Synthesis of a New Multidentate Phosphane Ligand $C_6H_2(CH_2PPh_2)_4$-1,2,4,5 – X-ray Structure of a Dinuclear Ruthenium(II)-Bridged Complex: [$\{RuCl_2(PPh_3)\}_2\{C_6H_2(CH_2PPh_2)_4$-1,2,4,5-*P,P′,P′′,P′′′*\}]

Pablo Steenwinkel[a], Sebastiaan Kolmschot[a], Robert A. Gossage[a], Paulo Dani[a], Nora Veldman[b], Anthony L. Spek[b][+], and Gerard van Koten*[a]

Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University[a],
Padualaan 8, NL-3584 CH Utrecht, The Netherlands
Fax: (internat.) + 31-30/252-3615
E-mail: g.vankoten@chem.ruu.nl

Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University[b],
Padualaan 8, NL-3584 CH Utrecht, The Netherlands

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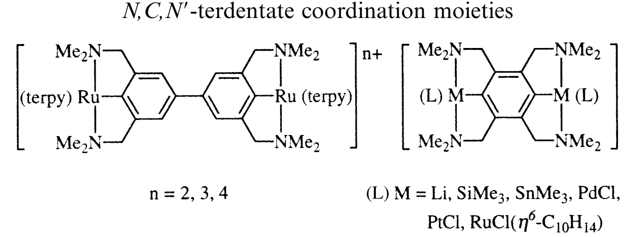
The tetrakis(phosphane oxide) $C_6H_2\{CH_2P(O)Ph_2\}_4$-1,2,4,5 (**5**), has been prepared in high yield from the Arbuzov reaction of $C_6H_2(CH_2Br)_4$-1,2,4,5 (**4**), with excess (7 equiv.) of Ph_2POEt. Subsequent reduction of **5** with $HSiCl_3$ (12 equiv.) in $C_6H_4Cl_2$-1,2 afforded the new tetraphosphane $C_6H_2(CH_2PPh_2)_4$-1,2,4,5 (**6**), in high yield. The reaction of **6** with $[RuCl_2(PPh_3)_4]$ in CH_2Cl_2 afforded the green dinuclear ruthenium(II) coordination complex $[\{RuCl_2(PPh_3)\}_2\{C_6H_2$-$(CH_2PPh_2)_4$-1,2,4,5-*P,P′,P′′,P′′′*$\}]\cdot 0.5\ CH_2Cl_2$ (**8**), in 39% isolated yield. The solid-state molecular geometry of **8**, determined by X-ray analysis, shows that the tetraphosphane is *ortho-P,P′*-chelated to each of the two $[Ru^{II}Cl_2(PPh_3)]$ units.

Introduction

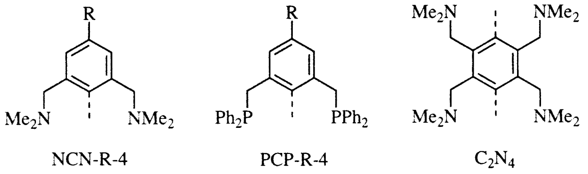
In recent years there has been an increasing interest in dinuclear organometallic complexes and such species have been used to model fundamental properties of multi- and polymeric organometallic materials[1] that have potential optical and/or electronic applications. Recently, we reported on the selective synthesis of 4,4′-biphenylene- and 1,4-phenylene-bridged bimetallic complexes of some platinum-group metals containing anionic *N,C,N′*-terdentate ligands (Figure 1)[2]. In addition to their interesting photochemical behavior[2a], these complexes have potential in the development of multimetallic materials, such as "molecular wires".

Figure 1. Some examples of 4,4′-biphenylene- and 1,4-phenylene-bridged organometallic complexes containing ligands with anionic *N,C,N′*-terdentate coordination moieties



We have also investigated the synthesis of ruthenium(II) complexes of monoanionic (functionalized) *N,C,N′*-terdentate ligands $[C_6H_2(CH_2NMe_2)_2$-2,6-R-4$]^-$ (= NCN-R-4) and *P,C,P′*-terdentate ligands $[C_6H_2(CH_2PPh_2)_2$-2,6-R-4$]^-$ (= PCP-R-4) (Figure 2). The use of these ligands, which can be derived from the aryl compounds $C_6H_3(CH_2ER'_2)_2$-1,3-R-5 (**1**), either by transmetallation (of **1a**-Li) or direct cyclometallation (of **1b**), has resulted in a new series of stable organoruthenium complexes (see Scheme 1)[3].

Figure 2. Schematic representation of the monoanionic aryl ligands NCN-R-4 (R = H, Ph, $Me_3SiC{\equiv}C$, Me_3Si) and PCP-R-4 (R = H, Ph) and the dianionic C_2N_4 ligand



The PCP-R-4 ruthenium(II) complexes **2b** can be obtained directly by cyclometallation[4] of the corresponding diphosphanes **1b** with $[RuCl_2(PPh_3)_4]$. In contrast, the NCN-R-4 ruthenium(II) complexes **2a** were prepared by transmetallation of organolithium reagents $[LiC_6H_2$-$(CH_2NMe_2)_2$-2,6-R-4$]_2$ derived from the aryldiamines **1a**. Some NCN-R-4 and PCP-R-4 ruthenium(II) complexes have also been used as catalysts in various hydrogen-transfer reactions[5].

