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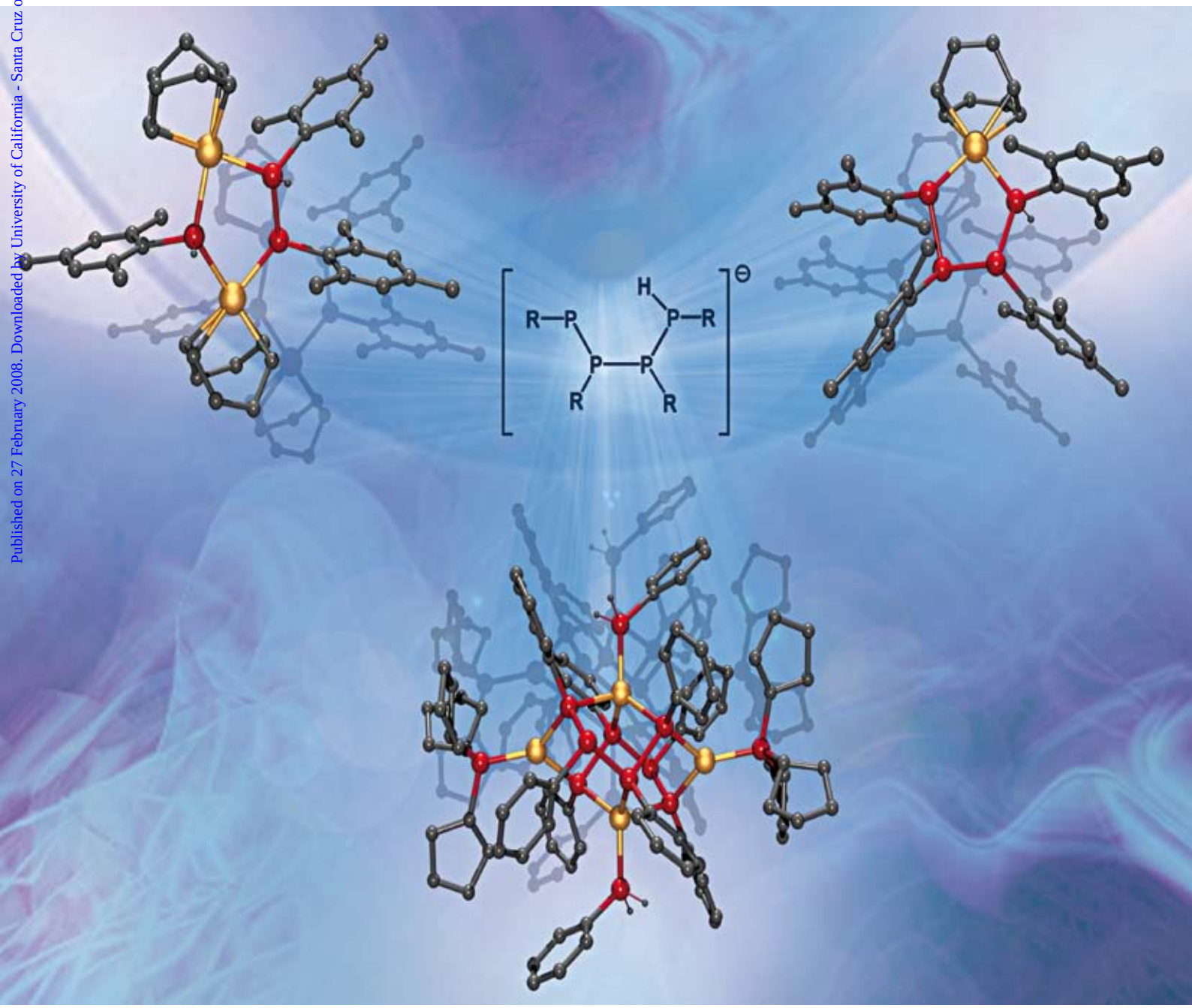

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Different transmetallation behaviour of [M(P$_4$HR$_4$)] salts toward rhodium(I) and copper(I) (M = Na, K; R = Ph, Mes; Mes = 2,4,6-Me$_3$C$_6$H$_2$)†

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[K$_2$(P$_4$Mes$_4$)] (**1**) or [Na$_2$(THF)$_4$(P$_4$Mes$_4$)] (**2**) (Mes = 2,4,6-Me$_3$C$_6$H$_2$) reacts with one equivalent of HCl and subsequently with 0.5 equivalents of [{RhCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) to give a mixture of rhodium complexes, from which [Rh(P$_4$HMes$_4$)(cod)] (**3**) and the secondary product [Rh$_2$(μ-P$_2$HMes$_2$)(μ-PHMes)(cod)$_2$] (**4**) were isolated and characterised by X-ray diffraction studies. Alternatively, the reaction of [K$_2$(P$_4$Ph$_4$)] (**5**) or [Na$_2$(THF)$_5$(P$_4$Ph$_4$)] (**6**) with one equivalent of HCl and subsequently with one equivalent of [CuCl(PCyp$_3$)$_2$] (Cyp = *cyclo*-C$_5$H$_9$) gave the complex [Cu$_4$(P$_4$Ph$_4$)$_2$(PH$_2$Ph)$_2$(PCyp$_3$)$_2$] (**7**), presumably *via* disproportionation of the monoanion (P$_4$HPh$_4$)$^-$.

