Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Palladium(II) complexes featuring a mixed Phosphine-Pyridine-Iminophosphorane pincer ligand : synthesis and reactivity

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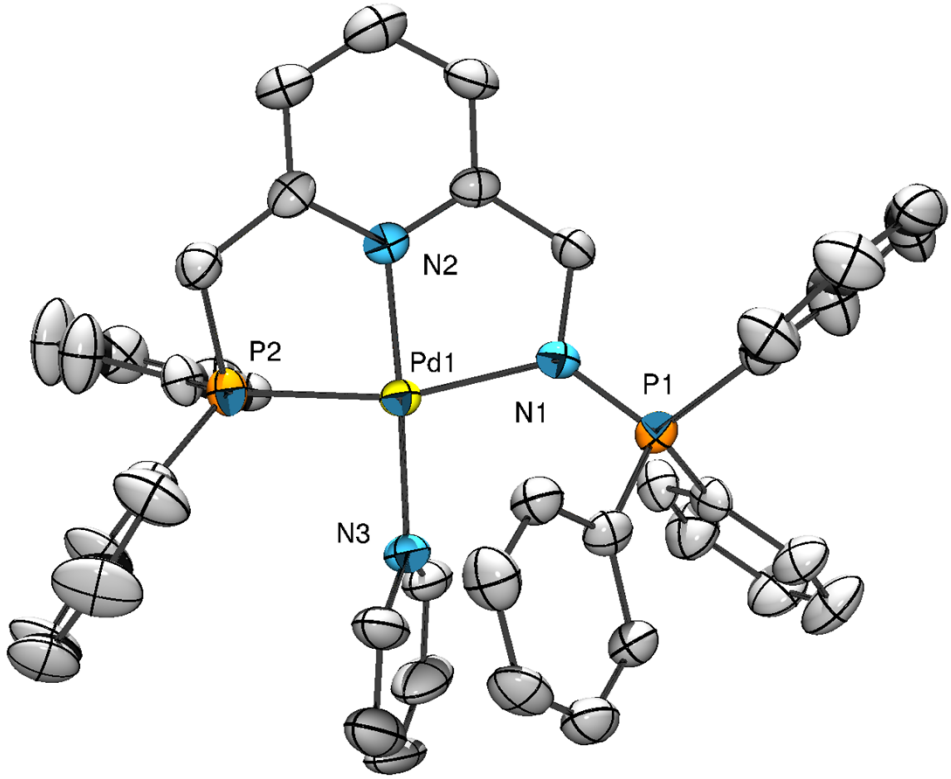


Figure S1.ORTEP of [**L**Pd(py)]$(BF_4)_2$ **2** – Hydrogen atoms and the two tetrafluroroborate anions were omitted for clarity. Selected bond lengths (Å) and angles (°): N1-P1 1,595(5), N1-Pd1 2,081(5), P2-Pd1 2,223(2), N2-Pd1 1,989(5), N3-Pd1 2,053(5) ; N1-Pd1-P2 163,8(1), N2-Pd1-N3 175,0(2), N1-Pd1-N2 80,7(2), P2-Pd1-N2 93,5(2), N1-Pd1-N3 102,5(2), P2-Pd1-N3 93,5(2).

