Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 691 (2006) 422–432
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis, coordination chemistry, and metal complex reactivity of (dimethylamino)methyl-substituted triarylphosphanes; X-ray study on [AuCl($PPh_{3-n}Ar_n$)] (Ar = 1-$C_6H_3(CH_2NMe_2)_2$-3,5, $n = 1, 3$; Ar = 1-$C_6H_4(CH_2NMe_2)$-4, $n = 3$)

Robert Kreiter [a], Judith J. Firet [a], Michel J.J. Ruts [a], Martin Lutz [b], Anthony L. Spek [b], Robertus J.M. Klein Gebbink [a,*], Gerard van Koten [a,*]

[a] *Debye Institute, Organic Chemistry and Catalysis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[b] *Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received 14 July 2005; received in revised form 31 August 2005; accepted 5 September 2005
Available online 19 October 2005

Abstract

The synthesis of the first series of 4-mono and 3,5-bis(dimethylamino)methyl-functionalized triarylphosphanes of the general formula $PPh_{3-n}Ar_n$ (Ar = 1-$C_6H_3(CH_2NMe_2)_2$-3,5 (NC(H)N), $n = 1$ (ligand **2**) or $n = 3$ (ligand **4**); Ar = 1-$C_6H_4(CH_2NMe_2)$-4 (NC(H)), $n = 3$ (ligand **7**)) is described. These phosphanes were used for the construction of complexes of the form [AuCl(P)] and [$PtCl_2(P)_2$]. In these complexes selective coordination of phosphorus to the metal ion is observed. The ^{31}P NMR data show the formation of *cis*-Pt complexes, even in the case of triarylphosphane **4**, which features a tris{3,5-bis(dimethylamino)methyl} substitution pattern. The structure of the gold complex of mono-3,5-functionalized triarylphosphane **2** in the solid state shows a striking resemblance to the structure of the corresponding complex [AuCl(PPh_3)]. The solid-state structure of the AuCl complex of tris-4-functionalized ligand **7** differs from that of [AuCl(PPh_3)] in the sign of the torsion angles. The amine functionalities in this class of gold compounds could be reacted selectively with either acid (HCl, H_3PO_4) to generate ammonium salts or with an alkylating agent (benzyl bromide) to afford benzyl ammonium salts, without the violation of the Au–P bond.

Keywords: Triarylphosphane; Amine; Au–P coordination; Pt–P coordination; Protonation; Alkylation

1. Introduction

Phosphorus-based ligands have found many applications, both in coordination chemistry and in homogeneous catalysis [1]. Among these, triphenylphosphane and its numerous derivatives are key examples that were implemented in many industrial applications. The reported triphenylphosphane modifications include anion or cation substitutions to arrive at water-soluble phosphanes [2]; the most successful example being tris-sulfonated triphenylphosphane (TPPTS) applied in the Rhône-Poulenc biphasic hydroformylation. Substitution of triarylphosphanes with fluorous alkyl chains has made those suitable for application in fluorous biphasic catalysis [3]. Furthermore, many examples apply increased steric bulk on the phenyl fragments thus rendering the ligands suitable candidates for high turnover C–C, C–N, or C–O coupling reactions [4]. The functionalization of arylphosphanes with potentially ligating groups opened up a new field of research, leading the way for secondary (ligand-to-metal) interactions or the formation of mixed metal complexes [5]. Examples of such ligands are the 2,6-bis(dimethylamino)methyl-substituted

* Corresponding authors. Tel.: +31 30 253 1889; fax: +31 30 2523615 (R.J.M. Klein Gebbink), Tel.: +31 30 2533120; fax: +31 30 2523615 (G. van Koten).
E-mail addresses: r.j.m.kleingebbink@chem.uu.nl (Robertus J.M. Klein Gebbink), g.vankoten@chem.uu.nl (G. van Koten).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.09.009

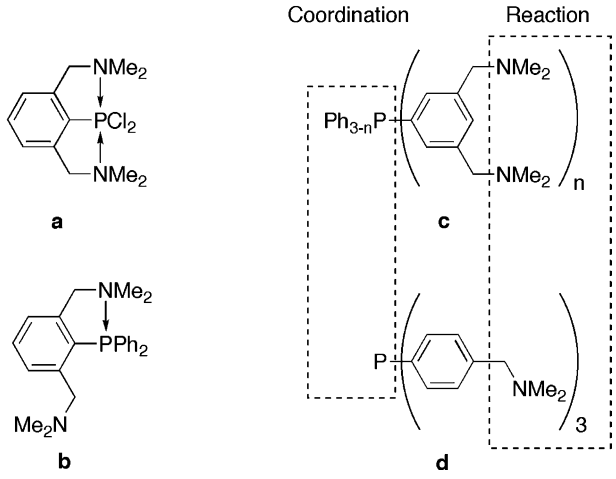


Fig. 1. Examples of (dimethylamino)methyl-substituted arylphosphanes reported by Cowley [6] (a), Corriu [7] (b), and in this report (c, d).

arylphosphanes (Fig. 1), reported by the groups of Cowley (a) [6] and Corriu (b) [7]. They showed that intramolecular N → P coordination in this type of mixed ligands takes place.

