Stoichiometry controlled self-assembly of tri- and octa-nuclear palladium–yttrium complexes†

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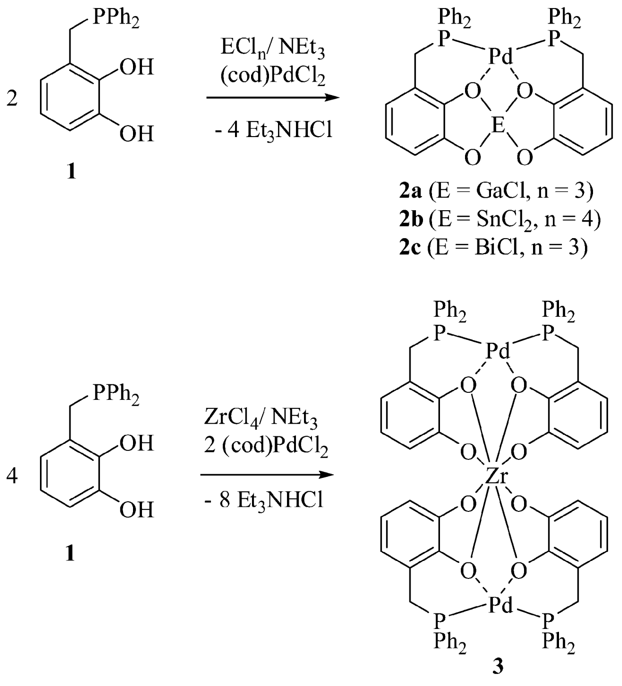
Palladium complexes with template-centred, bidentate bis-phosphine donors were prepared in a one-step process *via* base-assisted condensation of a ditopic catechol phosphine **1** (LH_2) with simple yttrium and palladium salts. It was found that the assembly of either one or two Pd-bisphosphine units on one template was possible in a controlled way by adjusting the stoichiometric ratio of the reactants. Thus, reaction of YCl_3, (cod)$PdCl_2$, and **1** in a 1 : 4 : 2 molar ratio produced a complex of composition $[Y(H_2L_2Pd)(L_2Pd)(dmf)]Cl$ whereas reaction of the same reactants in 1 : 2 : 1 molar ratio gave a polynuclear assembly $[O(YL_2Pd)_4(dmf)_4H]Cl_3$. Both products were characterised by single-crystal X-ray diffraction studies and spectroscopic data (NMR, ESI-MS) which indicated that the assemblies found in the crystalline state persist also in solution.

Introduction

Bidentate phosphines have a long standing in homogeneous catalysis because they often grant superior selectivity, activity, or stability of metal complex based catalysts.[1] Tuning a ligand to optimum performance in a catalytic reaction calls, however, for proper adjustment of its electronic and steric properties (like cone angles or natural bite angles[2]), and catalyst improvement may require screening of a whole family of tailored ligands. To be successful, efficient synthetic methods for ligands and complexes are needed. As one solution to this problem, modular syntheses permitting rational construction of ligand families with structurally diverse molecular backbones have been developed.[3] An alternative approach was recently introduced with the concept of supramolecular ligands.[4] Here, a bidentate donor forms spontaneously (*via* "self-assembly") upon mixing of two suitably functionalized monodentate ligands, creating the chelate backbone either directly by interaction of complementary binding motifs in both fragments, or by binding of both building blocks to a common template. Examples for the first approach involve the pairing of ligand components *via* hydrogen bonds[5] whereas template based supramolecular ligands were assembled *via* binding of ditopic fragments to a suitable metal ion,[6,7] or anion sequestering.[8]

Recently, we described a one-step synthesis of chelate complexes **2** *via* assembly of a simple palladium salt, a suitable template, and the ditopic catechol phosphine **1**[9] (further denoted as LH_2, Scheme 1).[10,11] As the formation of the target complexes relies on both the kinetic lability of the created template-oxygen bonds and the reversibility of the condensation step, the template-centred bis-phosphine donor was also considered a supramolecular ligand. Interestingly, it was found that its bite angle could be controlled by the choice of size and preferred coordination geometry of the template. Whereas use of a tetrahedral borate unit gave *trans*-chelating bisphosphine units with bite angles close to 180°,[10] larger triply or quadruply charged main-group elements (Ga^{3+}, Sn^{4+}, Bi^{3+}) produced complexes with *cis*-chelating ligands



Scheme 1

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and bite angles that shrunk continually from 102° to 97° with increasing template size.[12] An interesting case was the zirconium complex **3**[12] (Scheme 1) where binding of two palladium-bis-phosphine units to a relatively large and hard (in the sense of the HSAB formalism) template was observed.

In view of the structure directing influence of the template in the heterobimetallic assemblies **2** and **3**, it was expected that still larger templates than Zr^{4+} like Y^{3+} or lanthanide ions should be even more suitable for binding of a higher number of catechol units and might thus have considerable potential to act as nucleus for larger molecular assemblies with interesting architectures. As a first attempt along this line we have explored the use of Y^{3+} as template and report here on the outcome of these studies which indicate that stoichiometry control must be considered a further variable which controls the molecular structure of the complexes formed.

