Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Bisphosphine based Hetero-Capsules for the Encapsulation of Transition Metals

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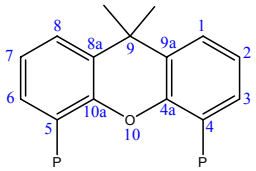
Outline

1. General

All reactions were carried out using standard Schlenk techniques under an atmosphere of purified nitrogen. Diethyl ether was distilled from sodium. Dichloromethane, methanol and acetonitrile were distilled from CaH_2. Compounds {[(*o*-tolyl)$_3$P]Pd(*p*-C_6H_4CN)Br}$_2$,[a] 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene tetrasodiumsalt **2**,[b] and 4,5-bis[bis(*p*-((diethylamino)methyl)phenyl)phosphino]-9,9-dimethylxanthene[c] were synthesized according to literature procedures. ^{13}CO was purchased from Praxair and all other reagents were purchased from Aldrich or Acros and used as received. NMR spectra were recorded on Varian Inova 500 (^{1}H NMR titrations, 1D-NOESY and DOSY measurements), Bruker DRX 300, and Varian Mercury 300 NMR spectrometers in CD_3OD unless otherwise specified. ^{31}P and ^{13}C spectra were measured ^{1}H decoupled. The coupling constant values *J* are given in Hz. High-resolution fast atom bombardment mass spectrometry (HRMS FAB) measurements were carried out on a JEOL JMS SX/SX 102A. Low-resolution

electrospray-ionization mass spectra (ESI-MS) in CH_3OH were recorded on a Shimadzu LCMS-2010A via direct injection. Infrared spectra were recorded on a Bruker Vertex 70 spectrophotometer.

Numbering of the diphosphine compounds:



2. Synthesis of 1a, 1b, 1c, 1d and 1d·2

Synthesis of 4,5-bis[bis(*p*-((diethylammoniumchloride)methyl)phenyl)phosphino]-9,9-dimethylxanthene, (*p*-(Et_2NHCl)CH_2-xantphos): **1a**

A 1 M solution of HCl in diethyl ether (3.10 mL, 3.10 mmol) was added dropwise to a solution of 4,5-bis[bis(*p*-((diethylamino)methyl)phenyl)phosphino]-9,9-dimethylxanthene **1** (0.57 g, 0.62 mmol) in 20 mL diethyl ether and a light yellow precipitation appeared immediate. After stirring for 45 min. the volatiles were removed *in vacuo* and **1a** was obtained as a light yellow powder in quantitative yield. δ_H(500 MHz; CD_3OD; Me_4Si) 7.59 (10 H, d, *J* 8.1, H_3 + PC_6H_4), 7.33-7.30 (8 H, m, PC_6H_4), 7.03 (2 H, t, *J* 7.7, H_2), 6.48 (2 H, d, *J* 7.6, H_1), 4.40 (8 H, s, CH_2N), 3.29-3.19 (16 H, m, CH_2CH_3), 1.68 (6 H, s, CCH_3), 1.38 (24 H, dt, *J* 3.0 and 7.5, CH_2CH_3); δ_H(500 MHz; $CDCl_3$; Me_4Si) 12.12 (4 H, s, NH^+); δ_P(202 MHz; CD_3OD; H_3PO_4) -16.8 (s); δ_P(202 MHz; dmso-d_6; H_3PO_4) -17.8 (s); δ_C(126 MHz; CD_3OD; Me_4Si) 153.2 (t, *J* 9.6, CO), 140.6 (t, *J* 7.2), 136.0 (t, *J* 10.9), 132.8 (s, C_1), 132.4 (t, *J* 3.2), 131.9 (s), 131.6 (s), 129.0 (s), 125.4 (t, *J* 8.9), 125.2 (s, C_2), 57.0 (s, CH_2N), 48.3 (s, CH_2CH_3), 48.2 (s, CH_2CH_3), 35.7 (s, CCH_3), 32.7 (s, CCH_3), 9.3 (s, CH_2CH_3), 9.2 (s, CH_2CH_3); HRMS (FAB+): [**1a** – 4Cl – 3H]$^+$: found 919.5573; calcd. ($C_{59}H_{77}ON_4P_2$) 919.5583; ESI-MS (CH_3OH): m/z = 307.05 [**1a** – 4Cl – 1H]$^{3+}$, 460.15 [**1a** – 4Cl – 2H]$^{2+}$, 919.25 [**1a** – 4Cl – 3H]$^{1+}$.

