## Making and Breaking of P–P Bonds with Low-Valent Transition-Metal Complexes

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The 1:1 or 1:2 stoichiometric reaction of  $[Na_2(thf)_4(P_4Mes_4)]$  $(1; Mes = 2,4,6-Me_3C_6H_2)$  with  $[{RhCl(cod)}_2]$  (cod = 1,5-cyclooctadiene) gave a mixture of compounds of which  $[Na(thf)_3]$ - $[Rh(P_3Mes_3)(cod)]$  (2) with a trimesityltriphosphane-1,3-diide ligand was structurally characterized. Density functional calculations on 2 confirmed the structural parameters obtained by X-ray diffraction studies. Shared electron number and natural bond orbital analyses indicated only weak interactions between Na and P, which were found to be even weaker than the Na-Rh interactions with covalent contribution. When an excess of 1 was used (3:1 or 4:1), 2 was also

### Introduction

Alkali-metal oligophosphanediides  $M_2(P_nR_n)$   $(n = 2-4)^{[1]}$ are versatile starting materials in the preparation of phosphorus-rich main-group and transition-metal complexes.<sup>[2]</sup> The chemistry of tetraaryltetraphosphane-1,4-diides  $(P_4R_4)^{2-}$  has proved to be as intriguing as that of alkalimetal cyclo-oligophosphanides.<sup>[3]</sup> Thus, in addition to the previously known group 4,<sup>[4]</sup> nickel,<sup>[5]</sup> and platinum<sup>[6]</sup> oligophosphanide complexes, we have observed that the dianions  $(P_4R_4)^{2-}$  (R = Ph or Mes; Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) remain intact in transmetallation reactions with late-transitionmetal halides such as  $[CuCl(PCyp_3)_2]$  (Cyp = cyclo-C<sub>5</sub>H<sub>9</sub>) to give  $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]^{[2a]}$  or with  $[PtCl_2(L)_2]$  to give complexes of the type  $[Pt(P_4Mes_4)_2(L)_2] [(L)_2 = cod, dppe;$  $L = C \equiv NtBu$ , and  $C \equiv NCy$ ; cod = 1,5-cyclooctadiene, dppe =  $Ph_2PCH_2CH_2PPh_2$ , and  $Cy = cyclo-C_6H_{11}$ .<sup>[2g]</sup> In addition, in the reaction of Na<sub>2</sub>(P<sub>4</sub>Ph<sub>4</sub>) with [Cp\*TaCl<sub>4</sub>]  $(Cp^* = C_5Me_5)$  tantalum was apparently reduced by the dianion, and subsequent rearrangement and oxidative addition gave the (phosphinidene)tantalum(V) complex [Cp\*Ta(Ph)(P<sub>6</sub>Ph<sub>5</sub>)].<sup>[2b]</sup> Furthermore, we observed oxidative P–P bond cleavage of the  $(P_4R_4)^{2-}$  (R = Ph, Mes) di-

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obtained as the major product together with small amounts of the side-products  $cyclo-P_6Mes_6$  (3) and  $[Na_3(Et_2O) (P_4Mes_4)(PHMes)]_{\infty}$  (4). Compounds 3 and 4 were only characterized by single-crystal X-ray diffraction studies. Their formation indicates that the reaction includes the breaking and making of P-P bonds to give (P<sub>3</sub>Mes<sub>3</sub>)<sup>2-</sup>, PHMes<sup>-</sup>, and cyclo-P<sub>6</sub>Mes<sub>6</sub>, although the mechanism is unclear. Furthermore, the reaction of 1 with 2 equiv. of  $[AgCl(PPh_3)_2]$  gave the tetranuclear compound  $[Ag_4(P_6Mes_6)_2]$  (5) in which the novel  $(P_6Mes_6)^{2-}$  ion also indicates degradation of the  $P_4$ chain followed by P-P bond formation.

anion by nickel(II) complexes in an intramolecular redox reaction that gave (diaryldiphosphene)nickel(0) complexes,<sup>[2d]</sup> whereas reductive P-P bond cleavage of tetraphenyltetraphosphane-1,4-diide by nickel(0) was observed to give the mixed-metal (s-block/d-block) complexes [Na(Et<sub>2</sub>O)<sub>3</sub>][Na<sub>3</sub>- $(Et_2O)_2Ni_3(\mu - P_2Ph_2)_2(P_2Ph_2)_3$ and [K(pmdeta)]<sub>2</sub>[Ni-(P<sub>4</sub>Ph<sub>4</sub>)(P<sub>2</sub>Ph<sub>2</sub>)] with Ni–Na and Ni–K interactions, respectively.<sup>[2f]</sup> The analogous protonated alkali-metal tetraaryltetraphosphanides  $(P_4HR_4)^-$  (R = Ph, Mes) also displayed very interesting transmetallation reactions with rhodium(I) and copper(I) salts, which led to phosphorus-rich complexes such as [Rh(P<sub>4</sub>HMes<sub>4</sub>)(cod)] and [Cu<sub>4</sub>(P<sub>4</sub>Ph<sub>4</sub>)<sub>2</sub>(PH<sub>2</sub>Ph)<sub>2</sub>-(PCyp<sub>3</sub>)<sub>2</sub>].<sup>[2e]</sup>

Herein we report the preparation of two novel metal oligophosphanide complexes [Na(thf)<sub>3</sub>][Rh(P<sub>3</sub>Mes<sub>3</sub>)(cod)] (2) with a trimesityltriphosphane-1,3-diide ligand and  $[Ag_4(P_6Mes_6)_2]$  (5) containing two hexamesitylhexaphosphane-1,6-diide ligands. Compounds 2 and 5 were obtained by the reaction of  $[Na_2(thf)_4(P_4Mes_4)]$  (1) with  $[{RhCl(cod)}_2]$  (1:1 or 2:1) and  $[AgCl(PPh_3)_2]$  (1:2), respectively. In addition, the structural characterization of two side-products obtained in addition to 2, namely, cyclo- $P_6Mes_6$  (3) and  $[Na_3(Et_2O)(P_4Mes_4)(PHMes)]_{\infty}$  (4), is also described.

