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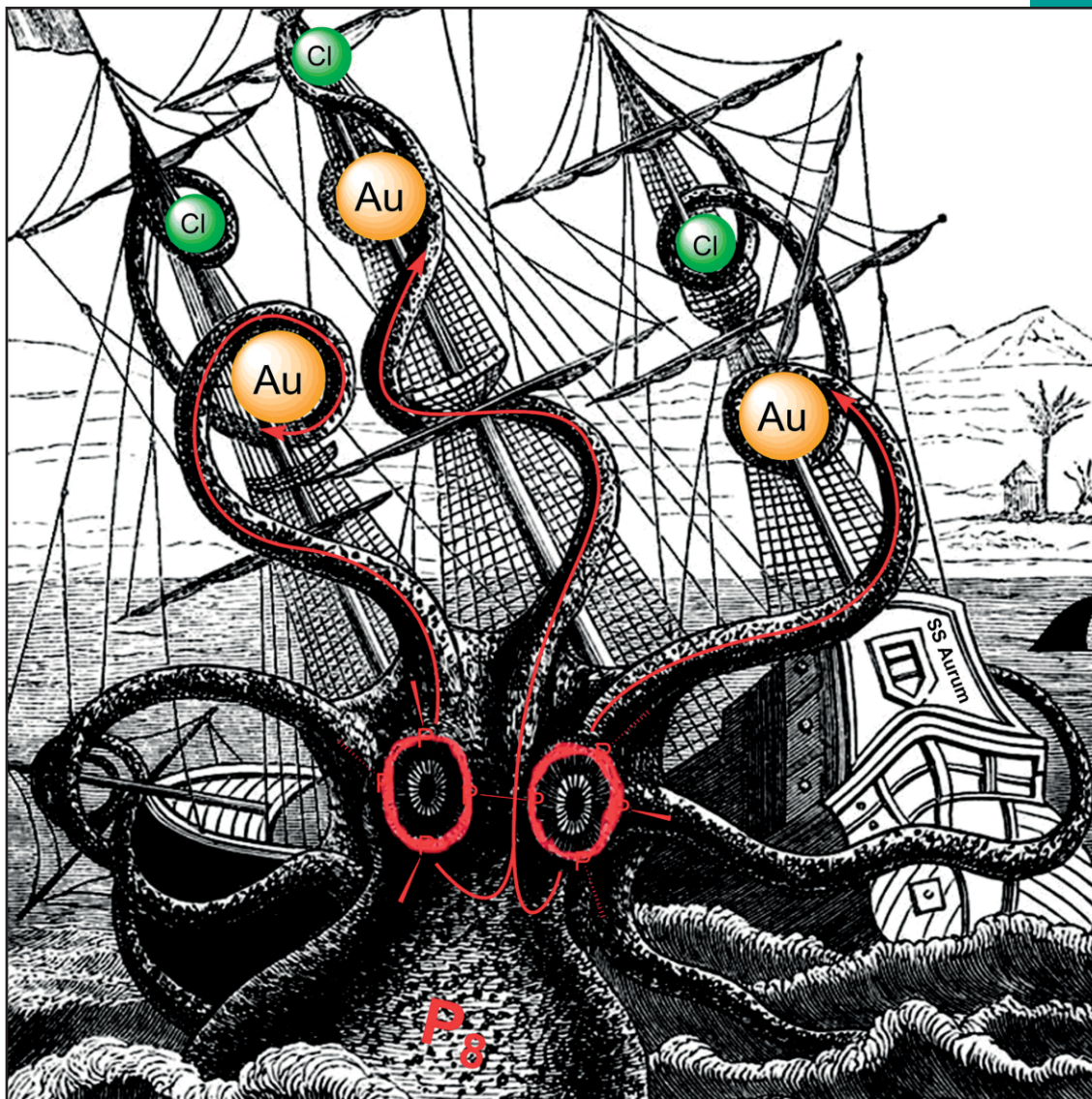
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## Front Cover

Toni Grell and Evamarie Hey-Hawkins

Dynamic Gold(I) Complexes of Hexa-*tert*-butyl-octaphosphane

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## Dynamic Gold(II) Complexes of Hexa-*tert*-butyl-octaphosphane



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Invited for the cover of this issue is the group of Evamarie Hey-Hawkins, Leipzig University, Germany. The cover image shows a huge octopus wrecking a ship, which symbolizes the coordination behavior of the studied ligand.