Synthesis of (*p*-(Et_2NHCl)CH_2-xantphos)Pd(*p*-C_6H_4CN)(Br):[d] **1b**

A yellow solution of {[(*o*-tolyl)$_3$P]Pd(*p*-C_6H_4CN)Br}$_2$ (148 mg, 0.125 mmol) and **1a** (266 mg, 0.250 mmol) in 10 mL of methanol-dichloromethane (1:10, v/v) was stirred overnight at room temperature. The orange solution was concentrated *in vacuo* to *ca.* 3 mL. Next, 10 mL of diethyl ether was added which resulted in the precipitation of a yellow powder. The suspension was filtered and the remaining powder was dried *in vacuo* to give **1b** (271 mg, 80%) as a yellow powder. δ_H(500 MHz; CD_3OD; Me_4Si) 7.90 (2 H, d, *J* 7.0, $H_{1,3}$), 7.52-7.43 (16 H, m, PC_6H_4), 7.33 (2 H, t, *J* 7.7, H_2), 7.22-7.19 (2 H, m, $H_{1,3}$), 6.99 (2 H, d, *J* 7.5, C_6H_4CN), 6.55 (2 H, d, *J* 7.2, C_6H_4CN), 4.36 (4 H, d, *J* 11.7, CH_2N), 4.32 (4 H, d, *J* 12.1, CH_2N), 3.28-3.10 (16 H, m, CH_2CH_3), 1.84 (6 H, s, CCH_3), 1.38 (12 H, t, *J* 7.0, CH_2CH_3), 1.37 (12 H, t, *J* 7.0, CH_2CH_3); δ_H(500 MHz; $CDCl_3$/CD_3CN 2/3; Me_4Si) 11.98 (4 H, s, NH^+); δ_P(202 MHz; CD_3OD; H_3PO_4) 9.4 (s); δ_P(202 MHz; dmso-d_6; H_3PO_4) 8.9 (s); δ_C(126 MHz; CD_3OD; Me_4Si) 168.1 (bs), 155.5 (t, *J* 5.9), 136.2 (bs), 135.7 (bs), 135.3 (t, *J* 6.6), 132.6 (t, *J* 22.6), 132.3 (s), 130.8 (t, *J* 5.0), 129.3 (s), 128.9 (s), 125.0 (s), 119.8 (s), 119.5 (t, *J* 22.9), 104.3 (s), 55.1 (s,

CH_2N), 47.4 (s, CH_2CH_3), 46.7 (s, CH_2CH_3), 36.4 (s, CCH_3), 27.9 (s, CCH_3), 8.0 (s, CH_2CH_3), 7.8 (s, CH_2CH_3); HRMS (FAB+): [**1b** – 4Cl – Br – 4H]$^+$: found 1126.4987; calcd. ($C_{66}H_{80}ON_5P_2Pd$) 1126.4895; ESI-MS (CH_3OH): m/z = 376.25 [**1b** – 4Cl – Br – 2H]$^{3+}$, 563.20 [**1b** – 4Cl – Br – 3H]$^{2+}$, 1126.20 [**1b** – 4Cl – Br – 4H]$^{1+}$.

Synthesis of [(*p*-(Et_2NHOTf)CH_2-xantphos)Pd(*p*-C_6H_4CN)]$^+$[OTf]$^-$:[d] 1c

