Coordination Chemistry

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A Cavity-Shaped Diphosphane Displaying "Oschelating" Behavior**

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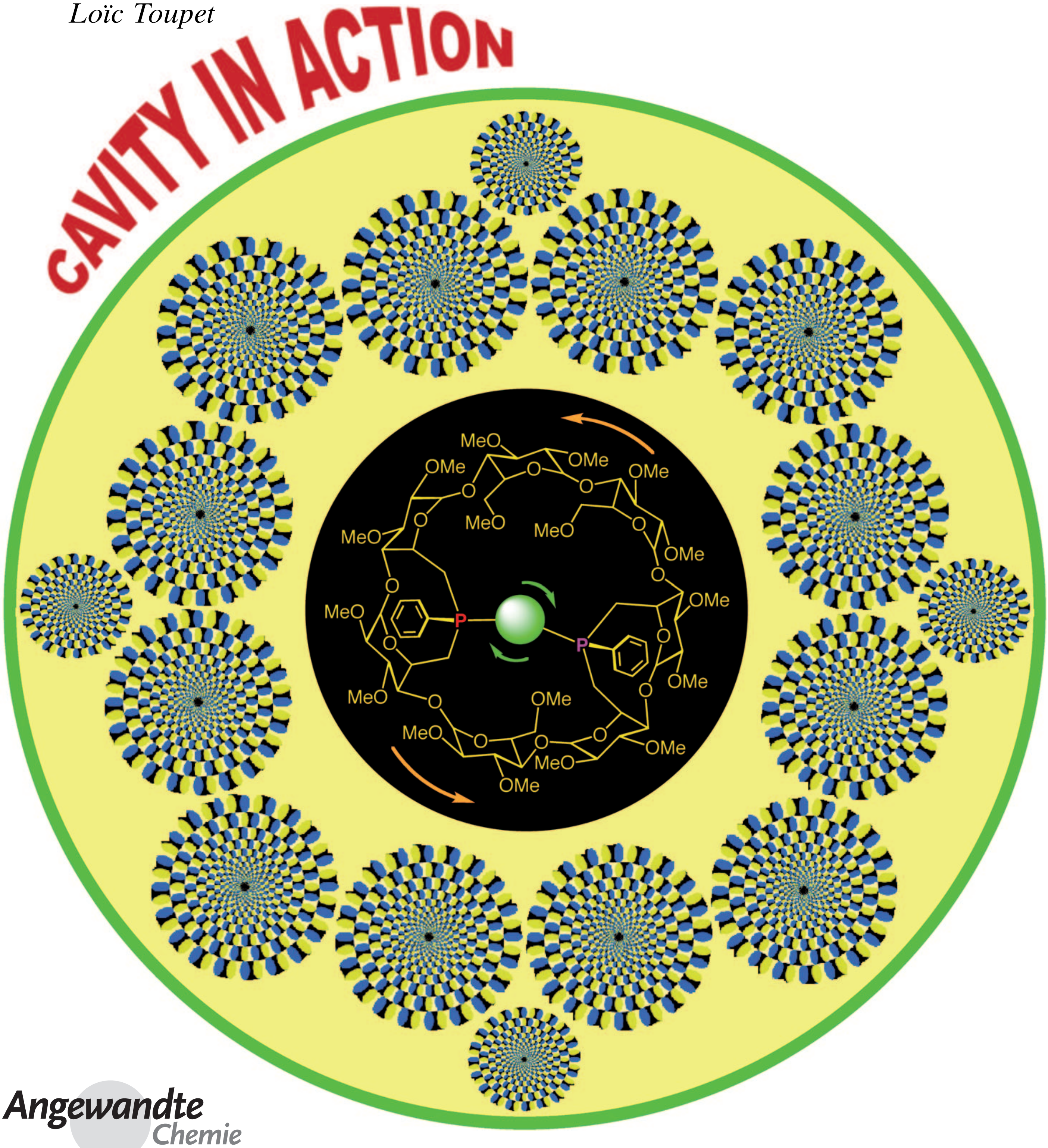

