Template assisted self-assembly of bidentate phosphine complexes with hemilabile coordination behaviour

Samir Chikkali, Dietrich Gudat*, Mark Niemeyer

Institut für Anorganische Chemie
Universität Stuttgart
Pfaffenwaldring 55, 70550 Stuttgart, Germany
Fax: (+)49 711 685 64241
E-mail: gudat@iac.uni-stuttgart.de

Supporting Information: Characterisation data for **2a** (solid-state NMR data, low-temperature ^{1}H NMR data of **2a** and **2a'**); synthetic procedure and spectroscopic data for **2b**; reaction conditions for the Sonogashira coupling with **2a,b** as catalyst; details on computational studies of **2a** and its adducts with formamide.

Characterisation data for 2a:
Solution NMR data:
^{1}H NMR (223K, DMF-d7; assignments were derived from ^{1}H-TOCSY, ^{1}H-NOESY, ^{1}H,^{31}P-HMQC NMR spectra):
2a: δ = 7.87, 7.73, 7.62 (all br, 10 H, C_6H_5), 7.57, 7.43, 7.28 (all br, 10 H, C_6H_5), 6.93 (br d, 2 H, C_6H_3), 6.55 (br t, 2 H, C_6H_3), 5.98 (br d, 2 H, C_6H_3), 4.64 (br m, 2 H, PCH_2), 3.86 (br m, 2 H, PCH_2).
2a': δ = 7.74, 7.68, 7.43 (all br, 10 H, C_6H_5), 7.6 – 6.5 (br, 6 H, C_6H_3), 4.16 (br, 4 H, PCH_2).

Solid state NMR data: Spectra were obtained from a sample of composition **2a** × DMF which constitutes obviously a pseudo-polymorph to the CH_2Cl_2 solvate in which the crystallographic equivalence between the phosphorus sites is removed.
^{119}Sn{^{1}H} CP-MAS NMR: δ_{iso} = -455.
^{31}P{^{1}H} CP-MAS NMR: δ_{iso} = 79.5, 74.1; J_{PP} = 41 Hz (from 2D-*J*-resolved).

Detailed synthetic procedure and characterisation data for 2b:
Dry DMF (20 ml) was added to a mixture of **L^{1}** (550 mg, 1.79 mmol) Me_2SnCl_2 (196 mg, 0.89 mmol), [(cyclooctadiene)$PdCl_2$] (**1**, 250 mg, 0.89mmol), and Et_3N (0.93 ml, 5.34 mmol). The reaction mixture was stirred for 3 h at room temperature to give a red suspension which was filtered through a celite bed in a P4 glass frit. The red filtrate was stored overnight at –28^{0}C. The colourless crystalline precipitate formed was separated by decantation, the solution diluted by addition of 50 ml of diethyl ether, and stored at +4^{0}C. Dark red crystals formed which were collected by decantation and dried in vacuum at 120^{0}C for 4 h to give 795 mg (95% yield) of **2b** of m.p. 310°C (dec.).
MS (ESI): m/e = 869.02(100%) (MH^+), 868.02(M^+).
^{31}P{^{1}H} NMR ($CDCl_3$, 303 K): δ = 74.6 (broad, s).
^{1}H NMR ($CDCl_3$, 303 K): δ = 7.96 (s, broad, 1H, DMF), 7.4 to 6.8 (m, 20 H, C_6H_5), 6.74 (d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, C_6H_3), 6.34 (t, $^{3}J_{HH}$ = 7.91 Hz, 2 H, C_6H_3), 5.61 (d, $^{3}J_{HH}$ = 7.8 Hz, 2 H, C_6H_3), 3.6 to 3.2 (broad, 4 H, CH_2), 2.89 (s, 3 H, DMF), 2.82 (s, 3 H, DMF), 0.53 (s, 6 H, SnMe).
^{13}C{^{1}H} NMR ($CDCl_3$, 303 K): δ = 162.6 (s, DMF), 154.5 (broad s), 148.9 (s), 132.4 (broad s), 131.7 (s), 128.5 (t, 4.6 Hz), 120.7 (s), 119.4 (s), 115.8 (s) 115.6 (s), 36.4 (s, DMF), 33.4 (broad, CH_2), 31.4 (s, DMF), 25.6 (s, CH_3).