### What is the most significant result of this study?

Even though merely one kind of metal precursor with rather unspectacular coordination behavior and one rather rigid ligand were chosen for this study, three complexes that exhibit an unusual coordination environment of the gold(II) atom and interesting dynamic behavior in solution were obtained. The main reason for this is the presence of multiple phosphorus atoms.

### What experimental technique is most powerful to you and why?

$^{31}\text{P}$  NMR spectroscopy is extremely powerful for our studies and the molecules seem to be made for it! The direct connection of the phosphorus atoms in these compounds results in very complex higher-order spectra, which are also amazingly beautiful. The simulation of these spectra delivers information about the constitution, configuration, and even conformation of our molecules. Additionally, single-crystal X-ray diffraction is an indispensable tool for verifying the identity of our molecules.

### What are the main challenges in the broad area of your research?

Making the ligands. The preparation of phosphorus-rich molecules is challenging because the syntheses are usually rather unselective and might also require a tedious workup (for an extreme example, see ZAAC, **1989**, 578, 7–17). This is also the reason why the coordination behavior of the octaphosphane in our current study has never been investigated, even though it was known before. Nevertheless, the current work shows that also the coordination behavior can be quite complex. Elucidating and understanding the mismatch between the solid-state and solution structures took us some time.

### Is your current research mainly fundamental or rather applied?

Unambiguously, it is rather fundamental, as we wish to understand the nature and properties of oligophosphane complexes. Nevertheless, these molecules are also suited for applications. In the past we could demonstrate that they can be converted to phosphorus-rich metal phosphides, which are very interesting materials that are otherwise difficult to obtain (e.g., *ChemPlus-Chem* **2012**, 77, 341–344), and shortly, we will publish further investigations of such precursors.

### Who pays the bill for the research highlighted on the cover?

We thank the Studienstiftung des deutschen Volkes (doctoral grant for T.G.) and the Graduate School BuildMoNa as well as Leipzig University for support.

### What is the inspiration of the cover design?

Most people do not know that an octopus has six arms and two legs (and not eight legs). Likewise, our **octa**phosphane has six arms (P atoms with a *t*Bu group) and two legs (P atoms without organic groups). While searching for pictures with octopuses, we stumbled across this old painting and found the analogy with the three-masted ship (three gold atoms) attacked by the octopus (coordinating ligand) to be just perfect. The attentive observer may also find another deadly animal in the background of the picture and wonder what it may symbolize...



Front Cover  
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Dynamic Gold(II) Complexes of Hexa-*tert*-butyl-octaphosphane



## Oligophosphane Complexes

Dynamic Gold(I) Complexes of Hexa-*tert*-butyl-octaphosphaneToni Grell<sup>[a]</sup> and Evamarie Hey-Hawkins<sup>\*[a]</sup>

**Abstract:** A facile synthesis for {*cyclo*-(P<sub>4</sub>tBu<sub>3</sub>)<sub>2</sub>} (**1**) is reported making the phosphane available for follow-up chemistry. Octaphosphane **1** reacts with [AuCl(tht)] (tht = tetrahydrothiophene) to give a monometallic {[AuCl(**1**-κ<sup>2</sup>P<sup>2</sup>,P<sup>4</sup>)]}, **2**, bimetallic {[AuCl]<sub>2</sub>(**1**-κ<sup>2</sup>P<sup>2</sup>,P<sup>4</sup>,κP<sup>2</sup>)}, **3** and trimetallic complex {[AuCl]<sub>3</sub>(**1**-κ<sup>2</sup>P<sup>2</sup>,P<sup>4</sup>,κP<sup>2</sup>,κP<sup>4</sup>)}, **4** in which up to four phosphorus atoms of the ligand are involved in coordination. In each of these com-

plexes one gold(I) atom is chelated in an unusual distorted T-shaped coordination mode which undergoes a rapid exchange between both donor atoms in solution. This mode of coordination in combination with the flexibility of the phosphane ligand moreover gives rise to an interesting dynamic behavior of the monometallic complex **2** which was elucidated by NMR spectroscopy, X-ray crystallography and DFT calculations.