### **Results and Discussion**

### Reactions of [Na<sub>2</sub>(thf)<sub>4</sub>(P<sub>4</sub>Mes<sub>4</sub>)] (1) with [{RhCl(cod)}<sub>2</sub>] in Ratios of 1:1 and 2:1

 $[Na(thf)_3][Rh(P_3Mes_3)(cod)]$  (2) was obtained as the major product in the mixtures obtained from the reaction

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Scheme 1.

of 1 or 2 equiv. of  $[Na_2(thf)_4(P_4Mes_4)]$  (1) with 1 equiv. of  $[{RhCl(cod)}_2]$  (Scheme 1). Crystals of **2** were obtained from thf in low yield and were always contaminated with  $[Rh(P_4HMes_4)(cod)]$  and  $[Rh_2(\mu-P_2HMes_2)(\mu-PHMes)-(cod)_2]$ ,<sup>[2e]</sup> which were also observed in the reaction mixtures by <sup>31</sup>P NMR spectroscopy. The ratio of **2**,  $[Rh(P_4HMes_4)(cod)]$ , and  $[Rh_2(\mu-P_2HMes_2)(\mu-PHMes)-(cod)_2]^{[2e]}$  in the mixtures depended on the stoichiometry. The amounts of the side-products were higher in the 1:1 reaction than in the 2:1 reaction.

Compound **2** was characterized by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy; characterization by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy was thwarted by severe overlap with the signals of [Rh(P<sub>4</sub>HMes<sub>4</sub>)(cod)] and [Rh<sub>2</sub>( $\mu$ -P<sub>2</sub>HMes<sub>2</sub>)( $\mu$ -PHMes)(cod)<sub>2</sub>].<sup>[2e]</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **2** in C<sub>6</sub>D<sub>6</sub>, [D<sub>8</sub>]thf, or C<sub>7</sub>D<sub>8</sub> exhibit two broad signals at  $\delta$  = -30 (P<sub>AA'</sub>) and -46 (P<sub>B</sub>) ppm both at room (C<sub>6</sub>D<sub>6</sub>, [D<sub>8</sub>]thf, or C<sub>7</sub>D<sub>8</sub>) and low temperature (-80 °C in [D<sub>8</sub>]thf or C<sub>7</sub>D<sub>8</sub>), which indicates that the Na–P interaction is retained in solution.<sup>[1g,1i]</sup>

Complex 2 crystallizes as orange plates in the triclinic space group  $P\bar{1}$  with two almost identical independent molecules in the asymmetric unit of which only one will be

discussed. The rhodium atom is coordinated in a distorted square-planar geometry by an  $\eta^4$ -cod ligand and a chelating  $(P_3Mes_3)^{2-}$  ligand, which coordinates through the two terminal phosphorus atoms (P1 and P3, Figure 1). The Rh1-P1 and Rh1-P3 bond lengths in 2 [232.9(2) and 231.5(1) pm] are similar to those observed in [Rh(P<sub>4</sub>- $HMes_4)(cod)]^{[2e]}$  and  $[Rh{cyclo-(P_5tBu_4)}(PPh_3)_2].^{[3b]}$  One of the two negative charges of the trimesityltriphosphane-1,3-diide ligand is counterbalanced by the sodium cation Na1, which interacts with the terminal phosphorus atoms of the P<sub>3</sub> chain [Na1-P1 315.7(2), Na1-P3 299.9(2) pm] and presumably with the rhodium atom [Na1-Rh1 310.5(2) pm]. The shorter Na1-P3 bond is in the range of those previously reported for sodium phosphanides,<sup>[1h,1i]</sup> whereas the Na1–P1 bond is somewhat longer and indicates a weaker Na-P interaction (Table 1). Furthermore, Na1 is coordinated by three thf molecules resulting in an unusual five-coordinate geometry.<sup>[7]</sup>

In reference to the short Na–Rh distance of 310.5(2) pm, an extensive literature search has shown that contacts between Rh and alkali metals are extremely rare,<sup>[8]</sup> and up to now short Rh…Li interactions with distances of 256.3, 261.3, and 264.4 pm have only been described by Andersen



Figure 1. Solid-state molecular structure of **2** (hydrogen atoms have been omitted for clarity).

and co-workers in the compounds [Li(tmeda)][Rh(CH<sub>2</sub>-SiMe<sub>3</sub>)<sub>2</sub>(cod)] (tmeda = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>) and [Rh<sub>2</sub>-(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>(cod)<sub>2</sub>( $\mu$ -Li)<sub>2</sub>].<sup>[8]</sup> Longer distances of about 288 pm were not considered as indicative of Rh–Li interactions by Cavell and co-workers for other related complexes.<sup>[9]</sup> However, to the best of our knowledge no evidence of Rh–Na interactions has been reported to date, and only longer distances [320.9(2) and 331.9(2) pm] have been observed in the sodium rhodate(III) complex Na[Rh(acac)<sub>2</sub>-Cl<sub>2</sub>]·H<sub>2</sub>O (acac = acetylacetonate),<sup>[10]</sup> probably due to packing effects.