Sonogashira coupling of phenylacetylene and 4-Iodo-nitrobenzene using 2a or 2b as catalyst:
Phenyl acetylene (44 mg, 0.44 mmol), copper iodide (33 mg, 0.16 mmol), and **2a** (30 mg, 0.033 mmol) were added to a solution of 4-iodo-nitrobenzene (98 mg, 0.44 mmole) in 15 ml of triethyl amine/DMF (2:1). The mixture was stirred for 20 hrs at room temperature. N-Hexane (20 ml) was then added and the precipitate filtered off. The filtrate was evaporated to dryness and the dark residue purified by column chromatography using neutral silca as stationary phase and dichloromethane/hexane (3:7) as eluent to give 88 mg (90%) of 4-nitrophenyl-phenylacetylene which was identified by ^{1}H NMR (^{1}H NMR ($CDCl_3$): δ = 8.22 (m, 2 H, $C_6H_4NO_2$), 7.67 (m, 2 H, $C_6H_4NO_2$), 7.55 (m, 2 H, Ph.), 7.35 - 7.45 (m, 3 H, Ph).
The corresponding reaction using **2b** as (pre)catalyst was performed under identical conditions. ^{31}P NMR spectra which were recorded after 1, 5 and 20 h in order to monitor the status of the catalyst showed a single resonance at 76 ppm confirming that **2b** remained intact during the reaction. After 24 h all volatiles were evaporated in vacuum. The residue was extracted with 10 ml of toluene. The suspension formed was allowed to settle for 15 min and the supernatant toluene layer decanted. The residue was dried in vacuum and dissolved in 5ml of DMF. The ^{31}P NMR spectrum of this solution still showed the resonance of **2b** at 76 ppm. The residue obtained after evaporation of the solvent was recovered and reused for further catalytic transformations.