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Molecules that combine the properties of a transition metal with those of an appended cavity have attracted a great deal of attention.[1–3] So far, research in this area has focused on four main objectives: 1) the design and synthesis of systems exploiting the binding properties of a receptor unit linked to a transition-metal center, with the aim of producing catalysts that mimic an enzyme;[4–8] 2) the study of metal-centered reactions taking place in a confined environment, thereby favoring highly regio-, stereo-, and shape-selective reactions;[9–13] 3) the metal-assisted entrapment and recognition of ionic species;[14–16] 4) the construction of sensors capitalizing on an electro- or photoactive metal unit covalently attached to a close, cavity-shaped receptor.[17,18]

While the coordination chemistry of many multitopic ligands giving rise to 3D architectures such as capsules, cages, bowls, and boxes has been thoroughly investigated,[19–25] the use of such ligands for generating oscillatory motion about a metal ion has not been considered yet, although examples of transition metals moving around the periphery of such an object are known.[26] Herein we show how a cavity bearing two introverted donor atoms may behave as a balance wheel swinging about a central metal unit. Our approach is based on the use of a rigid, cyclodextrin-based diphosphane characterized by a long P$\cdots$P separation, which results in highly unsymmetrical chelation.

Diphosphane **6** was obtained in 20 % overall yield according to Scheme 1. Its synthesis began with a regioselective double capping of native β-cyclodextrin (β-CD) using the bulky dialkylating reagent **1**.[27] The non-alkylated hydroxy groups were subsequently methylated with NaH/MeI, resulting in the *ABDE*-functionalized intermediate **2** (yield 50 %). Deprotection with HBF_4, leading to tetrol **3**, followed by reaction with mesyl chloride in pyridine afforded tetramesylate **4**. Reaction of the latter with Li_2PPh in THF gave diphosphane **6** in approximately 70 % yield along with two other, unidentified products. Workup required the preparation of the diborane adduct **5**, which was separated chromatographically. Finally, **5** was treated with $HNEt_2$ to afford **6** quantitatively. As expected, the ^{31}P NMR spectrum of **6** in C_6D_6 shows two very close singlets, seen at $\delta = -15.0$ and -15.2 ppm, respectively (in $CDCl_3$ the spectrum showed only a unique peak). Prolonged standing in air of a solution of **6** in MeOH produced the di(phosphane oxide) **7**, the structure of which was determined by an X-ray diffraction study (Figure 1). In the solid state, the two P=O vectors of **7** point towards the interior of the cavity, the P$\cdots$P separation being 6.91 Å. Two nonbridged glucose units are tipped towards the CD axis, reflecting some strain within the CD.

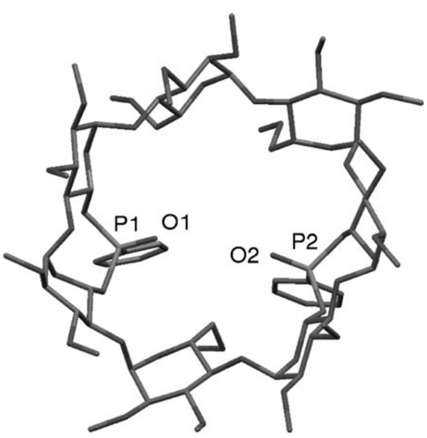

Figure 1. X-ray structure of the di(phosphane oxide) **7** (view from the secondary face). Solvent molecules have been omitted. Selected distances [Å]: P1–P2 6.91; O1–O2 4.32.

Despite the long separation between the two phosphorus atoms, diphosphane **6** turned out to be suitable for chelation. Thus, for example, reaction with $[Au(tht)(thf)]PF_6$ (tht = tetrahydrothiophene; thf = tetrahydrofuran) led quantitatively to complex **8** (Scheme 2). The mass spectrum of **8** showed an intense peak at m/z 1717.62 having exactly the isotopic profile expected for $[Au\cdot\mathbf{6}]^+$. Furthermore, the ^{31}P NMR (CD_2Cl_2, 25 °C) spectrum displayed an AB pattern with a J(PP) coupling constant of 326 Hz, which is in accord with a very large bite angle. In fact, molecular models indicate that the bite angle is close to 160°; in other terms the ligand cannot behave as a perfect *trans*-chelator. The good chelating properties of **6** were further confirmed by its reaction with $[PdCl_2(PhCN)_2]$, $[PtCl_2(PhCN)_2]$, and $[\{RhCl(CO)_2\}_2]$, leading to the chelate complexes **9**–**11**, respectively, in 100 % yield (Scheme 2 and the Supporting Information). As in **8**, the corresponding large J(PP′) coupling constants (see the Supporting Information) reflect the large bite angle of the ligand.[28,29]