Introduction

The chemistry of phosphorus-rich compounds is of much current interest, due to their similarities and differences to isolobal carbon counterparts.[1] In this context, there has been renewed interest in alkali metal oligophosphanides M{*cyclo*-(P$_n$R$_{n-1}$)} (n = 3–5) and M$_2$(P$_n$R$_n$) (n = 2–4; M = Li, Na, K).[2] Only recently have the interesting structural properties of these anions been fully unravelled, and their reactivity towards metals in different oxidation states explored.[3–7] Our initial efforts focussed on the targeted, high-yield synthesis of [Na{*cyclo*-(P$_5$*t*Bu$_4$)}],[4a,6a] its coordination and main group chemistry[6,7] and the preparation and reactivity of (P$_4$R$_4$)$^{2-}$ dianions (R = alkyl or aryl).[4a–c,5] In contrast, the chemistry of the monoprotonated anions (P$_n$HR$_n$)$^-$ (n = 2–4)[4e,8,9] has remained almost unexplored. Prior to this report, only [K(pmdeta)(P$_2$H*t*Bu$_2$)]$_2$[10] [pmdeta = MeN(CH$_2$CH$_2$NMe$_2$)$_2$] and [Li(thf)(P$_2$HPh$_2$)]$_4$[11] were isolated in pure form, while the potassium salts [K(crypt)][P$_2$HPh$_2$][4b] (crypt = 2,2,2-cryptand) and [{K(pmdeta)(P$_3$HMes$_3$)}$_2${K$_2$(P$_4$Mes$_4$)}] (Mes = 2,4,6-Me$_3$C$_6$H$_2$)[4e] and the related Cu^I complexes [Cu$_2$(P$_2$HMes$_2$)$_2$(PCyp$_3$)$_2$] and [Cu$_5$Cl(P$_2$HMes$_2$)$_3$(PHMes)(PCyp$_3$)$_2$] (Cyp = *cyclo*-C$_5$H$_9$) were only obtained in product mixtures and mainly characterised by X-ray diffraction studies.[4c] Moreover, the molybdenum complex [Cp°MoCl$_2$(P$_4$HCy$_4$)] (Cp° = C$_5$Me$_4$Et) containing the tetraphosphanide anion (P$_4$HCy$_4$)$^-$ was obtained in very low yield from the deprotonation of [Cp°MoCl$_4$(PH$_2$Cy)] with NEt$_3$, but the mechanism of its formation has remained unclear.[12]

Recently, we reported the targeted synthesis and unusual structural properties of the (P$_4$HMes$_4$)$^-$ anion, which partially disproportionates in solution and exhibits fluxional behaviour of its P–H proton. Possible synthetic applications of such tetraphosphanide anions might be complicated by their instability in solution.[8] To evaluate this hypothesis, we studied transmetallation reactions of the monoanions (P$_4$HR$_4$)$^-$ (M = Na, K; R = Ph, Mes) towards a variety of metal salts, and we now report the results of the reactions with rhodium(I) and copper(I) halides.

Results and discussion

[K$_2$(P$_4$Mes$_4$)] (**1**) or [Na$_2$(THF)$_4$(P$_4$Mes$_4$)] (**2**) reacts with one equivalent of HCl in polar solvents such as THF or diethyl ether, and the (P$_4$HR$_4$)$^-$ anion formed "*in situ*" was then treated with half an equivalent of [{RhCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) to give a mixture of products, from which two rhodium-containing complexes could be isolated by repeated crystallization from THF (Scheme 1). The more soluble component of this mixture was identified as [Rh(P$_4$HMes$_4$)(cod)] (**3**), and the other product as [Rh$_2$(μ-P$_2$HMes$_2$)(μ-PHMes)(cod)$_2$] (**4**). Complex **4** could be isolated as a pure compound, albeit as mixture of diastereomers because of the presence of chiral phosphorus centres, while **3** was always contaminated with a very small quantity of **4**. Compounds **3** and **4** were characterised by IR and multinuclear NMR spectroscopy, mass spectrometry and X-ray diffraction studies.

Complexes **3** and **4** show very complicated ^{1}H NMR spectra due to the asymmetry of the molecules and the presence of a mixture of isomers. The signals corresponding to the methyl groups of the mesityl moieties (some of which are slightly broadened) appear as singlets between 1.5 and 3.2 ppm, and the aromatic protons of the mesityl groups in the region between 6.4 and 6.9 ppm. The alkyl protons of the cod ligand could not be detected, probably due to overlap with the methyl signals of the mesityl substituents. Nevertheless, the olefinic protons of cod were observed as broad signals between 3.6 and 4.4 ppm. The P–H protons also appear as broad signals, between 3.6 and 6.3 ppm.

The high-resolution ^{31}P{^{1}H} NMR spectrum of the reaction mixture shows eight multiplets, four corresponding to **3** at *ca.* 38, −23, −35 and −61 ppm (ABCDX spin system) and four corresponding to the mixture of isomers of **4** at *ca.* 26, 10, −4 and −86 ppm (two ABCXY spin systems). Some additional, minor signals appeared when the mixture was stirred for a prolonged