In this context, the structure of **2** was investigated with the TURBOMOLE<sup>[11]</sup> suite. The calculations for **2** confirmed the structural parameters obtained by X-ray diffraction studies. A shared electron number (SEN) analysis was applied to investigate the Rh···Na interaction (see the Supporting Information). The SEN can be correlated to the covalent interaction between the investigated atoms. The two almost identical crystallographically independent molecules of **2** have SENs between Na and Rh of 0.35 and 0.37 electrons. Because the clearly covalent Rh–P1 and Rh–P3 interactions have values in the range of 0.55–0.59, covalency between Na and Rh may be assumed on the basis of our calculations. Further proof of a partially covalent bond is provided by the natural bond orbital (NBO) analysis.

The NBO analysis showed a low occupancy of the 3s orbital of Na, which indicates that the ionicity of Na is less than 100% and suggests a potential covalent contribution from Na. A covalent bond between Na and Rh becomes more likely when natural bond orbitals (NBOs), which are constructed as a linear combination of hybridized natural atomic orbitals of both atoms Na and Rh, are taken into account. The Na–Rh bond arises from an overlap of the 3s and 5s orbitals of Na and Rh, respectively. Occupancies of the antibonding NBOs  $\sigma^*_{Na-Rh}$  of 0.07 and 0.09 were

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Table 1. Selected bond lengths [pm] and angle
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	2	3	4	5
Rh1–Na1	310.5(2)			
Rh1–P1	232.9(2)			
Rh1–P3	231.5(1)			
Ag1-P1				256.3(2)
Ag1–P3				248.0(2)
Ag1–P3B				250.1(2)
Na1–P1	315.7(2)		278.37(9)	
Na1–P3	299.9(2)			
Na1–P4A			281.80(9)	
Na2–P2			308.48(8)	
Na2–P4			295.95(8)	
Na2–P5			282.86(8)	
Na3–P1			295.15(8)	
Na3–P3			305.77(8)	
Na3–P5A			288.79(8)	
P1-P2	222.0(2)	223.0(1)	218.05(6)	225.7(3)
P1-P3		223.2(1)		
P1–P3A				215.3(3)
P2–P2A				221.3(4)
P2-P3	221.4(2)		223.09(6)	
P2A-P3		222.7(2)		
P3–P4			218.26(6)	
P5–H1p			133(2)	
Ag1–P3–Ag1C				82.33(7)
P1–Rh1–P3	74.91(3)			
P1-Ag1-P3	~ /			123.94(8)
P1-Ag1-P3B				112.95(7)
P3–Ag1–P3B				112.54(6)
Na1–P1–Na3			105.83(2)	
Na2–P5–Na3B			111.26(3)	
P1-Na1-P3	54.54(4)			
P1-Na1-P4A			119.49(3)	
P1-P2-P3	79.14(5)		100.20(2)	
P1-P2-P2A				104.1(2)
P1-P3-P2A		96.40(5)		
P1A-P2A-P3		102.60(5)		
P2-P1-P3		97.56(5)		
P2-P1-P3A				104.8(2)
P2-P3-P4			102.08(2)	

calculated for the two independent molecules of **2**. The higher occupancy of the bonding NBO justifies the assumption of Na–Rh interactions with a covalent contribution (for further details, see the Supporting Information).

In addition, SEN studies on the Na-P bonds were carried out. The SENs range from 0.23 to 0.30 for the predefined Na-P bonds and indicate weak interactions, weaker even than the Na-Rh interaction (SEN values of 0.35 and (0.37). These results are consistent with those emerging from the NBO analysis. Indeed, bonding Na-P orbitals were found in both individual molecules. However, the contributions of Na to the NBOs were rather low, as indicated by the polarization coefficients ( $c_{Na} < 0.09$ ). Thus, the electrons of these orbitals are highly localized at P, corresponding to the P lone-pair of electrons. These results account for the weak interactions between Na and P and suggest a relatively high covalent contribution to the Na-Rh interaction, which is stronger than in the Na-P bonds (for further details, see the Supporting Information). To the best of our knowledge, no covalent bonds between Na and a transition metal have been reported to date; however, by using SEN

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and NBO methods, other authors have observed metalmetal bonds with covalent contributions that have been discussed in a way similar to the Na–Rh bond found in **2**.<sup>[12]</sup>

# Reactions of $[Na_2(thf)_4(P_4Mes_4)]$ (1) with $[\{RhCl(cod)\}_2]$ in Ratios of 3:1 and 4:1

To obtain further insight into the mechanism of the formation of **2**, the analogous reactions of 3 or 4 equiv. of 1 with 1 equiv. of  $[{RhCl(cod)}_2]$  were carried out. In addition to the formation of **2** as the major product and  $[Rh(P_4HMes_4)(cod)]$  and  $[Rh_2(\mu-P_2HMes_2)(\mu-PHMes)-$   $(cod)_2]^{[2e]}$  as side-products, small amounts of *cyclo*-P<sub>6</sub>Mes<sub>6</sub> (3) and  $[Na_3(Et_2O)(P_4Mes_4)(PHMes)]_{\infty}$  (4) were isolated. The formation of 2–4 indicates that the cleavage and formation of P–P bonds occurs in the course of the reaction to give  $(P_3Mes_3)^{2-}$ , PHMes<sup>-</sup>, and *cyclo*-P<sub>6</sub>Mes<sub>6</sub> (3). Compounds 3 and 4 could not be separated from 2 and were only characterized by X-ray diffraction studies.