Recently, we have also developed a synthetic strategy for the preparation of homo- and heterodinuclear organometallic complexes of the bis(*N,C,N′*-terdentate) coordinating dianionic 1,4-phenylene-bridging ligand $[C_6(CH_2NMe_2)_4$-2,3,5,6$]^{2-}$ (= C_2N_4; Figure 2)[6] and extension of this re-

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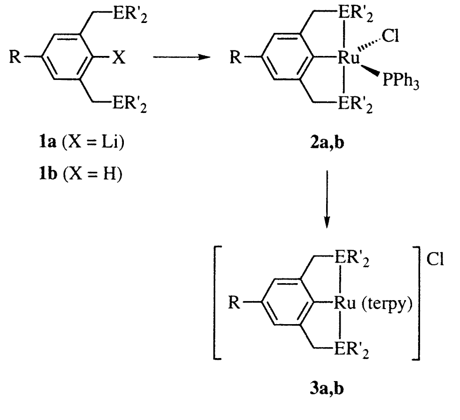
[+] Address correspondence pertaining to crystallographic studies to this author; E-mail: spea@xray.chem.ruu.nl

Scheme 1. Synthesis of ruthenium(II) complexes **2** and **3** derived from (functionalized) *N,C,N'*- and *P,C,P'*-terdentate-coordinating ligands **1**, by transmetallation (of **1a**-Li) or direct cyclometallation (of **1b**)



1a (X = Li)
1b (X = H)

2a,b

3a,b

1,2,3 a: ER'$_2$ = NMe$_2$; R = H, Ph, Me$_3$SiC≡C, Me$_3$Si

1,2,3 b: ER'$_2$ = PPh$_2$; R = H, Ph

search has been aimed at the generation of the related dianionic 1,4-phenylene ligand with two potentially *P,C,P'*-terdentate coordination motifs, i.e., an analog to the tetraaminophenylene dianion C_2N_4 shown in Figure 2. As part of this research we have explored the synthesis of the tetraphosphane $C_6H_2(CH_2PPh_2)_4$-1,2,4,5 (**6**), which is a potential precursor to the ligand $[C_6(CH_2PPh_2)_4\text{-}1,2,4,5]^{2-}$. We now report the successful synthesis of **6** and its complexation reaction with $[RuCl_2(PPh_3)_4]$.

Results

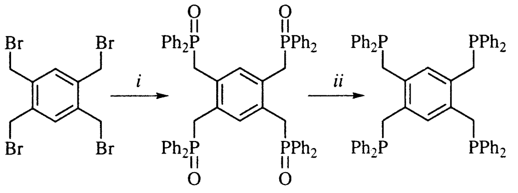
The target compound of this study is tetraphosphane-substituted benzene $C_6H_2(CH_2PPh_2)_4$-1,2,4,5 (**6**). The synthetic protocol used involves an Arbuzov reaction[7] of a phosphanic ester (i.e., Ph_2POEt) with a benzylic bromide [i.e., $C_6H_2(CH_2Br)_4$-1,2,4,5 (**4**)] to afford a P^V oxide compound, **5**[8]. The latter is then reduced to the corresponding desired tetraphosphane **6** (see Scheme 2).

Synthesis of $C_6H_2(CH_2PPh_2)_4$-1,2,4,5 (5)

Compound **5** can be obtained in high yield, as a white solid, by treatment of the known $C_6H_2(CH_2Br)_4$-1,2,4,5 (**4**)[9] with excess of ethyldiphenylphosphanite (Ph_2POEt) in *m*-xylene at 140°C in a slight modification of a previously described procedure that gives an improved yield[8]. The ^{1}H-NMR data of the poorly soluble tetrakis(phosphane oxide) **5** (in warm CD_3OD solution) were identical to those reported previously[8].

Typical procedures described for the reduction of phosphane oxides to phosphanes failed to completely reduce compound **5** to phosphane **6**. For example, $HSiCl_3$ reduction of **5** in benzene, toluene or xylene at reflux temperature[10] did not result in the formation of the desired phosphane. Similarly, $LiAlH_4$ (or $LiAlH_4 \cdot CeCl_3$) reductions[11] in THF also failed to reduce **5** selectively. In the latter case, a new product formed in ca. 10% yield with over 85% of the starting material still present. This new product has not been isolated in a pure form but on the basis of ^{31}P-NMR data of the crude material, its air stability and its water solubility we believe that it is likely to be an ionic phosphonium species (vide infra). It was felt that the poor reactivity of **5** in the attempted reduction reactions was possibly due to its inherent low solubility. Therefore, alternative solvents were examined and it has been found that for the reduction of **5** with $HSiCl_3$, hot 1,2-dichlorobenzene was the solvent of choice. In practice, a suspension of **5** in 1,2-dichlorobenzene was heated to 180°C and kept at this temperature for 10 min to dissolve all solid material. The solution temperature was then reduced to 140°C and $HSiCl_3$ was added by syringe. The reaction mixture was kept for 1 h at this temperature and, after appropriate work-up, the desired tetraphosphane **6** was obtained as a white solid in very good yield (96%). Compound **6** is air-sensitive and reasonably soluble in aromatic and chlorinated solvents. Analytically pure crystals of **6** can be obtained by slow diffusion of MeOH into a solution of **6** in benzene.