Since the synthesis of "Phosphabenzol" published by Köhler and Michaelis in 1877,<sup>[1]</sup> the chemical library of phosphorus-rich compounds was vastly extended, especially in the last four decades. Undoubtedly, the most important contribution was the pioneering work of Baudler who synthesized and characterized a large number of catenated, cyclic and polycyclic oligophosphanes<sup>[2,3]</sup> thereby revealing that phosphorus is capable of constitutional, configurational and conformational isomerism. As was shown later, also the formation of unsaturated<sup>[4]</sup> and even aromatic compounds<sup>[5]</sup> is possible which is one of the reasons why phosphorus is referred to as the carbon copy.<sup>[6]</sup>

Even though numerous phosphorus-rich compounds are known to date, their follow-up chemistry is considerably less investigated. One reason is their pronounced tendency to undergo transformation reactions to other phosphanes at much lower temperatures than organic molecules which can make the isolation of some of them virtually impossible, e.g. the hydrides P<sub>n</sub>H<sub>n+2</sub>.<sup>[3]</sup> The second reason is that the synthesis of many oligophosphanes is rather unselective, and extremely tedious procedures may be required to obtain a pure compound, as for instance in the isolation of {*cyclo*-(P<sub>4</sub>tBu<sub>3</sub>)<sub>2</sub>}PtBu.<sup>[7]</sup> Nevertheless, due to the variety of donor atoms and thus binding modes the coordination chemistry of these compounds is fascinating as the very few investigations already show.<sup>[2]</sup> For example, the reaction of P<sub>7</sub>Et<sub>3</sub> with [Cr(CO)<sub>5</sub>(thf)] yields five different mono-, bi-, tri- and tetrametallic complexes.<sup>[8]</sup>

Over the last years we have developed rational syntheses of phosphorus-rich ligands and investigated their coordination

chemistry. Selective syntheses for *cyclo*-(P<sub>5</sub>tBu<sub>4</sub>)<sup>-</sup> and (P<sub>4</sub>R<sub>4</sub>)<sup>2-</sup> (R = tBu, Ph, 2,4,6-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sup>[9]</sup> allowed the preparation of numerous novel metal complexes<sup>[10]</sup> as well as the discovery of several unexpected reactions thereof.<sup>[11]</sup> More recently, we shifted our attention to neutral cyclophosphanes like *cyclo*-(P<sub>5</sub>Ph<sub>5</sub>)<sup>[12]</sup> and found that even such simple and well-known molecules still hold surprises.<sup>[13]</sup> In this work, we report on the facile synthesis of {*cyclo*-(P<sub>4</sub>tBu<sub>3</sub>)<sub>2</sub>} (**1**) for which so far merely the preparation<sup>[14]</sup> and crystal structure<sup>[15,16]</sup> have been reported, but no reactivity studies.

Octaphosphane **1** was prepared by reductive coupling of *cyclo*-(P<sub>4</sub>tBu<sub>3</sub>Cl), which is prepared from *cyclo*-(P<sub>3</sub>tBu<sub>3</sub>) by a PCI insertion reaction,<sup>[17]</sup> in an overall yield of 28 %. The major advantage of this method compared to the procedure reported previously by Baudler is a higher yield and avoiding the highly reactive phosphorus hydride PHtBuPtBuPHtBu<sup>[18]</sup> as an intermediate.<sup>[19]</sup> In the solid state, an all-*trans* configuration of the tBu groups and a butterfly conformation of the four-membered rings are observed. We have studied the flexibility of the ligand by conducting a relaxed surface scan (PBE0-D3/def2-TZVP level, Figure S30, SI) of the dihedral angle between the bridge P atoms and their lone pairs of electrons (defined as τ). Two minima were thus identified corresponding to an *antiperiplanar* (τ = 180°, as in the solid state)<sup>[15,16]</sup> and a *gauche* (τ = 55°) conformation which are practically isoenergetic and are furthermore separated by low rotational barriers of ΔG<sub>act</sub> +13.7 kJ mol<sup>-1</sup>. An additional maximum with ΔG<sub>rel</sub> +29.5 kJ mol<sup>-1</sup> corresponding to a *synperiplanar* conformation (τ = 0) indicates that **1** can indeed freely rotate around the internal P–P bond.

