ESI for:

Supramolecular Bulky Phosphines Comprising of 1,3,5-Triaza-7-phosphaadamantane and Zn(salphen)s: Structural Features and Application in Hydrosilylation Catalysis

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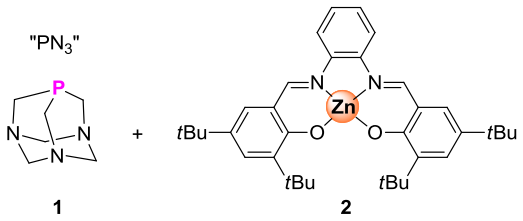
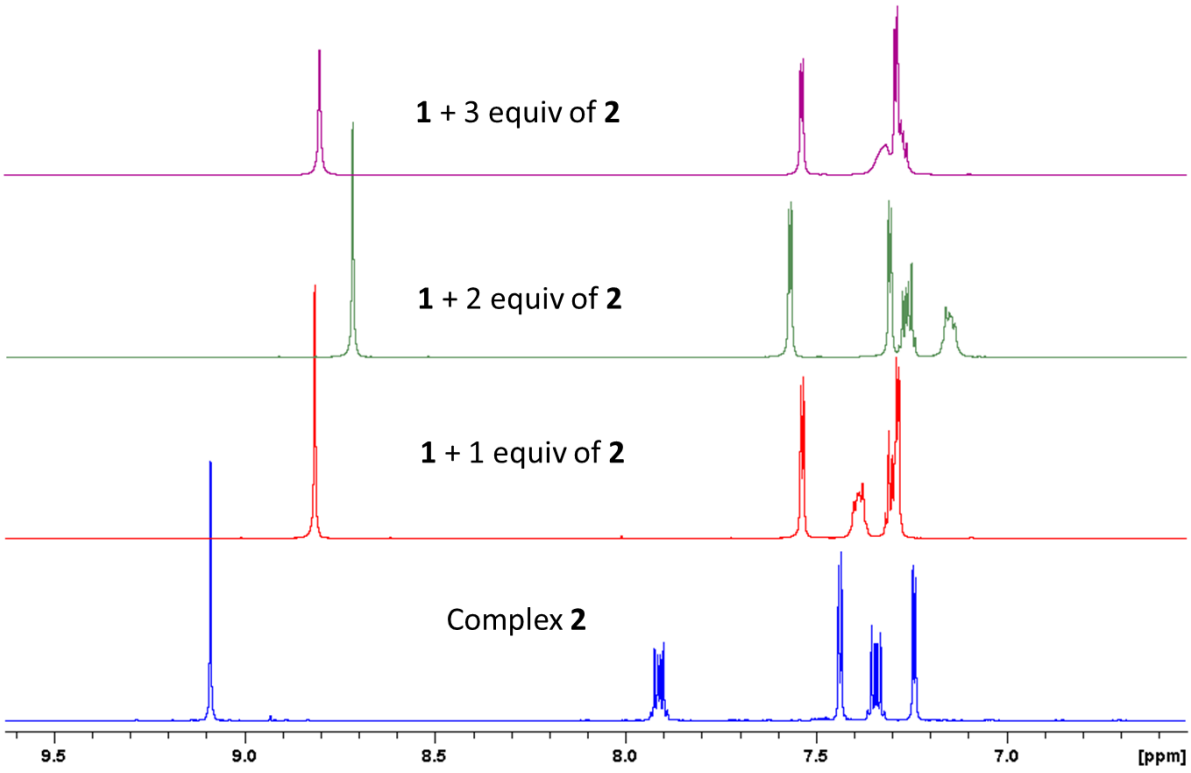
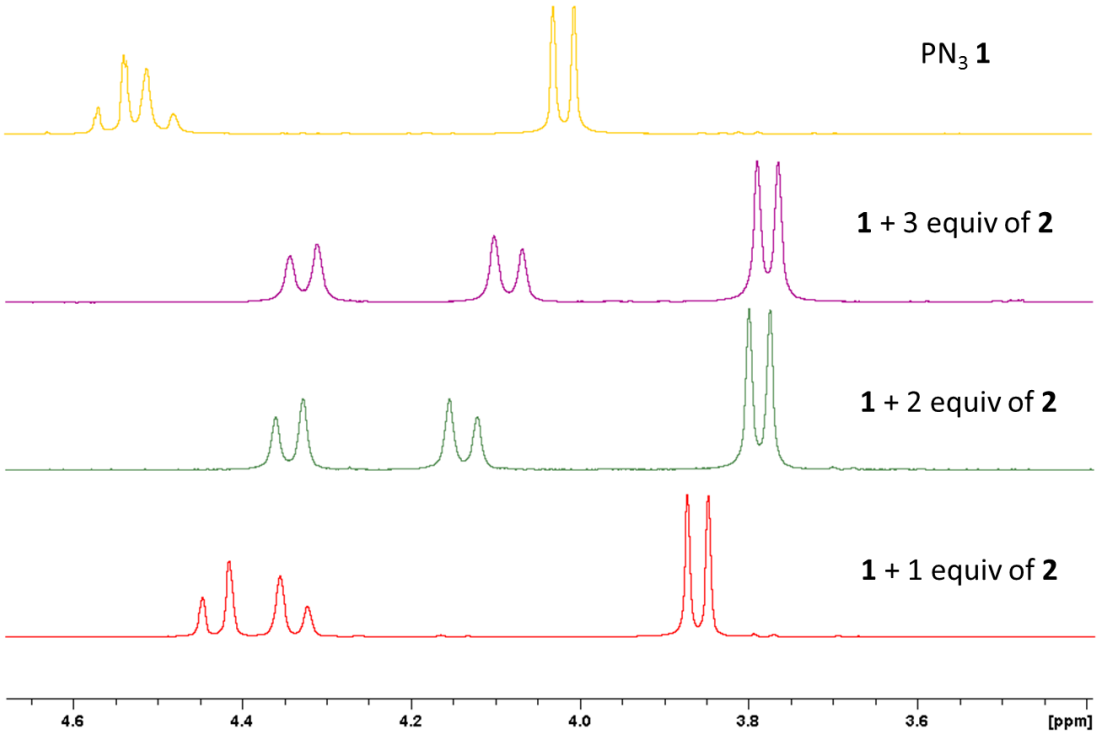
^{1}H and ^{31}P NMR spectral changes for the addition of complex **2** to the PN_3 ligand:



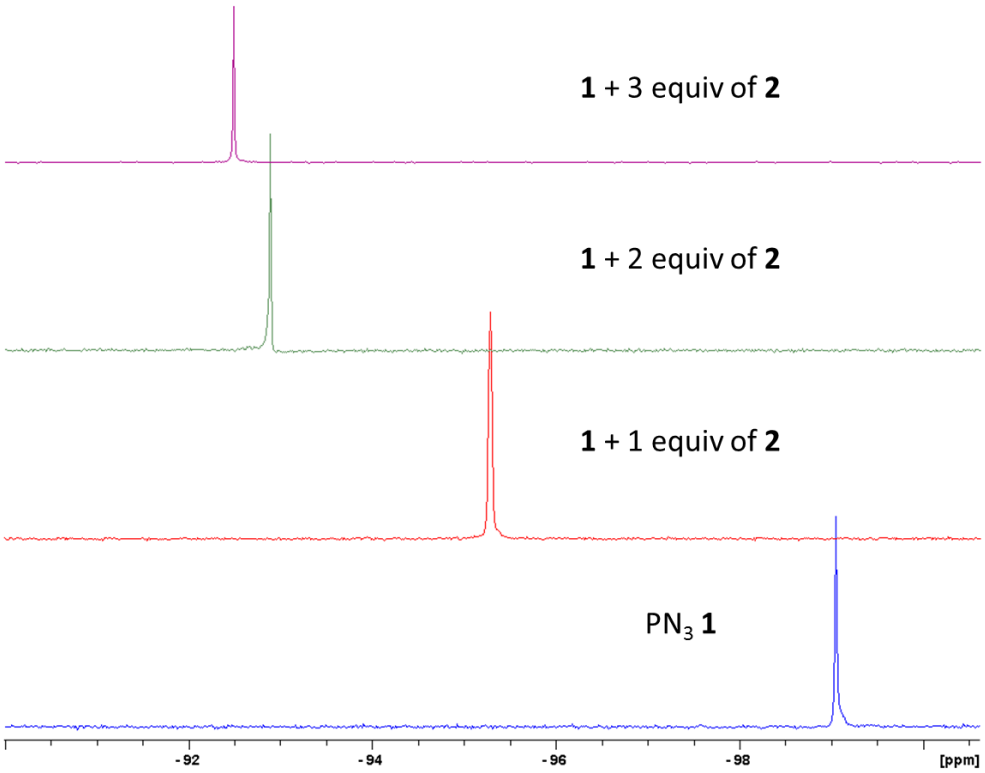
^{1}H NMR (d_6-acetone), aromatic region:



^{1}H NMR (d_6-acetone), aliphatic region:



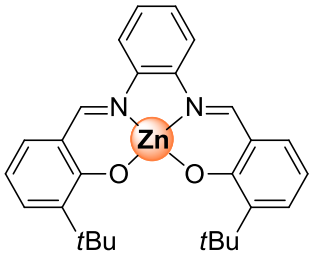
^{31}P{^{1}H} NMR (d_6-acetone):



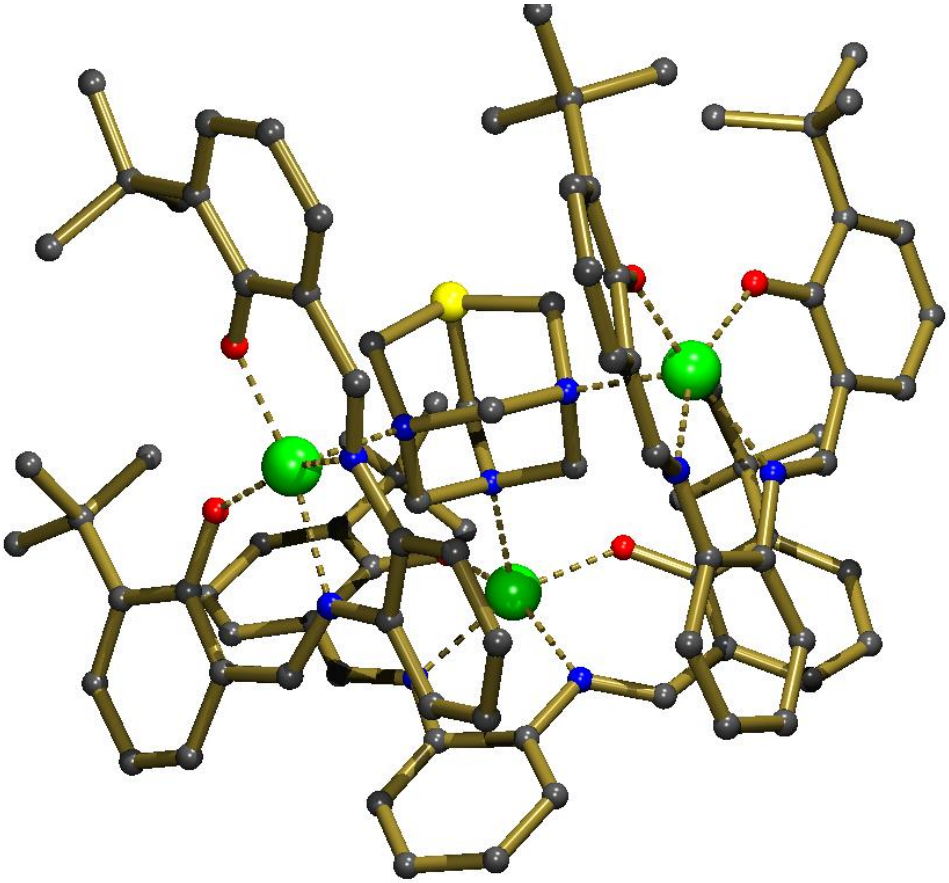
X-ray diffraction results for the PN_3 assemblies based on complexes **3**, **4**, **5**, **6** and **8**:

(in each case a POVRay image is provided.)