A solution of **1b** (160 mg, 0.118 mmol) and silver triflate (152 mg, 0.590 mmol) in 10 mL of dichloromethane-acetonitrile (5:1, v/v) was stirred in the dark for one hour. Next, Norit was added and the reaction mixture was stirred for another hour. The suspension was filtered through Celite filter aid and the filtrate was evaporated to dryness *in vacuo* yielding **1c** (170 mg, 77%) as a brown microcrystalline. δ_H(500 MHz; CD_3OD; Me_4Si) 8.06 (2 H, d, *J* 8.0, $H_{1,3}$), 7.70 (8 H, d, *J* 8.5, PC_6H_4), 7.67-7.63 (10 H, m, $H_{1,3}$ and PC_6H_4), 7.52 (2 H, t, *J* 7.7, H_2), 7.24 (2 H, d, *J* 8.5, C_6H_4CN), 7.16 (2 H, d, *J* 8.5, C_6H_4CN), 4.43 (8 H, s, CH_2N), 3.31-3.21 (16 H, m, CH_2CH_3), 1.86 (6 H, s, CCH_3), 1.37 (24 H, t, *J* 7.2, CH_2CH_3); δ_H(500 MHz; $CDCl_3$/CD_3CN 2/3; Me_4Si) 8.18 (4 H, bs, NH^+); δ_P(202 MHz; CD_3OD; H_3PO_4) 18.9 (s); δ_P(202 MHz; dmso-d_6; H_3PO_4) 18.7 (s); δ_C(126 MHz; CD_3OD; Me_4Si) 154.9 (t, *J* 8.1), 152.6 (m), 136.3 (s), 136.1 (bs), 135.8 (t, *J* 7.2), 135.3 (s), 134.8 (s), 133.8 (bs), 133.4 (t, *J* 5.8), 132.0 (s), 129.9 (t, *J* 26.0), 128.8 (bs), 125.7 (s), 123.2 (s), 120.7 (s), 119.9 (s), 119.3 (t, *J* 20.5), 118.3 (s), 109.1 (s), 56.6 (s, CH_2N), 48.5 (s, CH_2CH_3), 36.2 (s, CCH_3), 33.8 (s, CCH_3), 9.1 (s, CH_2CH_3); δ_F(282 MHz; CD_3OD; Cl_3CF) -80.2 (s); HRMS (FAB+): [**1c** – 1CF_3SO_3 – 1H]$^+$: found 1725.3197; calcd. ($C_{70}H_{83}O_{13}N_5F_{12}P_2S_4Pd$) 1725.3210; ESI-MS ($CH_3OH$): m/z = 376.85 [**1c** – 5CF_3SO_3 – 2H]$^{3+}$, 563.50 [**1c** – 5CF_3SO_3 – 3H]$^{2+}$, 1126.50 [**1c** – 5CF_3SO_3 – 4H]$^{1+}$, 426.85 [**1c** – 4CF_3SO_3 – 1H]$^{3+}$, 638.30 [**1c** – 4CF_3SO_3 – 2H]$^{2+}$, 476.80 [**1c** – 3CF_3SO_3]$^{3+}$, 713.80 [**1c** – 3CF_3SO_3 – 1H]$^{2+}$, –148.70 [CF_3SO_3]$^{1-}$.

Synthesis of [(*p*-(Et_2NHOTf)CH_2-xantphos)Pd(C(O)*p*-C_6H_4CN)]$^+$[OTf]$^-$:[e] 1d

Carbon monoxide was bubbled for 10 min. through a solution of **1c** in CD_3OD at room temperature, in a NMR tube. IR (CH_3OH, 20 °C): 1732 cm^{-1} [ν(C(O))]; δ_H(300 MHz; CD_3OD; Me_4Si) 8.02 (2 H, d, *J* 7.8, $H_{1,3}$), 7.85-7.60 (20 H, m, PC_6H_4, $H_{1,3}$ and H_2),7.49 (2 H, d, *J* 7.8, C_6H_4CN), 7.39 (2 H, d, *J* 8.1, C_6H_4CN), 4.40 (8 H, s, CH_2N), 3.29-3.10 (16 H, m, CH_2CH_3), 1.34 (21 H, t, *J* 7.2, CH_2CH_3); δ_C(75 MHz; CD_3OD; Me_4Si) 212.6 (s, PdC(O)); δ_P(121 MHz; CD_3OD; H_3PO_4) 11.5 (s).

Synthesis of capsule 1d·2

Carbon monoxide was bubbled for 10 min. through a solution of **1c·2** (**1c**:**2** = 1:2) in CD_3OD at room temperature, in a NMR tube. IR (CH_3OH, 20 °C): 1732 cm^{-1} [ν(C(O))]; δ_H(300 MHz; CD_3OD; Me_4Si) 7.93-7.45 (26 H, m, H_1, H_2, H_3, PC_6H_4), 7.43 (16 H, s, H_{meta} of **2**), 4.72 (8 H, d, *J* 12.6, H_{ax}), 4.28 (24 H, bs, CH_2N and $ArOCH_2$), 3.90 (16 H, t, *J* 5.0, $ArOCH_2CH_2$), 3.56 (16 H, q, *J* 6.9, OCH_2CH_3), 3.35 (8 H, d, *J* 13.8, H_{eq}), 3.05-2.90 (16 H, m, $NH^+(CH_2CH_3)_2$), 1.62 (6 H, s, CCH_3), 1.22 (24 H, t, *J* 7.2, OCH_2CH_3), 0.95-0.85 (24 H, m, $NH^+(CH_2CH_3)_2$); δ_C(75 MHz; CD_3OD; Me_4Si) 213.0 (s, PdC(O)); δ_P(121 MHz; CD_3OD; H_3PO_4) 12.1 (s).