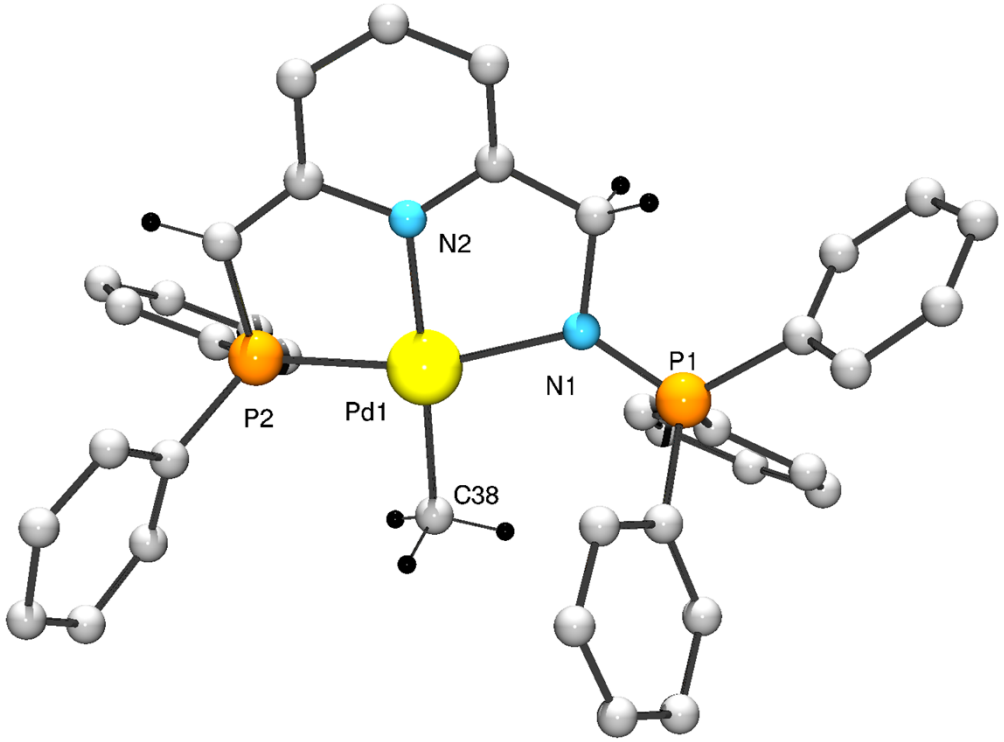


Figure S2. Solid-state connectivity of [**L***PdMe].

[**L***PdMe] crystallized as extremely thin needles, such shape prevents accurate data collection, no reflections can be find after *ca.* 2θ = 40°. The compound crystallized in the P-1 space group with the following cell parameters: a = 9.779(1), b = 12.328(1), c = 13.266(1); α = 97.909(1), β = 90.336(1), γ = 96.595(1). From these low quality data, the connectivity can be determined as presented above. Notably, no counter anion could be localized in the asymmetric unit cell. However, the structure cannot be refined in an anisotropic way because of an insufficient numbers of parameters leading to non-positive definite thermal ellipsoids for several carbon atoms.

Crystallographic data:

Compound	**1**	**2**	**3**	**5**
Formula	'$C_{37}H_{32}ClN_2P_2Pd$, C_7H_5N,Cl'	'$C_{42}H_{37}N_3P_2Pd$, $(BF_4)_2$'	'$C_{37}H_{31}ClN_2P_2Pd$'	'$C_{56}H_{34}BF_{15}N_2P_2Pd$'
Mw	847.00	925.70	707.43	1199.00
Space group	P 2_1/c	P b c a	P 21/n	P -1
λ(Å)	0.71069	0.71069	0.71069	0.71069
a(Å)	9.635(1)	12.601(1)	11.009(1)	14.503(1)
b(Å)	18.324(1)	16.725(1)	12.528(1)	14.797(1)
c(Å)	23.370(1)	41.916(1)	22.713(1)	17.647(1)
α(°)	90	90	90	78.966(1)
β(°)	108.913(3)	90	92.606(1)	69.404(1)
γ(°)	90	90	90	72.013(1)
V(Å^3)	3903.3(5)	8833.9(9)	3129.4(4)	3357.2(4)
Z	4	8	4	2
d(g-cm-3)	1.441	1.392	1.502	1.186
F(000)	1728	3744	1440	1200
μ(cm-1)	0.730	0.559	0.811	0.397
θ_{max}	27.482	25.024	27.455	30.032
Rflns measd	32353	42918	40877	36178
Unique data	8915	7611	7143	19127
Rint	0.0466	0.0386	0.1307	0.0333
wR2	0.0792	0.1557	0.1754	0.1241
R1	0.0391	0.0713	0.0704	0.0454
GoF	1.077	1.225	1.151	1.050
CCDC Number	1414327	1414328	1414329	1414330