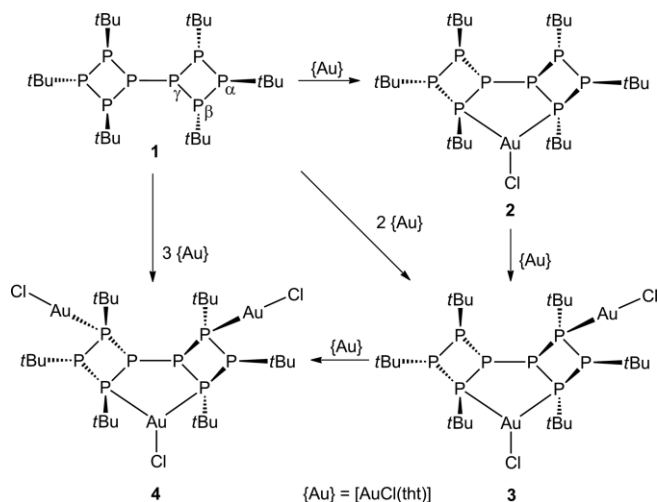
To study the coordination behavior of octaphosphane **1**, gold(I) was chosen as a metal ion as it usually favors low coordination numbers which, regarding the sterically demanding tBu groups, renders all eight P atoms potential donor atoms (three types labeled as α, β and γ in Scheme 1). When octaphosphane **1** is reacted with [AuCl(tht)] (tht = tetrahydrothiophene) a monometallic (**2**), bimetallic (**3**) and trimetallic complex (**4**) can be obtained where exclusively P atoms in β position are coordi-

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nating (Scheme 1). No further coordination was observed upon adding more equivalents of  $[\text{AuCl}(\text{tht})]$ .



Scheme 1. Reaction of phosphane **1** with  $[\text{AuCl}(\text{tht})]$  to give the  $\text{Au}^{\text{I}}$  complexes **2**, **3** and **4**.

The identity of homotrimetallic complex **4** was unambiguously verified by single crystal XRD. Ligand **1** adopts the *gauche* conformation [ $\tau = 104.15(2)^\circ$ ] and coordinates three gold(I) atoms (Figure 1), two of which are coordinated in an almost perfect linear fashion in accordance with a monodentate bonding mode of the ligand. The coordination environment of the chelated gold(I) atom ( $\text{Au1}$ ) on the other hand is unusual. While the  $\text{Au1-P1}$  bond length [ $2.236(4) \text{ \AA}$ ] is in a typical range for  $\text{Au-P}$  bonds,<sup>[20]</sup> the second bond,  $\text{Au1-P8}$ , is longer by approximately  $0.4 \text{ \AA}$  [ $2.629(4) \text{ \AA}$ ]. Nonetheless, an attractive interaction is evident as the  $\text{P1-Au1-Cl1}$  bond angle of  $156.4(2)^\circ$  indicates. Thus, the coordination environment of  $\text{Au1}$  can be described as a distorted T-shaped coordination.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **4** (Figure S19, SI) shows four symmetrical multiplets with chemical shifts expected for a coordination-induced shift. The spectrum is thus compatible with an  $\text{AA}'\text{BB}'\text{CC}'\text{DD}'$  spin system. Surprisingly, this is not consistent with the solid-state structure according to which nonequivalence of all P nuclei and thus eight different multiplets would be expected. This contradiction indicates a process, which causes effective  $\text{C}_2$  symmetry in solution. With respect to the molecular structure of the complex, this could obviously be achieved by a flip of the distorted T-shaped coordination mode of the chelated gold(I) atom by passing through a transition state with symmetrical Y-shaped<sup>[21]</sup> coordination environment (Scheme 2). DFT calculations (BP86-D3/def2-SVP level, SI) support a transition state which matches this expectation. In the corresponding structure (Figure S34, SI), both  $\text{Au-P}$  bond lengths (approx.  $2.4 \text{ \AA}$ , Table S7, SI) are equal and additionally lie precisely in-between the values observed for the molecular structure of the trimetallic complex. The same applies for the  $\text{P-Au-Cl}$  bond angles. Furthermore, the activation energy is only  $+10.0 \text{ kJ mol}^{-1}$  matching the observation that no significant change is observed when recording  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **4** down to  $-90 \text{ }^\circ\text{C}$ .