3. Chloride test of capsule 1a·2

Mixing water solutions of **1a** and **2** resulted in the precipitation of capsule **1a·2**. The chloride test with silver nitrate was used to determine the presence of sodium chloride in the precipitated capsule and the water filtrate, as is described below.

The molar solubility of AgCl in CH_3OH was visually determined by the addition of one drop of a saturated aqueous $AgNO_3$ solution to NaCl solutions in methanol (0.01 - 10 mM) and was found to be 0.50 mM. Next, one drop of the $AgNO_3$ solution was added to capsule **1a·2** formed *in situ* in methanol (**1a**/**2** = 1:1, 2 mM). As expected, AgCl precipitated immediately confirming the presence of chloride ions in solution. Subsequently equimolar water solutions of **1a** and **2** were mixed, the precipitate was filtered, washed with water (the water layers were combined), dried and re-dissolved in methanol. Upon addition of one drop of the $AgNO_3$ solution to the combined water layers AgCl precipitated immediately. However, addition of one drop of the $AgNO_3$ solution to the re-dissolved capsule in methanol (2 mM) did not result in any precipitation. The maximum concentration of NaCl that can be present in the solution of capsule **1a·2** is $\leq$ 0.50 mM, indicating that at most 6 % of the chloride that was initially present in **1a** (8 mM) is present in capsule **1a·2**. These chloride tests show that mixing equimolar water solutions of **1a** and **2** results in the precipitation of capsule **1a·2** in the absence of NaCl and the presence of NaCl in the water filtrate. This experiment was performed in duplo.

4. NMR characterization of capsules 1a·2, 1b·2, and 1c·2

The assignment of the ^{1}H NMR spectra of the capsules is fully supported by COSY NMR. Not all the proton resonances were visible in the ^{1}H NMR spectra because of overlap with other signals or because of H-D exchange with CD_3OD. ^{31}P NMR study of **1a**, **1b**, **1c**, **1a·2**, **1b·2**, and **1c·2** in CD_3OD, D_2O and dmso-d_6 confirms their stability in the different solvents.
^{31}P NMR, and upfield shifts ($\Delta\delta_H$) of the $CH_2NH^+(CH_2CH_3)_2$ protons of **1a**, **1b**, and **1c** upon capsule formation in different solvents:

Capsule 1a·2 (CD_3OD):

δ_P = -17.4 ppm, $\Delta\delta(CH_2C\mathbf{H_3})$ = 0.43 ppm, $\Delta\delta(C\mathbf{H_2}CH_3)$ = 0.33 ppm, $\Delta\delta(C\mathbf{H_2}N)$ = 0.25 ppm.

Capsule 1a·2 (dmso-d_6):

δ_P = -17.7 ppm, $\Delta\delta(CH_2C\mathbf{H_3})$ = 0.49 ppm, $\Delta\delta(C\mathbf{H_2}CH_3)$ = 0.32 ppm, $\Delta\delta(N\mathbf{H^+})$ = 1.40 ppm.

Capsule 1b·2 (dmso-d_6):

δ_P = 9.3 ppm, $\Delta\delta(CH_2C\mathbf{H_3})$ = 0.41 ppm, $\Delta\delta(C\mathbf{H_2}CH_3)$ = 0.27 ppm, $\Delta\delta(N\mathbf{H^+})$ = 1.14 ppm.

Capsule 1c·2 (CD_3OD):

δ_P = 19.4 ppm, $\Delta\delta(CH_2C\mathbf{H_3})$ = 0.58 ppm, $\Delta\delta(C\mathbf{H_2}CH_3)$ = 0.39 ppm, $\Delta\delta(C\mathbf{H_2}N)$ = 0.17 ppm.

Capsule 1c·2 (dmso-d_6):

δ_P = 19.0 ppm, $\Delta\delta(CH_2C\mathbf{H_3})$ = 0.70 ppm, $\Delta\delta(C\mathbf{H_2}CH_3)$ = 0.64 ppm, $\Delta\delta(N\mathbf{H^+})$ = 0.20 ppm.