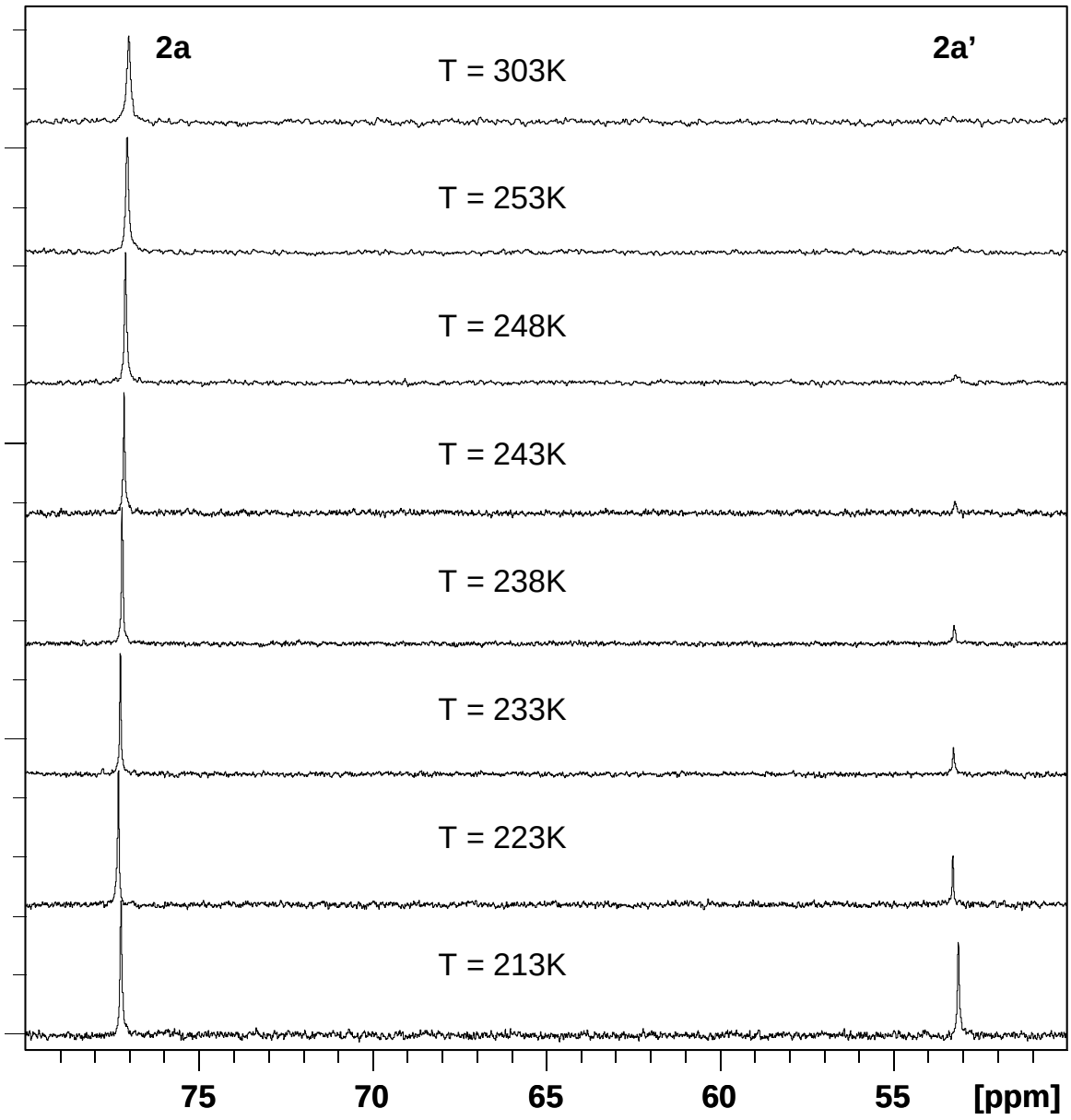

Figure ESI-1: VT $^{31}P\{^{1}H\}$NMR spectra (161.9 MHz, in DMF-d_7) of **2a** recorded at temperatures between –60°C (213K) and +30°C (303K) showing the resonances of **2a** and **2a'** (see labels).

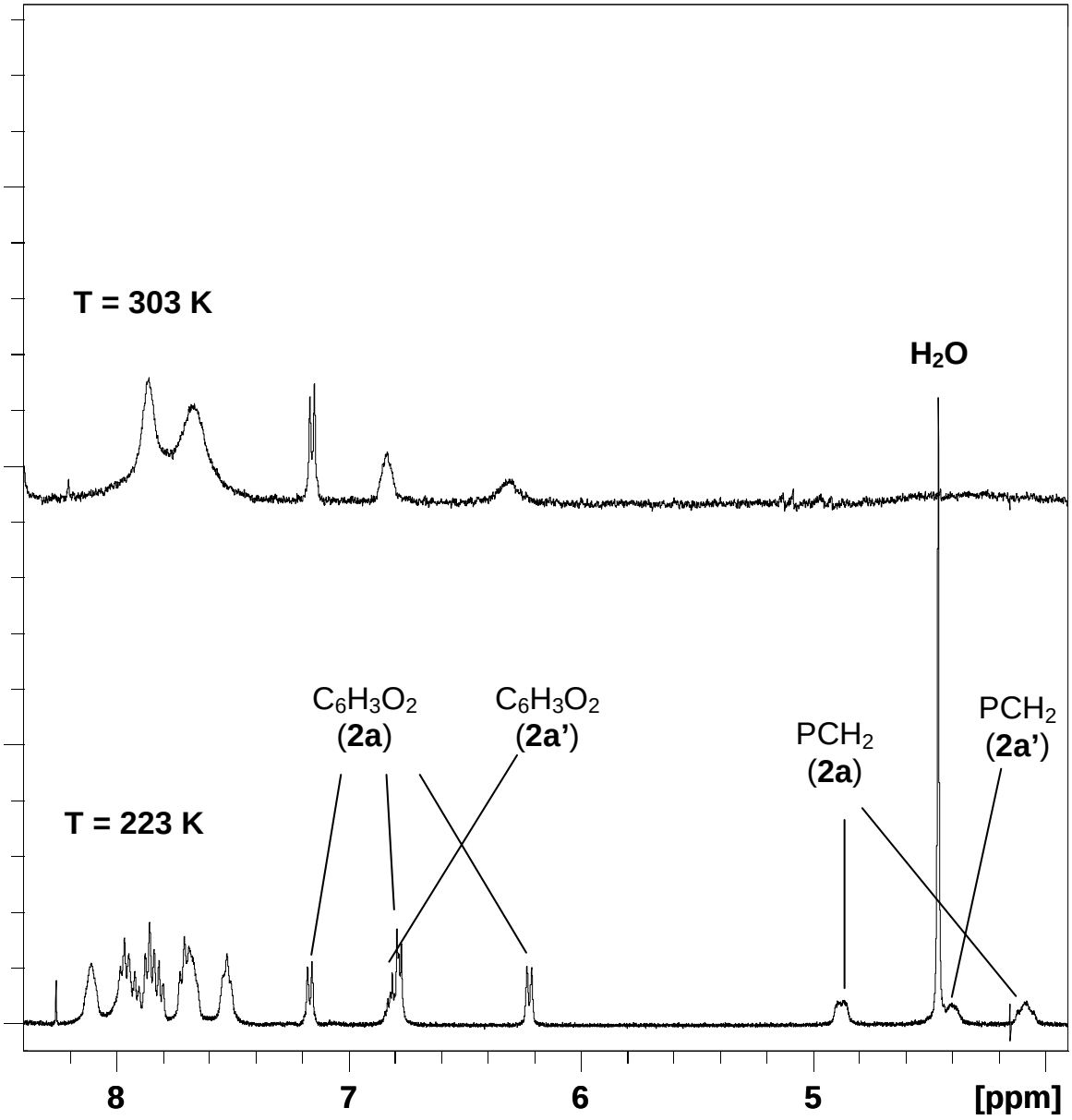

Figure ESI-2: ^{1}H NMR spectra (400.13 MHz, in DMF-d_7) of **2a**/**2a'** at 30°C (303K, top) and –50°C (223K, bottom). The signals attributable to the nuclei in the PCH_2 and the catechol moieties in **2a** and **2a'** are labeled . The resonance labeled as H_2O stems from residual water in the solvent.