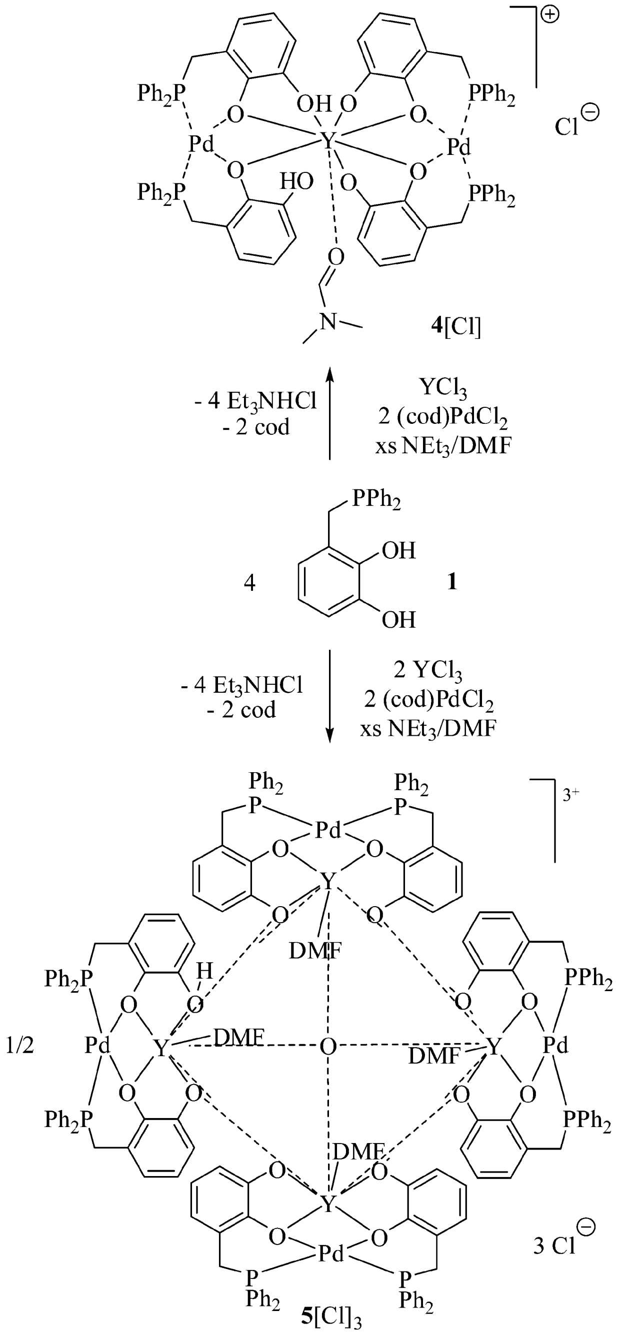
Results and discussion

To establish if the Y^{3+} template supports simultaneous binding of two L_2Pd fragments and may thus give rise to a similar architecture as found in the trinuclear $ZrPd_2$-complex **3**, we studied the reaction of yttrium trichloride (1 equiv.), cyclooctadiene palladium chloride (cod)$PdCl_2$ (2 equiv.), and phosphine **1** (4 equiv.) in the presence of excess triethyl amine under similar conditions as had been employed for the synthesis of **3**.[12] Work-up of the reaction mixture gave a dark red, solid product that was characterised by spectroscopic data and a single-crystal X-ray diffraction study.

The ^{31}P NMR spectrum of the isolated product showed two broad resonances at 71 and 66 ppm. The ^{1}H NMR spectrum displayed complicated patterns for aromatic and benzylic protons together with the signals of a co-crystallised solvent (DMF) and a singlet attributable to a free phenolic OH. The individual lines were likewise broad but analysis of the benzylic signals allowed to derive the presence of three distinguishable catechol phosphine units in 2 : 1 : 1 ratio. The ^{31}P chemical shifts and the observed diastereotopy of the benzylic CH_2-protons are characteristic features of complexes like **2** or **3** and suggest to assign all signals to ligands in chelate complexes although the presence of more than one distinguishable ligand environment has no precedence in these systems. The observation of temperature dependent changes in signal shapes confirmed that the line broadening in ^{1}H and ^{31}P NMR spectra owes presumably to mutual chemical exchange processes; however, as we were not able to reach the slow exchange regime in the accessible temperature range, these experiments did not provide further structural information.

The negative-mode ESI-MS showed a dominant signal attributable to an anion $(L_4Pd_2Y)^{-}$ whereas the positive-mode ESI-MS contained a series of pseudo-molecular ions of composition $(H_2L_4Pd_2Y)^{+}$, $(HL_4Pd_2YNa_2)^{2+}$, $(H_2L_4Pd_2YNa)^{2+}$, $(H_3L_4Pd_2Y)^{2+}$, and $(H_4L_4Pd_2Y)^{3+}$. As all these ions can be derived from a single precursor species which must contain two L_2Pd-units bound to a central yttrium template, the MS studies prove unambiguously the presence of the targeted trinuclear complex with a similar composition as **3**. An additional weak signal of a cation $(H_2L_2PdNa)^{+}$ in the (+)-ESI-MS is attributed to a decomposition product which arises presumably from slow hydrolysis. This interpretation is in accord with the observation of additional weak signals in the ^{31}P NMR spectra of aged solutions and suggests that the parent complex is only moderately stable in solution.