5. Job Plot

Equimolar solutions (2 mM) of **1a** and **2** in CD_3OD were prepared and mixed in various ratios. In this way the total concentration of **1a** and **2** was kept constant at 2 mM and only the **1a**/**2** ratio was varied. ^{1}H NMR spectra of the mixtures were recorded, and the chemical shifts of **1a** were analyzed by Job's method of continuous variation, *i.e.* a plot of the capsule concentration as a function of the mol fraction of **2** (Figure 1).[f] The maximum of the curve is clearly at a mol fraction of 0.5, confirming the 1:1 ratio assembly formed in solution.

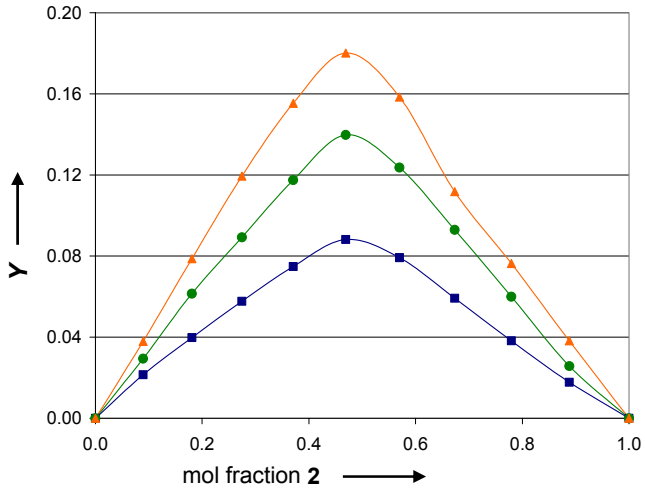


Figure 1. Job plot for the diphosphine ligand **1a** with the calix[4]arene **2** at a total concentration of 2 mM in CD_3OD at 298 K. The $C\mathbf{H_2}NH^+(C\mathbf{H_2}C\mathbf{H_3})_2$ protons of **1a** are reported; ▲ $CH_2C\mathbf{H}_3$, ● $C\mathbf{H}_2CH_3$, ■ $C\mathbf{H_2}N$; ($\Delta\delta_{\mathbf{1a}} = \delta_{obs} - \delta_0$ and $y = (\Delta\delta_{\mathbf{1a}})$*(mol fraction **1a**)).

6. ^{1}H NMR titrations

The ^{1}H NMR titrations of **2** with **1a** and of **2** with **1c** were measured in CD_3OD at 298 K under inert conditions. Because of solubility reasons the concentration of **2** was kept constant and low in all the samples (1 mM) whereas the concentrations of **1a** and **1c** were varied from 0 to 3 mM. The chemical shifts of the diphosphine protons $C\mathbf{H_2}NH^+(C\mathbf{H_2}C\mathbf{H_3})_2$ of **1a·2** and **1c·2**, relative to the chemical shifts of **1a** respectively **1c** were followed and fitted to a 1:1 binding model using a least-squares fitting procedure.[g] The association constants K for a single run were calculated as the mean of the values obtained for each of the followed diphosphine signals, weighted by the observed changes in chemicals shift (Figure 2).[h] The association constants from different runs were then averaged. The titrations were carried out *in duplo*. The association constant found for capsule **1a·2** is $K_{\mathbf{1a\cdot2}}=6\cdot10^4$ M^{-1} and for capsule **1c·2** is $K_{\mathbf{1c\cdot2}}=6\cdot10^3$ M^{-1}.