The compound *cyclo*- $P_6Mes_6$  (3) crystallizes in the monoclinic space group *P2/c* with half of the molecule located in the asymmetric unit and the other half generated by an inversion center. In addition, one half of a diethyl ether molecule was also located in the asymmetric unit with the oxy-



Figure 2. Solid-state molecular structure of 3 (hydrogen atoms have been omitted for clarity). Symmetry operations for A: -x, -y, -z.



Figure 3. Solid-state molecular structure of 4 (hydrogen atoms except at phosphorus atoms have been omitted for clarity). Symmetry operations for A: -x + 1/2, y + 1/2, -z + 1/2; for B: x - 1/2, -y - 1/2, z - 1/2.



Figure 4. Metallacycle formed by Na and P atoms. Symmetry operations for A: -x + 1/2, y + 1/2, -z + 1/2; for B: x - 1/2, -y - 1/2, z - 1/2.

gen atom located on a two-fold rotation axis. Like the  $C_6$  ring of cyclohexane, the  $P_6$  ring of **3** exhibits a chair conformation in which the mesityl groups occupy equatorial positions (Figure 2). The P–P bond lengths of the ring differ only slightly [with values between 222.7(2) and 223.2(1) pm] and are in the expected range,<sup>[13]</sup> whereas the endocyclic P–P–P bond angles vary between 96.40(5) and 102.60(5)°.

Compound 4 crystallizes in the monoclinic space group  $P2_1/n$ . It consists of co-crystallized Na<sub>2</sub>(P<sub>4</sub>Mes<sub>4</sub>) and Na-(Et<sub>2</sub>O)(PHMes), which also form the asymmetric unit. In spite of minor differences, the overall structural arrangement of the Na<sub>2</sub>(P<sub>4</sub>Mes<sub>4</sub>) core in **4** is similar to those observed in analogous compounds.<sup>[1h]</sup> The central  $(P_4Mes_4)^{2-1}$ dianion is in a syn arrangement with a P1-P2-P3-P4 torsion angle of around 78.8°. The sodium cation Na1 has an unusual three-coordinate environment (P1, P4, and the oxygen atom of the diethyl ether molecule), whereas Na2 and Na3 have a distorted tetrahedral geometry with coordination by three phosphorus atoms and  $\eta^2$  coordination of a mesityl group. Short Na-P distances are observed for Na2 and Na3 linked to the terminal and an internal phosphorus atom of the P<sub>4</sub> chain [Na3-P1 295.15(8), Na3-P3 305.77(8) and Na2-P2 308.48(8), Na2-P4 295.95(8) pm], which indicates a "quasicyclic structure", as was previously observed for alkali-metal tetramesityltetraphosphanediides.<sup>[1g,1h,2c]</sup> These Na<sub>2</sub>P<sub>4</sub> units are linked by PHMes<sup>-</sup> [bridging Na2 and Na3B with short Na-P bonds of 282.86(8) and 288.79(8) pm] and Na( $Et_2O$ )<sup>+</sup> [bridging P1 and P4A with Na1–P bond lengths of 278.37(9) (P1) and 281.80(9) pm (P4A)] resulting in a one-dimensional polymeric chain (Figure 3). Interestingly, P1-Na1-P4A-Na2A-P5A-Na3 form an almost planar six-membered ring in which only Na3 deviates by about 86 pm from the other co-planar atoms (Figure 4).

### [Ag<sub>4</sub>(P<sub>6</sub>Mes<sub>6</sub>)<sub>2</sub>]

 $[Ag_4(P_6Mes_6)_2]$  (5) was obtained as the main product in modest yield from the reaction of 1 equiv. of  $[Na_2(thf)_4-(P_4Mes_4)]$  (1) with 2 equiv. of  $[AgCl(PPh_3)_2]$  (Scheme 1). Compound 5 was crystallized from diethyl ether and characterized by spectroscopic methods and single-crystal X-ray diffraction studies.

It seems that complex 5 is formed by a redox reaction [Equation (1)] involving the formation of elemental silver, which was detected in the black precipitate formed in the reaction.

$$6 \text{ Ag}^{+} + 3 (\text{P}_{4}\text{Mes}_{4})^{2-} = 4 \text{ Ag}^{+} + 2 (\text{P}_{6}\text{Mes}_{6})^{2-} + 2 \text{ Ag}^{0}$$
 (1)

This reaction represents the first preparation of a  $P_6Mes_6^{2-}$  ligand, which, to the best of our knowledge, was previously unknown.