The remaining ambiguities in the structure elucidation were resolved by a single-crystal X-ray diffraction study on a sample obtained by recrystallisation from DMF/Et_2O (1 : 1) at room temperature. The crystals contained a cationic complex $[H_2L_4Pd_2Y(dmf)]^{+}$ (**4**, Scheme 2 and Fig. 1), a chloride, and three solvent molecules (DMF). Cation and anion are linked by a O–H···Cl hydrogen bond whereas the



Scheme 2 Synthesis of **4[Cl]** and **5[Cl]$_3$**; the extra H-atom in cation **5** has been arbitrarily attached to one of the catecholate oxygen atoms.

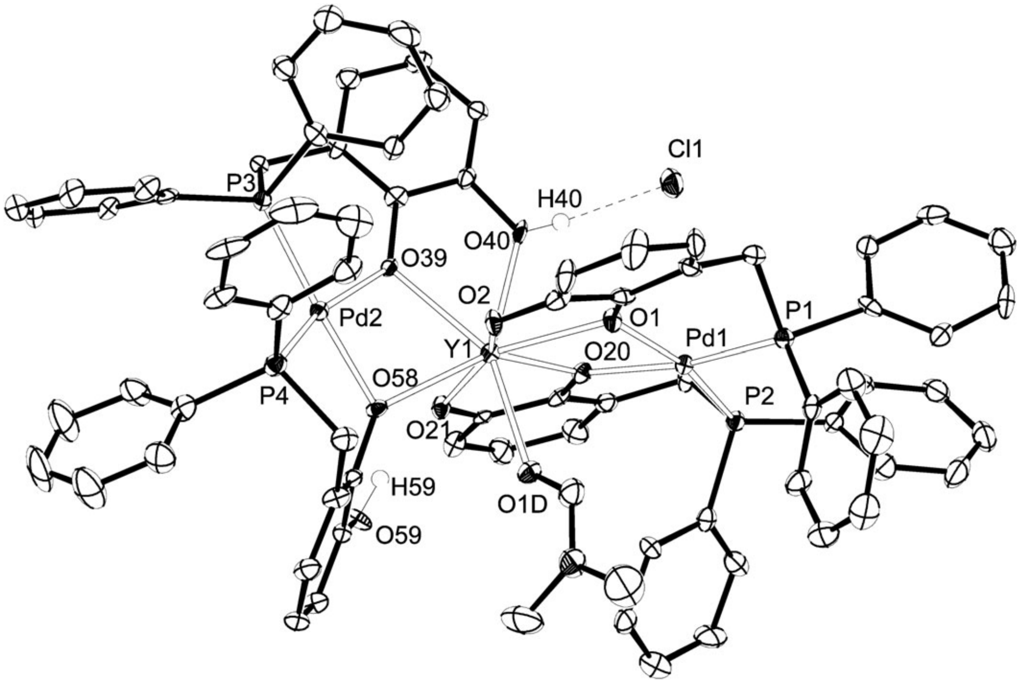


Fig. 1 Representation of **[4]Cl** in the crystal (H-atoms with exception of the OH-protons H40 and H59 were omitted for clarity; displacement parameters drawn at 50% probability level). Selected bond lengths [Å] and angles [°]: Y1–O21 2.280(4), Y1–O2 2.307(4), Y1–O1D 2.345(4), Y1–O1 2.355(4), Y1–O20 2.358(4), Y1–O58 2.371(4), Y1–O39 2.371(4), Y1–O40 2.435(5), Pd1–O20 2.048(4), Pd1–O1 2.070(4), Pd1–P1 2.227(2), Pd1–P2 2.231(2), Pd2–O39 2.074(4), Pd2–O58 2.101(4), Pd2–P4 2.226(2), Pd2–P3 2.232(2).

solvent molecules lack specific intermolecular interactions and serve merely to fill holes in the crystal packing.

The yttrium atom is coordinated by seven oxygen atoms of four catechol ligands and the oxygen atom of a coordinated DMF, resulting in a total coordination number of eight. Four of the catechol oxygen atoms (O1, O2, O20, O21) belong to a formally dianionic PdL_2-unit which differs from similar units in complexes **2** and **3**[12] in showing a coplanar arrangement of the two catecholate units. The yttrium atom lies 18 pm above this plane so that the whole bis-catecholate metal unit may be considered approximately planar. The position of the Pd1 atom deviates by approx. 63 pm from this coordination plane, and the chelate ring defined by Y1, O1, O20, and Pd1 is folded by 16° along the O1–O20 axis. The square planar coordination around the Pd1 atom and the Pd1–O (2.048(4)–2.070(4) Å) and Pd1–P (2.227(3)–2.231(3) Å) distances are similar as in **2** and **3** but both O1–Pd1–O20 (77.1(2)°) and P1–Pd1–P2 (102.6(1)°) angles are by some 2°–3° larger than the appropriate angles in **3** (O–Pd–O 75.1(1)°, P–Pd–P 99.7(1)°[12]), presumably reflecting different conformational strain in the fused ring systems of both species. Similar as in **2** and **3**, Y–O distances to terminal oxygen atoms (O2, O21) are shorter (2.280(4)–2.307(4) Å) than those to μ_2-bridging oxygen atoms (O1, O20; Y–O 2.355(4), 2.358(4) Å).