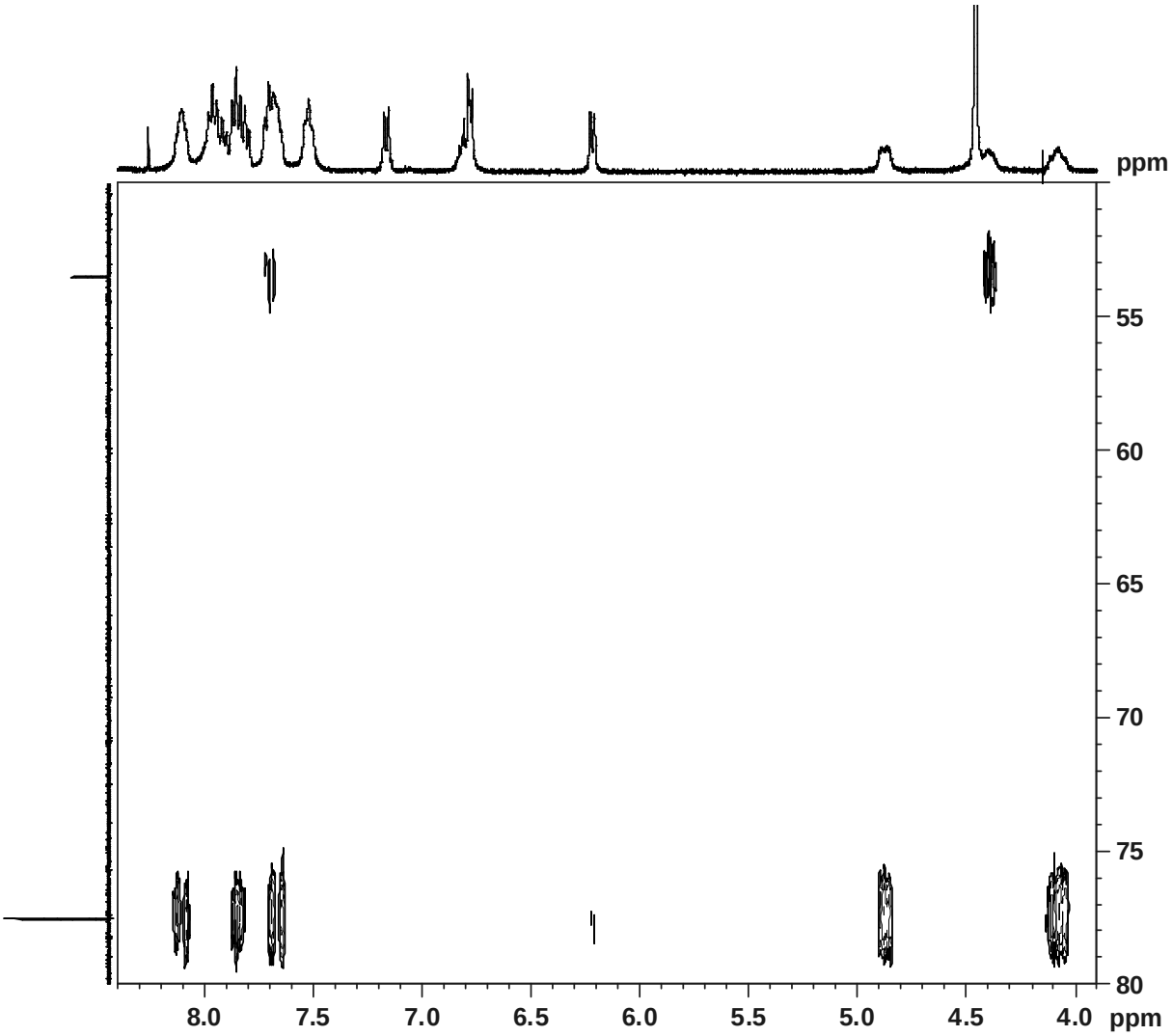

Figure ESI-3: $^{1}H,^{31}P$ gs-HMQC (400.13 MHz, in DMF-d_7) of **2a**/**2a'** at –50°C showing correlation signals connecting the o- and m-protons in the C_6H_5 rings and the geminal CH_2-protons with the phosphorus nuclei. The traces depict the 1D ^{1}H (top trace) and $^{31}P(^{1}H\}$ NMR-spectra of the same solution.