Scheme 2. Synthesis of the tetraphosphane $C_6H_2(CH_2PPh_2)_4$-1,2,4,5 (**6**). – *i:* Ph_2POEt, *m*-xylene, 140°C, $-EtBr$. – *ii:* $HSiCl_3$, $C_6H_4Cl_2$–1,2, 140°C, 1 h.



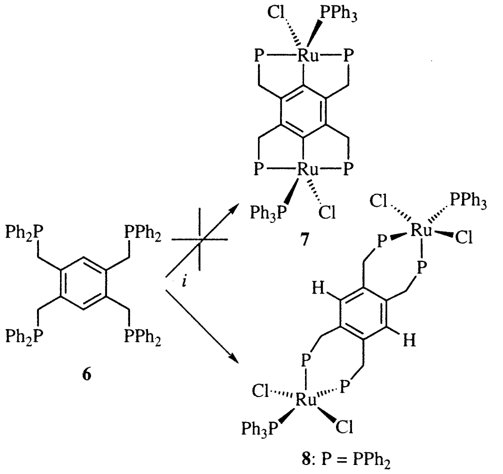
4 **5** **6**

Reaction of Tetraphosphane 6 with $[RuCl_2(PPh_3)_4]$

It was anticipated that phosphane **6** would be susceptible to cyclometallation and that with $[RuCl_2(PPh_3)_4]$[12] the product of this reaction would be a bimetallic species related to the ruthenium(II) complex **3b** (Scheme 1) obtained when $C_6H_3(CH_2PPh_2)_2$-1,3-R-5 (**1b**), is used as the phosphane[3c][3d]. To test the reactivity of the new tetraphosphane **6** towards $[RuCl_2(PPh_3)_4]$, these two species were mixed in a 1:2 molar ratio in CH_2Cl_2 (Scheme 3) at room temperature and after 1 h a green precipitate had been formed. After appropriate work-up, this precipitate was isolated as a green solid, whose poor solubility in common organic solvents (benzene, toluene, THF, CH_2Cl_2, etc.) has prevented us from identifying this material, **8**, by solution-NMR spectroscopy and also prevented successful recrystallization. However, elemental microanalysis data suggested that this crude product has an overall formula $[\{RuCl_2(PPh_3)\}_2(\mathbf{6})] \cdot 0.5\ CH_2Cl_2$.

In a second experiment, aimed at directly obtaining a purer, more crystalline product **8**, we carried out the original reaction under slightly different conditions. To this end, a CH_2Cl_2 solution of two equivalents of $[RuCl_2(PPh_3)_4]$ was carefully layered with a solution of tetraphosphane **6** in CH_2Cl_2 and the reaction mixture was left undisturbed for 24 h at room temperature. This produced analytically pure green crystals of **8** (isolated yield: 38%) which were suitable for an X-ray crystallographic study. This study afforded a solid-state structure (vide infra) which shows this product to be $[\{RuCl_2(PPh_3)\}_2\{C_6H_2(CH_2PPh_2)_4$-1,2,4,5-*P,P′,P′′,P′′′*$\}]\cdot 0.5\ CH_2Cl_2$ (**8**); the molecular geometry is depicted in Figure 3 and selected geometrical details are collected in Table 1. Complex **8** has a composition that corresponds to the original microanalytical data and it can be seen to be a dinuclear coordination complex of **6** in which this tetraphosphane functions as a bridging ligand that coordinates in a *P,P′*-bidentate manner to each of the identical metal centers. Thus, under the experimental conditions used or at reflux temperature in CH_2Cl_2, compound **6** does not undergo cyclometallation with the ruthenium(II) center to afford a product such as **7**. This behavior is different to that of aryldiphosphane $C_6H_4(CH_2PPh_2)_2$-1,3 which cyclometallates with $[RuCl_2(PPh_3)_4]$ under identical conditions to afford $[RuCl\{C_6H_3(CH_2PPh_2)_2$-2,6$\}(PPh_3)]$[3].

Scheme 3. Reactivity of **6** with $[RuCl_2(PPh_3)_4]$ in CH_2Cl_2 to afford coordination complex **8** rather than the cyclometallated species **7**. – *i:* 2 equiv. $[RuCl_2(PPh_3)_4]$, CH_2Cl_2, room temp., 1 h, –6 equiv. PPh_3.