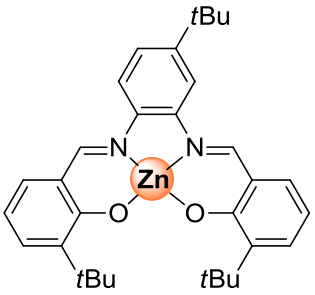
Structure based on complex **3**:



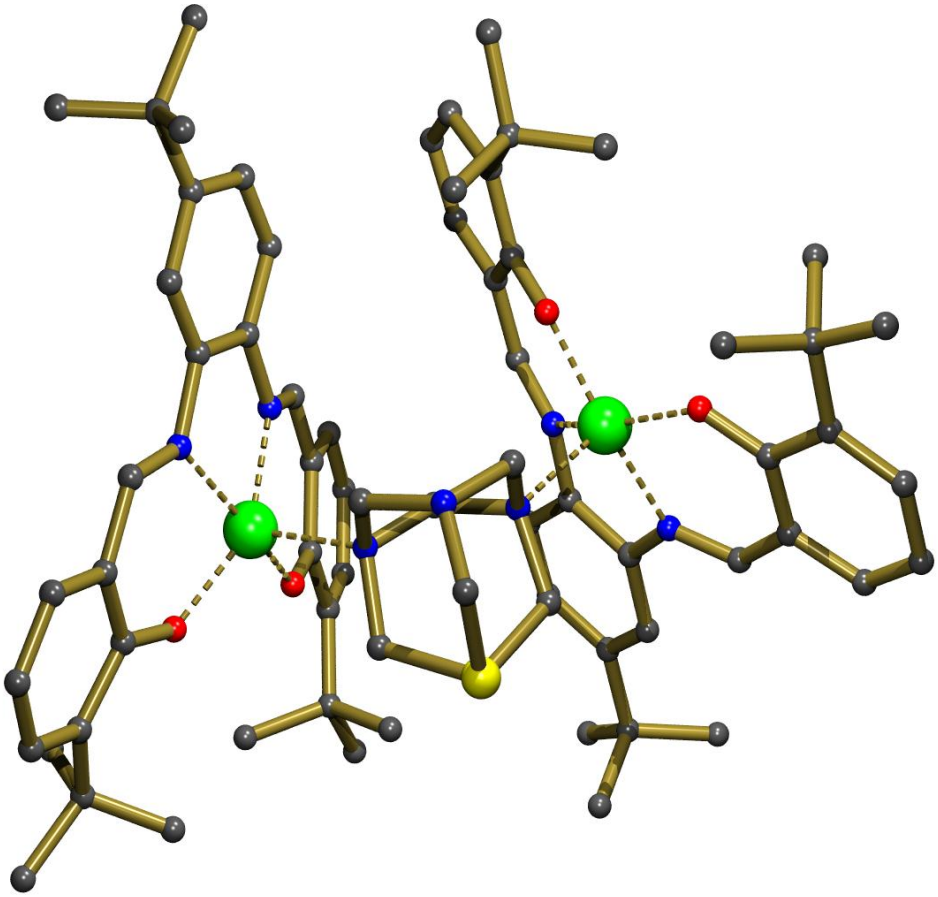
3



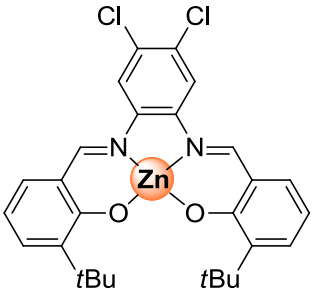
Structure based on complex **4**:



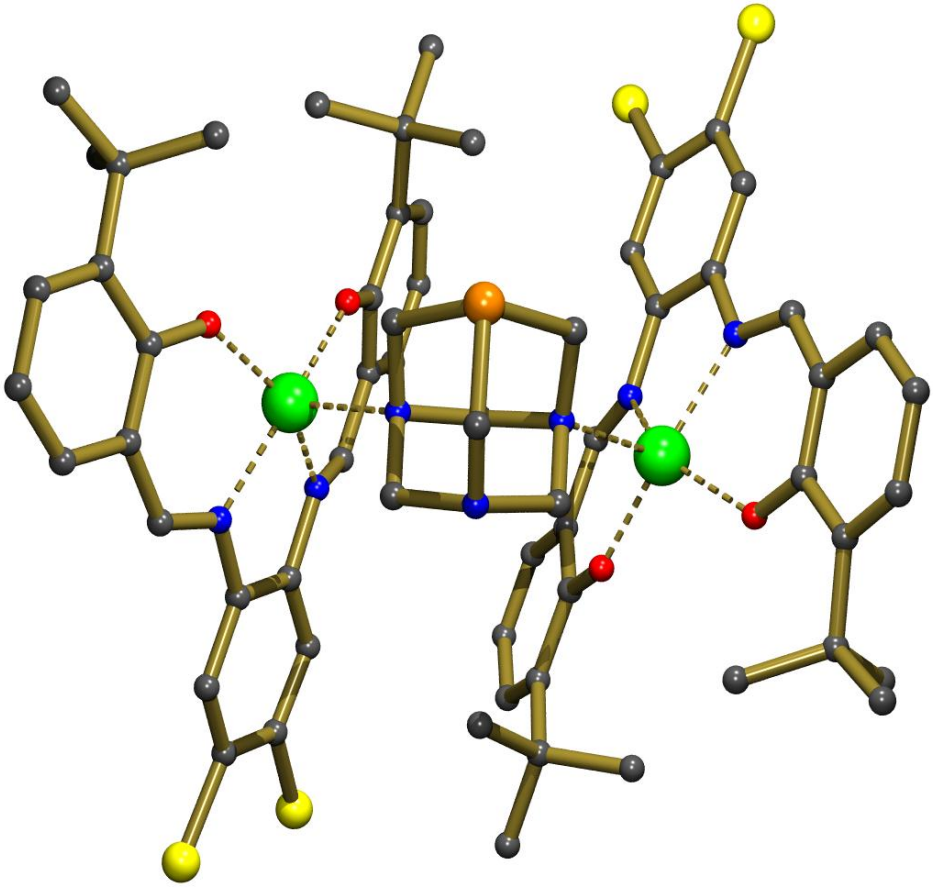
4



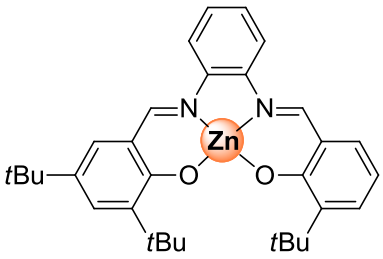
Structure based on complex **5**:



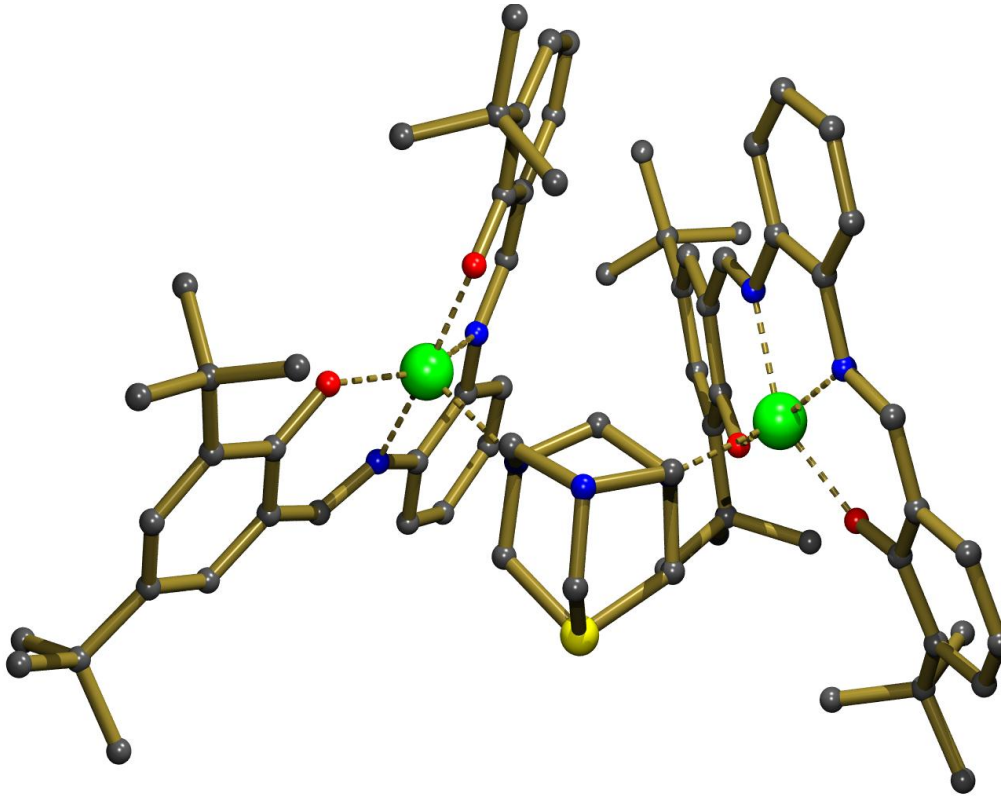
5



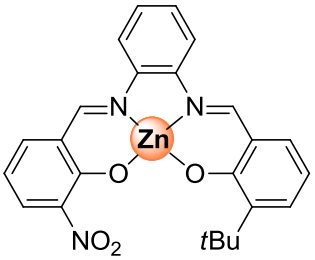
Structure based on complex **6**:



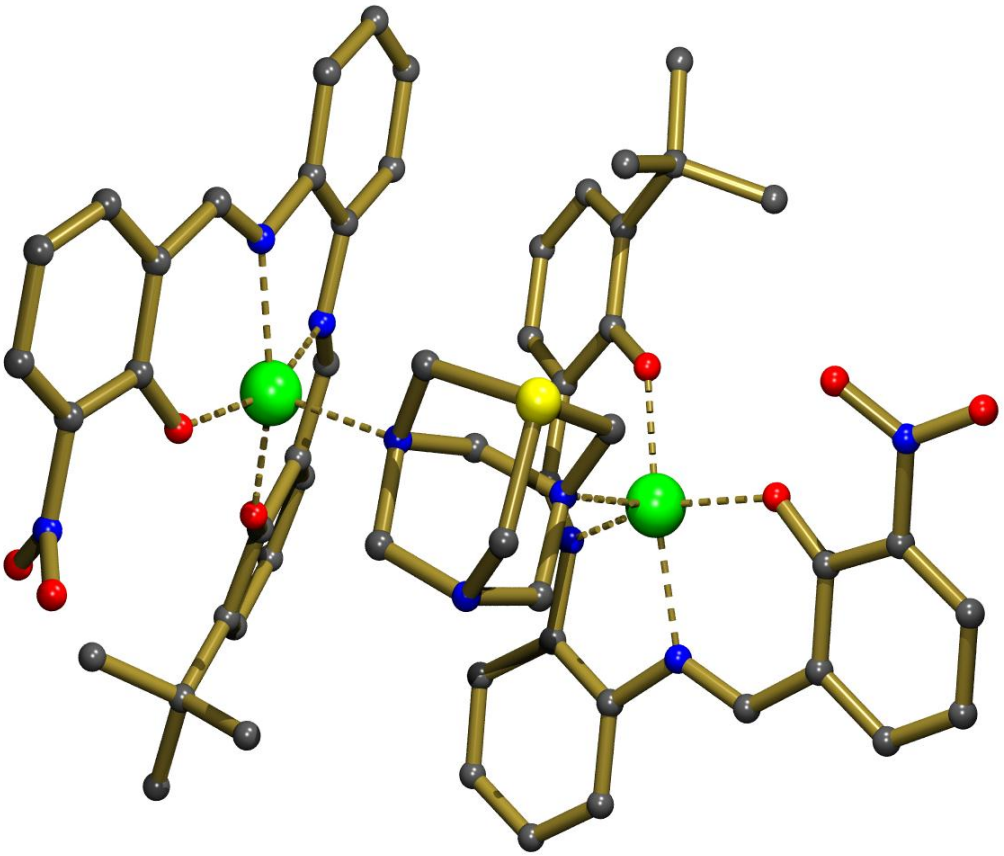
6



Structure based on complex **8**:[1]



8

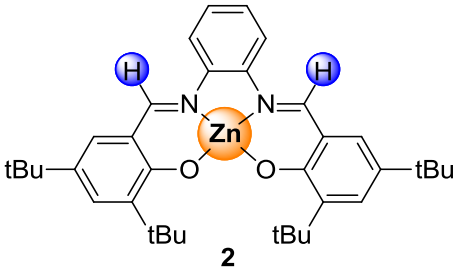


[1] Note that not a fully refined structure is presented here; a res-file can be made available from the authors via akleij@iciq.es.

Job plot data for the PN_3-based assemblies:[2]

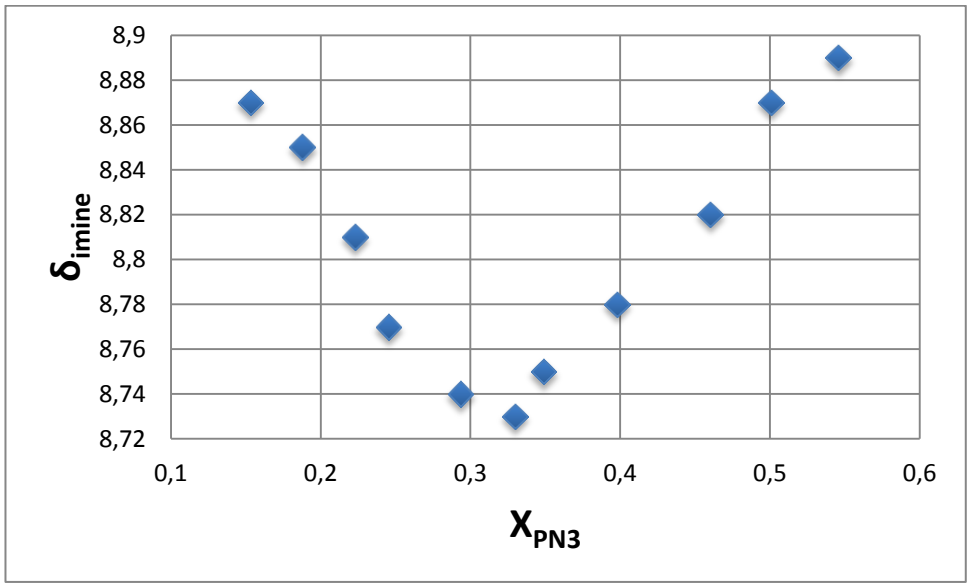
X_{PN3} = 0.33 refers to a 2:1 stochiometry.

X_{PN3} = 0.25 refers to a 3:1 stochiometry.

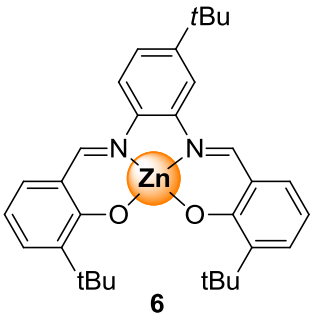


2

Corresponding Job plot (in $[D_6]$acetone):

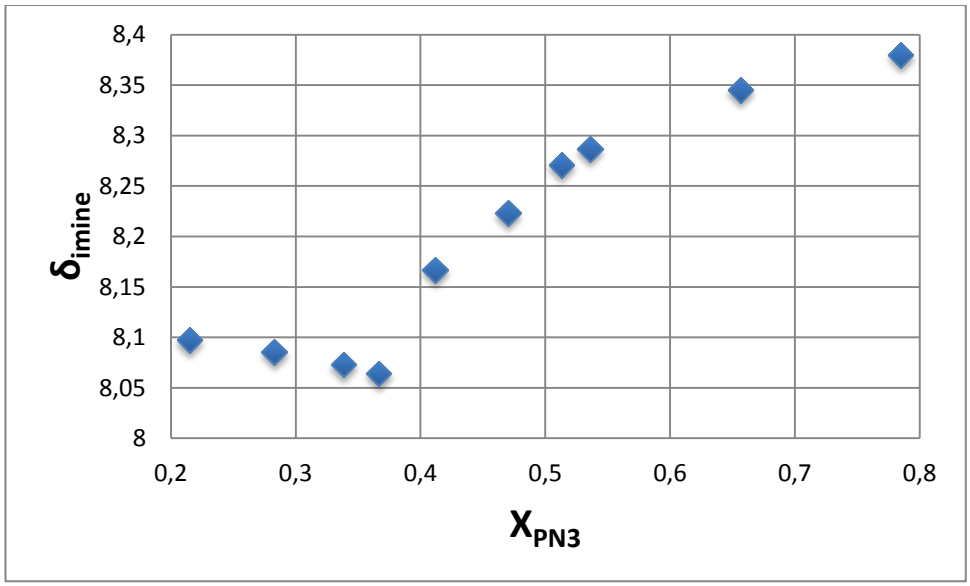


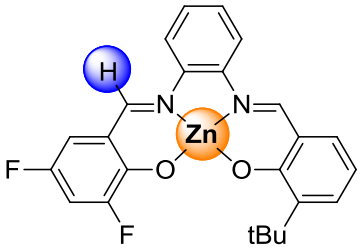
[2] The preferred stoichiometries in the case of complexes **3**-**5** were deduced from UV-vis titration experiments at lower concentrations as some solubility problems were encountered in the typical mM range for Job plot analyses using ^{1}H NMR.



6

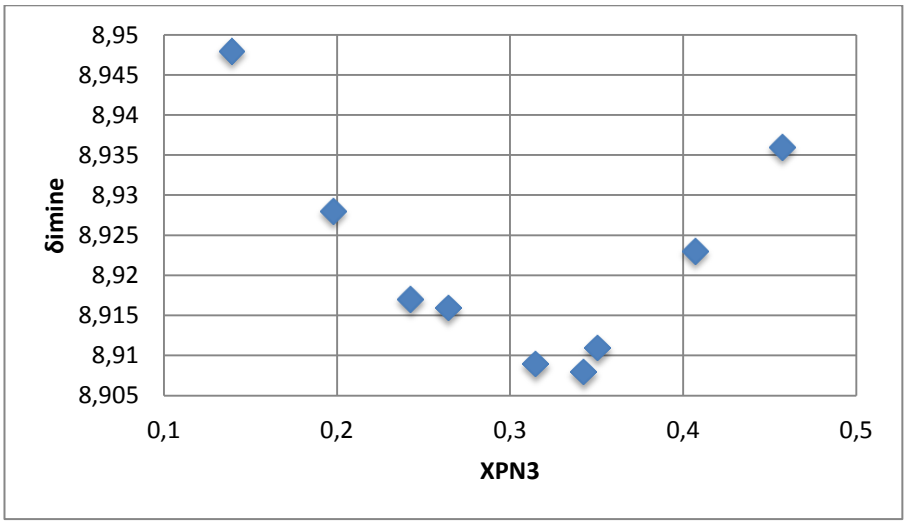
Corresponding Job plot (in [D_6]acetone):

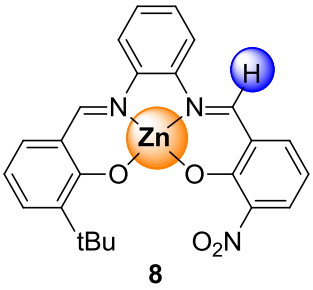




7

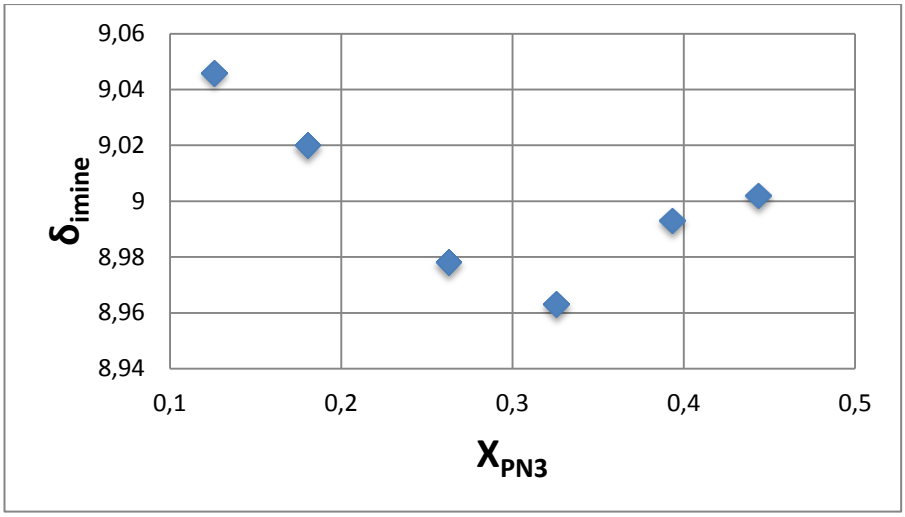
Corresponding Job plot (in [D_6]acetone):