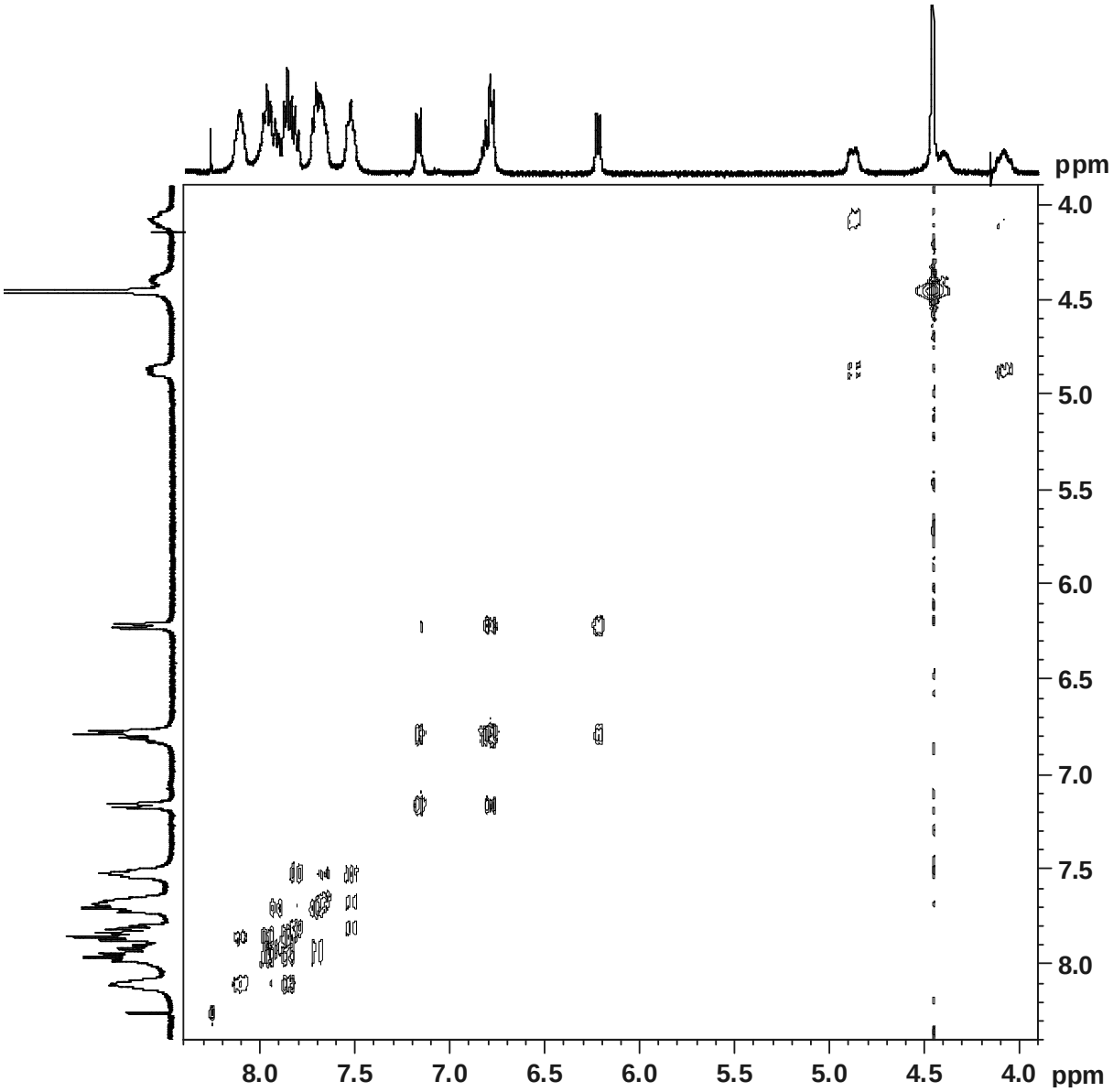

Figure ESI-4: ^{1}H gs-COSY (400.13 MHz, in DMF-d_7) of **2a**/**2a'** at –50°.