In the X-ray crystallographic structure of **8**, the tetraphosphane ligand bridges between the two identical 5-coordinate ruthenium(II) metal centers that have approximate square-pyramidal geometries; the molecule has a center of inversion positioned in the central aromatic ring of this tetraphosphane. The square pyramidal ligand array comprises in the basal plane plane two *trans*-Cl atoms [Cl(1) and Cl(2)] and two *trans*-P atoms [P(2) of the bridging ligand and P(3) of PPh_3] and at the apex there is a phosphorus atom P(1) of the bridging ligand. The bridging phosphane employs two mutually *ortho*-CH_2PPh_2 substituents for *ortho-P,P′* chelation to each metal center, thus forming a 7-membered chelate ring in which the bite angle P(1)–Ru(1)–P(2) is 97.46(9)°. The geometrical parameters found for **8**, including Ru–P bond lengths in the range of 2.208(3) to 2.391(2) Å and a Cl(1)–Ru(1)–Cl(2) bond angle of 160.96(9)°, are similar to those reported for related complexes with the general formula $[RuCl_2(Ph_2PR)_3]$[13a][13b] (see Discussion). The P–C_{aryl} bond lengths fall in the range of 1.815(10) to 1.853(9) Å and the Ru–P–C_{aryl} bond angles vary from 100.0(3) to 124.7(3)°. Interestingly, the proton H(31) situated on triphenylphosphane *ortho*-carbon atom C(31) is fairly close to the ruthenium(II) center with a Ru(1)···H(31) distance of 2.82 Å that is substantially shorter than the sum of the van der Waals radii (3.40 Å).

In further experimental studies aimed at promoting cyclometallation of the neutral phosphane **6** present in complex **8**, this latter complex was suspended in 1,2-dichlorobenzene and heated to 140°C together with PPh_3 and trioctylamine as a base. Although NMR-spectroscopic studies of the resulting solution indicated that a new orthometallated product had been formed, it was in fact the coordinated PPh_3 ligand, and not **6**, that had been cyclometallated. Unfortunately, a pure sample of this new cyclometallated product could not be separated for further identification.

Discussion

Synthesis of the Tetraphosphane

The choice of the Arbuzov-reaction/reduction sequence for the synthesis of tetraphosphane **6** is a consequence of the poor results that we achieved in preliminary experiments using the tetrabromide **4** as starting material in the well-known nucleophilic substitution of a benzylic bromide with $NaPPh_2$ in liquid ammonia[3c][14]. The main product of this latter reaction is not the desired phosphane **6**, but a mixture of phosphonium salts. These phosphonium salts are probably formed as a result of an intramolecular nucleophilic substitution reaction of a CH_2Br group with an *ortho*-positioned CH_2PPh_2 group that has been produced by an initially successful intermolecular nucleophilic substitution (see Scheme 4). The success of the route we employ to form **6** (Scheme 2) comes from the fact that the product of the Arbuzov reaction is a non-nucleophilic phosphane oxide and the initially formed $CH_2P(O)Ph_2$ unit is inert to intramolecular attack by an *ortho*-positioned benzylic bromide.

The solvent used in the $HSiCl_3$-mediated reduction reaction of the tetrakis(phosphane oxide) **5** to the tetraphosphane **6** was found to be crucial and the best experimental conditions that we found was the use of 1,2-dichlorobenzene at high temperature. It appears that for phosphane oxides like **5**, which have poor solubility characteristics, it is important to use a solvent that not only has a high boiling point but also one that has a good degree of polarity, and this combination of physical properties is found in 1,2-dichlorobenzene.

Solid-State Structure of 8

The complex formed by the undisturbed reaction of $[RuCl_2(PPh_3)_4]$ with **6** in CH_2Cl_2 was not one containing the expected cyclometallated tetraphosphane ligand **7**. In-

Figure 3. ORTEP drawing (50% probability atomic displacement ellipsoids) of [$\{RuCl_2(PPh_3)\}_2\{C_6H_2(CH_2PPh_2)_4$-1,2,4,5-*P,P′,P′′,P′′′*}] (**8**); hydrogen atoms and cocrystallized CH_2Cl_2 molecules have been omitted for clarity