Three oxygen atoms from the remaining catechol units (O39, O40, O58) and one (O1D) from the coordinated DMF form a second set of donor atoms that exhibit likewise a nearly coplanar arrangement. The angle between the two YO_4-coordination planes is 89°, and the whole yttrium coordination environment is thus best described in terms of two orthogonal crescents of which each is formed by four oxygen atoms. The catechol units containing the O39, O40, O58 atoms belong to a formally neutral H_2L_2Pd unit that connects to yttrium *via* two bridging oxygen atoms (O39, O58) and the oxygen atom (O40) of an intact hydroxyl function; the second hydroxyl group remains free but is stabilised by an intramolecular hydrogen bond (O59–H···O21 1.73(2)/2.561(6) Å) to a catecholate oxygen atom of the L_2Pd unit. The coordinated O40 atom is also involved in a O–H···Cl hydrogen bridging interaction with the chloride anion and exhibits a larger distance to the central yttrium atom (Y–O40 2.435(5) Å) than the catecholate oxygen atoms (Y–O39/O58 2.371(4) Å) and the oxygen atom in the coordinated DMF (Y–O1D 2.345(4) Å). The aromatic rings of the two catechol groups in the H_2L_2Pd unit are no longer coplanar, and the four-membered chelate ring through Y, O39, O58, Pd2 exhibits a larger deviation from planarity (fold angle 34°) than the ring including the other palladium atom (Pd1). The coordination geometry around Pd2 deviates from planarity and is best described as twisted (with a twist angle of 15° between the O58–Pd2–P4 and O39–Pd2–P3 planes; similar distortions of an ideal square planar environment have previously also been found for other Pd(II) complexes with chelating bis-phosphine ligands[13]), and the P3–Pd2–P4 bite angle (98.54(7)°) is smaller than its counterpart at Pd1.

In view of the fact that the (L_4Pd_2Y) core persists according to the ESI-MS studies in solution, it is reasonable to assume that the constitution of crystalline **4** can also serve as model for the solution structure. The signal multiplicities in solution ^1H and ^{31}P NMR spectra are then consistently explained by assuming a dynamic molecular structure that is characterised by rapid inversion of the conformationally flexible chelate ring system in the H_2L_2Pd-fragment (possibly in combination with rapid decomplexation and exchange of the coordinated DMF) and renders the catecholate units in the opposite L_2Pd-moiety chemically equivalent. The observed broadening of all ^{1}H and ^{31}P NMR signals suggests that also mutual exchange between bound and free OH-groups, or proton transfer between different catechol units, may take place; these processes must, however, occur at a rate that is slow on the NMR timescale as otherwise complete averaging of all signals should be observable.

In order to establish if beside **4** also yttrium-templated complexes with a similar structure as **2** and an Y : Pd ratio of 1 : 1 are available, we studied also the triethyl amine assisted reaction of yttrium trichloride, (cod)$PdCl_2$, and **1** in a molar ratio of 1 : 1 : 2. Work-up of the reaction mixture produced a dark red solid material which dissolved in DMF or DMSO but was only sparingly soluble in ether or acetonitrile, and was characterised by spectroscopic and analytical data and a single-crystal X-ray diffraction study.

The ^{31}P NMR spectrum of the isolated material displayed a sharp signal at 69.7 ppm, and the ^{1}H NMR spectrum contained the expected signals for aromatic and benzylic protons of ligand **1** together with a set of solvent resonances (DMF). All signals showed substantial broadening. Although the finding of ^{1}H NMR signals attributable to diastereotopic methylene protons and the observed ^{31}P chemical shift were taken as evidence for the presence of a chelate complex with a $M(\mu_2\text{-}L)_2Pd$ unit and similar local architecture as **2–4**,[10,12] the NMR data gave no clear picture of the ligand sphere around yttrium, and the constitutional assignment remained thus incomplete. Additional information was again available from (+)-ESI-mass spectra which showed peaks attributable to ions of composition $(L_8Pd_4Y_4OH)^{3+}$ and $(L_8Pd_4Y_4ONaF)^{2+}$ (where incorporated sodium and fluoride ions come from the solvent used) but gave at the same time no evidence for the presence of di- or trinuclear assemblies like **2–4**, respectively. All findings together suggested that a larger, presumably oxygen centred, polynuclear complex had formed.

This hypothesis was unambiguously confirmed by a single-crystal X-ray diffraction study. The dark-red, triclinic crystals (space group $P\bar{1}$) obtained by recrystallisation of the isolated product from a concentrated DMF solution contain a centrosymmetric complex with crystallographic C_i-symmetry which consists of four yttrium centres, eight PdL_2-units and four coordinated solvent molecules (DMF) (Fig. 2) as well as three chloride anions, 12 uncoordinated solvent molecules (DMF) and 5 hydrate water molecules per formula unit of the polynuclear complex.