II. NMR spectra

Figure S3. Deuteration of the benzylic position by MeOD-d^4 ($^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ in C_6D_6 spectra)

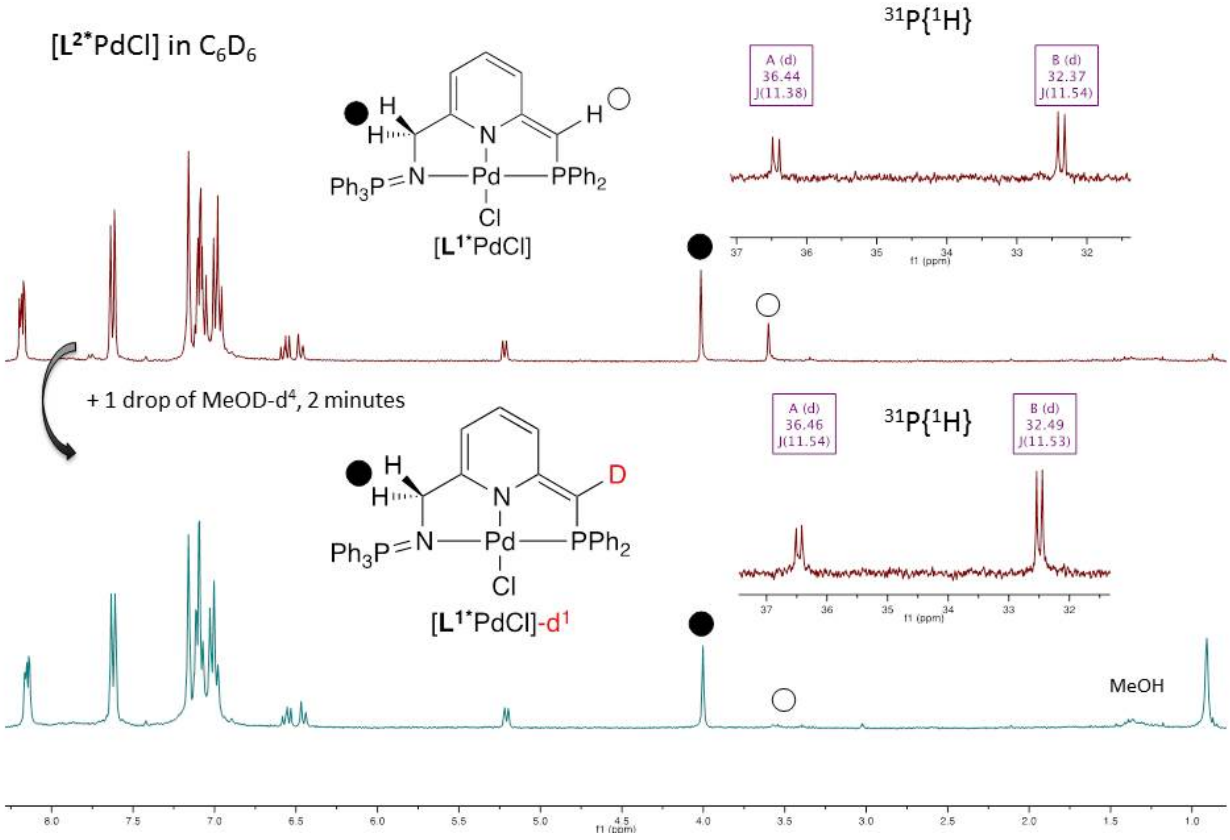
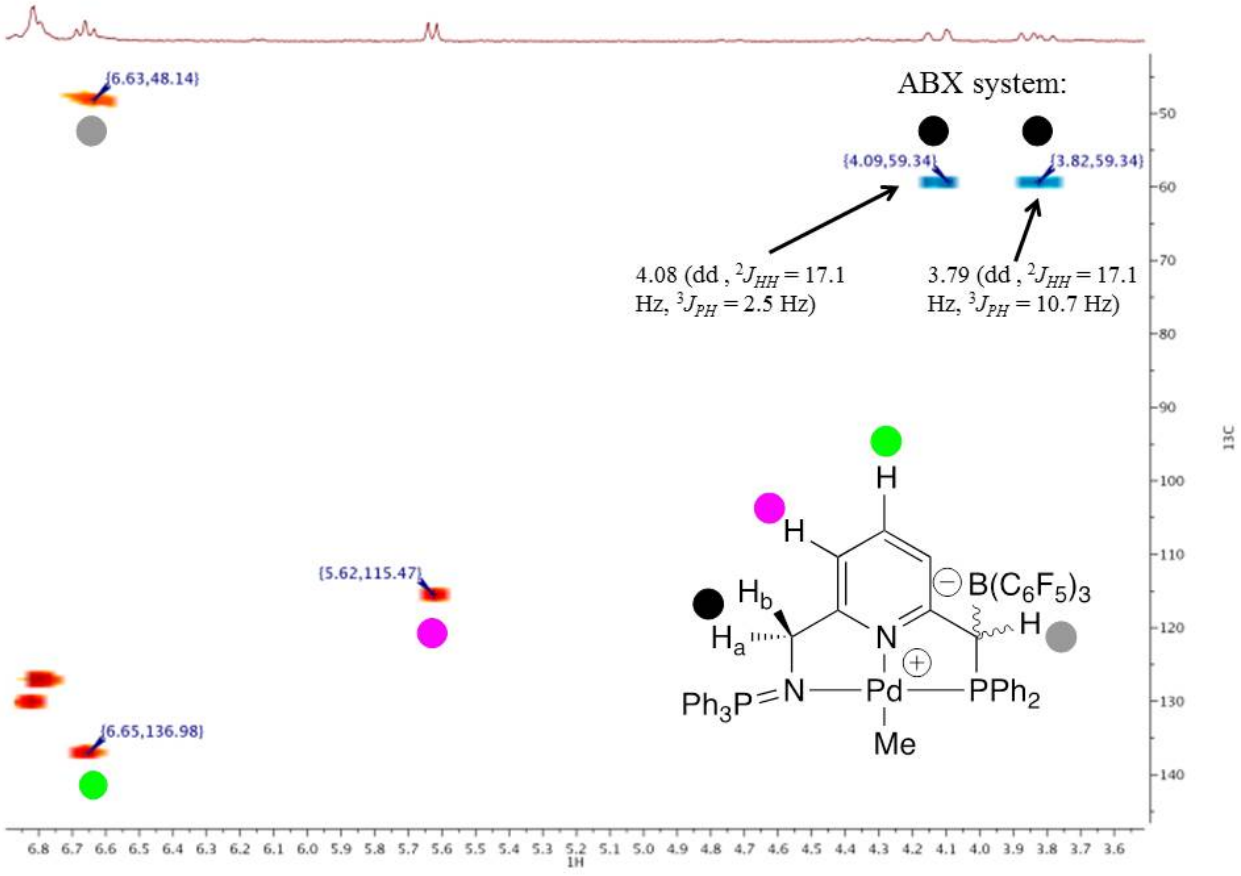