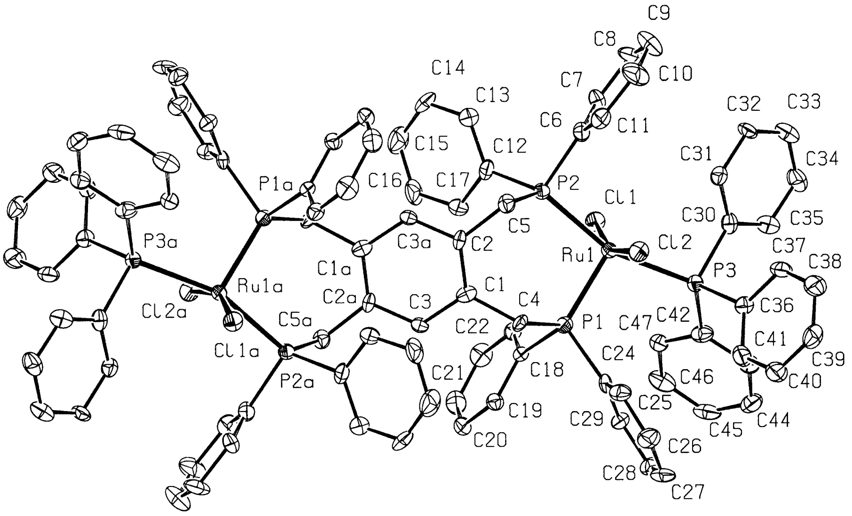
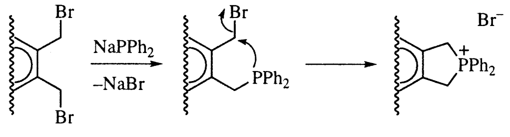


Table 1. Selected bond parameters of [$\{RuCl_2(PPh_3)\}_2$-$\{C_6H_2(CH_2PPh_2)_4$-1,2,4,5-*P,P′,P′′,P′′′*}] (**8**)

Bond lengths [Å]		Bond angles [°]	
Ru(1)−Cl(1)	2.389(2)	Cl(1)−Ru(1)−Cl(2)	160.96(9)
Ru(1)−Cl(2)	2.383(2)	P(1)−Ru(1)−P(2)	97.46(9)
Ru(1)−P(1)	2.208(3)	P(1)−Ru(1)−P(3)	101.74(9)
Ru(1)−P(2)	2.318(2)	P(2)−Ru(1)−P(3)	160.49(9)
Ru(1)−P(3)	2.391(2)	Ru(1)−P(1)−C(4)	114.8(3)
P(1)−C(4)	1.846(8)	Ru(1)−P(1)−C(18)	120.1(3)
P(1)−C(18)	1.853(9)	Ru(1)−P(1)−C(24)	116.3(3)
P(1)−C(24)	1.834(9)	Ru(1)−P(2)−C(5)	118.3(3)
P(2)−C(5)	1.847(9)	Ru(1)−P(2)−C(6)	100.0(3)
P(2)−C(6)	1.815(10)	Ru(1)−P(2)−C(12)	124.7(3)
P(2)−C(12)	1.816(10)	Ru(1)−P(3)−C(30)	103.1(3)
P(3)−C(30)	1.844(10)	Ru(1)−P(3)−C(36)	120.2(3)
P(3)−C(36)	1.828(8)	Ru(1)−P(3)−C(42)	121.5(3)
P(3)−C(42)	1.821(9)	P(3)−C(30)−C(31)	116.9(7)
Ru(1)···H(31)	2.8118	P(3)−C(30)−C(35)	123.5(7)
		P(3)−C(36)−C(37)	120.8(7)
		P(3)−C(36)−C(41)	120.6(7)
		P(3)−C(42)−C(43)	122.9(7)
		P(3)−C(42)−C(47)	118.9(7)

Scheme 4. Schematic formation of phosphonium species from the reaction of $NaPPh_2$ with *ortho*-bis(bromomethyl)arenes



stead, the product is a bimetallic coordination complex of neutral tetraphosphane **6** in which two *ortho*-positioned phosphane donor substituents are coordinated to a ruthenium(II) metal center. The related tetraphosphane ligand 1,2,4,5-tetrakis(diphenylphosphano)benzene has been reported to form similar, non-metallated, bridged bimetallic (and polymeric) coordination complexes with several transition metals[15]. It appears that this type of initial *P,P′*-chelation forms a species that is relatively inert to Ru−P bond cleavage and as a consequence the C_{aryl}−H bond of the central aromatic ring cannot approach the metal center for intramolecular activation and subsequent C−Ru bond formation.

Bisruthenium(II) complex **8** is one of only a few structurally characterized 5-coordinate ruthenium(II) species in which the ligand array comprises two halide atoms and three phosphanes. Moreover, in complex **8** the presence of a close contact between the metal center and an *ortho* H atom of one of the PPh_3 C_{aryl}−H units is a noteworthy feature; interestingly, the structure of [$RuCl_2(PPh_3)_3$] has a similar interaction which was concluded to be substantially repulsive,[13a] and not to be an agostic interaction[13c][13d] of this C_{aryl}−H bond with the metal center. The authors described the overall structure of this complex as a distorted square pyramid with this *ortho*-H atom occupying the open coordination site of an octahedral ligand array. More recently, Cotton and Matusz[13b] have reported the solid-state structure of another square-pyramidal ruthenium complex, [$RuCl_2(Ph_2PCH_2SiMe_3)_3$], in which this type of M···H−C interaction was not found and the bulky benzylic substituent would appear to be shielding the vacant sixth coordination site in this 16-electron species. Comparison of some selected bond lengths and interbond angles collected in Table 2, shows that the overall solid-state structures of bimetallic **8** with *P,P′*-chelation and the mononuclear complexes [$RuCl_2(Ph_2PR)_3$] (R = Ph, CH_2SiMe_3) with monodentate-bonded phosphanes are surprisingly similar.

