Supporting Information for

Synthesis, Structure and Computational Studies on a Cationic T-shaped Pd-Complex

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1. Computational Details

All computations were performed using the density functional method B97D as implemented in the Gaussian09 program.[1] For all main-group elements (C, H, N, O and P) the all-electron triple-z basis set (6-311G**) was used,[2] whereas for palladium (Pd) a small-core relativistic ECP together with the corresponding double-z valence basis set was employed (Stuttgart RSC 1997 ECP).[3]

Table S1. Energies of the optimized structures /B97D

Compound	E(0 K)[a] [Ha]	H(298 K)[b] [Ha]	G(298 K)[b] [Ha]
CH_4	-40.461047	-40.457229	-40.478383
H^+	0.000000	0.002360	-0.010000
P(*t*Bu)$_3$	-814.342356	-814.323976	-814.382865
[(*t*Bu$_3$P)Pd(Me)(Cl)]	-1442.701011	-1442.676679	-1442.750044
$[(t\mathrm{Bu_3P})_2\mathrm{PdMe}]^+$	-1796.622087	-1796.581170	-1796.686666
$[(t\mathrm{Bu_3P})_2\mathrm{Pd(CH_4)}]^{2+}$	-1796.859498	-1796.816810	-1796.926655
TS: $[(t\mathrm{Bu_3P})_2\mathrm{Pd(CH_4)}]^{2+}$ - CH_4	-1796.858488	-1796.815311	-1796.926653
$[(t\mathrm{Bu_3P})_2\mathrm{Pd}]^{2+}$	-1756.400152	-1756.360153	-1756.465018
$[(\mathrm{PONOP})\mathrm{Pd(CH_4)}]^{2+}$	-1878.918951	-1878.880383	-1878.984675

[a]DFT energy incl. ZPE.

[b]standard conditions T = 298.15 K and p = 1 atm.

Table S2. Energies of the optimized structures /PBE0

Compound	E(0 K)[a] [Ha]	H(298 K)[b] [Ha]	G(298 K)[b] [Ha]
CH_4	-40.425737	-40.421923	-40.443055
H^+	0.000000	0.002360	-0.010000
P(*t*Bu)$_3$	-813.915506	-813.896764	-813.956794

[(*t*Bu$_3$P)Pd(Me)(Cl)]	-1442.701011	-1442.676679	-1442.750044
[(*t*Bu$_3$P)$_2$PdMe]$^+$	-1796.622087	-1796.581170	-1796.686666
[(*t*Bu$_3$P)$_2$Pd(CH$_4$)]$^{2+}$	-1796.859498	-1796.816810	-1796.926655
[(*t*Bu$_3$P)$_2$Pd]$^{2+}$	-1755.222484	-1755.182559	-1755.287212
[(PONOP)Pd(CH$_4$)]$^{2+}$	-1877.746748	-1877.708572	-1877.813035

[a]DFT energy incl. ZPE.

[b]standard conditions T = 298.15 K and p = 1 atm.

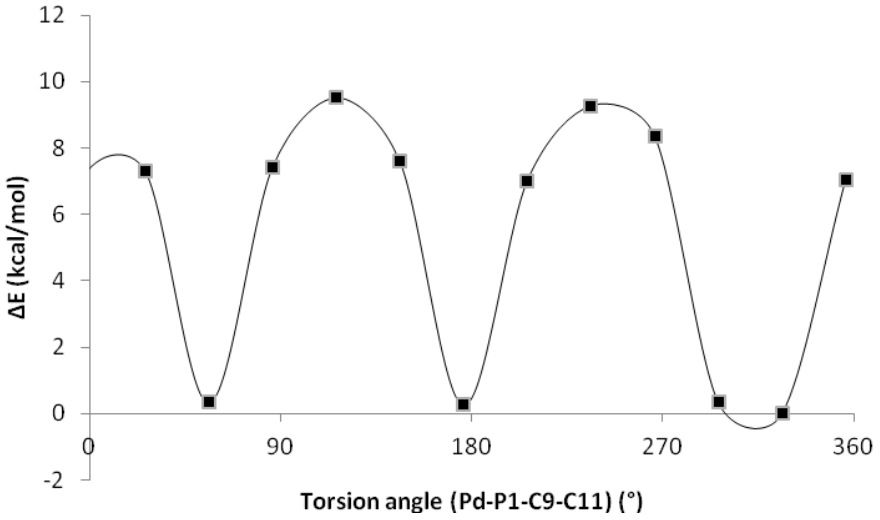

Figure S1. Scan along the dihedral angle Pd-P1-C9-C11

2. References

[1] Gaussian 09, Revision **A.1**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.;

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