As shown by a variable-temperature NMR study, complex **10** displays fluxional behavior in solution. The ^{31}P NMR (CD_2Cl_2) spectrum of **10**, measured at -80 °C, revealed the presence of two species (**10a** and **10b**) present in a 1:1 ratio, each characterized by an ABX pattern (^2J(AB) = 492 and 476 Hz, respectively; ^1J(PPt) coupling poorly resolved; Figure 2, bottom). Upon raising the temperature, the signals first broadened, then coalesced near -15 °C, and finally merged into a single ABX spectrum (^2J(AB) = 496 Hz, ^1J(PPt) = 2510 Hz; Figure 2, top). The observed data are consistent with exchange between two complexes both of which contain a close to linear P-Pt-P unit. A variable-temperature ^{1}H NMR study was also carried out which confirmed the 1:1 stoichiometry of the equilibrating species. Both series of experiments led to a free energy of activation $\Delta G^{\neq} = (11.3 \pm 0.2)$ kcal mol^{-1}. Interestingly, the low-temper-

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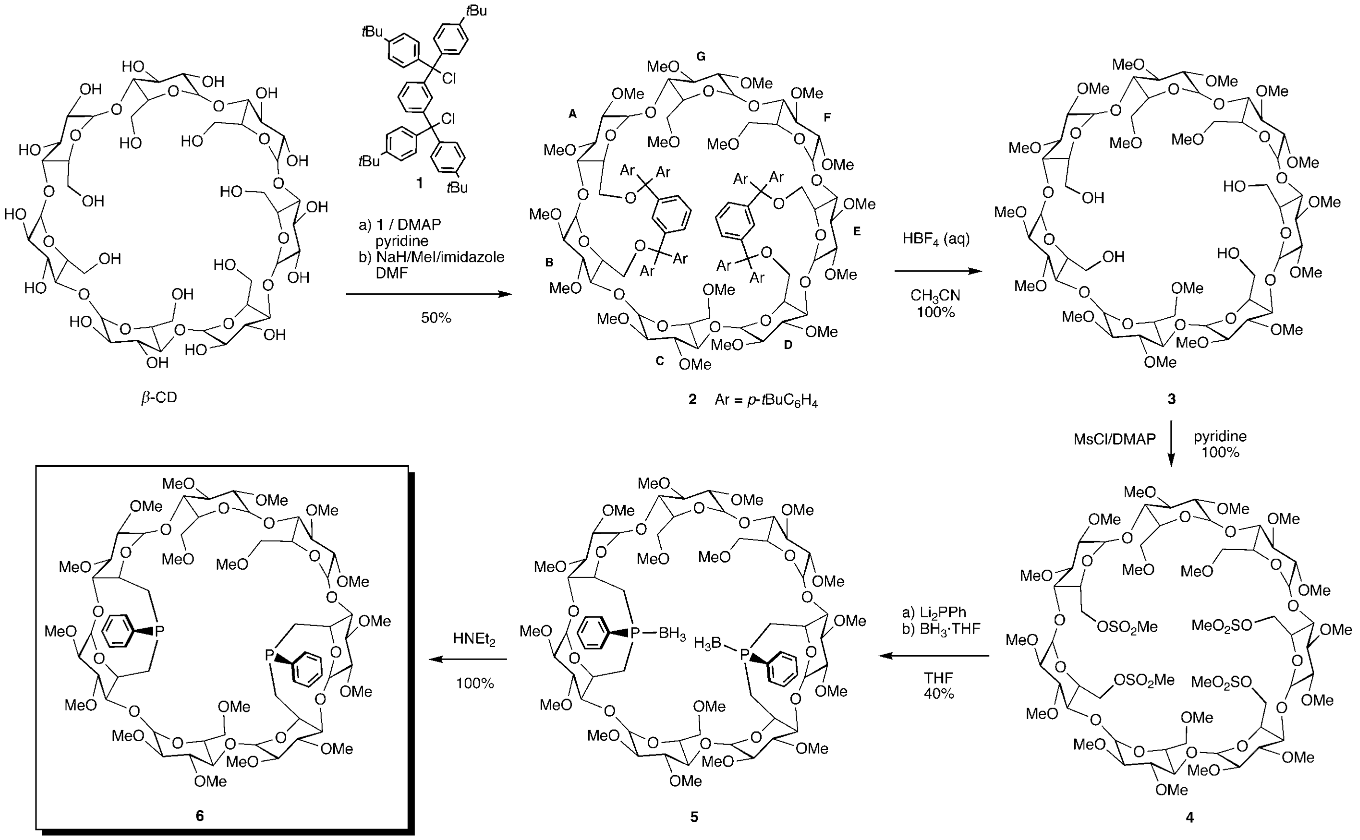