As crystalline complex **5** is poorly soluble in polar and nonpolar solvents, only very dilute solutions of **5** in C<sub>6</sub>D<sub>6</sub> could be analyzed. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **5** exhibits three broad multiplets at  $\delta = -100.6$ , -14.3, and 0.7 ppm at room temperature. The severe line-broadening, which precluded numerical analysis of the coupling patterns, may in part be due to the quadrupole moment of the silver nuclei. However, the presence of only these three signals in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and the <sup>1</sup>H NMR spectrum indicate that the molecular structure is also retained in solution.

Further analysis of this complex by ESI-MS was thwarted by its poor solubility, and other ionization techniques such as EI or CI led to severe fragmentation. However, the FAB mass spectrum showed a peak at m/z = 1331.6 of low relative intensity corresponding to the tetranuclear compound with loss of one P<sub>6</sub>Mes<sub>6</sub> ligand (see the Exp. Sect.).

Crystals of **5** obtained from diethyl ether were systematically twinned, and crystallization from other solvents did not lead to single crystals suitable for X-ray diffraction studies. However, in spite of the relatively poor quality of the crystals, the molecular structure of **5** was determined without ambiguity.

Complex 5 crystallizes in the tetragonal space group  $I\bar{4}_2d$ The asymmetric unit of 5 contains an AgP<sub>3</sub>Mes<sub>3</sub> unit, which, after application of an  $S_4$  axis, gives rise to the tetranuclear complex [Ag<sub>4</sub>(P<sub>6</sub>Mes<sub>6</sub>)<sub>2</sub>] (5). Six highly disordered diethyl ether molecules were also observed in the asymmetric unit, only two of which could be satisfactorily refined; the other four were removed by using the SQUEEZE program implemented in PLATON.<sup>[14]</sup>

In 5, two linear  $P_6Mes_6^{2-}$  ligands are bound by four phosphorus atoms (the most external ones P3 and P1) to four silver(I) atoms, which are coordinated in a distorted trigonal-planar fashion by three phosphorus atoms of two different  $P_6$  ligands (Figure 5). Interestingly, the 16-vertex polyhedron consists of four five-membered rings in an envelope conformation, formed by two silver atoms (e.g., Ag1 and Ag1B) and three phosphorus atoms of two different  $P_6$ ligands (e.g., P1, P3A, and P3B), and four six-membered rings in a boat conformation, formed by five phosphorus atoms of a  $P_6$  ligand (e.g., P1, P2, P2A, P1A, and P3) and a silver atom (e.g., Ag1). Two six-membered rings are fused to give a bicyclic  $Ag_2P_6$  fragment similar to bicyclo[2.2.2]-octane.



Figure 5. Solid-state molecular structure of 5 (with the omission of carbon and hydrogen atoms). Symmetry operations for A: -x, -y, +z; for B: -y + 1/2, x + 1/2, -z + 1/2; for C: y + 1/2, -x + 1/2, -z + 1/2.

The Ag–P bond lengths are between 248.0(2) and 256.3(2) pm, in the range of other reported Ag–P bonds,<sup>[3g]</sup> whereas the P–P distances of the P<sub>6</sub> ligand range from 215.3(3) (terminal P3 and P1A) to 225.7(3) pm and are also in the expected range.<sup>[13]</sup> The (P<sub>6</sub>Mes<sub>6</sub>)<sup>2–</sup> dianion shows P3–P1A–P2A–P2 and P1–P2–P2A–P1A torsion angles of about 108.1 and 69.7°, respectively, and P–P–P angles of about 104°. Silver(I) complexes often exhibit inter- or intramolecular Ag–Ag contacts (argentophilic interactions)<sup>[15]</sup> with distances of less than the sum of the van der Waals radii, which is 340 pm.<sup>[16]</sup> In **5**, the four Ag atoms are symmetry-related by an  $S_4$  axis and thus are located on the vertices of an imaginary tetrahedron (see Figure 6) with Ag···Ag distances of 327.9(2) and 334.6(2) pm, which indicate intramolecular contacts.



Figure 6. Tetrahedron formed by the Ag atoms of **5** with Ag···Ag distances [pm].

#### Conclusions

P–P bond-breaking and -making occur in the reactions of  $[Na_2(thf)_4(P_4Mes_4)]$  (1) with  $[{RhCl(cod)}_2]$  or  $[AgCl(PPh_3)_2]$ . Thus, 1 reacted with  $[{RhCl(cod)}_2]$  (1:1 or 2:1) to give a mixture of compounds from which  $[Na(thf)_3]$ - $[Rh(P_3Mes_3)(cod)]$  (2) was isolated, whereas the reactions with reagent ratios of 3:1 and 4:1 gave 2 as the major product together with small amounts of the neutral hexaphosphane *cyclo*-P<sub>6</sub>Mes<sub>6</sub> (**3**) and  $[Na_3(Et_2O)(P_4Mes_4)(PHMes)]_{\infty}$ (**4**) as side-products indicating that the reaction may involve cleavage of a P–P bond to give  $(P_3Mes_3)^{2-}$  and PHMes<sup>-</sup>. In addition, the formation of **3** may be possible by a rare coupling of two P<sub>3</sub> fragments. SEN and NBO analyses indicated only weak Na–P interactions in **2**, which are even weaker than the Na–Rh interactions with a bond length of 310.5(2) pm.

