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneN_2P)$(PH_3)_2$]$^{2+}$ *endo*-[Pd([9]aneN_2S)$(PH_3)_2$]$^{2+}$

$2a_{1g}$



endo-Pd([9]aneNPN)Cl_2 *endo*-Pd([9]aneNSN)Cl_2 *endo*-Pd([9]aneN_2P)Cl_2 *endo*-Pd([9]aneN_2S)Cl_2

$3a_{1g}$ (5s)



endo-Pd([9]aneNPN)Cl_2 *endo*-Pd([9]aneNSN)Cl_2 *endo*-Pd([9]aneN_2P)Cl_2 *endo*-Pd([9]aneN_2S)Cl_2

$2a_{1g}$

Table S3. Optimized average bond distances (Å), average atomic charges (NBO, au), and relative energies (eV) of the equilibrium structures {Pd([9]ane**B**$_2$**A**)**L**$_2$ and [Pd([9]ane**BAB**)**L**$_2$} at the B3P86//6-311+G(d,p) (3-21G(d) for Pd) levels.

Compound	Average distance				Average atomic charge				Relative energy	
	R^a_{Pd-N}	R^a_{Pd-P}	$R^b_{Pd\cdots N}$	$R^b_{Pd\cdots P}$	Q^c_{Pd}	Q^c_{PH3}	Q^d_N	Q^d_P	ΔE^c_{H-L}	$\Delta E^f_{BAB-B2A}$
endo-[Pd([9]aneNPN)$(PH_3)_2$]$^{2+}$	2.216	2.292	2.762		0.003	0.207	−0.687		3.46	0.29
endo-[Pd([9]aneN_2P)$(PH_3)_2$]$^{2+}$	2.153			2.789	0.099	0.249		0.576	2.76	0.00
	R^a_{Pd-N}	R^a_{Pd-S}	$R^b_{Pd\cdots N}$	$R^b_{Pd\cdots S}$	Q^c_{Pd}	Q^c_{PH3}	Q^d_N	Q^d_S		
endo-[Pd([9]aneNSN)$(PH_3)_2$]$^{2+}$	2.162	2.376	2.748		0.048	0.242	−0.686		3.16	0.12
endo-[Pd([9]aneN_2S)$(PH_3)_2$]$^{2+}$	2.148			2.867	0.129	0.244		0.307	2.73	0.00
	R^a_{Pd-N}	R^a_{Pd-P}	$R^b_{Pd\cdots N}$	$R^b_{Pd\cdots P}$	Q^c_{Pd}	Q^c_{Cl}	Q^d_N	Q^d_P		
endo-Pd([9]aneNPN)Cl_2	2.132	2.240	2.932		0.646	−0.616	−0.657		3.79	−0.18
endo-Pd([9]aneN_2P)Cl_2	2.107			2.959	0.341	−0.454		0.597	3.54	0.00
	R^a_{Pd-N}	R^a_{Pd-S}	$R^b_{Pd\cdots N}$	$R^b_{Pd\cdots S}$	Q^c_{Pd}	Q^c_{Cl}	Q^d_N	Q^d_S		
endo-Pd([9]aneNSN)Cl_2	2.110	2.357	2.786		0.254	−0.459	−0.701		3.35	−0.14
endo-Pd([9]aneN_2S)Cl_2	2.111			3.103	0.752	−0.583		0.225	3.49	0.00

[a]Bond length between the Pd^{II} center and equatorial binding atom of the tridentate ligand. [b]Bond length between the Pd^{II} center and axial binding site of the tridentate ligand. [c]Atomic charges of the Pd^{II} center and an binding atom of *trans* **L**-ligand. [d]Atomic charge of an apical binding atom. [e]Relative energy gap between HOMO and LUMO. [f]Energy gap between Pd([9]ane**B**$_2$**A**)**L**$_2$ and Pd([9]ane**BAB**)**L**$_2$ types. [g]Energy gap between *exo*- and *endo*-type structures.