The complex itself exhibits a core of four yttrium atoms which are arranged in a perfect square around a central μ_4-bridging oxygen atom lying on a centre of symmetry, with Y–μ_4-O–Y angles of 89.84(2)°–90.16(2)° and Y–O distances of 2.468(1)–2.472(1) Å. Each yttrium atom is further coordinated by the four catecholate oxygen atoms of a L_2Pd-subunit and the oxygen atom of an additional DMF. Whereas two of the catecholate oxygen atoms in each subunit act, as usual, as μ_2-bridging ligands towards the yttrium and the palladium atom in the same subunit, the remaining ones are involved in μ_2-bridging coordination with the yttrium atom of an adjacent subunit. The individual Y–O–Y bridges are distinctly asymmetric and are arranged in a way that the perimeter of the oxygen centred $(\mu_4\text{-}O)Y_4(\mu_2\text{-}OR)_8$-core is composed of an alternating array of shorter (2.286(4)–2.313(4) Å) and longer (2.338(4)–2.357(4) Å) Y–O bonds. The distances involving μ_2-O atoms in the Y–O–Pd bridges (Y–O 2.307(4)–2.357(4) Å, O–Pd 2.072(4)–2.097(3) Å) and the Pd–P bonds (2.241(1)–2.249(1) Å) are all very similar and compare well to the corresponding bond distances in **4**. In contrast to **4**, however, the four-membered YO_2Pd rings are essentially planar, and the bite angle of the supramolecular bidentate bisphosphine units is smaller (P–Pd–P 97.3(1)°–97.7(1)° *vs.* 99.7(1)° in **4**). The coordination geometry around the four yttrium atoms is best described as a doubly capped trigonal prism (Fig. 3).

Since the polynuclear assembly described so far must be considered a dication $[L_8Pd_4Y_4(dmf)_4O]^{2+}$ (**5**, Scheme 2) and the crystal contains three chloride anions per formula unit, electroneutrality requires the presence of another positive charge. In view of the observation of a peak attributable to a triply charged cation of composition $[L_8Pd_4Y_4OH]^{3+}$ in the ESI-MS, we suggest that the charge balance in the crystal is likewise achieved by protonation of the complex cation **5**. Although we were neither able to locate the additional proton directly in a difference Fourier map nor to deduce its position from careful analysis of bond distances, it is reasonable to assume that it resides either on the central oxygen atom or, like in **4**, on one of the μ_2-oxygens which connect adjacent yttrium atoms (in which case the absence of any marked irregularity in Y–O bond distances may be explained by a disorder of the protonation site over eight equivalent oxygen atom positions); both oxide and hydroxide centred lanthanide complexes with a central, square planar OM_4 core have precedence in the literature.[14] The infrared spectrum of **[5]Cl$_3$** displays a weak band around 3354 cm^{-1} which is in the range for alcoholic or phenolic OH-stretching frequencies, but lacks a sharp peak around 3580 cm^{-1} which had been previously assigned to the stretching of μ_3-OH groups.[14,15] Although this finding favours a structure with an oxide-centred core and one protonated catecholate unit, it must be noted that a μ-OH band is not always visible, in particular when additional water is present[16] (which is also the case here), so that unambiguous assignment of the protonation site remains unfeasible.

Formation of the polynuclear complex **5** can be rationalised in terms of the assembly of four YL_2Pd fragments that arise from spontaneous condensation of phosphine **1**, (cod)$PdCl_2$, and YCl_3 on an oxide or hydroxide template. The source of this template is a trace amount of water which was either serendipitously introduced with solvents or starting materials used, or was absorbed by the hygroscopic reaction mixture in the course of the reaction. If one assumes that the demand of the large Y^{3+} cation for high coordination numbers and the known preference of hard lanthanoid ions to form anion bridged polynuclear complexes[14] are strong driving forces for the assembly of both **4** and **5**, it appears that the outcome of the reaction depends critically on the relative ratio of Y^{3+} and catecholate ions, and that the stoichiometry of reactants employed has thus a strong impact on the product selectivity.