Furthermore, the reaction of **1** with 2 equiv. of  $[AgCl(PPh_3)_2]$  gave the tetranuclear compound  $[Ag_4-(P_6Mes_6)_2]$  (**5**) in which the presence of  $(P_6Mes_6)^{2-}$  indicates a redox reaction with P–P bond cleavage and formation involving the reduction of Ag<sup>+</sup> to Ag<sup>0</sup>. Ag<sup>...</sup>Ag distances of 327.9(2) and 334.6(2) pm indicate argentophilic intramolecular contacts in this compound.

### **Experimental Section**

General: All experiments were performed under dry argon by using standard Schlenk techniques. The NMR spectra were recorded with a Bruker Avance DRX 400 spectrometer. <sup>1</sup>H NMR (400.13 MHz): internal standard solvent, external standard TMS; <sup>31</sup>P NMR (161.9 MHz): external standard 85% H<sub>3</sub>PO<sub>4</sub>. FAB mass spectra were recorded with a MASPEC II spectrometer with 3-nitrobenzyl alcohol as matrix. EI-MS analyses were preformed with a MASPEC II instrument [II32/A302] (m/z = 50-1000). ESI-MS data were recorded with an FT-ICR MS Bruker Daltonics spectrometer (APEX II, 7 T, MASPEC II), and solutions of approximately 1 mg/mL of the compounds in dry thf/CH<sub>3</sub>CN (1:1) were injected. IR spectra: KBr pellets were prepared in a nitrogen-filled glove-box, and the spectra were recorded with a Perkin-Elmer System 2000 FTIR spectrometer in the range 400–4000 cm<sup>-1</sup>. All solvents were purified by distillation, dried, saturated with argon, and stored over a potassium mirror. [Na<sub>2</sub>(thf)<sub>4</sub>(P<sub>4</sub>Mes<sub>4</sub>)] (1),<sup>[1h]</sup> [{RhCl(cod)}2],[17] and [AgCl(PPh3)2][18] were synthesized according to literature procedures.

Synthesis of [Na(thf)<sub>3</sub>][Rh(P<sub>3</sub>Mes<sub>3</sub>)(cod)] (2): At -78 °C, a solution of 1 (0.75 g, 0.80 mmol) in thf (30 mL) was carefully added dropwise to a solution of  $[{RhCl(cod)}_2]$  (0.20 g, 0.40 mmol) in thf (50 mL). The brown solution that formed was allowed to warm to room temperature slowly over 2 h and then stirred for a further 2 h. The solvent was then removed under vacuum and the resulting dark brown oil extracted with Et<sub>2</sub>O ( $2 \times 50$  mL). The brown Et<sub>2</sub>O solution was filtered and the solvent evaporated in vacuo. The resulting brown solid was then recrystallized from thf (5 mL). A dark orange crystalline solid formed at -28 °C over 1 week. Complex 2 was always obtained contaminated with [Rh(P4HMes4)(cod)] and  $[Rh_2(\mu-P_2HMes_2)(\mu-PHMes)(cod)_2]$ ,<sup>[2e]</sup> and the signals in the <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H,<sup>31</sup>P}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra reported hereafter were assigned by comparison with the spectra of the pure side-products. Yield: 0.15 g (21%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 1.41 (12 H), 3.56 (12 H) (thf), 2.18 (12 H), 2.49 (3 H), 2.86 (6 H), 3.44 (br. s, 6 H, Me of Mes), 3.73 (2 H), 3.93 (1 H), 4.41 (br., 1 H, CH of cod), 6.46 (2 H), 6.96 (2 H), 7.06 (s, 2 H, aromatic CH of Mes) ppm (signals of the CH2 groups of cod were obscured by the signals of the methyl groups of mesityl).  ${}^{13}C{}^{1}H, {}^{31}P$  NMR ([D<sub>8</sub>]thf, 25 °C):  $\delta = 21.8, 21.9$  (*p*-Me in Mes), 29.2, 30.0, 30.5, 31.2, 32.2 (s, *o*-Me in Mes and CH2 of cod), 83.4, 86.0, 87.2, 87.8, 88.2, 94.1 (CH of cod in 2 and impurities), 127.7, 127.8, 128.0, 128.5, 129.0, 129.1 (C-3,5 in Mes), 134.3, 134.9, 136.2, 137.3, 138.3, 138.8, 140.0,

141.8, 143.1 (s, C-1,2,4,6 in Mes) ppm.  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = -30.3$  (br., P<sub>AA'</sub>), -46.3 (br., P<sub>B</sub>) ppm. IR (KBr):  $\tilde{v} = 3016$  (m), 2958 (s), 2915 (s), 2871 (s), 2727 (w), 1722 (w), 1601 (m), 1552 (w), 1455 (m), 1406 (w), 1375 (m), 1331 (w), 1289 (w), 1260 (m), 1176 (w), 1153 (w), 1096 (m), 1029 (s), 925 (w), 847 (s), 817 (m), 712 (w), 612 (m), 556 (m), 461 (w), 430 (w) cm<sup>-1</sup>. MS (EI): m/z (%) = 898.9 (0.8) [M + H]<sup>+</sup>, 795.0 (0.5) [M + H - cod]<sup>+</sup>, 335.1 (100) [Na(thf)<sub>2</sub>OPHMes]<sup>+</sup>. The elemental analysis data were not satisfactory due to the contamination of **2** with [Rh(P<sub>4</sub>HMes<sub>4</sub>)-(cod)] and [Rh<sub>2</sub>( $\mu$ -P<sub>2</sub>HMes<sub>2</sub>)( $\mu$ -PHMes)(cod)<sub>2</sub>].<sup>[2e]</sup> When using equimolar amounts of **1** (0.75 g, 0.80 mmol) and [{RhCl(cod)}<sub>2</sub>] (0.40 g, 0.80 mmol), the only significant difference was the proportion of the side-products [Rh(P<sub>4</sub>HMes<sub>4</sub>)(cod)] and [Rh<sub>2</sub>( $\mu$ -P<sub>2</sub>HMes<sub>2</sub>)( $\mu$ -PHMes)(cod)<sub>2</sub>]<sup>[2e]</sup> in the reaction mixture, which was higher than in the 2:1 reaction.