P,P′-Chelation versus Cyclometallation

Cyclometallation of aryldiphosphanes with ruthenium(II) species is a well-known reaction and has been successfully employed by us[3c] and others[3e] in earlier studies to form a series of complexes containing [$C_6H_2(CH_2PPh_2)_2$-2,6-R-4]$^-$, PCP-R-4 (Scheme 1). However, as reported here, the neutral tetraphosphane **6** has to date not been found to undergo such cyclometallation reactions and it is worthwhile considering the unique aspects of this compound that result in it having a different reactivity

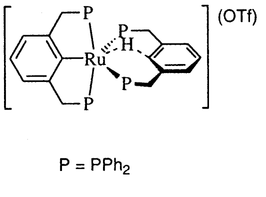
Table 2. Selected bond parameters of **8** and the known ruthenium(II) complexes $[RuCl_2(Ph_2PR)_3]$ (R = Ph, CH_2SiMe_3)

	8	$[RuCl_2(PPh_3)_3]$[a]	$[RuCl_2(Ph_2PCH_2SiMe_3)_3]$[b]
Bond lengths [Å]			
Ru(1)−Cl(1)	2.389(2)	2.387(7)	2.395(2)
Ru(1)−Cl(2)	2.383(2)	2.388(7)	2.390(2)
Ru(1)−P_A[c]	2.208(3)	2.230(8)	2.210(2)
Ru(1)−P_B[c]	2.318(2)	2.374(6)	2.348(2)
	2.391(2)	2.412(6)	2.379(2)
Ru(1)···H	2.8118	2.59	not present
Bond angles [°]			
Cl(1)−Ru(1)−Cl(2)	160.96(9)	157.2(2)	163.93(7)
P_B−Ru(1)−P_B[c]	160.49(9)	156.4(2)	165.91(7)
P_A−Ru(1)−P_B[c]	97.46(9)	101.1(2)	96.83(7)
	101.74(9)	101.4(2)	99.24(7)

[a] Data obtained from ref.[12a]. – [b] Data obtained from ref.[12b]. – [c] P_A and P_B are the apical and basal phosphorus atoms, respectively.

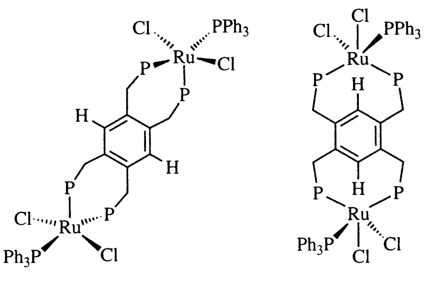
pattern. For reaction of the neutral aryldiphosphanes $C_6H_3(CH_2PPh_2)_2$-1,3-R-5 (**1b**), with $[RuCl_2(PPh_3)_4]$ we proposed that prior to cyclometallation an 8-membered cyclic coordination complex is formed by replacement of PPh_3 ligands of $[RuCl_2(PPh_3)_3]$ (vide supra) by the more basic phosphorus donor substituents of **1b**[3c]. In this resulting intermediate complex the two *meta*-positioned CH_2PPh_2 substituents are coordinated to the ruthenium(II) metal center in a bidentate *P,P'*-chelate mode. As a consequence the metal center is brought into proximity to the C−H bond which can then be activated. Because this intermediate has not been detected by NMR-spectroscopic methods we assume that the formation of this intermediate is rate-determining and that the following step, i.e. C−H bond cleavage and generation of the new Ru−C σ bond, is a much faster process. In one rare and unique case, an example of an agostic interaction of a C_{aryl}−H bond of an aryldiphosphane, **1b** (R = H), at an Ru^{II} center afforded by *P,P'*-chelate bonding has been confirmed by an X-ray crystallographic study[3d]; the molecular geometry of the monocationic complex reported in this study is schematically presented in Figure 4.

Figure 4. Schematic representation of aryl C−H bond activation at a Ru^{II} center in an intermediate whose structure has been determined by an X-ray crystallographic study



Tetraphosphane **6** should, like diphosphanes **1b**, displace PPh_3 from $[RuCl_2(PPh_3)_3]$ since the CH_2PPh_2 groups are more basic P donors than PPh_3. Several different coordination complexes could be formed, and two of these based on *P,P'*-chelation are the observed dinuclear coordination complex **8** as well as the alternative chelation complex **A** (See Figure 5). The difference between these complexes is that in **8** there is chelation of two *ortho*-positioned CH_2PPh_2 groups, whereas in **A** there is chelation two *meta*-positioned CH_2PPh_2 groups.