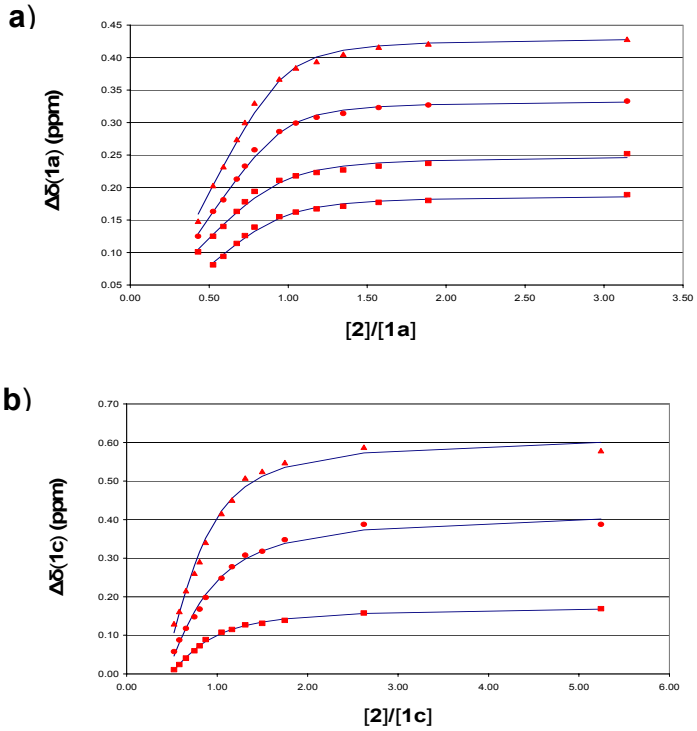


Figure 2. Fitting of the ^{1}H NMR titration data in CD_3OD at 298 K of ***a***) **2** with **1a**. ***b***) **2** with **1c**. Data points represent the absolute upfield shifts (Δδ) of $C\mathbf{H_2}NH^+(C\mathbf{H_2}C\mathbf{H_3})_2$ protons of **1a·2** and **1c·2** relative to the chemical shifts of free **1a** resp **1c**; lines are best-fit curves calculated by nonlinear regression; ▲ $CH_2C\mathbf{H_3}$, ● $C\mathbf{H_2}CH_3$, ■ $C\mathbf{H_2}N$ (the protons in the diethylammoniummethyl groups are diastereotopic).[c]

7. 1D-NOESY measurements

Transient 1D-NOESY experiments (DPFGSE) of capsule **1a·2** (1:2, [**1a**] = 3mM, CD_3OD), capsule **1b·2** (1:2, [**1b**] = 3mM, CD_3OD), capsule **1c·2** (1:2, [**1c**] = 3mM, dmso-d_6) were carried out at 296 K. Negative NOE enhancements were observed between the $NH^+(CH_2C\mathbf{H_3})_2$ protons of **1a**, **1b** and **1c**, and the aromatic protons of **2**.[i]

8. DOSY measurements

In all the DOSY experiments of the free building blocks as well of the capsules, the concentrations of **1a**, **1b**, **1c** and **2** were kept constant at 2 mM, this resulted in a 1:1 ratio of the capsules building blocks **1** and **2**. The $NH^+(CH_2C\mathbf{H_3})_2$ protons of **1a**, **1b** and **1c** and the $OCH_2C\mathbf{H_3}$ protons of **2** were used for the calculation of the diffusion coefficients. The diffusion measurements were carried out on a Varian Inova 500 equipped with a Performa II pulsed gradient unit able to produce magnetic field pulse gradients of about 30 Gcm^{-1} in the *z*-direction. The ^1H DOSY experiments were carried out in a 5 mm inverse probe at 296 K. The magnetic field pulse gradients were of 1.5 ms duration followed by a stabilization time of 2 ms. The diffusion delay was set to 0.2 s. The magnetic field pulse gradients were incremented from 0 to 25 Gcm^{-1} in ten steps and the stimulated spin echo experiment was performed with compensation for convection. The pulse sequence was developed by Evans and Morris (University of Manchester). The diffusion coefficients *D* are calculated according to the Stejskal-Tanner equation:[j] $\ln(I/I_0) = -[\gamma^2\delta^2G^2(\Delta-\delta/3)]D$, where *I* is the peak area, I_0 is the peak area in the absence of gradients, γ the magnetogyric ratio of the observed nucleus, δ is the gradient duration, *G* the strength of the gradient pulse in T/m, Δ the diffusion time and *D* the diffusion coefficient (Table 1).

Table 1. Diffusion coefficients *D* of the free building blocks **1a**, **1b**, **1c** and **2**, and of capsules **1a·2**, **1b·2** and **1c·2**.[i, ii]

Entry	Compounds	Solvent	D / 10^{-6} cm^2s^{-1}
1	Free **1a**	CD_3OD	3.35
2	Free **1c**	CD_3OD	3.21
3	Free **2**	CD_3OD	3.55
4	Capsule **1a**·2	CD_3OD	2.46
	Capsule 1a·**2**	CD_3OD	2.44
5	Capsule **1c**·2	CD_3OD	2.04
	Capsule 1c·**2**	CD_3OD	2.00
6	Free **1b**	dmso-d_6	1.01
7	Free **2**	dmso-d_6	1.04
8	Capsule **1b**·2	dmso-d_6	0.74
	Capsule 1b·**2**	dmso-d_6	0.74

