# Template controlled self-assembly of bidentate phosphine complexes with hemilabile coordination behaviour†

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**Template-assisted self-assembly of ditopic catechol phosphines creates complexes containing a chelating diphosphine ligand, which display hemilabile coordination properties with prospects for applications in catalysis.**

Chelating bidentate phosphines are extremely useful ligands in catalysis due to their ability to enforce a rigid coordination environment at the metal and induce thus improved regio- and enantioselectivity.[1] In order to circumvent laborious syntheses which are often required to construct bidentate ligands with covalent backbones, lately a new concept based on the self-assembly of monodentate fragments in the coordination sphere of a metal atom was introduced.[2] The ligand backbone is hence formed *via* non-covalent interactions such as hydrogen bonding between fragments with complementary binding motifs,[2,3] or by the assembly of two fragments on a template. Available strategies for the latter include formation of coordinative bonds to a catalytically inactive metal ion such as $Zn^{2+}$,[2,4] or anion sequestering.[5]

We have recently reported[6] the synthesis of the phosphine $L^1$ (Scheme 1) which has the potential to act as a ditopic ligand with a hard catecholate and a soft phosphine binding site. Some time ago it has been demonstrated that the disposition of a related catechol phosphine $L^2$ for site-selective binding of hard and soft metal ions can be exploited for the designed synthesis of supramolecular heterometallic clusters[7] or the immobilisation of catalytically active complexes on metal oxide supports.[8] In view of the closer proximity of the donor centres and higher conformational flexibility of $L^1$ as compared to rigid $L^2$ we wondered if assembly of the catechol moieties of two molecules of $L^1$ to a suitable template and simultaneous binding of the phosphine units to a soft metal might allow the formation of molecular complexes in which the template-supported phosphine fragments mimic a chelate

ligand. Here, we describe the feasibility of accessing such species by self-assembly on a main-group template, and demonstrate that the bisphosphine ligand in the assembly formed shows hemilabile behaviour.

In view of the existence of stable spirocyclic catecholate complexes of tin[9] we began to study reactions of two molar equivalents of the phosphine $L^1$ with [PdCl$_2$(COD)] (**1**) and SnCl$_4$ or Me$_2$SnCl$_2$, respectively. The reaction proceeded readily in DMF–NEt$_3$ *via* self-assembly to afford the complexes **2a,b** (Scheme 2) which were isolated in moderate to good yield.‡ Both products were characterised by analytical and spectroscopic data and **2a** as well by a single-crystal X-ray diffraction study.§ The formation of **2a,b** was also observed when the reaction was carried out with an excess, or less than the stoichiometric quantity, of **1**.

The crystals of **2a** (Fig. 1) contain discrete complexes that lie on a crystallographic $C_2$ axis along with disordered solvent molecules (CH$_2$Cl$_2$). The tin atom features a distorted octahedral coordination by the oxygen atoms of two chelating catechol units and two chlorides. The oxygen atoms O1/O1′ act as μ$_2$-bridging ligands towards Sn and Pd, with the Sn–O1 bonds in the resulting planar SnO$_2$Pd-ring being distinctly longer (2.17 Å) than the Pd–O1 bonds (2.09 Å) or the Sn–O2 bonds to the terminal oxygen atoms (2.03 Å). The square-planar coordination sphere at Pd is completed by the two phosphorus atoms. The constraints of the polycyclic structure inflict a strictly pyramidal coordination at the μ$_2$-bridging oxygen atoms (sum of angles 323°) with a
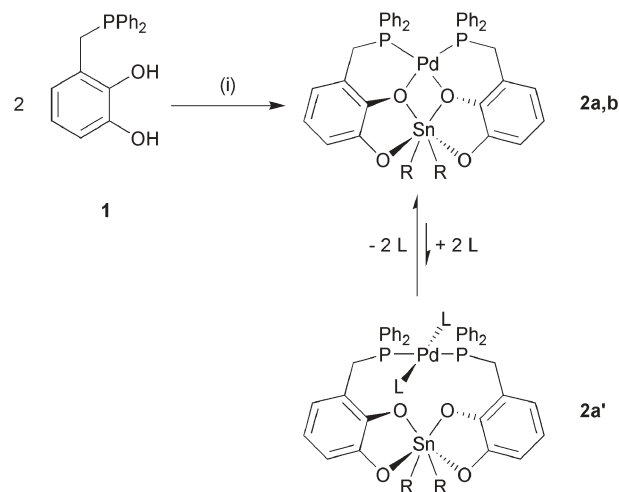