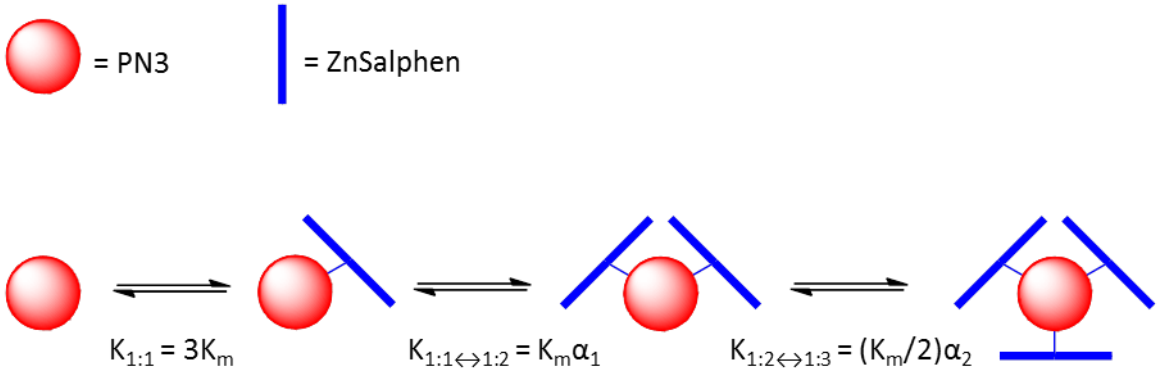
8

Corresponding Job plot (in [D_6]acetone):

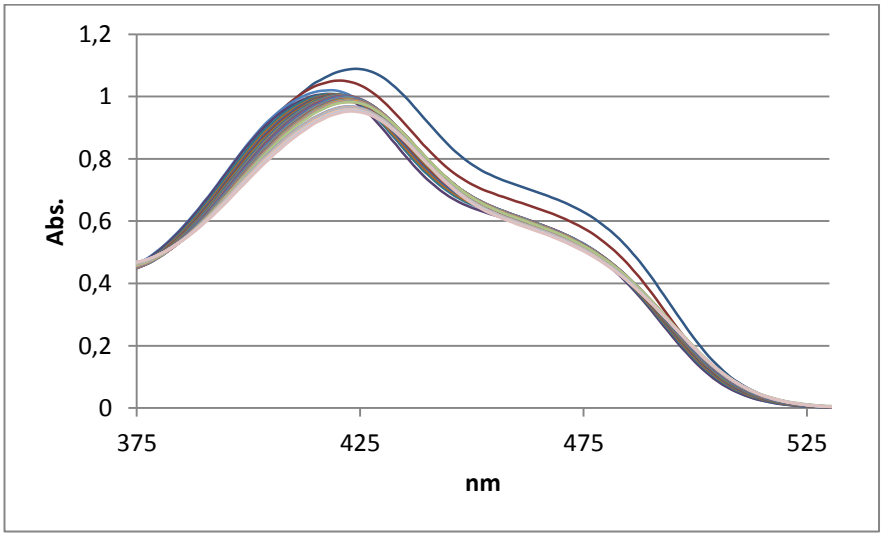


UV-vis titration of Zn(salphen)s **2** with PN_3 **1** and data fitting using Specfit/32:

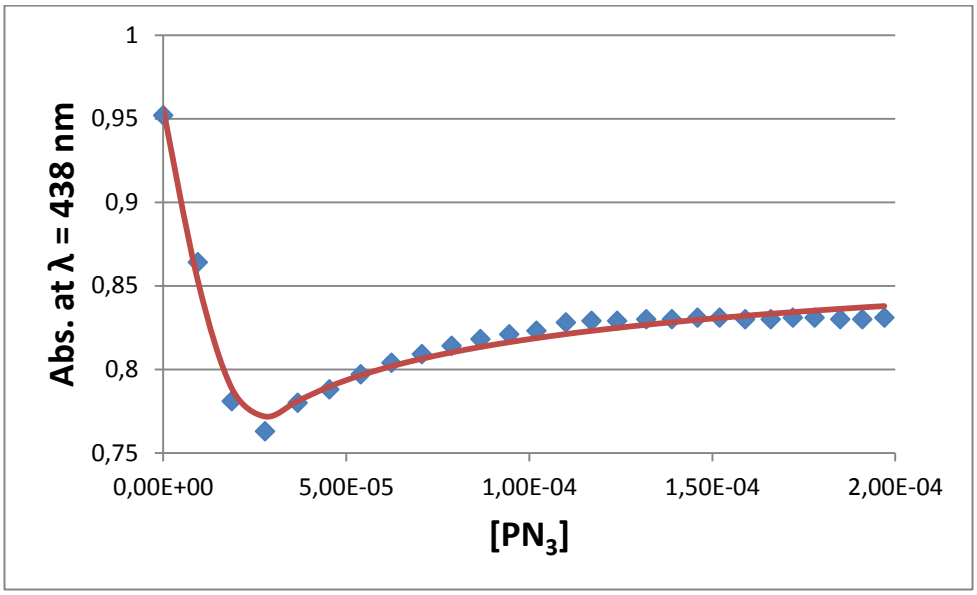
UV-vis titration: Aliquots between 20–520 μL of a solution of PN_3 (9.54×10^{-4} M) and Zn(salphen) complex **2** (5.38×10^{-5} M) in dry toluene were added stepwise to 2.00 mL of a solution of the host **2** in dry toluene in a 1.00 cm quartz cuvette. After each addition, a UV-vis spectrum was acquired. The titration data obtained were analyzed using Specfit/32 by fitting to a binding model reported in Scheme S1 which includes four colored species (free Zn(salphen) **2**, and the assembled species with stochiometries 1:1, 1:2 and 1:3).



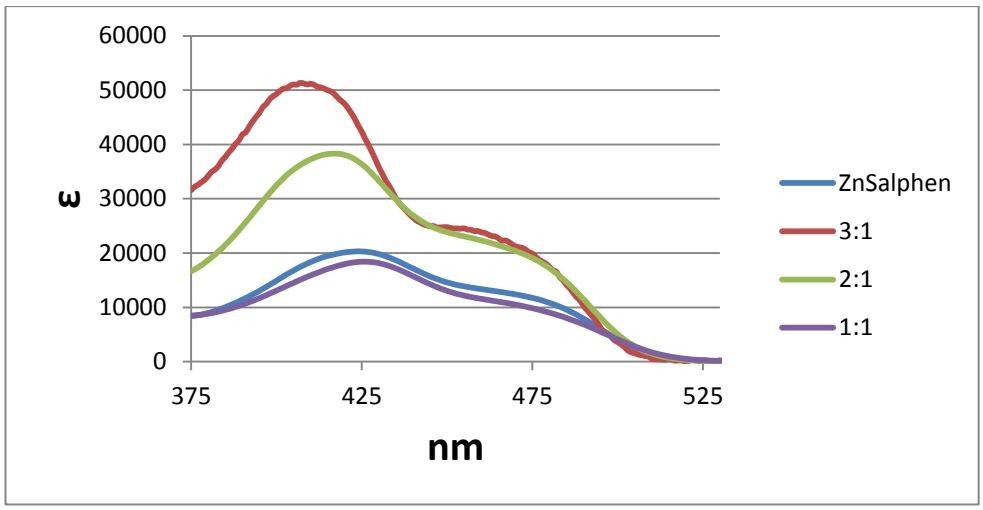
Scheme S1. Involved species in the titration of PN_3 **1** to Zn(salphen) complex **2**. $K_{1:1}$ is the stability constant of the 1:1 complex, $K_{1:1\leftrightarrow1:2}$ and $K_{1:2\leftrightarrow1:3}$ are the stepwise constants. All constants are related to statistical correction factors, the microscopic binding constant (K_m) and the cooperativity factor (α).



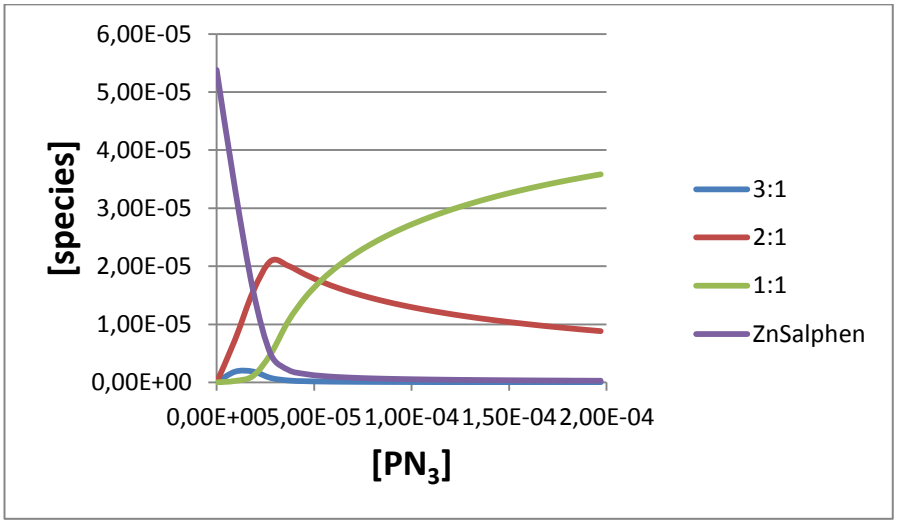
Spectral changes upon the addition of PN_3 **1** to complex **2** carried out in toluene at [**2**] = 5.38×10^{-5} M.



Titration curve and data fit at λ = 438 nm.



Simulated spectra for this titration at the specified equilibrium constants.