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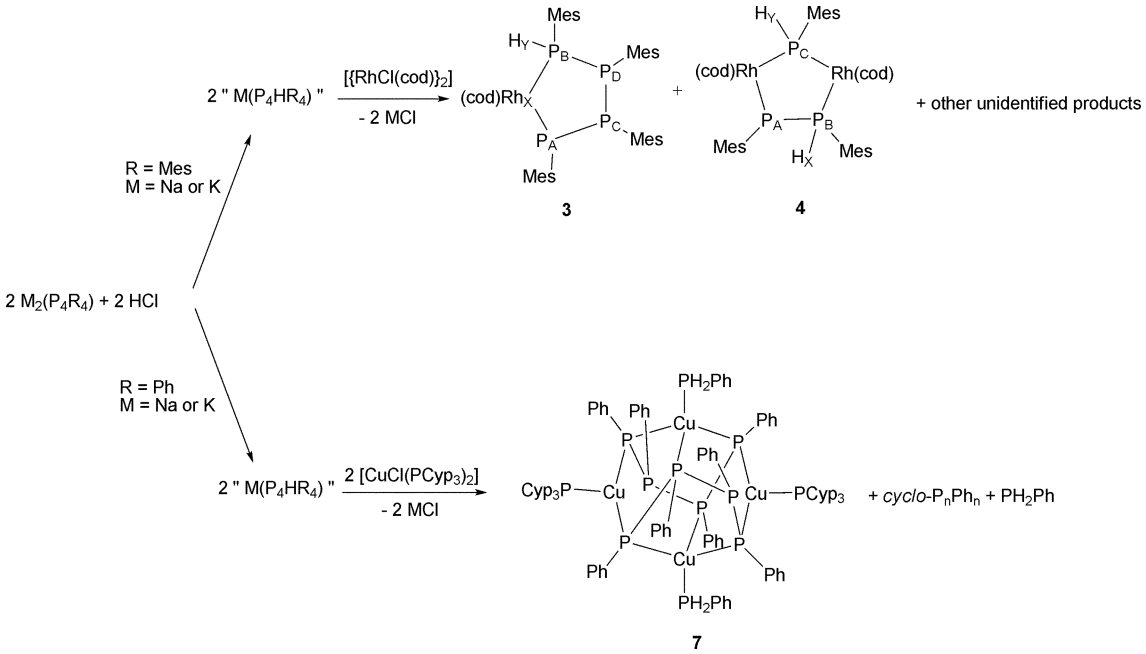
† Electronic supplementary information (ESI) available: 1: Simulated and experimental ^{31}P NMR spectrum of [Rh(P$_4$HMes$_4$)(cod)] (**3**). 2: Variable-temperature ^{31}P{^{1}H} NMR spectra of [Rh$_2$(μ-P$_2$HMes$_2$)(μ-PHMes)(cod)$_2$] (**4**). CCDC reference numbers 666346 (**3**), 666347 (**4**) and 666348 (**7**) see DOI: 10.1039/b718727k



Scheme 1

period and coincide with those observed in the reaction mixture of one equivalent of [{RhCl(cod)}$_2$] with one equivalent of **1**. In the proton-coupled ^{31}P NMR spectrum of **3** one of the signals (P_B) is further split by coupling to hydrogen, an ABCDXY spin system is observed and the ^{31}P NMR parameters could be obtained *via* simulation using the program SPINWORKS[13] (see experimental section and electronic supplementary information for details). The $^1J_{PP}$ (167.55–272.71 Hz) and $^2J_{PP}$ (16.54–57.96 Hz) coupling constants are in the expected ranges and the $^1J_{RhP}$ coupling constants (85.32 and 160.60 Hz) are of the same order of magnitude as, for example, observed for the related complex [Rh{*cyclo*-(P_5tBu$_4$)}(PPh$_3$)$_2$].[6b] In addition, a very large $^1J_{PH}$ coupling constant (335.24 Hz) unequivocally supports the presence of a P–H proton at P_B. Attempts to simulate the ^{31}P{^{1}H} NMR spectrum of **4** failed due to the severe overlap of signals from two different isomers which presumably contain the two P–H protons in mutual *cis* and *trans* arrangements.

Complex **3** crystallises as orange plates in the space group $P\bar{1}$ with two molecules in the unit cell. The X-ray crystal structure determination reveals that the rhodium atom has a distorted square-planar geometry in which a cod ligand is η^4 coordinated and the $(P_4HR_4)^-$ ligand chelates the metal centre *via* its two terminal phosphorus atoms (P1 and P4, Fig. 1). Selected bond lengths and angles are given in Table 1. Similar to the structure of [Rh{*cyclo*-(P_5tBu$_4$)}(PPh$_3$)$_2$],[6b] the Rh(1)–P(1) bond length in **3** is 229.89(8) pm, while the Rh(1)–P(4) distance of 225.66(9) pm is somewhat shorter, as it corresponds to a coordinated phosphane. The P–P distances [219.9(1)–222.3(1) pm] indicate single bonds.[14] The P_4 chain is in a *syn* arrangement (torsion angle P(1)–P(2)–P(3)–P(4) −44.3°) and is clearly unsymmetrical, with the proton bound to the terminal phosphorus atom P(4) [P(4)–H(4P) 126(3) pm, the position of this proton was located from the Fourier difference map and refined freely]. The four phosphorus atoms are significantly pyramidalised and form a five-membered ring

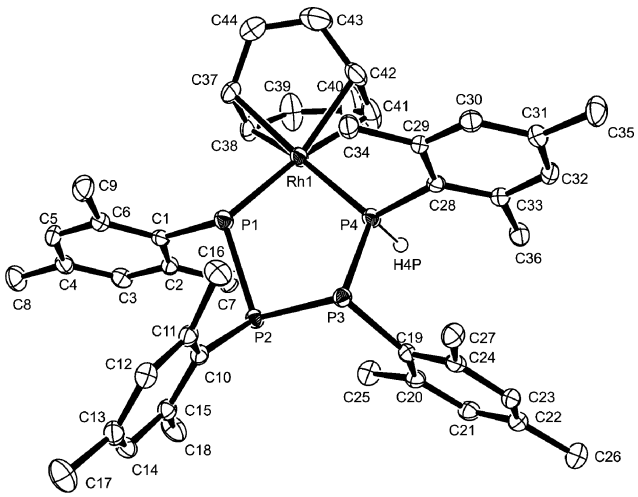


Fig. 1 Molecular structure and atom labelling scheme for **3** with thermal ellipsoids at 50% probability (hydrogen atoms, except at phosphorus, are omitted for clarity).

with the rhodium atom, which is in an envelope conformation with P(2) deviating by −45.6 pm from the mean plane formed by Rh(1)–P(1)–P(3)–P(4).