**Scheme 1** Catechol phosphines.

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† Electronic supplementary information (ESI) available: Descriptions of the syntheses and spectroscopic data of **2a,b**; details of catalytic and computational studies. See DOI: 10.1039/b616102b



**Scheme 2** Molecular bimetallic chelate complexes by self-assembly. R = Cl (**2a**), Me (**2b**); L = solvent (DMF or formamide). *Reagents and conditions*: (i) 1 equiv. R$_2$SnCl$_2$, 1 equiv. [(cyclooctadiene)PdCl$_2$], DMF–NEt$_3$.
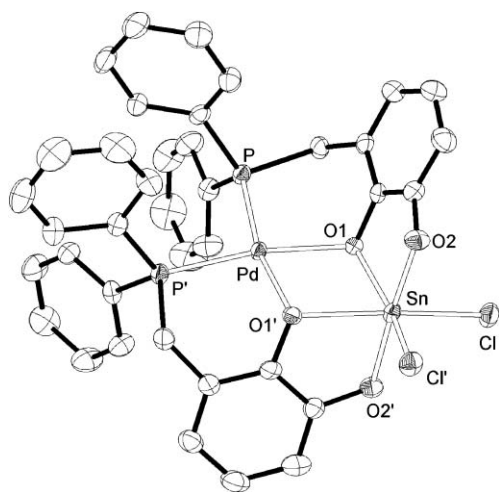
**Fig. 1** Molecular structure of **2a** in the crystal (H-atoms omitted; 50% probability thermal ellipsoids; atom labels with a prime (′) character indicate that these atoms are at equivalent position $(2 - x, y, 1/2 - z)$); selected distances (Å) and angles (°): Pd–O1 2.088(2), Pd–P 2.2519(10), O1–Sn 2.171(2), O2–Sn 2.033(3), Sn–Cl 2.3901(10); O1–Pd–O1′ 76.95(14), O1–Pd–P 168.55(7), P–Pd–P′ 98.78(5), O1–Sn–O1′ 73.49(13), Cl–Sn–Cl′ 104.28(5), O2–Sn–O1 103.58(11), O2–Sn–Cl 91.46(9).

*trans*-arrangement of the exocyclic O–C bonds at the SnO$_2$Pd-ring and a *cis*-arrangement of the phosphine moieties at Pd. The same constraints are presumably responsible for the substantial bond angle distortions around tin and palladium (*cf.* Fig. 1) which suggest that the assembly of the complex goes along with the build-up of some ring strain.

The $^{31}$P NMR spectra of **2a,b** at 30 °C in DMF show broadened lines ($\delta$ 76.4 (**2a**), 74.6 (**2b**)) at substantially higher chemical shifts than in the complex [*trans*-PdCl$_2$(**L$^1$**)$_2$] ($\delta$ 19.1) which is accessible from reaction of **L$^1$** and **1**; similar deshieldings had previously been observed for chelate complexes of related phosphinoalcohol ligands.[10] The observation of tin-satellites in the $^{31}$P{$^1$H} and a triplet in the $^{119}$Sn{$^1$H} NMR spectrum of **2b** ($\delta$ −199.4, $J_{Sn,P}$ = 15 Hz) disclosed that the bimetallic aggregate remains kinetically stable and does not undergo ligand exchange (a $^{119}$Sn NMR signal of **2a** was unobservable in solution owing to its much lower solubility but the $^{119}$Sn CP-MAS NMR spectrum of a solid sample shows one isotropic line at $\delta_{iso}$ = −455).