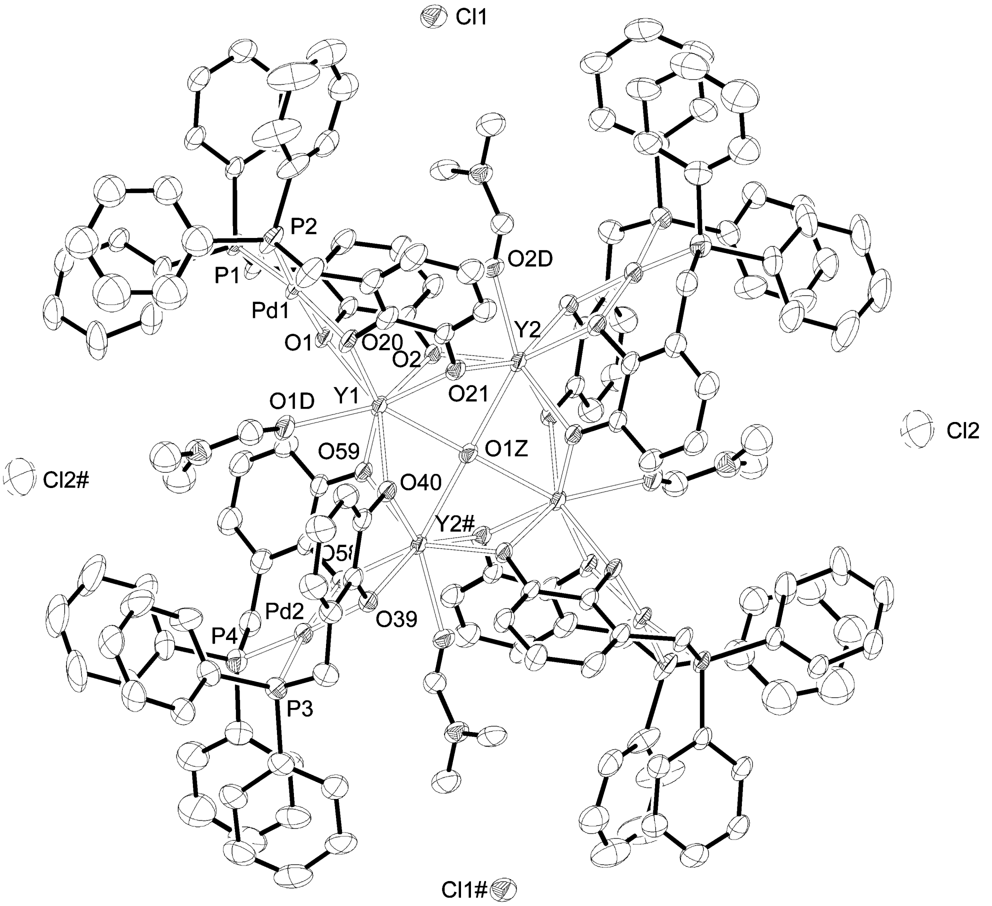


Fig. 2 Representation of **[5]Cl$_3$** in the crystal (H-atoms were omitted for clarity; displacement parameters drawn at 50% probability level). Y1/Y1# and Cl2/Cl2# denote pairs of crystallographically equivalent atoms related by a centre of symmetry (# symmetry code $-x$, $1-y$, $1-z$). Anions Cl2/Cl2# have a site occupation factor of 0.5. Selected bond lengths [Å] and angles [°]: Y1–O59 2.307(4), Y1–O40 2.313(4), Y1–O1D 2.338(4), Y1–O1 2.346(3), Y1–O2 2.349(4), Y1–O20 2.349(4), Y1–O21 2.357(4), Y1–O1Z 2.4722(5), Y2–O2# 2.286(4), Y2–O21# 2.305(4), Y2–O39 2.324(3), Y2–O59 2.339(4), Y2–O2D 2.340(4), Y2–O58 2.348(4), Y2–O40 2.357(4), Y2–O1Z 2.4675(5), Pd1–O1 2.076(4), Pd1–O20 2.097(3), Pd1–P2 2.247(2), Pd1–P1 2.249(2), Pd2–O39 2.072(4), Pd2–O58 2.095(3), Pd2–P4 2.241(2), Pd2–P3 2.249(2).

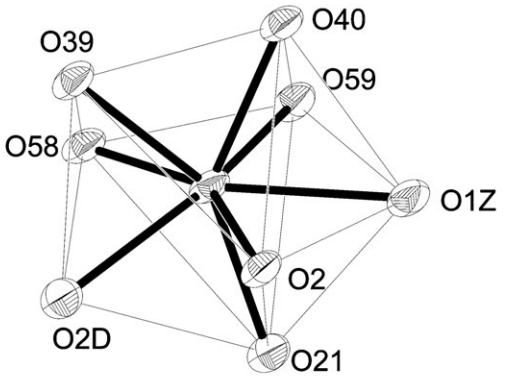


Fig. 3 Representation of the coordination sphere of the Y2 atom of **5**. Thin lines highlight the doubly capped trigonal prismatic coordination polyhedron.

The unusual coordination geometries around the Y^{3+} ion of **4** and the central μ_4-oxygen atom of **5** can be explained if one assumes that the interactions of ligands with these centres are predominantly electrostatic in character, and that the ligand arrangement is strongly directed by the demands to minimise the ring strain in the peripheral PdL$_2$-moieties and the mutual repulsion between these groups. The structure of **4** appears interesting as the unusual η^3-coordination of the formally neutral H$_2$LPd-unit can be regarded as snapshot on the way to the formation of a genuine ML$_2$Pd-chelate.

