Calculations Details:

We have evaluated the robustness of the calculated isomer energies to changes in the functional, basis set, and compared optimisation *in vacuo* with a continuum dielectric field as described in the manuscript. Re-optimisation of the geometries with different functionals also provided us with an indication of the impact of small structural changes on isomer energies. The results have been summarised in Table S1.

Table S1: Calculated isomer energies and structural features for representative complexes considered in this work

Complex	**Method**	**Isomer Energy, kcal mol^{-1}**	**M-PPh$_2$ (Å)**	**M-PR$_2$ (Å)**	**M-Me (Å)**	**M-Cl (Å)**	**P-M-P (°)**
4a	PW91, MeOH solv.	0.00	2.249	2.444	2.115	2.437	101.2
4b	PW91, MeOH solv.	3.05	2.411	2.300	2.106	2.449	100.2
4a	PW91, MeOH solv., 6-311G**+/LACV3P**+	0.00	2.245	2.445	2.116	2.443	101.8
4b	PW91, MeOH solv., 6-311G**+/LACV3P**+	3.61	2.408	2.295	2.108	2.467	101.2
4a	PW91, in vacuo	0.00	2.242	2.433	2.116	2.409	101.2
4b	PW91, in vacuo	4.00	2.398	2.294	2.107	2.417	99.9
4a	SVWN, MeOH solv.	0.00	2.210	2.362	2.08	2.377	100.7
4b	SVWN, MeOH solv.	3.01	2.337	2.252	2.073	2.384	99.5
4a	B3LYP, MeOH solv.	0.00	2.262	2.499	2.113	2.459	101.6
4b	B3LYP, MeOH solv.	3.11	2.451	2.317	2.106	2.483	100.9
13a	PW91, MeOH solv.	0.00	2.252	2.393	2.111	2.434	102.3
13b	PW91, MeOH solv.	-1.03	2.393	2.265	2.106	2.434	98.0
13a	PW91, in vacuo	0.00	2.241	2.380	2.113	2.406	101.8
13b	PW91, in vacuo	1.66	2.382	2.256	2.101	2.404	97.3
13a	SVWN, MeOH solv.	0.00	2.212	2.329	2.077	2.371	102.2
13b	SVWN, MeOH solv.	0.21	2.326	2.220	2.069	2.376	100.4
13a	B3LYP, MeOH solv.	0.00	2.266	2.424	2.112	2.450	101.6
13b	B3LYP, MeOH solv.	-0.18	2.434	2.281	2.106	2.455	99.3
7a	PW91, MeOH solv.	0.00	2.270	2.476	2.105	2.441	101.4
7b	PW91, MeOH solv.	4.15	2.441	2.333	2.095	2.444	100.6
7a	SVWN, MeOH solv.	0.00	2.214	2.370	2.067	2.370	101.2
7b	SVWN, MeOH solv.	4.20	2.343	2.264	2.058	2.372	99.9

7a	B3LYP, MeOH solv.	0.00	2.300	2.536	2.099	2.464	101.0
7b	B3LYP, MeOH solv.	3.78	2.495	2.371	2.088	2.465	100.2
$[Pd(CH_3)ClL_{nBu}]$, a	PW91, MeOH solv.	0.00	2.269	2.413	2.102	2.428	102.1
$[Pd(CH_3)ClL_{nBu}]$, b	PW91, MeOH solv.	-0.92	2.415	2.281	2.094	2.436	100.6

Method References:

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