Details and results of computational studies:
All DFT-computations were performed with the B3LYP functional and using a normal grid for numeric integration. Energy optimisations of **2a** and of two different adducts with two molecules of formamide were carried using a 3-21g* basis set. The relative energies E_{rel} of both adducts were obtained by computing the energy-optimised molecular structure of formamide at the same level of theory and evaluating the difference E_{rel} = E(adduct) – E(**2a**) – 2 E(formamide). Attempts to locate a structure with *trans*-coordination of the Chloride ligands at Sn did not lead to a minimum. Attempts to locate a complex with a *cis*-coordination of formamide ligands at Pd produced a strongly distorted structure with very low energy gradient at high relative energy (E_{rel} = 28.7 kcal mol^{-1}) which is not reported here.

Atomic coordinates (in Å) and absolute energies (in Hartree):

Complex **2a** (point group C_2); E = -14270.3118843 Hartree

atom	x	y	z
Pd	0.000000	0.000000	0.129668
O	0.737526	1.163633	1.718517
O	-0.737526	-1.163633	1.718517
Sn	0.000000	0.000000	3.471649
Cl	-1.359462	-1.283530	4.970347
Cl	1.359462	1.283530	4.970347
P	1.122326	1.436627	-1.311595
P	-1.122326	-1.436627	-1.311595
O	-1.463503	1.445900	3.236658
O	1.463503	-1.445900	3.236658
C	1.490626	2.970701	-0.287997
C	0.344133	3.306258	0.637709
C	0.000694	2.354209	1.594718
C	-1.144810	2.474955	2.409558
C	-1.908343	3.642500	2.292224
C	-1.548155	4.627440	1.368937
C	-0.438754	4.466006	0.530787
C	-1.490626	-2.970701	-0.287997
C	-0.344133	-3.306258	0.637709
C	-0.000694	-2.354209	1.594718
C	1.144810	-2.474955	2.409558
C	1.908343	-3.642500	2.292224
C	1.548155	-4.627440	1.368937
C	0.438754	-4.466006	0.530787
C	0.317493	2.040562	-2.821765
C	-0.726286	2.980440	-2.706840
C	-1.387787	3.432434	-3.847411
C	-1.024989	2.953291	-5.109578
C	0.000000	2.013218	-5.228271
C	0.668164	1.552510	-4.091896
C	-0.317493	-2.040562	-2.821765
C	0.726286	-2.980440	-2.706840
C	1.387787	-3.432434	-3.847411
C	1.024989	-2.953291	-5.109578
C	0.000000	-2.013218	-5.228271
C	-0.668164	-1.552510	-4.091896
C	2.749521	0.786496	-1.780252
C	3.628564	1.515817	-2.601809
C	4.908263	1.028200	-2.862565
C	5.325192	-0.183610	-2.303193
C	4.460378	-0.910424	-1.483390
atom	x	y	z
C	3.176223	-0.430155	-1.222260
C	-2.749521	-0.786496	-1.780252
C	-3.628564	-1.515817	-2.601809
C	-3.176223	0.430155	-1.222260
C	-4.908263	-1.028200	-2.862565
C	-5.325192	0.183610	-2.303193
C	-4.460378	0.910424	-1.483390
H	2.384972	2.714596	0.291743
H	1.721332	3.799987	-0.964512
H	-2.777449	3.757227	2.926313
H	-2.143071	5.530804	1.298040
H	-0.172595	5.233847	-0.187331
H	-2.384972	-2.714596	0.291743
H	-1.721332	-3.799987	-0.964512
H	2.777449	-3.757227	2.926313
H	2.143071	-5.530804	1.298040
H	0.172595	-5.233847	-0.187331
H	-1.012404	3.359087	-1.731424
H	-2.185488	4.159481	-3.750912
H	-1.540047	3.310185	-5.993697
H	0.284146	1.638016	-6.204562
H	1.460342	0.821401	-4.190658
H	3.312316	2.457690	-3.035916
H	5.581988	1.594974	-3.494339
H	6.323223	-0.555630	-2.502452
H	4.782791	-1.845077	-1.040706
H	2.506577	-0.989277	-0.576784
H	1.012404	-3.359087	-1.731424
H	2.185488	-4.159481	-3.750912
H	1.540047	-3.310185	-5.993697
H	-0.284146	-1.638016	-6.204562
H	-1.460342	-0.821401	-4.190658
H	-3.312316	-2.457690	-3.035916
H	-5.581988	-1.594974	-3.494339
H	-6.323223	0.555630	-2.502452
H	-4.782791	1.845077	-1.040706
H	-2.506577	0.989277	-0.576784