Complex **4** crystallises as very thin orange plates in the space group $P\bar{1}$ with two molecules of **4** and two THF molecules in the unit cell. Both rhodium atoms have a distorted square-planar geometry with one η^4-coordinated cod ligand at each rhodium atom and bridging $(P_2HMes_2)^-$ and $PHMes^-$ anions (Fig. 2). The Rh(1)–P(1) and Rh(2)–P(2) bond lengths [228.8(2) and 228.8(2) pm] are similar to those of **3**, while the Rh(1)–P(3) and Rh(2)–P(3) distances [237.1(2) and 237.2(2) pm] are significantly longer. The P(1)–P(2) bond length of 216.8(2) pm is typical for complexes containing $(P_2HR_2)^-$ anions.[4b,c,10,11] The positions of the P–H

Table 1 Selected bond lengths (pm) and angles (°) for **3** and **4**

	3	**4**
Rh(1)–P(1)	229.89(8)	228.8(2)
Rh(1)–P(3)		237.1(2)
Rh(1)–P(4)	225.66(9)	
Rh(2)–P(2)		228.8(2)
Rh(2)–P(3)		237.2(2)
P(1)–P(2)	222.3(1)	216.8(2)
P(2)–P(3)	221.2(1)	
P(3)–P(4)	219.9(1)	
P(2)–H(2P)		111(7)
P(3)–H(3P)		126(6)
P(4)–H(4P)	126(3)	
P(1)–P(2)–P(3)	95.91(4)	
P(2)–P(3)–P(4)	96.80(4)	
Rh(1)–P(1)–P(2)	113.75(4)	113.13(9)
Rh(1)–P(4)–P(3)	119.48(4)	
P(1)–Rh(1)–P(4)	88.16(3)	
P(1)–Rh(1)–P(3)		87.67(6)
P(2)–Rh(2)–P(3)		84.76(6)
Rh(2)–P(2)–P(1)		115.72(9)
Rh(1)–P(3)–Rh(2)		128.31(8)

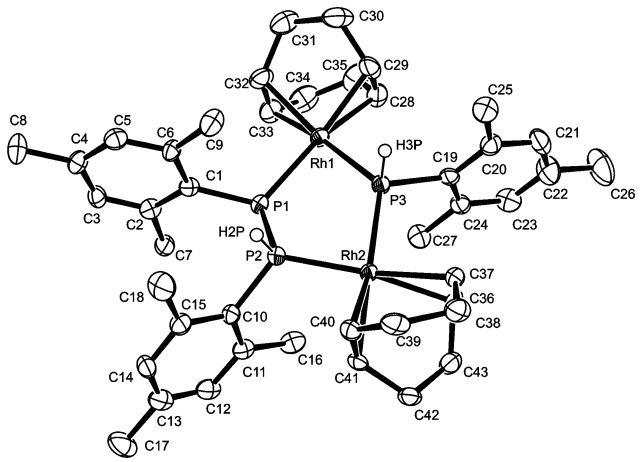


Fig. 2 Molecular structure and atom labelling scheme for **4** with thermal ellipsoids at 50% probability (hydrogen atoms, except at phosphorus, are omitted for clarity).

protons were located from the Fourier difference map, and their free refinement yielded reasonable P(2)–H(2P) and P(3)–H(3P) distances of 111(7) and 126(6) pm, respectively.

In the FAB mass spectrum of **3** the molecular ion peak and characteristic fragments such as $[M - cod]^+$, $[M - cod - PHMes]^+$ and $[M - cod - P_2HMes_2]^+$ (100.0%) were observed. Similar fragments were also observed for **4** in addition to the molecular ion peak and, interestingly, the organyl-free fragments $[Rh_2P_3]^+$ and $[Rh_2P_2]^+$. The P–H stretching frequencies were observed in the expected region at *ca.* 2360 cm^{-1} in the IR spectrum of **3** and **4**.

The complex $[Cu_4(P_4Ph_4)_2(PH_2Ph)_2(PCyp_3)_2]$ (**7**) was obtained from the reaction of one equivalent of $[K_2(P_4Ph_4)]$ (**5**) or $[Na_2(THF)_5(P_4Ph_4)]$ (**6**) with one equivalent of HCl followed by subsequent reaction with one equivalent of $[CuCl(PCyp_3)_2]$ (Scheme 1). The desired $(P_4HPh_4)^-$ anion is not present in **7**. Instead, two $(P_4Ph_4)^{2-}$ dianions are coordinated to four copper(I) cations. One of the possible explanations for this phenomenon could be the disproportionation of two equivalents of the "*in situ*"-generated $(P_4HPh_4)^-$ monoanion before or after the transmetallation step to give one equivalent of $(P_4Ph_4)^{2-}$ and one equivalent of $P_4H_2Ph_4$. The latter is very unstable in solution and decomposes rapidly to give a mixture of the phosphanes *cyclo*-(P_nPh_n), $P_2H_2Ph_2$ and PH_2Ph,[15] the last-named of which is found as a ligand in **7**. Nevertheless, an alternative metal-mediated mechanism cannot be discounted.

The complex crystallises in the centrosymmetric space group $P2_1/c$ and selected bond lengths and angles are given in Table 2. Its molecular structure (Fig. 3) is similar to that of the previously reported $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$, which was obtained from the reaction of two equivalents of $[CuCl(PCyp_3)_2]$ with one equivalent of **6**,[5a] with the difference that instead of a third $PCyp_3$ ligand two PH_2Ph ligands are present in **7**. This leads to a centrosymmetric arrangement of the Cu_4P_8 cluster core which differs significantly from that in $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$ (Fig. 4).