Scheme 1. Stepwise buildup of **6**. DMAP = 4-dimethylaminopyridine; Ms = methanesulfonyl.

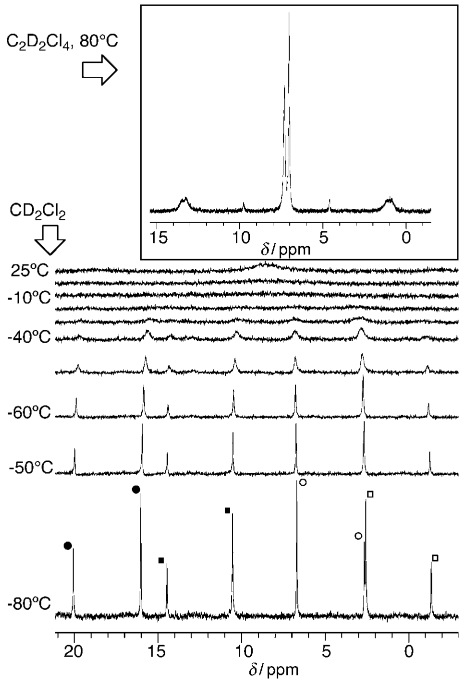
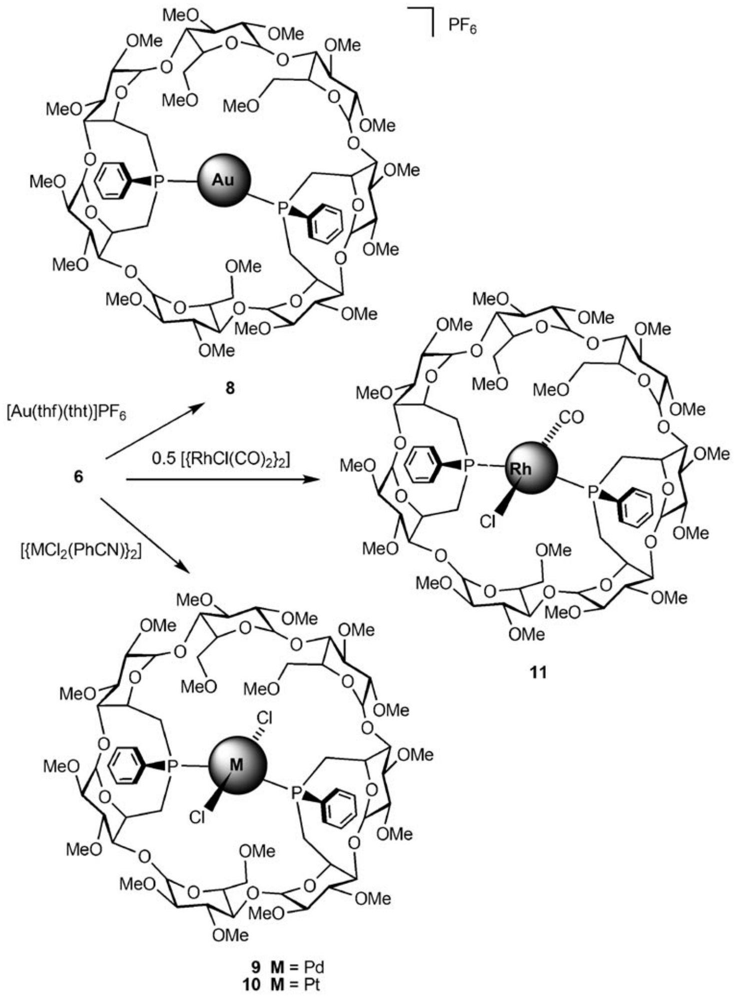