Figure 5. Schematic representation of two different coordination complexes **8** and **A** which could be formed from **6** and $[RuCl_2(PPh_3)]_4$



8 P = PPh2 **A**

In complex **A**, there are two 8-membered chelate rings that allow the metal centers to be brought close to the aryl C−H bonds at positions 3 and 6 on the central aromatic ring; as a result of geometric (steric) restraints each ring has limited flexibility. In contrast, complex **8** contains two 7-membered chelate rings that have a good degree of conformational flexibility, and therefore this situation is energetically more favorable than that in **A**. However, unlike the situation in **A** the ruthenium(II) centers in **8** are unable to approach the central C−H bonds to undergo cyclometallation and form complex **7** (Scheme 3). The favorable situation found in complex **8** is emphasized by the fact that this complex does not undergo cycloruthenation during the synthetic procedure. In principle, the excess of free PPh_3 present in the reaction mixture (see Scheme 2) could induce the formation of an η^1-*P*-coordinated ligand **6** in complex **8**, and this would be sufficient to generate a situation where the an aryl C−H bond (as in **A**) is close enough to the metal center for cyclometallation to occur. However, the poor solubility characteristics of **8** in common organic solvents prevents the possibility of this situation.

Conclusion

In this report we have shown that the new neutral tetraphosphane ligand $C_6H_2(CH_2PPh_2)_4$-1,2,4,5 (**6**) can be easily prepared in high yield. The synthetic strategy, which involves an Arbuzov reaction, has great potential as an alternative (and less hazardous) route to many other aryl- and alkylphosphanes. In this strategy the choice of 1,2-dichlorobenzene as a high-temperature solvent for the reduction of the corresponding phosphane oxide was crucial. With ruthenium(II) centers the new tetraphosphane **6** affords *P,P'*-bidentate chelation from two *ortho*-positioned, rather than *meta*-positioned, CH_2PPh_2 substituents such that C−H bond activation and formation of a *P,C,P'*-terdentate-coordinated ruthenium(II) species does not occur.

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Table 3. Crystal Data and Details of the Structure Determination for $[\{RuCl_2(PPh_3)\}_2\{C_6H_2(CH_2PPh_2)_4\text{-}1,2,4,5\text{-}P,P',P'',P'''\}]$ (**8**)

	Crystal Data		
empirical formula	$C_{94}H_{80}Cl_4P_6Ru_2 \cdot 8\ CH_2Cl_2$		
formula weight	2418.92	crystal size [mm]	0.15 × 0.15 × 0.63
crystal system	triclinic	space group	$P\bar{1}$ (no. 2)
a [Å]	10.2378(13)		
α [°]	106.139(10)		
b [Å]	14.227(2)		
β [°]	97.707(10)		
c [Å]	20.237(2)		
γ [°]	106.822(11)		
V [Å^3]	2635.4(6)	$D_{calcd.}$ [g cm^{-3}]	1.524
Z	1	$F(000)$ [e]	1226
μ(Mo-K_α) [cm^{-1}]	9.3		
	Data Collection		
T [K]	150		
θ_{min}, θ_{max} [°]	1.1, 25.0		
wavelength (Mo-K_α) [Å]	0.71073	scan range [°]	1.10 + 0.00 tanθ
hor. aperture	3.00	vert. aperture	4.00
data set	−8/12, −17/17, −25/25		
total data	10839		
total unique data	9273		
observed data [$I > 2.0\ \sigma(I)$]	5094		
	Refinement		
N_{ref}, N_{par}	9273, 586	final $R1$[a]	0.0748
final $wR2$[b]	0.1660	goodness of fit	1.01
w^{-1}	$\sigma^2(F^2) + (0.0474P)^2 + 1.8922P$, where $P = (F_o^2+2F_c^2)/3$		
$(\Delta.\sigma)_{av}$, $(\Delta.\sigma)_{max}$	0.00, 0.00		
min. and max. resid. density [e Å^{-3}]	−0.74, 0.64		

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. – [b] $wR2 = [(|F_o|^2-|F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$.

Experimental Section

General: All synthetic procedures were performed under dry dinitrogen. Hexane and benzene were freshly distilled from sodium benzophenone ketyl, CH_2Cl_2 from CaH_2, and xylenes and 1,2-dichlorobenzene from molecular sieves (5 Å). – Spectroscopic measurements (^{1}H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR) were performed with a Bruker AC200 or AC300 spectrometer, with chemical shifts referenced to either Me_4Si or 85% H_3PO_4. – Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim, Germany. – The compounds $C_6H_2(CH_2Br)_4$-1,2,4,5 (**4**)[9], Ph_2POEt[16], and $[RuCl_2(PPh_3)_4]$[17] were prepared according to previously described methods. $RuCl_3 \cdot 3\ H_2O$ was purchased from Degussa.