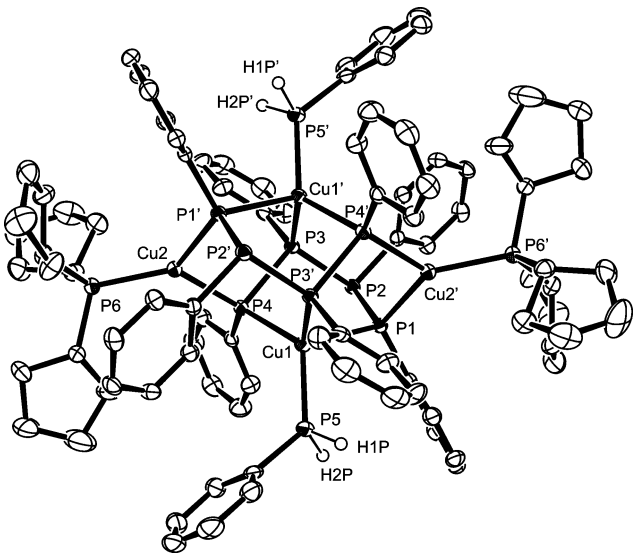


Fig. 3 Molecular structure and atom labelling scheme for **7** with thermal ellipsoids at 50% probability (hydrogen atoms, except at phosphorus, and labels for carbon atoms are omitted for clarity). Symmetry transformation to generate equivalent atoms: $2 - x, y, 1 - z$.

Table 2 Selected bond lengths (pm) and angles (°) for **7**[a]

Cu(1)–P(1)	230.1(1)	P(1)–P(2)	218.6(1)
Cu(1)–P(4)	233.38(8)	P(2)–P(3)	220.5(1)
Cu(1)–P(5)	222.72(8)	P(3)–P(4)	218.6(1)
Cu(2)–P(1)′	227.56(8)	P(5)–H(1p)	130(3)
Cu(2)–P(4)	228.47(8)	P(5)–H(2p)	130(3)
Cu(2)–P(6)	222.64(9)		
P(6)–Cu(2)–P(1)′	127.39(3)	P(3)–P(4)–Cu(1)	100.25(4)
P(6)–Cu(2)–P(4)	133.20(3)	Cu(2)–P(4)–Cu(1)	109.73(3)
P(1)′–Cu(2)–P(4)	99.31(3)	P(1)–P(2)–P(3)	101.46(3)
P(5)–Cu(1)–P(1)	124.13(3)	P(1)–P(2)–Cu(1)′	105.23(3)
P(5)–Cu(1)–P(2)′	108.74(3)	P(3)–P(2)–Cu(1)′	125.35(4)
P(1)–Cu(1)–P(2)′	108.03(2)	P(2)–P(1)–Cu(2)′	104.09(3)
P(5)–Cu(1)–P(4)	106.14(3)	P(2)–P(1)–Cu(1)	90.31(3)
P(1)–Cu(1)–P(4)	107.02(3)	Cu(2)′–P(1)–Cu(1)	116.31(3)
P(2)′–Cu(1)–P(4)	100.15(2)	Cu(1)–P(5)–H(1P)	113(2)
P(4)–P(3)–P(2)	95.54(4)	Cu(1)–P(5)–H(2P)	116(2)
P(3)–P(4)–Cu(2)	110.92(3)	H(1P)–P(5)–H(2P)	96(2)

[a] Symmetry transformation to generate equivalent atoms: $2 - x, y, 1 - z$.

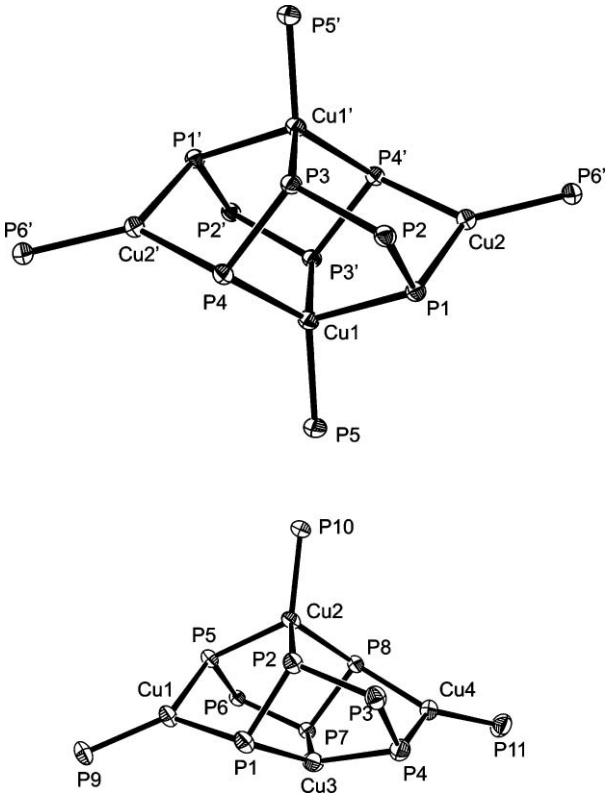


Fig. 4 Comparison of the core structures of **7** (top) and $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$ (bottom).

From a heuristic viewpoint, the structure of **7** may be viewed as a "crownlike", ten-membered $[Cu_2(P_4Ph_4)_2]^{2-}$ macrocycle which coordinates two further copper ions through two terminal phosphorus atoms of the same P_4 chain and one internal phosphorus atom of the other P_4 chain. Although unusual, such an aggregation is not completely unprecedented, as other copper(I) phosphanido compounds generally form four- to eight-membered Cu_nP_n rings, depending on the size of the substituents on phosphorus.[16] Two distinct coordination environments can be distinguished for copper: Cu(1) shows a tetrahedral geometry and Cu(2) is in a trigonal-planar environment (sum of bond angles at Cu(2): 359.90°). Both crystallographically independent Cu atoms are coordinated by two terminal phosphorus atoms from the $(P_4Ph_4)^{2-}$ chains. However, Cu(1) is coordinated by two terminal P atoms from the *same* P_4 chain, giving rise to the formation of five-membered CuP_4 chelate rings, while Cu(2) bridges two terminal P atoms from different chains. The coordination sphere of Cu(1) is completed by coordination of an internal phosphorus atom of the second $(P_4Ph_4)^{2-}$ ligand and a PH_2Ph ligand. Cu(2) is further coordinated by a $PCyp_3$ ligand.