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR study of platinum complex **10**. The AB patterns of the two equilibrating species are represented by dots and squares. Filled symbols are for the A parts, open symbols for the B parts.

ature ^{31}P NMR spectra revealed two AB patterns with a large separation between the A and B parts (ca. 12 ppm), indicating that the two P atoms of each complex are coordinated to the platinum atom with unequal strength. Note that one of the phosphorus signals appears near the midpoint between the signal of the free ligand and that of the other signal. As shown by an off-resonance $^{31}P\{^1H\}$-$^{31}P\{^1H\}$ ROESY NMR experiment (see the Supporting Information), the "strongly" coordinated phosphorus atom of each species is in exchange with the "weakly" coordinated phosphorus atom of the other isomer.

Overall, the best way to describe these findings is to consider that the $d_{x^2-y^2}$ orbital involved in formation of the M−P bonds changes its orientation in a pendular fashion so as to adopt in alternation different overlaps with each of the two convergent, but nonaligned phosphorus lone pairs. Consequently, metal binding to the two phosphorus donors is nonequivalent in a given species (Scheme 3). The observed isomerization is probably also accompanied by a slight displacement of the metal center. Thus, being unable to form an authentic *trans* complex (i.e. with a P-M-P angle of 180°), diphosphane **6** may be regarded as a frustrated chelator, which compensates the metal electron deficiency generated at one coordination site by oscillating about the complexed metal ion. We propose to term this type of bidentate ligand an oschelating (contraction of "oscillating" and "chelating") species. It is worth mentioning here that the



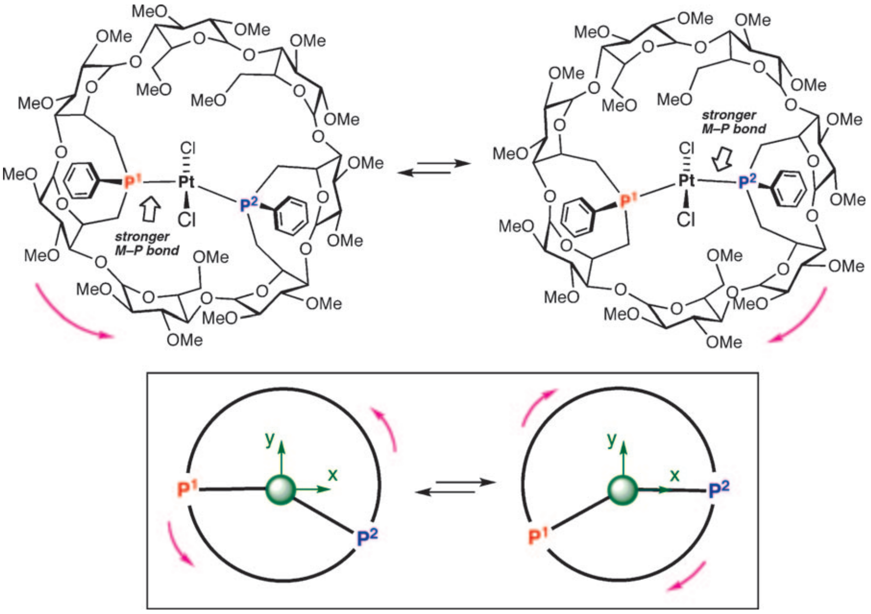
Scheme 2. Synthesis of complexes **8**–**11**.

observed fluxionality is different from that found in complexes containing hemilabile ligands, the latter leading to intermediates in which one end is totally dissociated.[30–33] It should be emphasized that similar dynamics (with comparable activation energies) were observed for all three oschelated complexes **8**, **9**, and **11**. Furthermore, for all four complexes investigated, the $J(PP')$ coupling constants persisted over the temperature range −80 °C to +80 °C. In other words, the observed dynamic behavior occurs without dissociation of the M−P bonds. This phenomenon may be regarded as a variant of bond-stretch isomerism.[34,35]