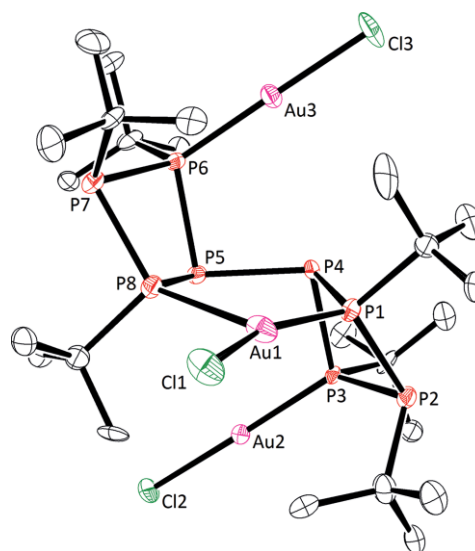
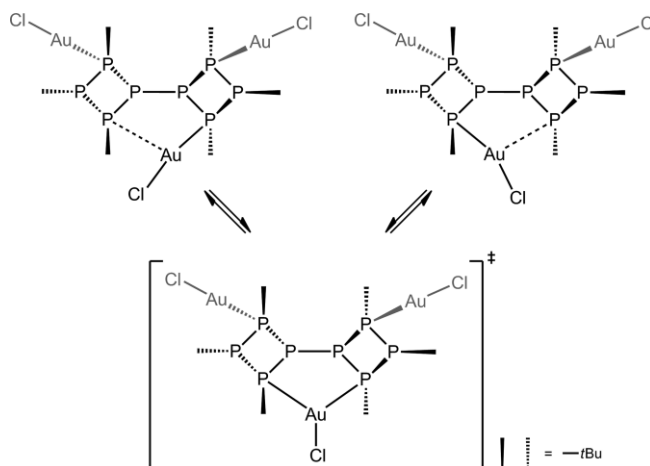


Figure 1. Molecular structure of complex **4** (H atoms omitted for clarity). Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]:  $\text{Au1-P1}$  2.236(4),  $\text{Au1-P8}$  2.629(4),  $\text{Au2-P3}$  2.227(3),  $\text{Au3-P6}$  2.232(3),  $\text{P1-Au1-Cl1}$  156.4(2),  $\text{P8-Au1-Cl1}$  105.5(1),  $\text{P1-Au1-P8}$  98.2(1),  $\text{P3-Au2-Cl2}$  176.9(2),  $\text{P6-Au3-Cl3}$  175.5(2),  $\tau$  104.15(2).



Scheme 2. Representation of the Y-shape coordination flip of the chelated gold(I) atom in complexes **2-4**.

A CSD search yielded three complexes with gold(I) in a similar distorted T-shaped coordination environment (Table S2, SI). Remarkably, despite the asymmetric coordination in the solid state, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra show equivalence of the respective P atoms in all cases, which indicates the presence of similar fluctuational processes. Furthermore, VT  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of one of the complexes (CSD code **TIJLEF**) showed no decoalescence until  $-83 \text{ }^\circ\text{C}$ ,<sup>[22]</sup> which points to an equally low activation barrier. No indications for gold in a symmetrical coordination were found during structure refinement in any of the crystal structures including **4**. Obviously, the thermal energy is too low for the Y-shape coordination flip at the temperatures of the measurements ( $-143 \text{ }^\circ\text{C}$  and below), even though packing effects in the solid state cannot be ruled out. It is noted that the CSD search also yielded a much larger number of complexes with *symmetrical* Y-shaped coordination environment (corre-

sponding to the transition state structure); yet no structural parameter in the ligands could be identified which causes the coordination of the gold(I) atom to be asymmetrical.