Complex **2a** × 2 Formamide (Coordination at Sn) (point group C_2)
E = -14608.2311568 Hartree

atom	x	y	z
Pd	0.000000	0.000000	-0.469620
O	0.838770	1.061962	1.096131
O	-0.838770	-1.061962	1.096131
Sn	0.000000	0.000000	3.187288
Cl	-1.947199	-1.398212	3.793585
Cl	1.947199	1.398212	3.793585
P	1.280057	1.341708	-1.894523
P	-1.280057	-1.341708	-1.894523
O	-1.316048	1.527947	2.610791
O	1.316048	-1.527947	2.610791
C	1.794865	2.824507	-0.857688
C	0.670141	3.248215	0.056418
C	0.231093	2.299165	0.982351
C	-0.902783	2.525518	1.793464
C	-1.560508	3.756203	1.682653
C	-1.105906	4.723211	0.779434
C	0.000000	4.477449	-0.039627
C	-1.794865	-2.824507	-0.857688
C	-0.670141	-3.248215	0.056418
C	-0.231093	-2.299165	0.982351
C	0.902783	-2.525518	1.793464
C	1.560508	-3.756203	1.682653
C	1.105906	-4.723211	0.779434
C	0.000000	-4.477449	-0.039627
C	0.573752	2.044536	-3.417826
C	-0.339237	3.112762	-3.318120
C	-0.939734	3.630890	-4.464815
C	-0.647127	3.090799	-5.720260
C	0.247048	2.023849	-5.824875
C	0.853597	1.498379	-4.682038
C	-0.573752	-2.044536	-3.417826
C	0.339237	-3.112762	-3.318120
C	0.939734	-3.630890	-4.464815
C	0.647127	-3.090799	-5.720260
C	-0.247048	-2.023849	-5.824875
C	-0.853597	-1.498379	-4.682038
C	2.844701	0.544223	-2.367956
C	3.799050	1.180970	-3.181328
C	5.021209	0.562547	-3.443157
C	5.305007	-0.691645	-2.893732
C	4.364681	-1.328334	-2.082277
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C	-2.844701	-0.544223	-2.367956
C	-3.799050	-1.180970	-3.181328
C	-3.138588	0.715067	-1.819492
C	-5.021209	-0.562547	-3.443157
C	-5.305007	0.691645	-2.893732
C	-4.364681	1.328334	-2.082277
H	2.645072	2.467646	-0.264804
H	2.119516	3.637215	-1.515114
H	-2.430234	3.940499	2.300874
H	-1.621726	5.674713	0.713338
H	0.347954	5.230677	-0.738745
H	-2.645072	-2.467646	-0.264804
atom	x	y	z
H	-2.119516	-3.637215	-1.515114
H	2.430234	-3.940499	2.300874
H	1.621726	-5.674713	0.713338
H	-0.347954	-5.230677	-0.738745
H	-0.574645	3.534915	-2.347113
H	-1.636835	4.456233	-4.377526
H	-1.115224	3.497515	-6.609174
H	0.476320	1.599046	-6.795520
H	1.543691	0.668853	-4.770855
H	3.584039	2.153194	-3.610668
H	5.753227	1.059117	-4.069552
H	6.257791	-1.167162	-3.095754
H	4.582455	-2.297238	-1.649072
H	2.408442	-1.201286	-1.180716
H	0.574645	-3.534915	-2.347113
H	1.636835	-4.456233	-4.377526
H	1.115224	-3.497515	-6.609174
H	-0.476320	-1.599046	-6.795520
H	-1.543691	-0.668853	-4.770855
H	-3.584039	-2.153194	-3.610668
H	-5.753227	-1.059117	-4.069552
H	-6.257791	1.167162	-3.095754
H	-4.582455	2.297238	-1.649072
H	-2.408442	1.201286	-1.180716
O	0.716762	-1.055699	5.147893
C	1.852788	-1.576785	5.281916
H	2.539679	-1.661007	4.443949
N	2.279561	-2.079104	6.454181
H	3.198892	-2.492596	6.549476
H	1.671685	-2.031683	7.266871
O	-0.716762	1.055699	5.147893
C	-1.852788	1.576785	5.281916
H	-2.539679	1.661007	4.443949
N	-2.279561	2.079104	6.454181
H	-3.198892	2.492596	6.549476
H	-1.671685	2.031683	7.266871