We anticipated that the dynamic nature of **6** in the chelate complexes would weaken the P−M bonds. In fact, treatment of **9** with $[PdCl_2(PhCN)_2]$ led formally to insertion of a $PdCl_2$ fragment into one of the Pd−P bonds of **9**. The resulting complex **12** crystallized with a water molecule coordinated to one of the palladium atoms (Scheme 4, Figure 3). It is likely that owing to its rigidity, diphosphane **6** cannot adapt to a $\{Pd_2Cl_2(\mu\text{-}Cl)_2\}$ fragment having the usual flat or roof structure and therefore prefers to cap a $\{Pd_2Cl_4\}$ unit having only a single chlorido bridge. Another reaction directly related to the oschelating behavior of **6** is the reaction between **9** and O_2/H_2O in methanol, leading to equimolar amounts of complexes **13** and **14** (Scheme 4). Complex **13**, which was characterized by an X-ray diffraction study, is seemingly formed by cleavage of one of the Pd−P bonds and its substitution by a bond to H_2O, followed by oxidation of the dissociated P atom. Complex **14**, the structure of which was unambiguously determined by multidimensional NMR analysis,[36] corresponds to a complex in which the other Pd−P bond has been cleaved, but in this case the phosphane oxide moiety formed is coordinated to the metal atom, as deduced from the existence of a $^3J(PP')$ coupling constant (4.4 Hz).

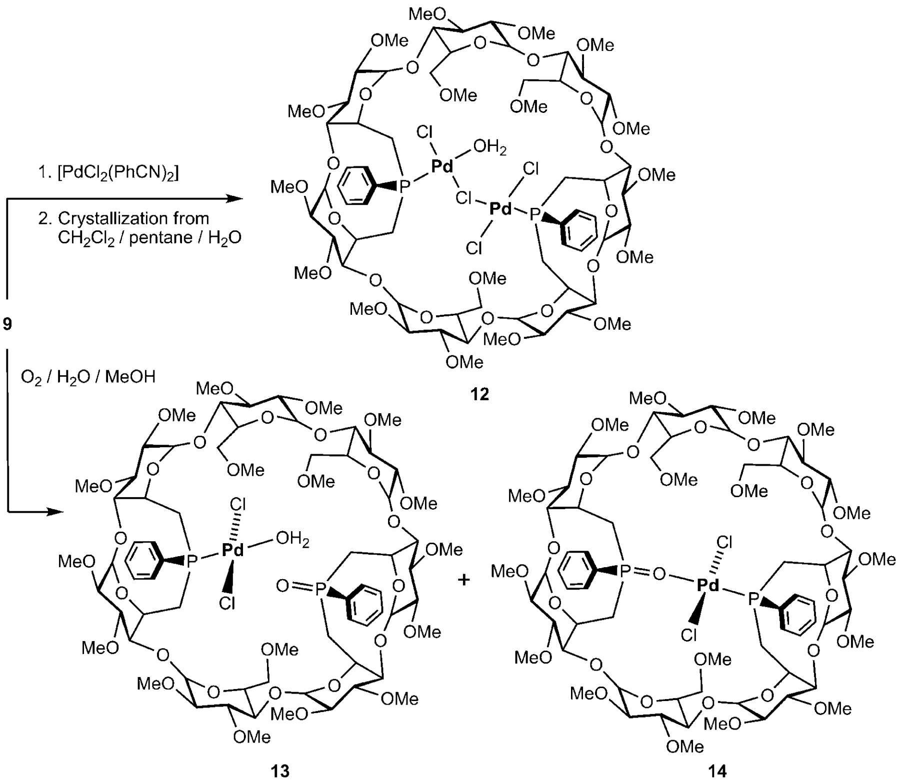
It is interesting to note that complexes **12** and **13** both contain a "$\{(\text{phosphane})PdX_2(H_2O)\}$" unit, thus constituting rare examples of $[LL'PdX_2]$ complexes containing a unique monophosphane ligand. Overall, the coordinative properties of **6** are markedly different from those of the previously reported α-CD analogue (TRANSDIP).[37]

In conclusion, by using a capping methodology that relies on the use of the bulky dialkylating agent **1**, we have synthesized the first large-bite-angle diphosphane (**6**) based on a β-CD backbone. Owing to the rigidity of this ligand as well as the large



Scheme 3. Balance wheel movement of ligand **6** in complex **10** (view along the CD axis). The green arrows in the lower part indicate the orientations of the $d_{x^2-y^2}$ orbital involved in formation of the two M−P bonds.

separation between the phosphorus atoms, **6** behaves towards transition-metal ions as an unsymmetrical chelator, inducing rapid oscillation of the chelate about the coordinated metal center. This phenomenon occurs without dissociation of the phosphorus atoms. The unprecedented chelating behavior of **6** enables the formation of monophosphane complexes located inside a CD, thereby opening a way to the further study of organometallic catalysts operating in a confined environment.