The $^{31}$P NMR signals of **2a,b** sharpened eventually upon cooling to −30 °C. Surprisingly, further cooling of a solution of **2a** lead to the appearance of a new $^{31}$P NMR signal ($\delta$ 55.5) which grew in intensity when the temperature was lowered to −55 °C. All changes were reversible upon warming to ambient temperature. We attribute the new signal to a second species **2a′** which is, according to 2D $^{31}$P EXSY spectra, in dynamic exchange with **2a**. Assuming that this exchange can be described as a pseudo-unimolecular reaction **2a** ⇆ **2a′**, evaluation of the temperature dependence of the equilibrium constant $K$ = [**2a′**]/[**2a**] yields values of $\Delta H$ = −5.4 kcal mol$^{-1}$ and $\Delta S$ = −26 cal mol$^{-1}$ K$^{-1}$. Careful analysis of the results of low-temperature NMR studies of solutions of **2b** suggested that similar dynamic equilibria are likewise present even if the unambiguous identification of a transient species was in this case precluded due to its much lower concentration.

The $^1$H NMR signals of the CH$_2$ and phenyl protons of **2a** are likewise broad at 30 °C and decoalesce at −50 °C into two sets of signals, indicating that the geminal protons and phenyl rings in the Ph$_2$PCH$_2$-units become chemically inequivalent. The analogous $^1$H NMR signals of **2a′** (which were identified in 2D NMR spectra) did not split up but it is currently unclear if this results from the failure to reach the slow-exchange regime (because of accidental near-degeneracy of the chemical shifts at exchanging sites), or if the geminal protons and phenyl rings remain equivalent.

Interpretation of the dynamic phenomena observed is feasible by assuming that **2a′** arises from coordination of extra solvent molecules to **2a** in a process which is favoured by enthalpy and disfavoured by entropy. As the available experimental data allow no unequivocal assignment of the molecular structure of **2a′**, we performed DFT calculations[11] in order to model the interaction of **2a** with formamide in the gas phase and decide if the new donors bind preferably to tin or to palladium. The results of these studies suggested that formation of a macrocyclic complex with *trans*-configuration at Pd (*cf.* Scheme 2 and Fig. 2) is favoured by 3.6 kcal mol$^{-1}$ over coordination of formamide to tin. Since all attempts to locate further stationary points on the energy hypersurface (*e.g.* representing complexes with *cis*-configuration at Pd or *trans*-configuration at Sn) failed, we conclude that the found molecular structure is most likely to represent that of the transient complex **2a′**. The failure to resolve the diastereotopic CH$_2$ protons in the low-temperature $^1$H NMR spectra and the high $^{31}$P chemical shift of **2b** compared to [PdCl$_2$(**L$^1$**)$_2$] impose no plain contradictions to this assignment as it cannot be ruled out that the former is caused by rapid dynamic racemisation of the chiral coordination environment at tin (which is facilitated by the dissociation of the O-donors from Pd and removes the inequivalence between diastereotopic geminal sites)[12] or accidental near-degeneracy of chemical shifts whereas the latter is attributable to the zwitterionic nature of **2b**.

In view of the easy replacement of the catechol oxygens from Pd, **2a** can be viewed as a Pd-complex with a hemilabile ligand that can switch between tetradentate O$_2$P$_2$ and bidentate P$_2$
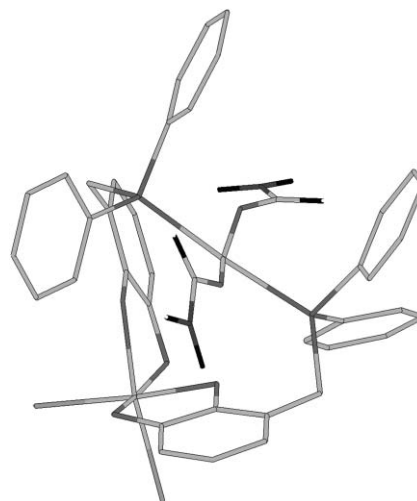


**Fig. 2** Wire-model of the energy optimised molecular structure of the solvent adduct **2a**·2H$_2$NCHO (at the b3lyp/3-21g* level of theory).

coordination. As it appears likely that the solvent molecules in **2a′** are further displaceable by other donors, a similar catalytic activity as for other Pd-phosphine complexes is anticipated. A first confirmation of this hypothesis was obtained from the successful application of **2a,b** as catalysts in the Sonogashira coupling[13] of *para*-iodonitrobenzene with phenyl acetylene. The stability of the bimetallic complex under catalytic conditions was, in the case of **2b**, indicated by the finding that the catalyst could be recovered during the work-up and reused for further catalytic transformations.