Complex **2** × 2 Formamide (coordination at Pd, *trans*-isomer) (point group C_2)
E = -14608.2368014 Hartree

atom	x	y	z
Pd	0.000000	0.000000	-0.903227
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O	-0.739995	-1.248562	1.497439
Sn	0.000000	0.000000	3.076336
Cl	-1.206554	-1.342325	4.689782
Cl	1.206554	1.342325	4.689782
P	1.766099	1.601164	-0.987049
P	-1.766099	-1.601164	-0.987049
O	-1.600602	1.325946	2.827605
O	1.600602	-1.325946	2.827605
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C	0.435558	3.468569	0.665052
C	0.000000	2.404520	1.445086
C	-1.224418	2.452273	2.149965
C	-1.967554	3.632445	2.102634
C	-1.519761	4.724441	1.334927
C	-0.327510	4.643250	0.602153
C	-1.737568	-3.228580	-0.052824
C	-0.435558	-3.468569	0.665052
C	0.000000	-2.404520	1.445086
C	1.224418	-2.452273	2.149965
C	1.967554	-3.632445	2.102634
C	1.519761	-4.724441	1.334927
C	0.327510	-4.643250	0.602153
C	1.785793	2.056914	-2.753999
C	1.104748	3.209533	-3.187254
C	0.982078	3.492046	-4.548355
C	1.526819	2.627568	-5.499723
C	2.187043	1.468244	-5.083702
C	2.308320	1.180779	-3.725249
C	-1.785793	-2.056914	-2.753999
C	-1.104748	-3.209533	-3.187254
C	-0.982078	-3.492046	-4.548355
C	-1.526819	-2.627568	-5.499723
C	-2.187043	-1.468244	-5.083702
C	-2.308320	-1.180779	-3.725249
C	3.400346	0.904998	-0.589027
C	4.544174	1.159202	-1.367762
C	5.779383	0.625584	-0.994972
C	5.888380	-0.153949	0.160608
C	4.759142	-0.394139	0.946683
C	3.517806	0.130799	0.582508
C	-3.400346	-0.904998	-0.589027
C	-4.544174	-1.159202	-1.367762
C	-3.517806	-0.130799	0.582508
C	-5.779383	-0.625584	-0.994972
C	-5.888380	0.153949	0.160608
atom	x	y	z

C	-4.759142	0.394139	0.946683
H	2.543413	3.116024	0.683260
H	1.999940	4.043567	-0.734181
H	-2.884678	3.693918	2.675111
H	-2.086113	5.650253	1.342294
H	0.019402	5.490173	0.019224
H	-2.543413	-3.116024	0.683260
H	-1.999940	-4.043567	-0.734181
H	2.884678	-3.693918	2.675111
H	2.086113	-5.650253	1.342294
H	-0.019402	-5.490173	0.019224
H	0.654407	3.877426	-2.462885
H	0.460745	4.388197	-4.864817
H	1.433780	2.851271	-6.555899
H	2.604259	0.787552	-5.816837
H	2.811901	0.272528	-3.416562
H	4.469913	1.773235	-2.257217
H	6.656591	0.830095	-1.598365
H	6.850945	-0.559241	0.451365
H	4.827032	-0.981022	1.855006
H	2.661450	-0.066473	1.214629
H	-0.654407	-3.877426	-2.462885
H	-0.460745	-4.388197	-4.864817
H	-1.433780	-2.851271	-6.555899
H	-2.604259	-0.787552	-5.816837
H	-2.811901	-0.272528	-3.416562
H	-4.469913	-1.773235	-2.257217
H	-6.656591	-0.830095	-1.598365
H	-6.850945	0.559241	0.451365
H	-4.827032	0.981022	1.855006
H	-2.661450	0.066473	1.214629
O	-1.275328	1.688022	-1.244713
O	1.275328	-1.688022	-1.244713
C	-2.466172	2.055488	-1.461180
H	-3.160051	1.457229	-2.057363
N	-2.965626	3.200694	-1.003234
H	-3.936035	3.443575	-1.173720
H	-2.421223	3.761950	-0.331206
C	2.466172	-2.055488	-1.461180
H	3.160051	-1.457229	-2.057363
N	2.965626	-3.200694	-1.003234
H	3.936035	-3.443575	-1.173720
H	2.421223	-3.761950	-0.331206

Formamide (point group C_s)
E = -168.9476573 Hartree

atom	x	y	z
O	1.219230	0.230780	0.000000
C	0.000000	0.420040	0.000000
H	-0.464520	1.422082	0.000000
N	-0.954235	-0.559299	0.000000
H	-0.666568	-1.532720	0.000000
H	-1.943105	-0.340742	0.000000

Relative Energies E_{rel} (in kcal mol^{-1}):

	E_{rel} (in kcal mol^{-1}):
Complex **2a** + 2 Formamide:	0.0
Complex **2a** × 2 Formamide (coordination at Pd, *trans*-isomer)	-15.0
Complex **2a** × 2 Formamide (Coordination at Sn)	-18.6