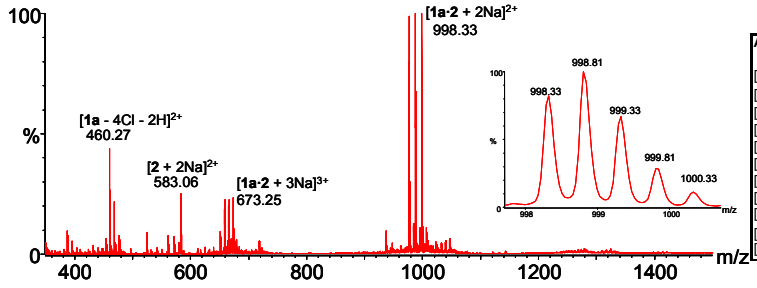
[i] The protons of the building blocks in Bold were used for the calculation of *D*.
[ii] As the free and bound building blocks exchange fast on the NMR timescale, the observed diffusion coefficients of the capsules are the weighted average of the diffusion coefficients of the free and bound building blocks.

9. ESI-MS measurements

Samples of the supramolecular capsules **1a·2**, **1b·2**, and **1c·2** (building blocks ratio 1:1) with initial concentrations of 100-250 μM were diluted in 70% MeOH sometimes with the addition of formic acid to a final concentration of 1%. Nanoelectrospray MS and collision induced dissociation (CID) MSMS were performed on a Q-Tof (Micromass, Waters, Whyttenshawe, UK) mass spectrometer with a Z-Spray orthogonal ESI source. EconoTips (New Objective, Woburn, MA) were used to create an off-line nanospray. From the survey MS spectra individual candidate ions were selected for CID with Argon as collision gas. The survey MS and the resulting MSMS spectra were processed and deconvoluted with software tools embedded in Masslynx software (Micromass, Waters, Whyttenshawe, UK). Additional isotopic pattern analysis was performed with the use of the Bruker Daltonics Isotope Pattern software program (Bruker Daltonik, Bremen, Germany, version 1.0.125.0).

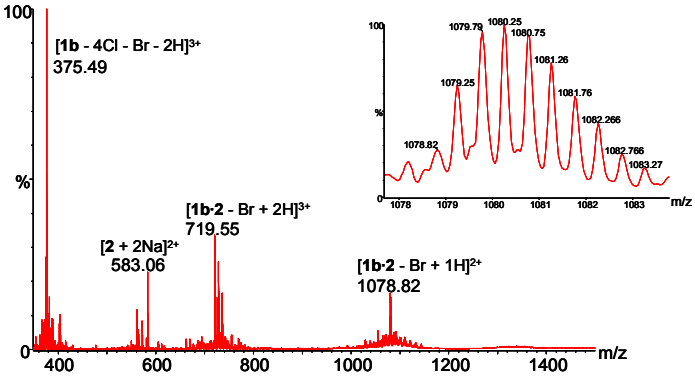
Comparison of the measured isotope pattern of capsules **1a·2**, **1b·2**, and **1c·2** with the calculated ones confirms the elemental composition and charge state. The capsules ion peaks correspond to 1:1 complexes and no ion peaks for higher aggregates were detected. Deconvolution of the mass spectra gave for all the capsules the expected singly charged monoisotopic ion peaks at *m/z* 1995.7 for $[\mathbf{1a{\cdot}2} - 1H + 2Na]^{1+}$, *m/z* 2156.7 for $[\mathbf{1b{\cdot}2} - Br]^{1+}$ and *m/z* 2157.1 for $[\mathbf{1c{\cdot}2} - CF_3SO_3]^{1+}$. The assignment of the capsule's ion peaks is confirmed by collision experiments. Upon collision induced dissociation (CID) of the capsule's ion peaks product peaks appeared that correspond to the diphosphine building blocks **1a**, **1b**, and **1c** respectively at *m/z* 460.4 for $[\mathbf{1a} - 4Cl - 2H]^{2+}$, at *m/z* 562.8 for $[\mathbf{1b} - 4Cl - Br - 3H]^{2+}$, and at 562.9 for $[\mathbf{1c} - 5CF_3SO_3 - 3H]^{2+}$ (Figure 3). Comparison of the ESI-MS spectra of **1b** (see synthesis) and of capsule **1b·2** shows in both cases a heterolytic splitting of the Pd-Br bond.