This fluxional process is crucial to understand the properties of the monometallic complex **2** in solution. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2**, unexpectedly, shows only three multiplets with a relative intensity of 2:1:1. This is not compatible with a monometallic complex as it corresponds to a coordination of all four  $\beta$ -P atoms. However, mass spectrometry and elemental analysis clearly point to the presence of only one Au–Cl fragment. Therefore, a dynamic process, which renders all four  $\beta$ -P atoms equivalent, must take place. In fact, VT  $^{31}\text{P}\{^1\text{H}\}$  NMR measurements (Figure S9, SI) reveal a typical decoalescence for the multiplet ( $-16.1$  ppm,  $I_{\text{rel}} = 2$ ) which can be assigned to these P atoms. The spectrum at  $-85$  °C shows four multiplets with equal relative intensity as well as pronounced fine structure and is thus consistent with an AA'BB'CC'DD' spin system. In analogy to the trimetallic complex **4**, this points to the same Y-shape coordination flip for the chelated gold(I) atom in complex **2**.

Since the rotation around the internal P–P bond presents the sole degree of freedom in phosphane **1**, a relaxed surface scan (BP86-D3/def2-SVP level, SI) was performed to elucidate the mechanism of the dynamic process of complex **2**. The obtained rotational profile (Figure 2,  $\tau'$  for  $360^\circ$  range) shows three major minima which correspond to a monodentate complex with an *antiperiplanar* conformation similar to the solid-state structure of the free phosphane<sup>[15,16]</sup> (**2c**,  $\tau' = 160^\circ$ ), a bidentate complex with *synperiplanar* conformation (**2b**,  $\tau' = 24^\circ$ ) as well as a *gauche* conformation (**2a**,  $\tau' = 272^\circ$ ), which is structurally analogous to **4**. Complex **2a** moreover represents the energetically most favored form and is thus the only species observable at  $-85$  °C. The rotamers **2a–c** are separated by maxima representing rotational barriers that lie between  $+34.5$  and  $+53.9$  kJ mol $^{-1}$  matching well with the temperature range in which decoalescence is observed in the NMR spectrum. As both bidentate complex conformers **2a** and **2b** feature the same asymmetrical environment of the gold(I) atom, the transition states of the Y-shape coordination flip was also calculated for these molecules and yielded similar structures and activation energies ( $+13.7$  and  $+17.6$  kJ mol $^{-1}$ , Figure S34, Table S7, SI).

Based on these results, the dynamic process can be rationalized as a combination of the rotation around the internal P–P bond and the Y-shape coordination flip (Figure 2,  $\beta$ -P atoms arbitrarily labeled P $^1$  to P $^4$  for clarity). Starting from the *gauche* complex **2a**, rotation of the four-membered ring leads to the secondary coordination of the  $\beta$ -P atom from the other ring (P $^4$ ) which corresponds to rotamer **2b**. A Y-shape coordination flip of the gold(I) atom from P $^1$  to P $^4$  enables rotation of the other four-membered ring resulting in formation of the enantiomer of the initial complex **2a**. Further Y-shape coordination flips and rotations cause all four  $\beta$ -P atoms, on average, to be identical.