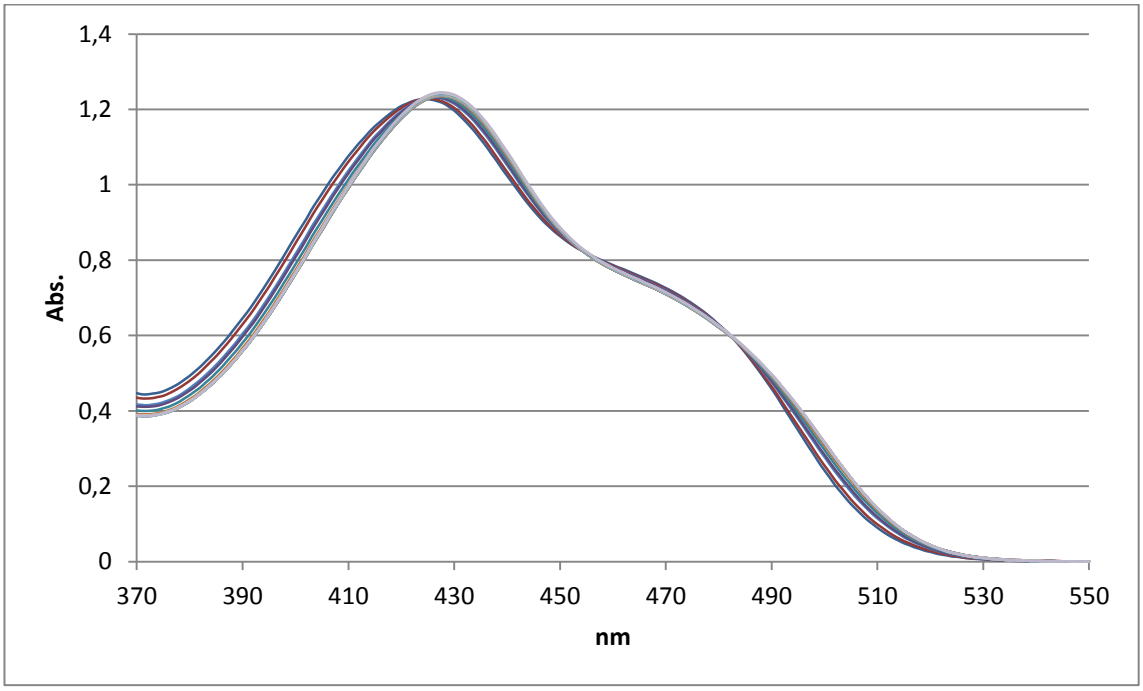


Simulated concentration profiles for this titration at the specified equilibrium constants.

Table S1: Stepwise stability constants and cooperativity factors (α) for the PN_3-Zn(salphen) assemblies based on the direct titration of Zn(salphen) **2** with PN_3 **1**.

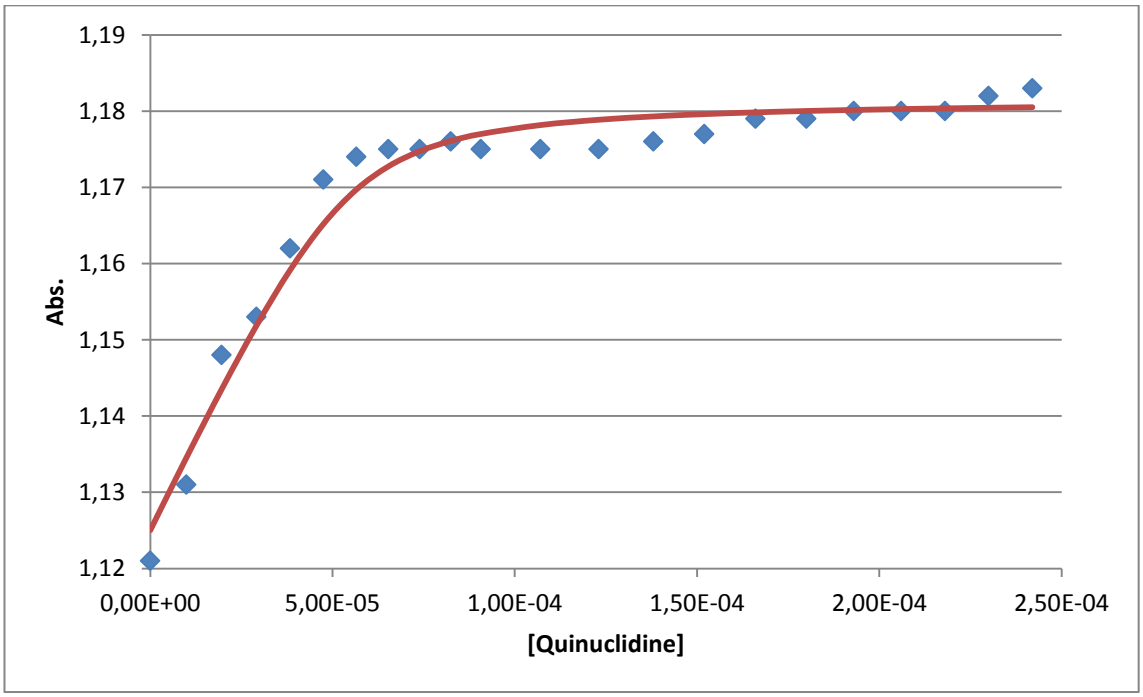
	1:1	1:1↔1:2	1:2↔1:3
K (M^{-1})	**8.45×10^5**	**8.85×10^5**	**7.51×10^3**
α	-	**1.047**	**0.053**

For a first estimate of $K_{1:1}$, we titrated **2** with quinuclidine, see below for details:



Spectral changes of complex Zn(salphen) **2** upon the addition of quinuclidine carried out in toluene at [**2**] = 5.46×10^{-5} M.

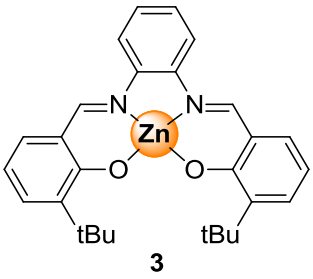
From these data we obtained the following titration curve, which was fitted to a 1:1 model using Specfit/32 giving $K_{1:1}$ as used as a starting point for the data-fit of the titration of **2** with PN_3 **1**.



Titration curves and data fits at λ = 435 nm.

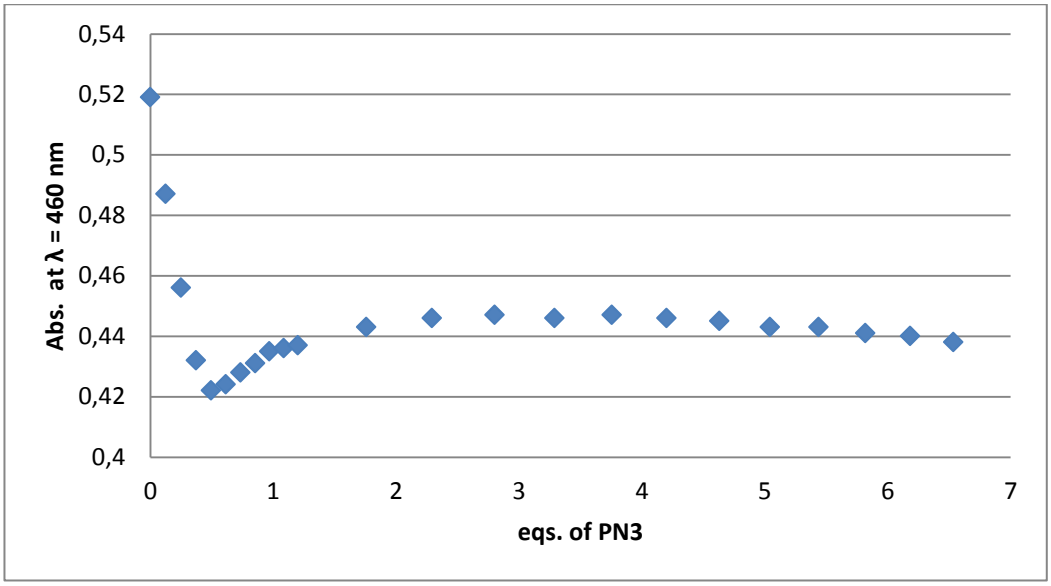
$$K_{1:1} = K_m = 2.82 \times 10^5\ M^{-1}$$

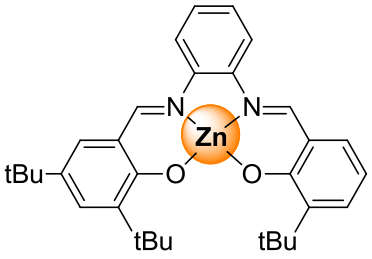
UV-vis titrations of Zn(salphen)s **3-5** with PN_3 **1**:



3

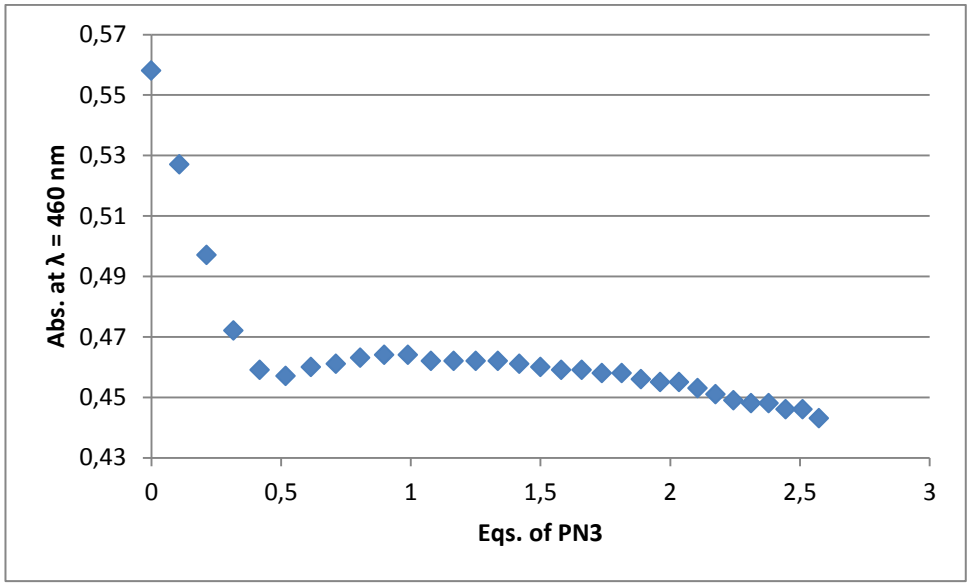
[**3**] = 3.86×10^{-5} in pre-dried toluene:



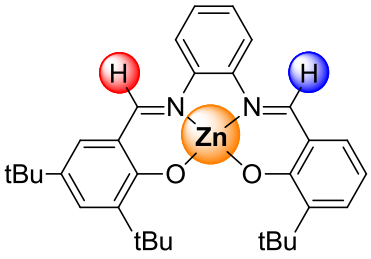


4

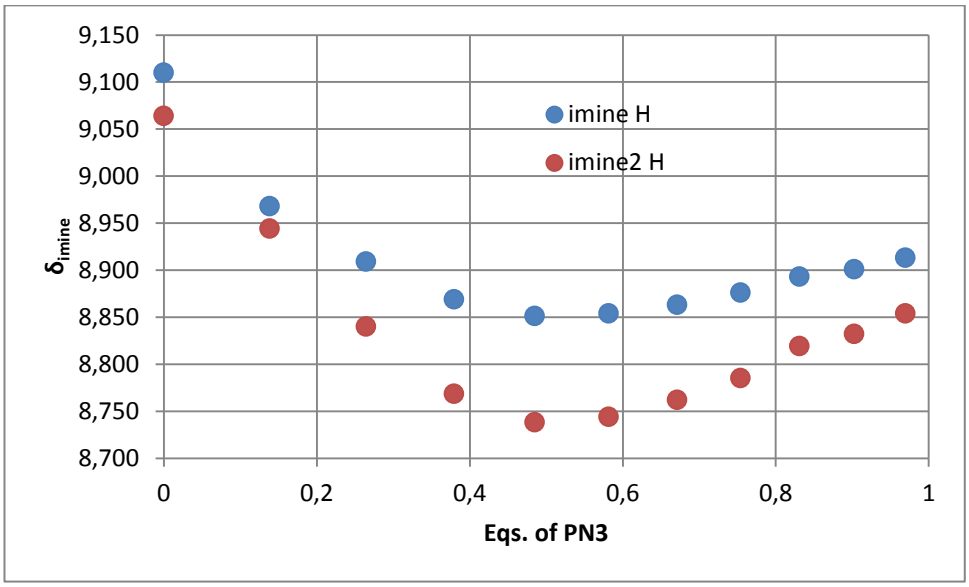
[**4**] = 4.56×10^{-5} in pre-dried toluene:



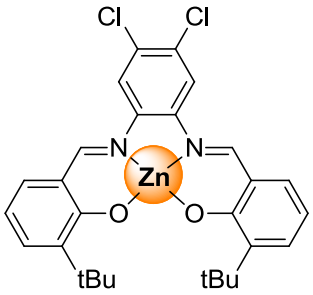
The Zn(salphen) complex **4** was also titrated with PN_3 **1** at a higher concentration using NMR spectroscopy, with [**4**] = 5.02×10^{-3} in [D_6]acetone. The chemical shifts values for both magnetically unequal imine-H were used and the corresponding plots can be found below:



4

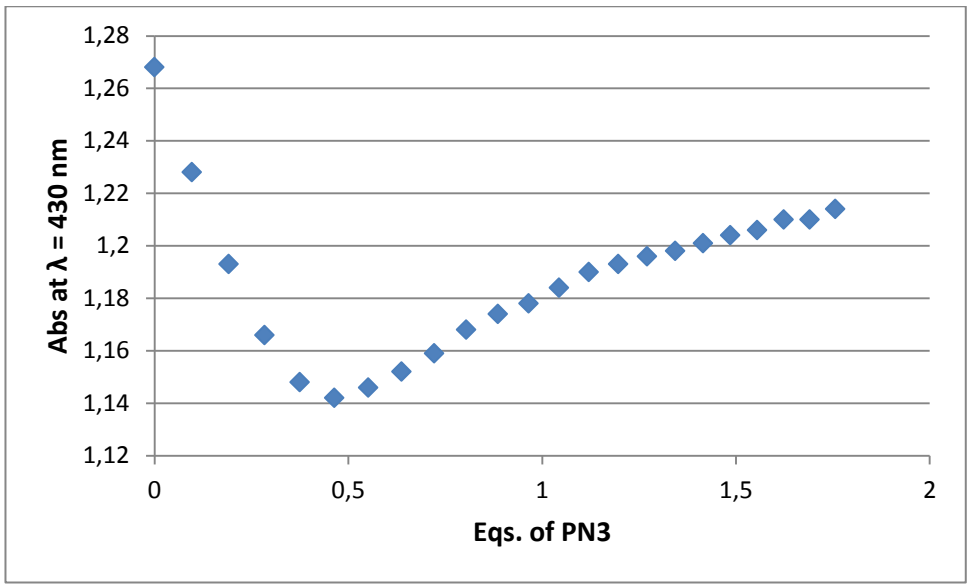


Again a 2:1 stoichiometry seems to be the preferred one.



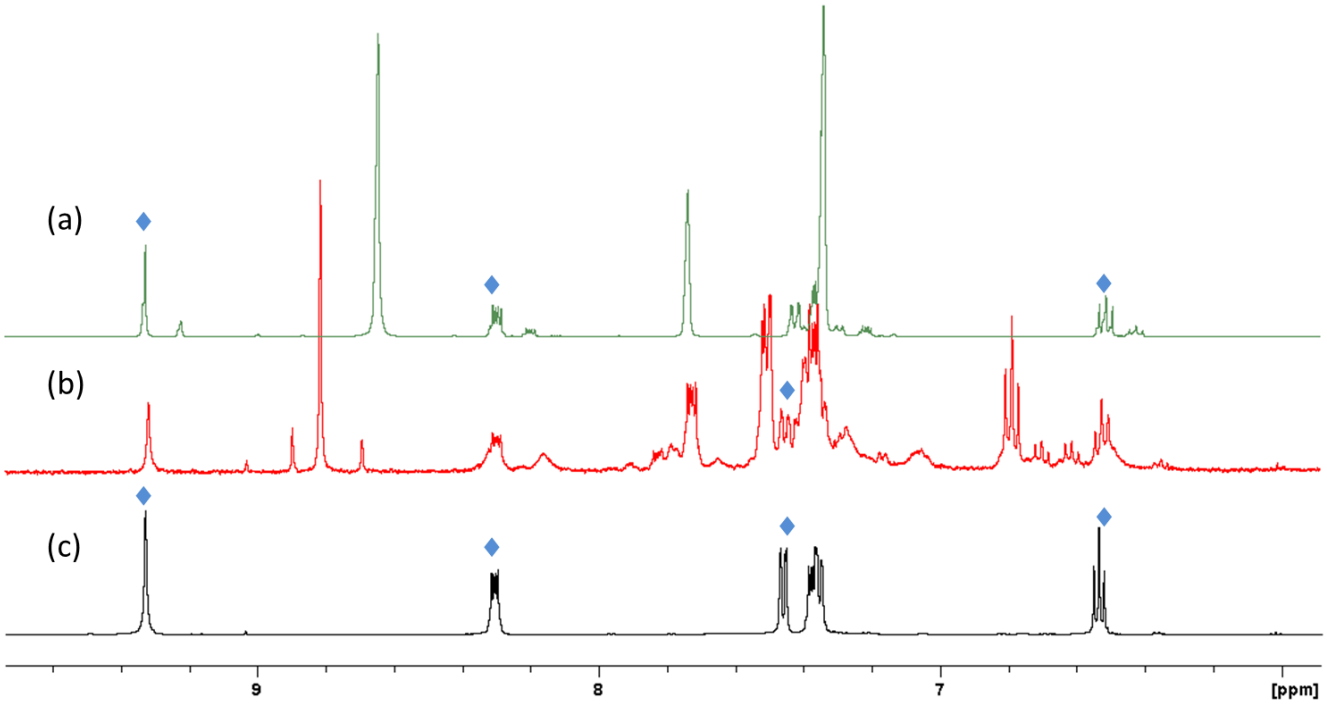
5

[**5**] = 4.64×10^{-5} in pre-dried toluene:



NMR details for the assembly formation between PN_3 **1** and Ru(CO)salphen **9**.

^{1}H NMR comparison (only aromatic region shown here):

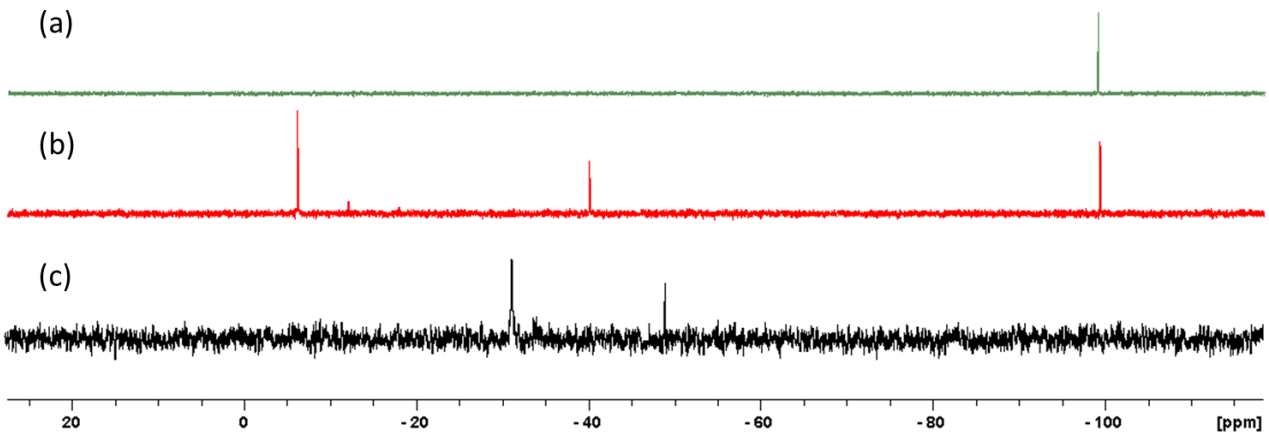


(a) 3 equiv Ru(CO)salphen **9** + 1 equiv PN_3 **1** + 20% v/v [D_5]pyridine

(b) 3 equiv Ru(CO)salphen **9** + 1 equiv PN_3 **1**

(c) Ru(CO)salphen **9**

^{31}P NMR comparison:



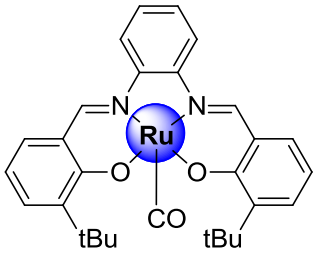
(a) PN_3 **1**

(b) PN_3 **1** + 3 equiv Ru(CO)salphen **9** + 20% v/v [D_5]pyridine

(c) PN_3 **1** + 3 equiv Ru(CO)salphen **9**

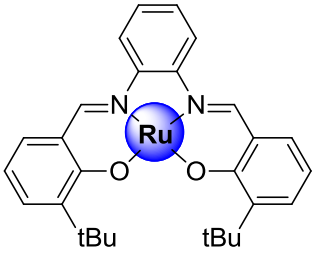
* Note that the peak at $\delta \sim -6$ ppm refers tot he phosphine oxide based on PN_3 **1**.