ESI Q-TOF MS Spectrum of capsule **1a·2**
(inset: measured isotope pattern)



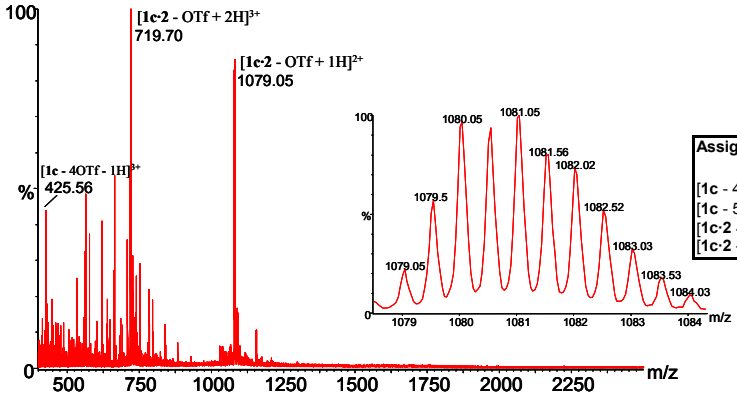
Assignment	Found m/z mono isotope	Calculated m/z mono isotope
[**1a** - 4Cl -2H]2+	460.267	460.282
[**2** + 2H]2+	561.101	561.084
[**2** + 1H + 1Na]2+	572.096	572.075
[**2** + 2Na]2+	583.055	583.065
[**1a·2** + 3H]3+	651.263	651.265
[**1a·2** + 2H + 1Na]3+	658.602	658.593
[**1a·2** + 1H + 2Na]3+	665.921	665.920
[**1a·2** + 3Na]3+	673.251	673.247
[**1a·2** + 2H]2+	976.354	976.394
[**1a·2** + 1H + 1Na]2+	987.327	987.385
[**1a·2** + 2Na]2+	998.325	998.375

ESI Q-TOF MS Spectrum of capsule **1b·2**
(inset: measured isotope pattern)



Assignment	Found m/z mono isotope	Calculated m/z mono isotope
[**1b** - 4Cl - 2H - Br]3+	375.488	375.501
[**2** + 2H]2+	561.074	561.084
[**2** + 1H + 1Na]2+	572.068	572.075
[**2** + 2Na]2+	583.055	583.065
[**1b·2** + 2H - Br]3+	719.549	719.576
[**1b·2** + 1H + 1Na - Br]3+	726.881	726.909
[**1b·2** + 2Na - Br]3+	734.219	734.230
[**1b·2** + 1H - Br]2+	1078.823	1078.860

ESI Q-TOF MS Spectrum of capsule **1c·2**
(inset: measured isotope pattern)



Assignment	Found m/z mono isotope	Calculated m/z mono isotope
[**1c** - 4OTf - 1H]3+	425.563	425.487
[**1c** - 5OTf - 3H]2+	562.873	562.747
[**1c·2** - OTf + 2H]3+	719.696	719.576
[**1c·2** - OTf + 1H]2+	1079.045	1078.860

Figure 3. ESI-MS spectra of capsules **1a·2**, **1b·2**, and **1c·2** in CH_3OH.

10. References

a) R. A. Widenhoefer, H. A. Zhong and S. L. Buchwald, *J. Am. Chem. Soc*., 1997, **119**, 6787.

b) R. Fiammengo, P. Timmerman, F. de Jong and D. N. Reinhoudt, *Chem. Commun*., 2000, 2313; R. Fiammengo, P. Timmerman, J. Huskens, K. Versluis, A. J. R. Heck D. N. Reinhoudt, *Tetrahedron*, 2002, **59**, 757.

c) A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. W. Elgersma, K. Goubitz and J. Fraanje, *Organometallics*, 1997, **16**, 3027.

d) M. A. Zuideveld, B. H. G. Swennenhuis, M. D. K. Boele, Y. Guari, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz , A. L. Spek and P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.*, 2002, 2308.

e) P. W. N. M. van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz and A. L. Spek, *J. Am. Chem. Soc*., 2003, **125**, 5523.

f) P. Job, *Ann. Chim.* **1928**, *9*, 113-203. M. T. Blanda, J. H. Horner, M. Newcomb, *J. Org. Chem.* **1989**, *54*, 4626-4636.

g) F. Corbellini, S. Mulder, A. Sartori, M. J. W. Ludden, A. Casnati, R. Ungaro, J. Huskens, M. Crego-Calama, D. N. Reinhoudt, *J. Am. Chem. Soc.*, 2004, **126**, 17050.

h) P. Bisson, C. A. Hunter, J. C. Morales and K. Young, *Chem. Eur. J.*, 1998, **4**, 845.

i) D. Neuhaus and M. P. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis, Second Edition*, **2000**.

j) E. O. Stejskal and J. E. Tanner, *Journal of Chemical Physics* 1965, **42**, 288.