Even though the proposed mechanism (Figure 2) is intramolecular, also an *intermolecular* process is conceivable. We, therefore, performed reactions of the compounds **1–4** with each other (Equations 1 - 3) which in fact show that an exchange of Au–Cl units is possible. However, these reactions re-

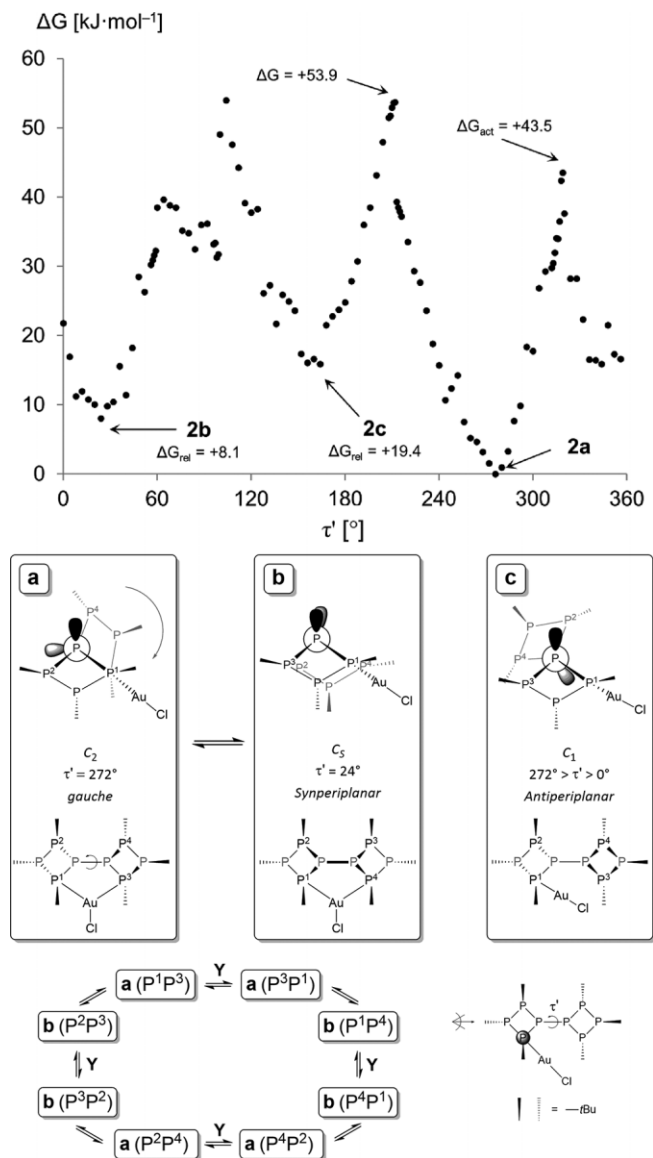
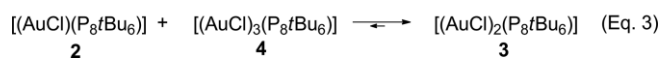
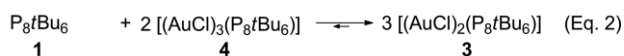
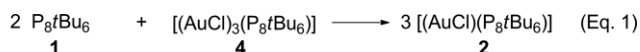


Figure 2. Illustration of the dynamic process of complex **2**. **Top**: Rotational profile from DFT; **Middle**: Crucial rotation step; with molecular symmetry of rotamers. **Bottom**: Demonstration of the equivalence of  $\beta$ -P atoms on average. The Y symbolizes the Y-shape coordination flip.

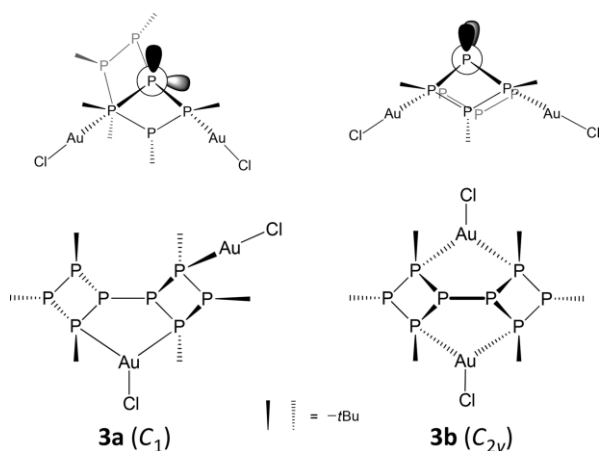
quire a few minutes and thus take too long to be responsible for the observations on the NMR time scale. Additional spectroscopic observations also support an *intramolecular* process: The decoalescence temperature of **2** is independent of the concentration of the complex in solution, and furthermore, no chemical shift change occurs for the NMR signals of **2** when different amounts of phosphane **1** are added to the solution (further details in SI). Lastly, an *intermolecular* process is also unlikely as this should lead to dynamic effects in the trimetallic complex **4** for which no such experimental evidence is found. Hierso et al. reported a homobimetallic gold(I) complex which also exhibits a dynamic behavior. In contrast to complex **2**, however, this is achieved by a so-called shuttling process of the Au–Cl fragments and not by the motion of a flexible ligand.<sup>[23]</sup>