The P–P bond lengths range from 218.6(2) to 220.5(1) pm and are in the expected range for single bonds.[14] The P_4 chains of the $(P_4Ph_4)^{2-}$ ligands are in a *syn* arrangement and display rather large torsion angles as a consequence of the coordination of an internal phosphorus atom to one copper atom in each of the ligands (P(1)–P(2)–P(3)–P(4) 67.53, *cf*. P(1)–P(2)–P(2)′–P(1)′ 32.18° in **6**).[4a]

The ^{1}H NMR spectrum of **7** is similar to that reported for $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$ and shows three broad signals between 1.0 and 2.0 ppm corresponding to the cyclopentyl groups of the $PCyp_3$. The signal corresponding to the protons of the PH_2Ph groups is observed as a broad doublet at *ca.* 4.4 ppm.

The aromatic protons are observed as broad signals between 6.0 and 7.5 ppm. As observed previously for $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$, the room-temperature $^{31}P\{^1H\}$ NMR spectrum is very complicated, displaying broad peaks at 19.9, 11.3, 7.8, −5.0, −9.7, −24.7, −46.5, −70.3, −79.5 and −94.0 ppm of varying intensity, and it appears unlikely that the molecular structure of **7** is retained in solution. The FAB mass spectrum of this complex does not show the molecular ion peak, but typical fragments for this molecule derived from the loss of organic substituents (Ph, Cyp) and copper tricyclopentylphosphane units as well as the fragment $[Cu_3P_8]^+$ are observed. Finally the IR spectrum shows the typical P–H stretching bands at 2330 and 2326 cm^{-1}.

Conclusions

While previous attempts to employ $M(P_4HMes_4)$ salts in transmetallation reactions with transition metal halides showed the presence of $(P_4HMes_4)^-$-containing complexes in the reaction mixtures, which could not be separated, the preparation of the rhodium complex $[Rh(P_4HMes_4)(cod)]$ (**3**) now represents the first targeted synthesis (albeit in low yield) of a transition metal complex containing a tetraphosphanide anion. Thus, the $(P_4HMes_4)^-$ anion is apparently stable enough to be transmetallated successfully in spite of its lability in solution.[8] However, this lability leads to the formation of the secondary product $[Rh_2(\mu\text{-}P_2HMes_2)(\mu\text{-}PHMes)(cod)_2]$ (**4**).

In contrast, the $(P_4HPh_4)^-$ anion did not remain intact in the attempted transmetallation reaction of $M(P_4HPh_4)$ with $[CuCl(PCyp_3)_2]$. The complex $[Cu_4(P_4Ph_4)_2(PH_2Ph)_2(PCyp_3)_2]$ (**7**) was obtained instead, which indicates preferred formation of the $[Cu_4(P_4Ph_4)_2]$ entity. This has previously been observed in the complex $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$[5a] and may thus be a favoured structural unit for copper(I) tetraphosphanediido complexes. The difference in reactivity between the $M(P_4HMes_4)$ and $M(P_4HPh_4)$ salts may be attributed to the lower amount of steric shielding provided by the phenyl substituents in the $(P_4HPh_4)^-$ anion, which facilitates rearrangement processes. The outcome of transmetallation reactions of $M(P_4HR_4)$ salts thus depends on careful tuning of a number of different parameters, including the substituents of the $(P_4HR_4)^-$ anion and the type of transition metal halide employed.

Experimental

General remarks

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. The NMR spectra were recorded on a Bruker AVANCE DRX 400 spectrometer. ^{1}H NMR (400.13 MHz): internal standard solvent, external standard TMS; ^{31}P NMR (161.9 MHz): external standard 85% H_3PO_4; IR spectra: KBr pellets were prepared in a nitrogen-filled glove box and the spectra were recorded on a Perkin-Elmer System 2000 FTIR spectrometer in the range 350–4000 cm^{-1}. FAB-MS spectra were recorded in a MASPEC II spectrometer with 3-nitrobenzyl alcohol as matrix. All solvents were purified by distillation, dried, saturated with argon and stored over potassium mirror. $[\{RhCl(cod)\}_2]$,[17] $[CuCl(PCyp_3)_2]$,[5a] $K_2(P_4Mes_4)$ (**1**), $Na_2(P_4Mes_4)$ (**2**), $K_2(P_4Ph_4)$ (**5**)

and $Na_2(P_4Ph_4)$ (**6**)[4a,c,e,i] were synthesised according to literature procedures. Simulation of the ^{31}P NMR spectrum of **3** was carried out using the program SPINWORKS.[13]

Data collection and structural refinement of 3, 4 and 7. The data of **3**, **4** and **7** were collected on a CCD Oxford Xcalibur S diffractometer (λ(Mo-Kα) = 0.71073 Å) using ω and ϕ scan mode. Semi-empirical from equivalents absorption corrections were carried out with SCALE3 ABSPACK[18] and the structures were solved with direct methods.[19]

Structure refinement was carried out with SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically, the H atoms bonded to phosphorus were localised and refined freely and the other hydrogen atoms were placed in calculated positions and refined with calculated isotropic displacement parameters. Crystallographic data for **3**, **4** and **7** are presented in Table 3.