Conclusions

It has been demonstrated that palladium complexes with template-centred bis-phosphine donors are accessible in one-step *via* base-assisted condensation of catechol phosphine **1** (LH$_2$) with simple yttrium and palladium salts. The relatively large Y^{3+} template can support binding of one or two Pd-bisphosphine units, yielding either a complex [Y(H$_2$L$_2$Pd)(L$_2$Pd)(dmf)]Cl or a polynuclear assembly [O(YL$_2$Pd)$_4$(dmf)$_4$H]Cl$_3$, respectively. Formation of the products occurs in a controlled way, and the architecture of the product formed can be addressed by adjusting the stoichiometric amounts of reactants employed. Single-crystal X-ray diffraction studies revealed that binding of two bisphosphine-Pd units to one Y^{3+}-template in [Y(H$_2$L$_2$Pd)-(L$_2$Pd)(dmf)]Cl resulted in an interesting coordination topology that was characterised by the presence of two sets of four donor atoms arranged in two mutually orthogonal coordination planes. The structure of this product contained further a κ^3-O,O′,O″-coordinated, formally neutral H_2LPd-unit that is unprecedented for this class of compounds and can be regarded to provide a snapshot on the way to the formation of a genuine ML_2Pd-chelate. Spectroscopic studies (NMR, ESI-MS) indicated that the assemblies found in the crystalline state persist in solution.

Experimental section

General remarks

All reactions were carried out under dry argon using standard Schlenk techniques. Solvents were dried by standard procedures unless otherwise mentioned. The catechol phosphine **1** (denoted as LH_2)[9] and cyclooctadiene palladium dichloride[17] were prepared as previously reported. Commercially available anhydrous YCl_3 (Sigma-Aldrich) was used. Solution NMR spectra were recorded at 30 °C on Bruker Avance 400 (^{1}H: 400.1 MHz, ^{13}C: 100.5 MHz, ^{31}P: 161.9 MHz) or Avance 250 (^{1}H: 250 MHz, ^{13}C: 62.8 MHz, ^{31}P: 101.2 MHz) spectrometers; chemical shifts are referenced to ext. TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P). Coupling constants are given as absolute values. Protons of phenyl and catechol rings are denoted by Ph and C_6H_3, respectively. ESI-MS spectra were measured on a Bruker Daltonics-micro-TOF-Q instrument using alkali halide containing MeOH as solvent. Observed ions were unequivocally identified by comparison of measured and simulated isotope patterns. IR spectra were measured on a Nicolet 6700 FT-IR spectrometer equipped with a diamond ATR unit. Elemental analyses were measured with a Perkin-Elmer 2400 CHSN/O analyser; deviations from calculated values are in case of solvates attributable to non-stoichiometric amounts of solvent. Melting points were determined in sealed capillaries.

Synthesis of [4]Cl

Dry DMF (12 ml) was added to a mixture of **1** (450 mg, 1.40 mmol), YCl_3 (68.3 mg, 0.35 mmol), $(COD)PdCl_2$ (208 mg, 0.70 mmol) and triethyl amine (0.51 ml, 3.65 mmol) and the resulting mixture was stirred at room temperature for 3 h. The dark-red suspension was filtered through a glass frit and the filtrate was stored overnight at −28 °C. White, needle like crystals of $[Et_3NH]Cl$ were removed by decantation. The supernatant solution was diluted with the same amount of diethyl ether, and the solution stored at room temperature until dark red, prismatic crystals separated. Filtration and drying of the solid product in vacuum (4 h at 100 °C) gave 741 mg (yield 65%) of product, mp 197 °C. ^{1}H NMR ($CDCl_3$): δ = 8.2 (broad s, DMF), 7.65 (broad m, 2 H, C_6H_5), 7.33 (broad m, 2 H, C_6H_5), 7.2–6.6 (m, 45 H, Ph and C_6H_3), 6.3–6.1 (m, 3 H, C_6H_3), 6.04 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, C_6H_3), 5.93 (d, $^3J_{HH}$ = 7.3 Hz, 1 H, C_6H_3), 5.85 (broad, s, 1 H, OH), 5.70 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, C_6H_3), 5.63 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, C_6H_3), 3.80–3.50 (br m, 3 H, CH_2), 3.34 (dd, $^2J_{PH}$ = $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 3.06 (d, $^2J_{PH}$ = 15 Hz, 2 H, CH_2), 2.73 (br, 1 H, CH_2), 2.95 (s, DMF), 2.81 (s, DMF), 2.48 (dd, $^2J_{PH}$ = $^2J_{HH}$ = 15 Hz, 1 H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 71 (broad), 66 (broad). (+)-ESI-MS: m/z = 1529.06 $(H_2L_4Pd_2Y)^+$, 787.01 $(HL_4Pd_2YNa_2)^{2+}$, 776.05 $(H_2L_4Pd_2YNa)^{2+}$, 765.03 $(H_3L_4Pd_2Y)^{2+}$, 743.07 $(H_2L_2PdNa)^+$, 510.36 $(H_4L_4Pd_2Y)^{3+}$. (−)-ESI-MS: m/z = 1527.06 $(L_4Pd_2Y)^-$.