Figure S4. HSQC ^{1}H-^{13}C spectrum of **5** (blue = CH_2, red = CH, CH_3):



III. ^{1}H DOSY NMR of **L**.LiCl

The ^{1}H PGSE (DOSY) experiments were performed on the same spectrometer. The experiment was measured using the ledbpgp2s pulse program (Bruker) at a temperature of 293 K. A relaxation delay of 10 s was employed along with a diffusion time (Δ) of 50 ms and an eddy current delay of 5 ms. Bipolar gradient pulses (δ/2) of 2.2 ms and homospoil gradient pulses of 1.1 ms were used. The gradient strength of the 2 homospoil pulses were -17.13 % and -13.17 % respectively. Sixteen experiments of sixteen scans each were collected with the bipolar gradient strength, initially at 2 % (1st experiment), linearly increased to 98 % (16th experiment). All gradient pulses were sine shaped and after each application a recovery delay of 200 µs was used. Further processing was achieved using the MestReNova software.

The DOSY spectrum of **L**.LiCl in THF-d_8 is presented below, a diffusion coefficient of 7.43.10^{-6} cm^2.s^{-1} is found, assuming a dynamic viscosity η = 0.48 cP for the THF at 20°C, a hydrodynamic radius of 6 Å is obtained, corresponding to a volume of about 900 Å^3 for the approximating sphere.

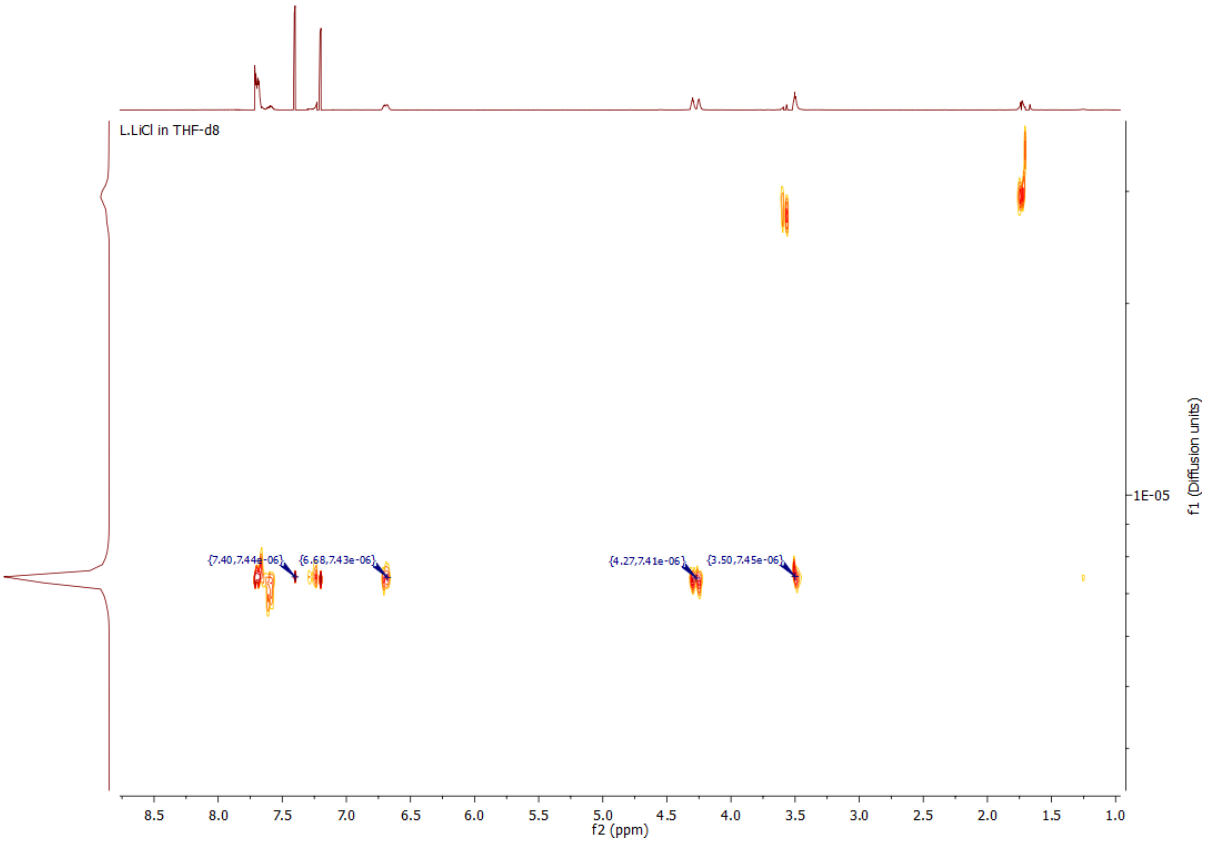


Figure S5. ^{1}H DOSY NMR spectrum of **L**.LiCl in THF-d_8

The DOSY spectrum of **L**.LiCl in $CDCl_3$ in presented below, a diffusion coefficient of 5.42.10^{-6} cm^2.s^{-1} is found, assuming a dynamic viscosity η = 0.563 cP for the chloroform at 20°C, a hydrodynamic radius of 7 Å is obtained corresponding to a volume of about 1400 Å^3 for the corresponding sphere.