CCDC reference numbers 666346 (**3**), 666347 (**4**) and 666348 (**7**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718727k

Synthesis of [Rh(P_4HMes_4)(cod)] (3) and [Rh_2(μ-P_2HMes_2)(μ-PHMes)(cod)$_2$] (4). A solution of HCl in Et_2O (2 M) (0.34 mL, 0.70 mmol) in diethyl ether (10 mL) was carefully added to an orange solution of $K_2(P_4Mes_4)$ (0.46 g, 0.70 mmol) in THF (10 mL). A red suspension formed which was allowed to warm to room temperature slowly over 2 h and stirred for 5 h. The mixture was filtered and subsequently the filtrate was added carefully to a solution of [{RhCl(cod)}$_2$] (0.17 g, 0.35 mmol) in THF (40 mL) at −78 °C, and the deep red solution turned brown. The mixture was stirred for 3 h, and the solvent was removed under vacuum. The resulting dark brown oil was extracted twice with Et_2O (40 mL) and filtered. The combined extracts were reduced to *ca.* 15 mL. An orange solid formed over one week at −30 °C, which was isolated and characterised as a mixture of **3** and **4** (ratio *ca.* 1 : 3). This solid was recrystallised from THF (15 mL). Orange crystals were obtained from this solution, which were isolated by filtration and identified as **4**. The filtrate was evaporated in vacuum and the resulting solid analysed and identified as **3**. Yield of **3**: 0.15 g (26%); mp 111–113 °C; ^1H NMR ([D$_8$]THF, 25 °C, for the predominant isomer): δ 1.63 (6H), 1.97 (6H), 2.01 (12H), 2.98 (6H), 3.03 (6H) (br s, Me of Mes), 3.75 (1H), 3.99 (2H), 4.37 (1H) (br, CH of cod), 4.4–6.3 (several broad signals, P–H), 6.45 (3H), 6.56 (1H), 6.72 (1H), 6.80 (3H), (s, aromatic CH of Mes), CH_2 of cod obscured by other signals; $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 25 °C, for the predominant isomer): δ 19.6, 19.9 (br s, *p*-Me in Mes), 21.0, 21.6 (br s, *p*-Me in Mes), 27.1, 27.4, 27.6, 27.8 (s, *o*-Me in Mes), 29.8, 30.1, 30.2, 30.8, 31.2, 32.3, 32.4 (s, *o*-Me in Mes and CH of cod), 80.7, 85.5, 90.7, 93.3 (br s, CH of cod), 127.4, 127.6, 127.7, 128.1, 128.3, 128.5, 128.7 (s, 3,5-C in Mes), 132.3–142.9 (several s, 1,2,4,6-C in Mes); ^{31}P NMR ([D$_8$]THF, 25 °C, for the predominant isomer): δ 39.34 (m, P_A, $^1J_{AC}$ = 167.55, $^1J_{AX}$ = 85.32, $^2J_{AB}$ = 16.54, $^2J_{AD}$ = 57.96, $^3J_{AY}$ = 5.29 Hz), −23.31 (m, P_B, $^1J_{BD}$ = 272.71, $^1J_{BX}$ = 160.60, $^1J_{BY}$ = 335.24, $^2J_{BC}$ = 55.29), −34.41 (m, P_C, $^1J_{CD}$ = 205.56), −61.16 (m, P_D); FAB-MS, matrix: 3-NBA; *m*/*z* (%): 813.3 (42.3) [M + H]$^+$, 812.3 (2.4) [M]$^+$, 704.2 (5.6) [M − cod]$^+$, 553.1 (53.4) [M − cod − PHMes]$^+$, 401.0 (100.0) [M − 2H − cod − P_2HMes_2]$^+$; IR (cm^{-1}): 3018 m, 2962 s, 2917 s, 2868 m, 2729 w, 2362 w, 1603 s, 1554 m, 1452 s, 1408 m, 1376 m, 1289 m, 1261 s, 1096 s, 1028 s, 846 s, 805 s, 713 w, 614 m, 554 m, 462 w. Elemental analysis (%): found (calc. for $C_{44}H_{57}P_4Rh$, M = 812.69): C 64.35 (65.02); H 7.03 (7.07).

Yield of **4**: 0.10 g (16%); mp 143–148 °C; ^1H NMR ([D$_8$]THF, 25 °C, for the predominant isomer): δ 1.67, 1.80, 1.83, 2.01, 2.02, 2.11, 2.41, 2.85, 2.92 (s, each 3H, Me of Mes), 3.62 (2H), 4.15 (4H), 4.27 (2H) (br, CH of cod), 4.70–6.19 (several broad signals, P-H), 6.42, 6.70, 6.74 (s, each 2H, aromatic CH of Mes), CH_2 of cod obscured by other signals; $^{13}C\{^1H\}$ NMR (THF[D$_8$], 25 °C, for the mixture of isomers): δ 20.0, 20.8, 21.2, 21.4, 21.8 (s, *p*-Me in Mes), 27.5–27.7 (several s, *o*-Me in Mes), 29.1, 29.5, 30.0, 30.3, 30.4, 30.5, 31.0, 31.3, 32.2, 32.5 (s, *o*-Me in Mes and CH

Table 3 Crystallographic data for **3**, **4** and **7**

	3	**4**	**7**
Empirical formula	$C_{44}H_{57}P_4Rh$	$C_{47}H_{67}OP_3Rh_2$	$C_{90}H_{108}P_{12}Cu_4$
M	812.69	946.74	1815.56
Crystal dimensions/mm^3	0.4 × 0.05 × 0.05	0.50 × 0.02 × 0.01	0.30 × 0.10 × 0.10
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/pm	822.5(2)	1262.7(5)	1420.8(5)
b/pm	1190.2(2)	1294.1(5)	1853.6(5)
c/pm	2153.6(4)	1560.4(5)	1692.3(5)
α/°	105.21(1)	74.908(5)	90
β/°	94.20(1)	84.544(5)	107.519(5)
γ/°	92.75(1)	67.189(5)	90
V/nm^3	2.0241(6)	2.270(2)	4.250(2)
Z	2	2	2
T/K	130(2)	130(2)	130(2)
D_c/Mg m^{-3}	1.333	1.386	1.419
μ/mm^{-1}	0.610	0.866	1.258
F(000)	852	984	1888
Reflns collected/unique	38404/9977	35456/9985	99893/9374
R_{int}	0.0568	0.0582	0.0592
Data/restraints/parameters	9977/0/458	9985/6/471	9374/0/486
Final $R1/wR2$ [$I > 2\sigma(I)$]	0.0430/0.0823	0.0495/0.1530	0.0306/0.0523
Final $R1/wR2$ (all data)	0.0731/0.0843	0.0904/0.1728	0.0660/0.0786
$\Delta\rho_{max/min}$/e Å^{-3}	0.537/−0.496	2.156/−0.866	0.797/−0.564