MS details for Ru(CO)(salphen) complex **9**:



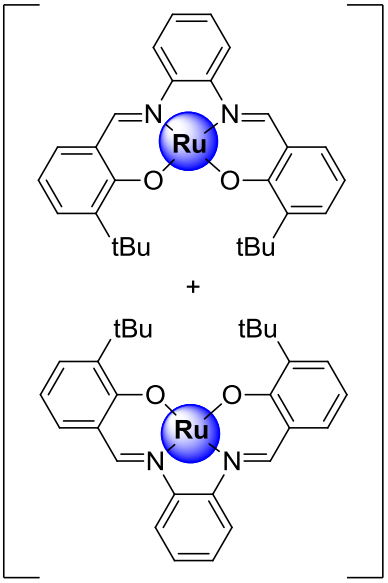
9

Molecular Weight: 556,64
M^+(calcd) = 557.14



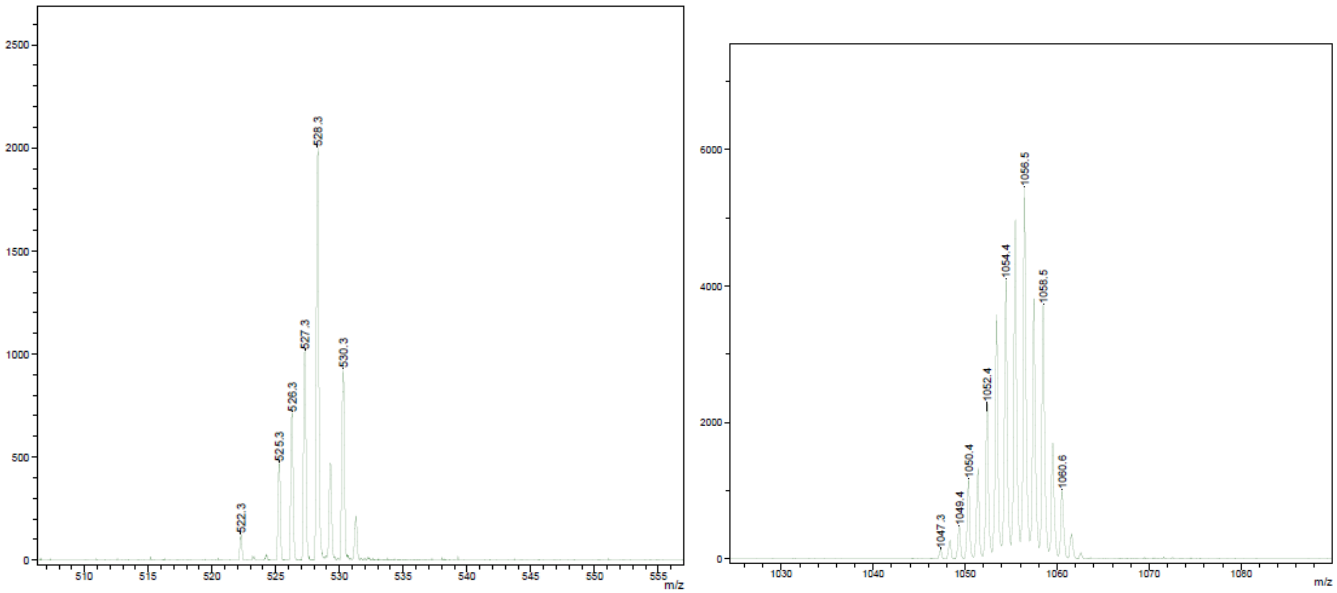
[**9** - CO]

Molecular Weight: 527,62
M^+(calcd) = 528.14



(**9** - CO)$_2$

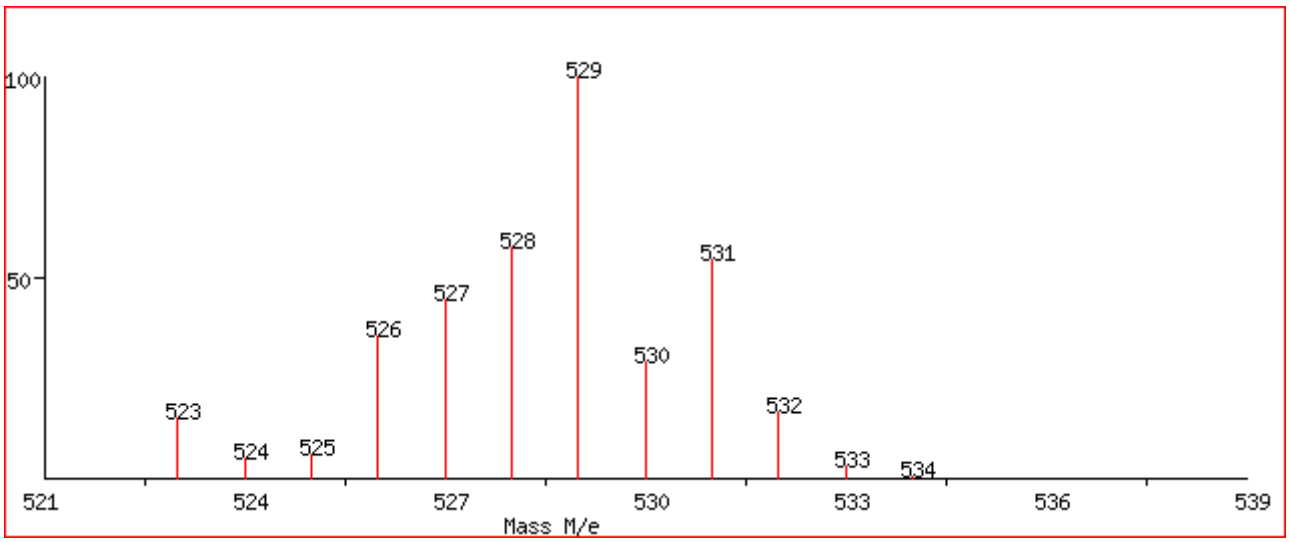
Molecular Weight: 1055.24
M^+(calcd) = 1056.27



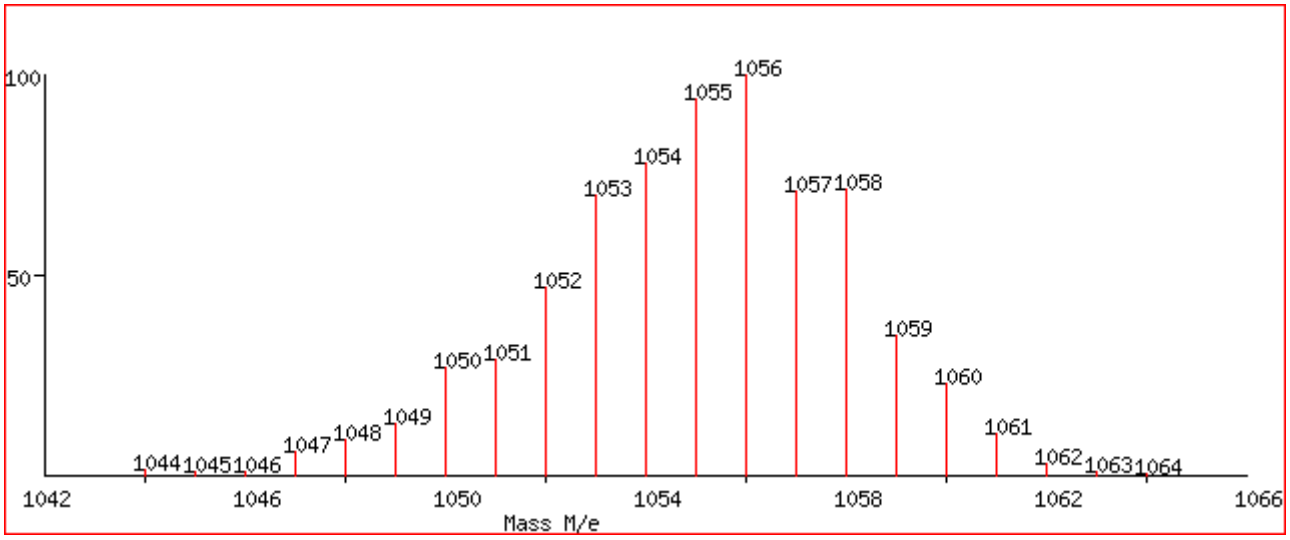
Observed isotopic patterns for both the monomeric (left) as well as dimeric Ru-complex (right) observed by MALDI+ using pyrene as matrix.

Calculated theoretical isotopic patterns fort he mono-Ru and bis-Ru species observed:

Mono-Ru complex, formula $C_{28}H_{30}N_2O_2Ru$:



Bis-Ru complex, formula $C_{56}H_{60}N_4O_4Ru_2$:



Hydroformylation catalysis details:

A typical experiment was carried out in a stainless steel autoclave (150 mL) charged with an insert suitable for 8-14 reaction vessels equipped with Teflon mini stirring bars for performing parallel reactions. Each vial was charged with an appropriate amount of ligand, template and substrate (0.1 mmol). A solution of [Rh(acac)$(CO)_2$] (0.0005 mmol) in toluene (0.1 mL) and toluene (0.9 mL) were added. The substrate was filtered over basic alumina prior to its use to remove possible peroxide impurities. The toluene was distilled from sodium prior to use. Before starting the catalysis, the charged autoclave was purged three times with 10 bar of syngas (H_2/CO = 1/1) and then pressurized to 20 bar and heated 96 h at 40ºC. Then, the autoclave was cooled down to 0ºC, the pressure was reduced to 1.0 bar and a few drops of tri-n-butylphosphite were added in each reaction vessels to prevent any further reaction. The reaction mixtures were not filtered over basic alumina to remove catalyst residues, because filtration may cause retention of the aldehydes and thus influence the GC-results. The mixtures were diluted with dichloromethane for GC-analysis. Gas chromatographic analysis were run on a Shimadzu GC-17A apparatus (split/splitless injector, SUPELCO SPB-1, 30 m column, 0.32 mm diameter, film thickness 3.0 μm, carrier gas 70 kPa He, FID Detector).