Scheme 4. Breaking the P–Pd bonds of **9**.

Experimental Section

Full experimental details including X-ray structural data are given in the Supporting Information. CCDC 756653 (**7**), 758028 (**12**), and 770728 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6: $^{31}\text{P}\{^{1}\text{H}\}$ NMR (202.5 MHz, C_6D_6, 25 °C): $\delta = -15.0$ (s), -15.2 ppm (s).

8: $^{31}\text{P}\{^{1}\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2, −80 °C): $\delta = 40.6$ and 31.6 (AB system, $^{2}J_{P1,P2} = 326$ Hz), 38.0 and 33.8 (AB system, $^{2}J_{P1,P2} = 326$ Hz), −144.3 ppm (hept, $^{1}J_{P,F} = 716$ Hz).

9: $^{31}\text{P}\{^{1}\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2, −80 °C) = 21.7 and 11.4 (2 d, AB system, $^{2}J_{P1,P2} = 564$ Hz), 17.7 and 5.6 ppm (2 d, AB system, $^{2}J_{P1,P2} = 549$ Hz).

10: $^{31}\text{P}\{^{1}\text{H}\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 8.9$ ppm (br s with br Pt satellites, $^{1}J_{P,Pt} \approx 2500$ Hz); $^{31}\text{P}\{^{1}\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2, −80 °C) = 0.97 and 12.20 (2 d, AB system, $^{2}J_{P1,P2} = 476$ Hz), 5.02 and 17.76 ppm (2 d, AB system, $^{2}J_{P1,P2} = 492$ Hz) ($^{1}J_{Pt,P}$ poorly resolved); $^{31}\text{P}\{^{1}\text{H}\}$ NMR (202.5 MHz, $C_2D_2Cl_4$, +80 °C) = 7.04 and 7.35 ppm (2 d with Pt satellites, ABX system, $^{1}J_{Pt,P1} = 2507$ Hz, $^{1}J_{Pt,P2} = 2481$ Hz, $^{2}J_{P1,P2} = 496$ Hz).

11: $^{31}\text{P}\{^{1}\text{H}\}$ NMR (162.0 MHz, CD_2Cl_2, −80 °C) = 28.0 and 9.4 (2 dd, ABX system, $^{2}J_{P1,P2} = 354$ Hz, $^{1}J_{P,Rh} = 118$ and 118 Hz), 16.4 and 9.4 ppm (2 dd, ABX system, $^{2}J_{P1,P2} = 354$ Hz, $^{1}J_{P,Rh} = 118$ and 118 Hz).

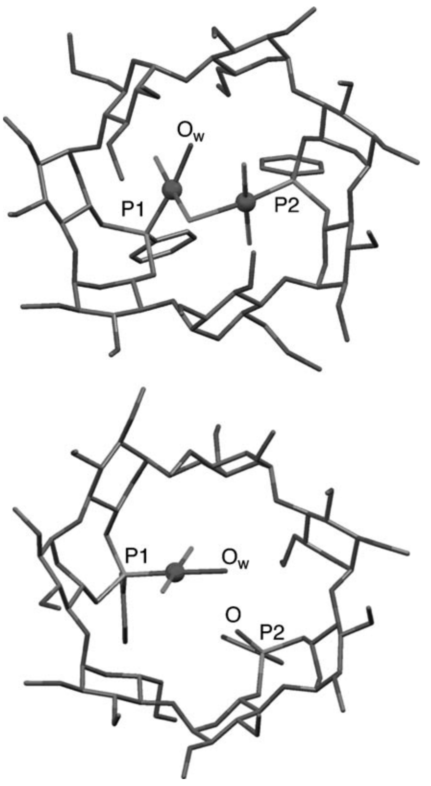


Figure 3. X-ray crystal structures of dinuclear complex **12** (top) and the monophosphane Pd complex **13** (bottom). Distances between the phosphorus atoms [Å]: 6.29 (**12**) and 6.60 (**13**) (cf. 6.91 Å in **7**). The short $O_{water}\cdots O(P)$ separation (2.61 Å) in **13** is indicative of a hydrogen bond between the coordinated water molecule and the phosphoryl group.

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