$C_6H_2(CH_2P(O)Ph_2)_4$-1,2,4,5 (**5**): A modification of a procedure described in the literature[8] was used. In a two-necked 100-ml round bottom flask, a stirred colorless solution of Ph_2POEt (20.52 g, 89 mmol) and $C_6H_2(CH_2Br)_4$-1,2,4,5 (5.35 g, 11.9 mmol) in xylenes (20 ml) was heated at 140°C for 0.5 h, while a gentle stream of nitrogen was bubbled through the reaction mixture. After this time, the reaction mixture was cooled to 50°C (ice bath) and the white solid which had precipitated was filtered off. This solid was washed once with hot benzene (100 ml), filtered off and dried in vacuo to afford the tetraphosphoryl compound **5** as a white solid which was sufficiently pure for further synthesis. Yield: 9.53 g (86%), mp > 220°C (ref.[8]: 315–317°C). – ^{1}H NMR (CD_3OD, 200 MHz, 335 K): δ = 7.62 (m, 40 H, ArH), 6.42 (s, 2 H, ArH), 3.52 (d, 8 H, $^2J_{P\text{-}H}$ = 12 Hz, CH_2P). – $^{31}P\{^1H\}$ NMR (CD_3OD, 81 MHz, 335 K): δ = 32.4 (s).

$C_6H_2(CH_2PPh_2)_4$-1,2,4,5 (**6**): In a two-necked 100-ml round bottom flask equipped with a reflux condensor and a septum, was heated a stirred suspension of the tetraphosphoryl compound **5** (1.89 g, 2.02 mmol) in 1,2-dichlorobenzene (50 ml) at reflux temperature until all solids had dissolved. The resulting clear solution was then allowed to cool to 140°C and $HSiCl_3$ (2.46 ml, 24.4 mmol) was carefully added through the septum over a period of 5 min by means of a syringe. The reaction mixture was then stirred at 140°C for 1 h, after which a clear solution was obtained. This solution was then cooled to 0°C with an ice bath. Degassed aqueous NaOH (50 ml, 4 M) was carefully added through the septum over a period of 5 min by means of a syringe while the mixture was stirred vigorously. This resulted in the formation of a two-layer system, from which the organic layer was collected. The aqueous layer was extracted with CH_2Cl_2 (2 × 25 ml) and the combined organic fractions were dried with $MgSO_4$ and filtered. The filtrate was concentrated in vacuo to ca. 10 ml. Hexane (50 ml) was slowly added, which induced the crystallization of a white solid. This solid was collected by filtration, washed with hexane (2 × 25 ml) and dried in vacuo to afford analytically pure tetraphosphane **6** as white crystals. Yield: 1.68 g (96%), mp 125°C. – ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.28 (m, 40 H, ArH), 6.22 (s, 2 H, ArH), 2.96 (s, 8 H, CH_2P). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298 K): δ = 138.4 (d, $^1J_{P\text{-}C}$ = 16 Hz, Ar), 133.0 (d, $^2J_{P\text{-}C}$ = 19 Hz, Ar), 131.2 (d, $^3J_{P\text{-}C}$ = 12 Hz, Ar), 128.4 (d, $^3J_{P\text{-}C}$ = 23 Hz, Ar), 32.6, 32.4 (d, $^1J_{P\text{-}C}$ = 15 Hz, CH_2P). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz, 298 K): δ = −12.3 (s). – $C_{58}H_{50}P_4$: calcd. C 79.99, H 5.79; found C 79.84, H 5.72.

$[\{RuCl_2(PPh_3)\}_2\{C_6H_2(CH_2PPh_2)_4\text{-}1,2,4,5\text{-}P,P',P'',P'''\}] \cdot 0.5\ CH_2Cl_2$ (**8**): A colorless solution of tetraphosphane **6** (0.38 g, 0.44 mmol) in CH_2Cl_2 (20 ml) was added to a brown solution of $[RuCl_2(PPh_3)_4]$ in CH_2Cl_2 (20 ml) at room temperature and the resulting reaction mixture was stirred for 2 h at this temperature. During this time a green precipitate formed. After 2 h, the green precipitate was filtered off, washed with CH_2Cl_2 (2 × 20 ml) and dried in vacuo to afford the pure bisruthenium(II) complex **8** in 38% yield as a green insoluble solid (mp > 200°C). – $C_{94}H_{78}Cl_4P_6Ru_2 \cdot 0.5\ CH_2Cl_2$: calcd. C 63.69, H 4.58; found C 63.83, H 4.65. – When a CH_2Cl_2 solution of $[RuCl_2(PPh_3)_4]$ was

layered with a CH_2Cl_2 solution of tetraphosphane **6** and the resulting reaction mixture was left undisturbed for 24 h, green-brown X-ray quality crystals (mp > 200°C) of bisruthenium complex **8** were obtained. These crystals were collected by filtration, washed with CH_2Cl_2 (2×20 ml), dried in vacuo and subsequently subjected to an X-ray structure determination.

X-ray Structure Determination of **8**: X-ray data were collected with an ENRAF-NONIUS CAD4 diffractometer on rotating anode for a needle-shaped green-brown crystal. Numerical data are collected in Table 3. The structure was solved by Direct Methods (SHELXL86)[18] and refined on F^2 using SHELXL96[19]. Data were corrected for absorption effects using the DIFABS algorithm as implemented in PLATON[20]. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. Geometrical calculations and the ORTEP illustration were done with PLATON.

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