Reaction of 1 with [{RhCl(cod)}<sub>2</sub>] in Ratios of 3:1 and 4:1: Crystallization of the Mixture of [Na(thf)<sub>3</sub>][Rh(P<sub>3</sub>Mes<sub>3</sub>)(cod)] (2), cyclo- $P_6Mes_6$  (3), and  $[Na_3(Et_2O)(P_4Mes_4)(PHMes)]_{\scriptscriptstyle \infty}$  (4): At –78 °C, a solution of 1 (1.13 g, 1.20 mmol) in thf (50 mL) was carefully added dropwise to a solution of [{RhCl(cod)}<sub>2</sub>] (0.20 g, 0.40 mmol) in thf (50 mL). The brown solution that formed was allowed to warm to room temperature slowly over 2 h and then stirred for a further 2 h. The solvent was then removed under vacuum and the resulting dark brown oil extracted with  $Et_2O$  (2×50 mL). The brown  $Et_2O$ solution was filtered and concentrated to ca. 5 mL. A crystalline solid comprising colorless prisms of 3, yellow cubes of 4, and orange plates of 2 formed at -28 °C over 1 week. A small amount of the crystals obtained was transferred into perfluoro ether oil, separated by hand under the microscope, and subjected to X-ray diffraction. No significant differences were observed when using the stoichiometry 4:1.



Synthesis of [Ag<sub>4</sub>(P<sub>6</sub>Mes<sub>6</sub>)<sub>2</sub>] (5): At -78 °C and in the dark, a solution of 1 (0.75 g, 0.80 mmol) in thf (50 mL) was carefully added dropwise to a suspension of [AgCl(PPh<sub>3</sub>)<sub>2</sub>] (1.07 g, 1.60 mmol) in thf (50 mL). An orange solution formed that was allowed to warm to room temperature slowly over 2 h and then stirred for a further 6 h. The solvent was then removed under vacuum and the resulting dark orange oil extracted with Et<sub>2</sub>O (20 mL). The orange Et<sub>2</sub>O solution was filtered and concentrated to ca. 5 mL. Orange crystals formed at -28 °C over about 1 month. Once the crystals were isolated, they were poorly soluble in solvents such as benzene, toluene, diethyl ether, thf, n-hexane, n-pentane, dimethoxyethane, and dioxane. Yield: 0.090 g (17%); m.p. 233–235 °C (brown oil). <sup>1</sup>H NMR  $(C_6D_6, 25 \text{ °C}): \delta = 1.64 (6 \text{ H}), 1.66 (6 \text{ H}), 1.77 (6 \text{ H}), 2.16 (6 \text{ H}),$ 2.18 (6 H), 2.43 (6 H), 2.79 (6 H), 3.08 (6 H), 3.99 (s, 6 H, Me of Mes), 6.17 (2 H), 6.23 (2 H), 6.32 (2 H), 6.49 (2 H), 6.85 (2 H), 7.08 (s, 2 H, aromatic CH of Mes) ppm.  ${}^{13}C{}^{1}H, {}^{31}P{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 20.3, 20.4, 21.0, 22.9, 23.0, 24.0, 25.1, 28.3$  (Me of Mes), 129.1, 129.5, 129.6 (C-3,5 in Mes), 133.7, 133.9, 134.0 (C-4 in Mes), 136.9, 137.7, 137.8 (C-1 in Mes), 143.8, 144.3, 144.7 (C-2,6 in Mes) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = -100.6$  [br. m, appears as br. sext,  $P_{AA'}$ , J(P-P) = 230.0 Hz], -14.3 [br. m, appears as br. sext,  $P_{BB'}$  J(P-P) = 228.4 Hz], 0.7 [br. m, appears as br. q,  $P_{CC'}$  J(P-P) = 205.7 Hz] ppm. IR (KBr):  $\tilde{v}$  = 3014 (m), 2958 (s), 2930 (m), 2867 (s), 1626 (m), 1602 (m), 1549 (w), 1458 (s), 1373 (m), 1289 (w), 1261 (s), 1178 (w), 1145 (m), 1097 (s), 1021 (s), 917 (w), 847 (m), 804 (s), 745 (w), 711 (w), 709 (w), 607 (w), 549 (m), 473 (w), 446 (w), 404 (w) cm<sup>-1</sup>. MS (FAB): m/z (%) = 1331.6 (0.7) [M - $P_6Mes_6]^+$ , 345.2 (100)  $[AgP_2Mes_2 - 4 Me - H]^+$ .  $C_{108}H_{132}Ag_4P_{12}$ (2233.36): C 58.08, H 5.96; found C 57.72, H 5.65.