In summary, the synthesis of discrete complexes containing a hard main-group and a soft transition metal by self-assembly of simple metal precursors and bifunctional phosphine–catecholate ligands has been demonstrated. The products are distinguished from known heterobimetallic complexes of phosphinoalcohols in requiring neither the dedicated synthesis of a polydentate chelate ligand[14] nor the need for introducing the metal atoms in separate reaction steps.[15] The coordination of the soft Pd-atom by μ-bridging catecholate oxygen atoms that are easily displaceable by donor solvents can be viewed in terms of hemilabile coordination properties. Studies of the impact of the hemilabile behaviour on the catalytic properties of such complexes as well as the assembly of complexes containing other main-group and transition-metal atoms are currently under investigation.

## Notes and references

‡ *Experimental procedure*: A mixture of **L**[1] (600 mg, 1.95 mmol), SnCl$_4$ (1.1 ml, 0.97 mmol), **1** (280 mg, 0.97 mmol) and NEt$_3$ (0.8 ml, 5.7 mmol) in dry DMF (20 ml) was stirred for 24 h at room temperature. The red suspension was filtered through Celite. Solvents were evaporated in vacuum and the residue washed with CH$_2$Cl$_2$ (10 ml) and dissolved in a small amount of DMF. The same volume of CH$_2$Cl$_2$ and, finally, small portions of diethyl ether were added until a precipitate began to form. The mixture was stored overnight at 4 °C to yield a microcrystalline solid which was collected by filtration and dried in vacuum for 4 h at 70 °C to yield 40% of **2a**, mp 214 °C (decomp.). Elemental analysis (%). Calc. for **2a**·DMF: C 50.16, H 3.80, N 1.43. Found: C 49.92, H 3.77, N 1.58. **2b** was obtained by an analogous procedure from **L**[1], **1** and Me$_2$SnCl$_2$, and isolated as red crystals (mp 310 °C (decomp.)) in 95% yield. Elemental analysis (%). Calc. for **2b**·DMF: C 54.78, H 4.81, N 1.49. Found: C 54.68, H 4.78, N 1.41. Detailed descriptions of synthetic procedures and characterisation data are available as ESI.†

§ *Crystal structure analysis*: single crystals of a solvate **2a**·3CH$_2$Cl$_2$ were obtained from DMF–CH$_2$Cl$_2$ (4 : 1); Siemens P4 diffractometer, $T$ = 173(2) K, Mo-Kα radiation ($\lambda$ = 0.710 73 Å), SHELX97 for structure solution (direct methods) and refinement (full-matrix, least squares refined against $F^2$). The positions of the hydrogen atoms were refined with a riding model; the contribution of the severely disordered CH$_2$Cl$_2$ molecules in solvent accessible cavities of the structure was eliminated from the reflection data, using the BYPASS method[16] as implemented in the SQUEEZE routine of the PLATON98 package; orange–red crystals, C$_{38}$H$_{30}$Cl$_2$O$_4$P$_2$PdSn; $M$ = 908.56; crystal size 0.40 × 0.15 × 0.08 mm; monoclinic, space group P2/c (no. 13), $a$ = 12.227(2), $b$ = 11.707(2), $c$ = 16.475(3) Å, $\beta$ = 102.516(12)°, $V$ = 2302.2(7) Å$^3$, $Z$ = 2, $\mu$ = 1.149 mm$^{-1}$, semi-empirical absorption correction by using ψ-scans, min/max. abs. 0.589/0.923, $F(000)$ = 900, $\theta_{max}$ = 28°; 6056 reflections of which 5523 were independent; $R_1$ = 0.045 (for $I > 2\sigma(I)$), w$R_2$ = 0.125 (all data). CCDC 616084. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616102b

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