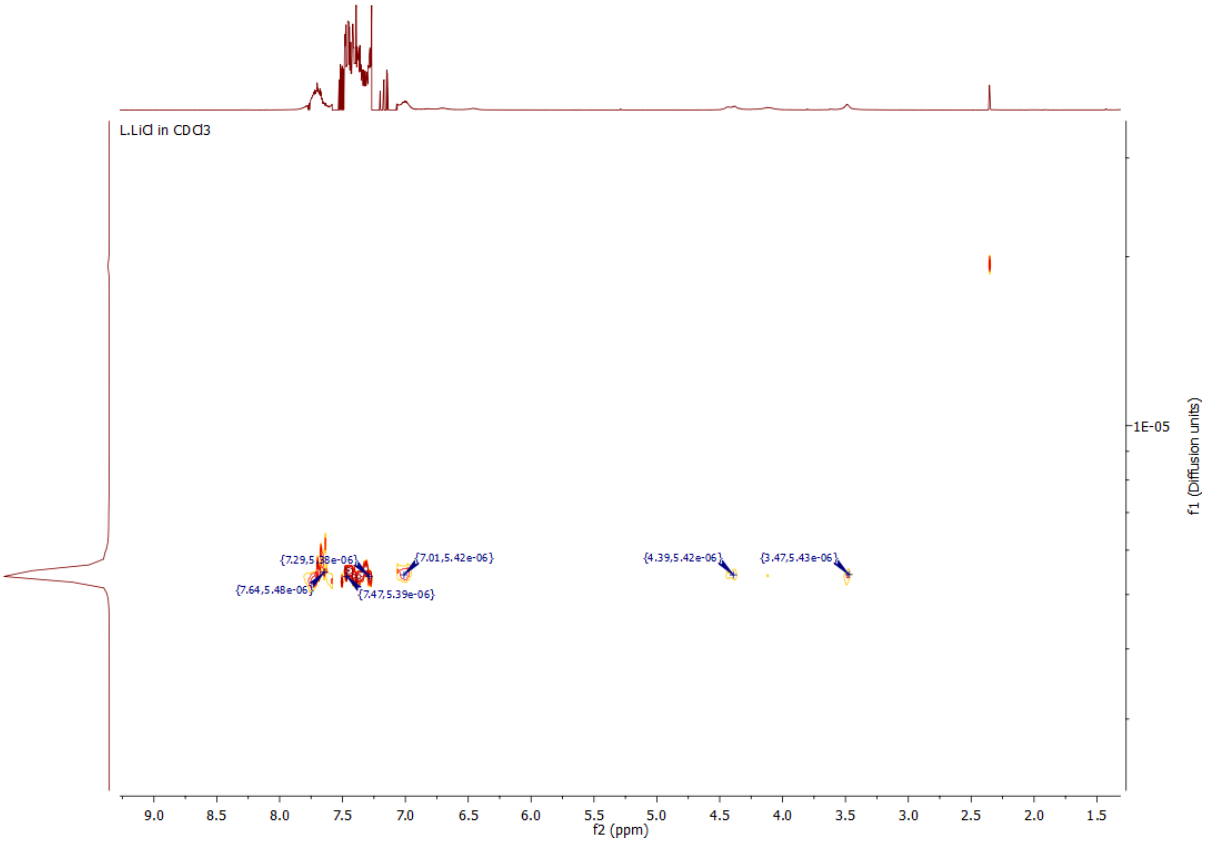


Figure S6. ^{1}H DOSY NMR spectrum of **L**.LiCl in $CDCl_3$