of cod), 81.1, 82.4, 84.3, 85.0, 85.1, 85.8, 85.9, 88.9, 91.0, 92.7, 93.0, 96.2, 97.1, 97.2 (s, CH of cod), 127.0, 128.1, 128.4, 128.6, 129.3, 129.4 (s, 3,5-C in Mes), 133.7, 134.8, 136.0, 136.7, 137.1, 138.0, 138.1, 138.2, 138.4, 140.1, 140.3, 141.5, 142.7, 142.9, 143.0, 144.1, 144.5 (s, 1,2,4,6-C in Mes); $^{31}P\{^{1}H\}$ NMR ([D$_8$]THF, 25 °C, for the mixture of isomers): δ 26.0 (m), 9.7 (m), −4.5 (m), −86.1 (m); FAB-MS, matrix: 3-NBA; *m/z* (%): 875.2 (24.7) $[M + H]^+$, 874.2 (2.0) $[M]^+$, 721.1 (5.0) $[M - H - PHMes]^+$, 662.2 (13.6) $[M - Rh - cod]^+$, 656.0 (6.0) $[M - 2H - 2cod]^+$, 571.0 (39.3) $[M - 2H - P_2HMes_2]^+$, 401.0 (100.0) $[M - 2H - Rh - cod - PHMes]^+$, 298.9 (18.8) $[M - 2H - 2cod - 3Mes = Rh_2P_3]^+$, 267.7 (22.7) $[M - H - PHMes - 2cod - 2Mes = Rh_2P_2]^+$; IR (cm^{-1}): 3021 m, 2965 s, 2920 s, 2868 m, 2728 w, 2370 m, 2361 w, 1601 s, 1549 m, 1462 w, 1451 s, 1408 m, 1376 m, 1299 w, 1289 m, 1262 s, 1099 s, 1028 s, 846 s, 802 s, 711 w, 611 m, 555 m, 461 w. Elemental analysis (%): found (calc. for $C_{43}H_{59}P_3Rh_2$, $M = 874.66$): C 58.66 (59.05); H 6.68 (6.80).

Synthesis of $[Cu_4(P_4Ph_4)_2(PH_2Ph)_2(PCyp_3)_2]$ (7). A solution of HCl in Et_2O (2 M) (0.68 mL, 1.40 mmol) in THF (25 mL) was carefully added to a red solution of $Na_2(P_4Ph_4)$ (1.16 g, 1.40 mmol) in THF (30 mL). An orange suspension formed, which was allowed to warm to room temperature slowly over 2 h and stirred for 5 h. The mixture was filtered, the filtrate was added carefully to a solution of $[CuCl(PCyp_3)_2]$ (0.80 g, 1.40 mmol) in THF (30 mL) at −78 °C and the deep red solution turned brown. The mixture was stirred for 16 h and the solvent was completely evaporated. The resulting dark brown oil was extracted twice with toluene (75 mL) and filtered. The combined filtrates were reduced to *ca.* 20 mL. Yellow crystals formed over two weeks at room temperature, which were isolated by filtration. Yield: 0.25 g (40%); mp 159–162 °C; ^{1}H NMR ([D$_8$]THF, 25 °C): δ 0.87–1.97 (br, 54H, Cyp), 4.43 (br d, 4H, $^{1}J_{PH} = 276$ Hz, PH_2), 6.67–8.28 (br, 50H, Ph). $^{13}C\{^{1}H\}$ NMR ([D$_8$]THF, 25 °C): δ 25.2–25.7 (br s, CH_2 of Cyp), 29.7, 30.4 (br s, CH_2 of Cyp), 35.0, 35.2 (br s, CH of Cyp); 124.7–148.8 (several br s, Ph); $^{31}P\{^{1}H\}$ NMR ([D$_8$]THF, 25 °C): δ 19.9 (br t, J(P,P) = 212.5), 11.3 (br d, J(P,P) = 73.0), 7.78 (br s), −5.0 (br s), −9.7 (br s), −24.7 (m), −46.5 (br s), −70.3 (br s), −79.5 (br s), −94.0 (br s); FAB-MS, matrix: 3-NBA; *m/z* (%): 1293.0 (1.2) $[M - CuPCyp_3 - 2PH_2Ph]^+$, 819.2 (4.9) $[M - Cu - 2PH_2Ph - 2PCyp_3 - 3Ph = Cu_3P_8]^+$, 628.2 (79.8) $[M - 2Cu - 2PH_2Ph - PCyp_3 - PCyp_2 - P_4Ph_4 = Cu_2P_4Ph_4Cyp]^+$; IR (cm^{-1}): 3045 m, 2954 s, 2864 s, 2330 m, 2326 w, 1950 w, 1576 m, 1473 m, 1430 m, 1304 s, 1260 s, 1183 m, 1101 s, 1024 s, 908 w, 854 m, 804 s, 736 s, 693 s, 516 w, 494 w, 460 w. Elemental analysis (%): found (calc. for $C_{90}H_{108}P_{12}Cu_4$, $M = 1815.56$): C 58.99 (59.53); H 6.11 (6.00).

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