**Data Collection and Structural Refinement of 2–5:** The data for 2– 5 were collected with a CCD Oxford Xcalibur S diffractometer

	Table 2.	Crystallog	graphic	data	for	2-5
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	2	3	4	5
Empirical formula	C47H69NaO3P3Rh	C <sub>58</sub> H <sub>76</sub> OP <sub>6</sub>	C49H66Na3OP5	C <sub>148</sub> H <sub>232</sub> Ag <sub>4</sub> O <sub>10</sub> P <sub>12</sub>
M	900.83	975.01	894.84	2974.46
$T[\mathbf{K}]$	130(2)	130(2)	130(2)	130(2)
Crystal system	triclinic	monoclinic	monoclinic	tetragonal
Space group	ΡĪ	P2/c	$P2_1/n$	$I\bar{4}_2d$
a [pm]	1192.1(5)	1331.12(5)	1237.11(2)	1895.90(1)
b [pm]	1969.9(5)	852.68(3)	1628.58(3)	1895.90(1)
c [pm]	2087.8(5)	2454.24(7)	2512.24(4)	5054.71(8)
	70.537(5)	90	90	90
β[°]	79.200(5)	97.469(3)	96.223(2)	90
γ [°]	80.798(5)	90	90	90
V [nm <sup>3</sup> ]	4.52(1)	2.7620(2)	5.0317(2)	18.1688(3)
Z	4	2	4	4
Crystal size [mm]	$0.4 \times 0.18 \times 0.01$	$0.30 \times 0.20 \times 0.10$	$0.60 \times 0.20 \times 0.20$	$0.60 \times 0.15 \times 0.05$
$\rho_{\rm calcd.}  [{\rm Mgm^{-3}}]$	1.325	1.172	1.181	1.087
F(000)	1904	1044	1904	6272
Absorption coefficient [mm <sup>-1</sup> ]	0.533	0.232	0.241	0.575
hkl range	$-15 \le h \le 14$	$-16 \le h \le 16$	$-16 \le h \le 16$	$-22 \le h \le 22$
	$-24 \leq k \leq 24$	$-10 \le k \le 10$	$-21 \le k \le 21$	$-20 \le k \le 22$
	$-26 \le l \le 26$	$-30 \le l \le 30$	$-33 \le l \le 33$	$-60 \le l \le 59$
$2\theta_{\rm max}$ [°]	53.46	52.74	56.56	50.56
Reflections collected/unique	105139/19133	59610/5655	49467/12482	69054/8185
<i>R</i> (int)	0.0690	0.0677	0.0443	0.1116
Data/restraints/ parameters	19133/820/893	5655/0/292	12482/0/584	8185/16/291
Goodness of fit on $F^2$	0.965	1.035	0.917	1.178
$R_1/wR_2 [I > 2\sigma(I)]$	0.0415/0.0992	0.0640/0.1998	0.0351/0.0767	0.0780/0.1882
$R_1/wR_2$ (all data)	0.0787/0.1148	0.0990/0.2220	0.0752/0.0878	0.0944/0.2032
Largest difference peak/hole [eÅ-3]	0.865/-1.138	0.937/-0.532	0.342/-0.224	1.271/-0.847
Flack parameter	-	-	_	-0.05(6)

 $[\lambda(Mo-K_{\alpha}) = 71.073 \text{ pm}]$  by using  $\omega$ - and  $\phi$ -scan modes. Semi-empirical equivalence absorption corrections were carried out with SCALE3 ABSPACK,<sup>[19]</sup> and the structures were solved by direct methods by using SHELXS-97.[20] Structure refinement was carried out with SHELXL-97.<sup>[21]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined at idealized positions by using the riding model. Table 2 lists the crystallographic data for complexes 2-5. For 2, some carbon atoms of the thf molecules were disordered and were refined over split positions with constrained geometry and fixed atomic displacement parameters (SADI and EADP instructions). For 5, only two of the six diethyl ether molecules found in the asymmetric unit could be satisfactorily refined, and the other four were removed by using the program SQUEEZE implemented in Platon.<sup>[14]</sup> CCDC-793271 (2), -793272 (3), -793273 (4), and -793274 (5) 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.

Calculations: All electronic structure calculations were carried out with the TURBOMOLE suite.[11] The final optimized structure was obtained by employing the BP86 density functional, and the resolution of identity approximation was used.<sup>[22]</sup> A TZVP basis set was applied to all atoms. In the geometry optimization the convergence criterion of the DFT energy and the magnitude of the gradient vector were set to 10<sup>-8</sup> Hartree and 10<sup>-4</sup> Hartree/Bohr, respectively. The SEN analysis was performed with the TURBOMOLE suite on the basis of the precalculated wavefunctions. Gaussian 03<sup>[23]</sup> was employed for the NBO analysis with the TZVP basis set and the BP86 functional in which the recommended VWN-V-LDA correlation was employed.<sup>[24]</sup> Thereby localized Lewis bonds and interactions between bonds were sought for. When Gaussian 03 default settings were employed, a number of second-order perturbation interactions were indicated, but no Na-Rh single bond was assigned. By predefinition of an Na-Rh single bond, however, covalent interactions between both metal atoms could be supported. No clues to a conceivable Na-Rh-P three-center bond were obtained. For further details see the Supporting Information.

**Supporting Information** (see footnote on the first page of this article): Full details of the calculation of 2 and a complete picture of the molecular structure of 5.

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