Table S1:

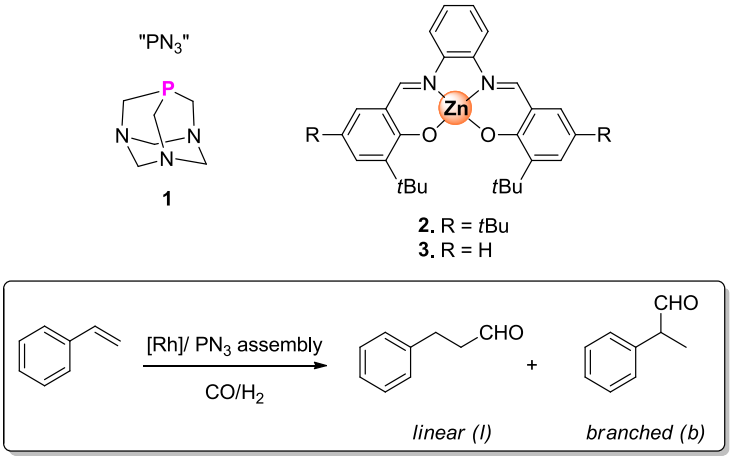


Table S1. Rhodium-catalyzed hydroformylation of styrene using the supramolecular PN_3 assemblies as ligands.[a]

Entry	Ligand	Equiv. of [Zn]	Conv. [%][b]	branched [%][b]	linear [%][b]	b/l[c]
1	–	0	>99.9	90	10	9
2	**1**	0	7	>99	n.d.	>99
3	**2**	10	3	>99	n.d.	>99
4	**1·2**[d]	2	>99.9	97	3	32
5	**1·2**[e]	10	>99.9	96	4	24
6	**1·2**[f]	12	>99.9	97	3	32
7	**3**	10	13	78	22	3.5
8	**1·3**[d]	3	>99.9	91	9	10
9	**1·3**[e]	10	>99.9	89	11	8.1
10	**1·3**[f]	13	>99.9	88	12	7.3
11	**4**	10	>99.9	81	19	4.3
12	**1·4**[e]	3	>99.9	96	4	24
13	**1·4**[e]	10	>99.9	96	4	24

[a] Conditions: [Rh] = 0.5 mM in toluene, ligand/metal ratio = 5, substrate/rhodium = 200, 40 ºC, 20 bar, CO/H_2 = 1:1, 96 h. [b] Conversion and products distribution determined by GC. [c] Branched/linear product ratio. [d] Discrete/pre-isolated assembly used. [e] In situ prepared assembly using the indicated amount of Zn(salphen) **2**, **3**, or **4**. [f] Discrete assembly combined with indicated amount of Zn(salphen) **2** or **3.**

Table S2:

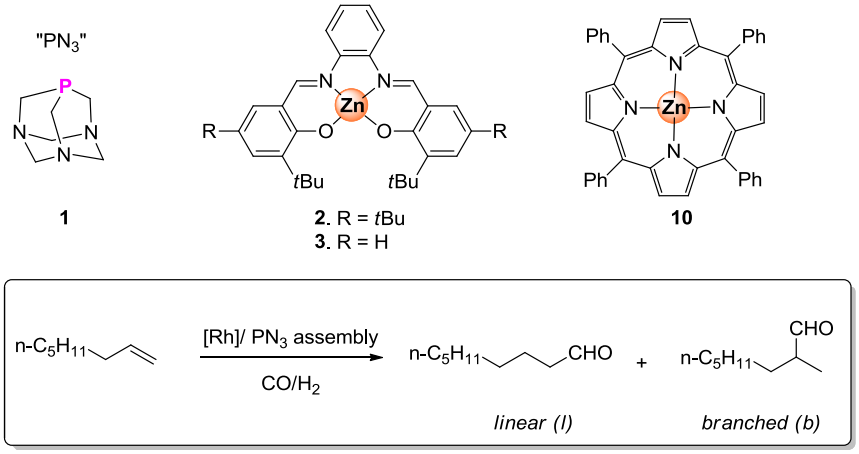
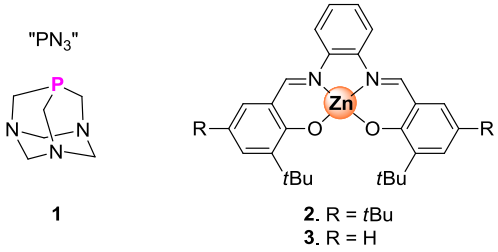


Table S2. Rhodium-catalyzed hydroformylation of 1-octene using the supramolecular PN_3 assemblies as ligands.[a]

Entry	Ligand	Equiv. of [Zn]	Conv. [%][b]	Iso [%][b]	branched [%][b]	linear [%][b]	l/b[c]
1[d]	–	0	>99.9	12	39	49	1.3
2	**1**	0	0	0	0	0	–
3	**2**	10	20	5.5	30.5	64	2.1
4	**1·2**[e]	2	79	0	33	67	2.0
5	**1·2**[f]	10	>99.9	0	35	65	1.9
6	**1·2**[g]	12	>99.9	0	34	66	1.9
7	**3**	10	79	25	24	51	2.1
8	**1·3**[e]	3	>99.9	0	23	77	3.3
9	**1·3**[f]	10	>99.9	0	25	75	3.0
10	**1·3**[g]	13	>99.9	0	25	75	3.0
11	**4**[d]	10	>99.9	17	40	43	1.1
12	**1·4**[f]	3	26	0	28	72	2.6
13	**1·4**[f]	10	>99.9	0	30	70	2.3
14	**1·10**	2	83	0	29	71	2.4
15	**1·10**	3	96	0	29	71	2.4

[a] Conditions: [Rh] = 0.5 mM in toluene, ligand/metal ratio = 5, substrate/rhodium = 200, 40 ºC, 20 bar, CO/H_2 = 1:1, 96 h. [b] Conversion and products distribution determined by GC. [c] Linear/branched product ratio. [d] Note that in this case also some C3 (2-ethylheptanal) and C4 aldehyde (2-propylhexanal) were observed; this as a result of isomerization of the alkene prior to hydroformylation. [e] Discrete/pre-isolated assembly used. [f] In situ prepared assembly using the indicated amount of Zn(salphen) **2**, **3** or **4**. [g] Discrete assembly combined with 10 equiv of Zn(salphen) **2**, **3** or **4**.

Table S3:



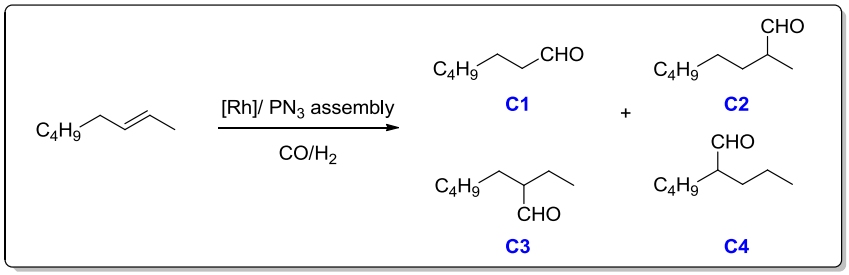


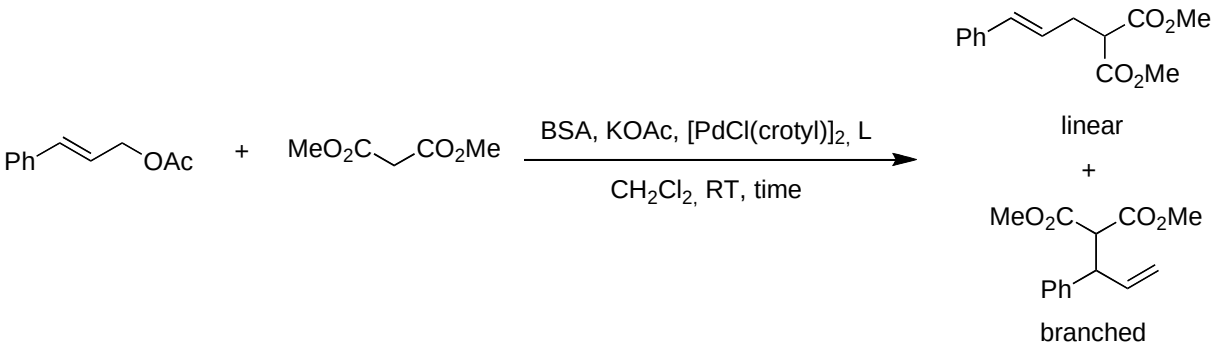
Table S3. Rhodium-catalyzed hydroformylation of *trans*-2-octene using the supramolecular PN_3 assemblies as ligands.[a]

Entry	Ligand	Eq. [Zn]	Conv. [%][b]	**C1** [%]	**C2** [%]	**C3** [%]	**C4** [%]
1	**–**	0	>99.9	9	52	23	16
2	**1**	0	0	0	0	0	0
3	**2**	10	0	0	0	0	0
4	**1·2**[c,d]	2	94.1	8	50	20	11
5	**1·2**[e]	12	0	0	0	0	0
6	**1·2**[f]	5	0	0	0	0	0
7	**1·2**[f]	10	0	0	0	0	0
8	**3**	10	0	0	0	0	0
9	**1·3**[c,d]	3	64	0	53	35	4
10	**1·3**[e]	13	0	0	0	0	0
11	**1·3**[f]	5	21	0	57	43	0
12	**1·3**[f]	10	34	0	49	51	0
13	**4**	10	0	0	0	0	0
14	**1·4**[f]	3	40	0	57	43	0
15	**1·4**[f]	10	48	0	57	43	0

[a] Conditions: [Rh] = 0.5 mM in toluene, ligand/metal ratio = 5, substrate/rhodium = 200, 40 ºC, 20 bar, CO/H_2 = 1:1, 96 h. [b] Conversion and products distribution determined by GC. [c] Discrete/pre-isolated assembly used. [d] 11% (entry 4) and 8% (entry 9) of 2-octene isomerization noted. [e] Discrete assembly combined with 10 equiv of Zn(salphen) **2**, **3** or **4**. [f] In situ prepared assembly using the indicated amount of Zn(salphen) **2**, **3** or **4**.

Table S4:

Experimental procedure for allylic alkylation reactions: A solution of $[PdCl(crotyl)]_2$ (0.49 mg, 0.00125 mmol, 0.5 mol%) in dichloromethane (0.5 mL) was added to a solution of the supramolecular ligand PN_3/Zn(salphen) in dichloromethane (0.5 mL). After stirring 30 min at room temperature, a solution of cinnamyl acetate (0.042 mL, 0.25 mmol), dimethyl malonate (0.086 mL, 0.75 mmol), bis(trimethylsilyl)acetamide (0.185 mL, 0.75 mmol) in dichloromethane (1 mL) and a pinch of KOAc were added. After stirring at room temperature for 16 h, a sample was filtered over Celite and analysed by ^{1}H NMR spectroscopy and GC.



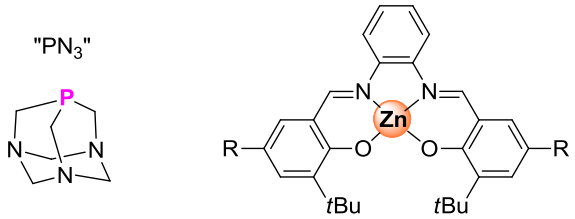


Table S4. Palladium-catalyzed allylic alklylation of cinnamyl acetate with dimethyl malonate using the supramolecular PN_3 assemblies as ligands.[a]

Entry	L	L [mol%]	t [h]	Conv. [%][b]	linear [%]	branched [%]
1	–	–	16	–	–	–
2	**1**	1	2	100	77	23
3	**2**	6	16	–	–	–
4	**3**	6	16	–	–	–
5	**1**(**2**)$_2$	1	16	18	70	30
6	**1**(**2**)$_2$	2	16	100	64	36
7	**1**(**3**)$_3$	1	16	3	n.d.	n.d.
8	**1**(**3**)$_3$	2	16	100	66	34

[a] Conditions: $[PdCl(crotyl)]_2$ = 0.5 mol%, cinnamyl acetate/dimethyl malonate/BSA = 1/3/3, 20 ºC. [b] Conversion and products distribution determined by ^{1}H NMR spectroscopy and GC. Results averaged over two runs.