Synthesis of [O(Y(dmf)L$_2$Pd)$_4$H]Cl$_3$ ([5]Cl$_3$)

Phosphine **1** (320 mg, 1.04 mmol), YCl_3 (101 mg, 0.52 mmol), $(COD)PdCl_2$ (148 mg, 0.52 mmol) and triethyl amine (0.36 ml, 2.59 mmol) were placed in a 100 ml Schlenk tube, DMF (8 ml) was added, and the reaction mixture was stirred at room temperature for 3 h. The dark red suspension was filtered through a glass frit and the filtrate was stored overnight at −28 °C. A precipitate of white, needle-like crystals of $[Et_3NH]Cl$ was formed and was separated by decantation. The supernatant solution was stored at room temperature until red crystals separated which were collected by filtration and dried in vacuum at 120 °C for 4 h to give 275 mg (60% yield) of product of mp 345 °C. ^{1}H NMR ($CDCl_3$): δ = 7.95 (s, broad, DMF), 7.7–6.7 (m, 80 H, Ph), 6.25 (t, $^3J_{HH}$ = 7.2 Hz, 8 H, C_6H_3), 6.13 (m, $^3J_{HH}$ = 8.7 Hz, 8 H, C_6H_3), 5.79 (t, $^3J_{HH}$ = 6.7 Hz, 8 H, C_6H_3), 4.2–4.0 (d, broad, 8 H, CH_2), 3.1–2.9 (d, broad, 8 H, CH_2), 2.9–2.85 (broad, DMF); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 69.8 (s). (+)-ESI-MS: m/z = 1644.95 $(OY_4L_8Pd_4NaF)^{2+}$, 1082.7 $(OY_4L_8Pd_4H)^{3+}$. FT-IR: 3354 (w), 3047 (w), 3009 (w), 1660 (m), 1572 (m), 1467 (s), 1454 (s), 1435 (s), 1318 (s), 1280 (s), 1223 (m), 1096 (m), 1010 (m), 865 (m), 735 (s), 688 (s) cm^{-1}. $C_{164}H_{148}Cl_3N_4O_{21}P_8Pd_4Y_4$ (3646.45, **5** × 4DMF): calcd C 54.02, H 4.09, N 1.54%, found C 53.14, H 4.04, N 1.20%.

Crystal structure determination

Suitable single crystals for X-ray diffraction studies were grown from concentrated solutions in DMF (**[5]Cl$_3$**) or DMF/Et_2O (1 : 1) (**[4]Cl**) at room temperature. Single-crystal X-ray diffraction studies were carried out on Bruker-Nonius Kappa CCD diffractometer at 123 K (**[4]Cl**) and 100 K (**[5]Cl$_3$**), respectively, using Mo-Kα radiation (λ = 0.71073 Å). Direct methods (SHELXS-97[18]) were used for structure solution and refinement (SHELXL-97,[18] full-matrix least-squares on F^2). Hydrogen atoms were refined using a riding model (H(O) in **[4]Cl** free). One free dmf in **[4]Cl** is disordered. One phenyl ring, one coordinated dmf, and hydrate water molecules in **[5]Cl$_3$** are disordered.

[4]Cl: red crystals, $[C_{76}H_{62}O_8P_4Pd_2Y\text{–}dmf]^+\cdot Cl^-$, 3 free dmf, M = 1856.68, crystal size 0.25 × 0.15 × 0.10 mm, monoclinic, space group $P2_1/n$ (No. 14): a = 19.804(4) Å, b = 20.246(4) Å, c = 21.280(4) Å, β = 98.08(2)°, V = 8448(3) Å^3, Z = 4, ρ (calcd) = 1.460 Mg m^{-3}, $F(000)$ = 3800, μ = 1.27 mm^{-1}, 56 587 reflections ($2\theta_{max}$ = 50°), 14 752 unique [R_{int} = 0.085], semi-empirical absorption correction from equivalents, max. and min. transmission 0.883 and 0.635, 1015 parameters, 171 restraints, R_1 ($I > 2\sigma(I)$) = 0.063, wR_2 (all data) = 0.120, GooF = 1.110, largest diff. peak and hole 0.72 and −0.84 e Å^{-3}.

[5]Cl$_3$: red crystals, $[C_{152}H_{121}O_{17}P_8Pd_4Y_4\text{–}4dmf]^{3+}\cdot 3Cl^-$, 12 free dmf, 5 hydrate water ($C_{200}H_{243}Cl_3N_{16}O_{38}P_8Pd_4Y_4$), M = 4614.45, crystal size 0.30 × 0.20 × 0.08 mm, triclinic, space group $P\bar{1}$ (No. 2): a = 16.3740(2) Å, b = 18.8825(2) Å,

c = 20.6120(3) Å, α = 67.152(1)°, β = 70.115(1)°, γ = 74.181(1)°, V = 5449.58(12) Å^3, Z = 1, ρ (calcd) = 1.406 Mg m^{-3}, $F(000)$ = 2370, μ = 1.54 mm^{-1}, 121 719 reflections ($2\theta_{\text{max}}$ = 56°), 26 720 unique [R_{int} = 0.119], numerical absorption correction, max. and min. transmission 0.877 and 0.646, 976 parameters, 603 restraints, R_1 ($I > 2\sigma(I)$) = 0.075, wR_2 (all data) = 0.214, GooF = 1.03, largest diff. peak and hole 1.64 and -1.52 e Å^{-3}.

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