Single crystal XRD analysis of the bimetallic complex **3** showed the molecular structure (Figure S24, SI) to be analogous



to the trimetallic complex **4** without a third Au–Cl fragment. The substance is phase pure as was confirmed by comparing the experimental PXR diffractogram with the theoretical pattern calculated from the single crystal structure. Surprisingly, in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of a solution of crystalline **3**, significant quantities of phosphane **1** and complexes **2** and **4** can be detected indicating intermolecular processes. In fact, the NMR spectra of the reactions of complex **4** with phosphane **1** or complex **2** in the right ratio (Equations 2 and 3) are identical to the one obtained from the reaction of **1** with 2 equiv. of  $[\text{AuCl}(\text{tht})]$ . Similar observations, but to a lesser extent, are also made for complex **2**, therefore leading to the conclusion that these complexes exist in equilibria in solution.

Even though the PXR diffractogram as well as mass spectrometry and elemental analysis clearly confirm the identity of the bimetallic complex **3** observed in the solid state, the results from NMR spectroscopy which give information on the behavior in solution are less conclusive. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of a solution of **3** shows seven signals (Figure S16, SI) which can be attributed to two sets considering their intensity and the results from  $^{31}\text{P}\{^1\text{H}\}$ - $^{31}\text{P}\{^1\text{H}\}$  COSY NMR spectroscopy. One signal set consists of four equally intense signals which are compatible with an AA'BB'CC'DD' spin system. The second set includes three signals with a relative intensity of about 2:1:1. We conclude that the activation barriers for a rotation around the internal P–P bond in this complex is high enough to render conformers on the NMR time scale discernible at room temperature. Thus, we propose a complex with *gauche* conformation as observed in the solid state (**3a**) and one with *synperiplanar* conformation where both gold(I) atoms are chelated (**3b**) (Scheme 3, further explanation in SI).



Scheme 3. Conformers of complex **3** in solution.

Complexes **2–4** show that the  $\beta$ -P atoms in octaphosphane **1** are the most favorable ones for coordinating gold(I). This is

in accordance with DFT calculations (details in SI) performed on hypothetical monodentate complexes with an Au–Cl fragment attached to the  $\alpha$ - ( $\Delta G = -87.3 \text{ kJ mol}^{-1}$ ),  $\beta$ - ( $\Delta G = -100.4 \text{ kJ mol}^{-1}$ ) and  $\gamma$ -P atom ( $\Delta G = -82.3 \text{ kJ mol}^{-1}$ ). The reason why no more than three gold(I) atoms can be coordinated can be answered by inspecting the MO energies of complexes **2–4** (Table S6, SI). Upon subsequent addition of gold(I) atoms to phosphane **1** the energies of the molecular orbitals that present the lone pairs are continuously decreasing, obviously making the reaction to a tetrametallic complex energetically unfavorable. This is also reflected in the complex formation energies (Table S8, SI) which steadily decrease for every additional gold(I) atom in the molecule ( $\Delta\Delta G \approx 30\text{--}50 \text{ kJ mol}^{-1}$ ). Nevertheless, other oligophosphanes which contain further phosphorus atoms should be capable of coordinating more than three metal atoms and very likely exhibit an equally interesting coordination chemistry which will be discovered in future studies.

CCDC 1946813 (for **1**), 1946817 (for **3**), and 1946818 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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**Keywords:** Phosphanes · Oligophosphanes · Gold · Phosphorus · Fluxionality

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