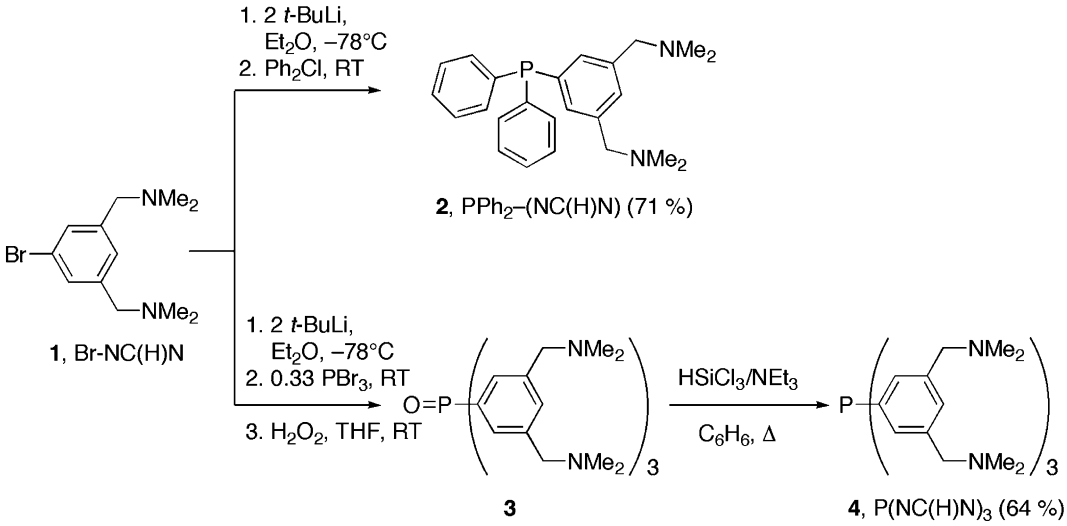
In our research, we set out to design and prepare bifunctional arylphosphanes of the general formula $PPh_{3-n}Ar_n$ (Ar = 1-$C_6H_3(CH_2NMe_2)_2$-3,5 (NC(H)N); or Ar = 1-C_6H_4-(CH_2NMe_2)-4 (NC(H))) (Fig. 1(c) and (d)) which on the one hand could function as typical triarylphosphane ligands, i.e., coordinate via the phosphorus center to a metal ion, while at the same time being substituted with (dimethylamino)methyl groups at either the *para*- or at both *meta*-positions. The latter NC(H)N-motif could serve either for the introduction of a metal atom via a M–C-bond (via bis-*ortho*-metalation or transmetalation) or for the use as Lewis basic functionalities (CH_2NMe_2), i.e., as extension of the triarylphosphane scaffold by quaternization or by reversible protonation/deprotonation. This paper discusses the synthesis of the first series of 4-mono and 3,5-bis(dimethylamino)methyl-functionalized triarylphosphanes and shows selective coordination of the phosphorus center in these ligands to gold(I) chloride and platinum(II) dichloride. Moreover, protonation and quaternization with alkyl halides of the CH_2NMe_2-functionalities is discussed.

2. Results

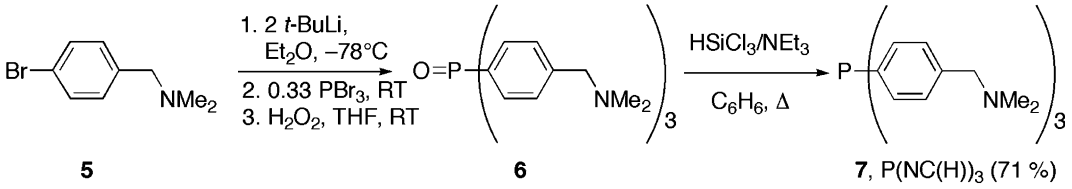
2.1. Preparative results

Using a previously described protocol [8], mono{3,5-bis[(dimethylamino)methyl]phenyl}-diphenylphosphane (**2**, PPh_2–(NC(H)N)) and tris{3,5-bis[(dimethylamino)-methyl]phenyl}phosphane (**4**, $P(NC(H)N)_3$) were prepared. The procedure started from 1-bromo-3,5-bis[(dimethylamino)methyl]benzene (**1**, Br–(NC(H)N)) [9], which was converted into the respective phosphanes **2** and **4** via lithium–bromide exchange followed by reaction with chlorodiphenylphosphane or phosphorus tribromide (Scheme 1). In the case of **2**, the crude product was obtained as a yellow oil, which could be purified by bulb-to-bulb distillation, affording the pure phosphane as a dark yellow oil in a yield of 71%. In the case of hexa-functionalized ligand **4**, the product was partially oxidized to phosphane oxide **3** during work-up of the reaction. Therefore, the crude product was completely oxidized with H_2O_2 in THF, and after isolation reduced to free phosphane **4** by treatment with $HSiCl_3$ and NEt_3 in refluxing benzene. This procedure afforded pure **4** as a light yellow sticky solid. Both ligands feature a triarylphosphane core having a 3,5-bis(dimethylamino)methyl substitution pattern on one or all three of the aryl rings. This moiety is potentially useful as a terdentate NCN-pincer ligand, which is able to bind as a mono-anion to a metal site [10].

The corresponding tris{4-[(dimethylamino)methyl]-phenyl}phosphane (**7**, $P(NC(H))_3$) was prepared in a similar fashion (Scheme 2). Lithiation of 4-bromobenzylamine



Scheme 1. Synthesis of 3,5-bis(dimethylamino)methyl-substituted triarylphosphanes, PPh_2–(NC(H)N) (**2**) and $P(NC(H)N)_3$ (**4**).



Scheme 2. Synthesis of 4-(dimethylamino)methyl-substituted triarylphosphane $P(NC(H))_3$ (**7**).

followed by a quench with phosphorus tribromide and subsequent oxidation afforded phosphane oxide **6**. The free phosphane **7** was obtained after reduction.

In order to study the coordination behavior of the phosphanes PPh_2–(NC(H)N) (**2**), $P(NC(H)N)_3$ (**4**), and $P(NC(H))_3$ (**7**), they were reacted with Au(I) and Pt(II) metal complexes. To this end, ligand **2** was mixed with one equivalent of [AuCl(THT)] in CH_2Cl_2. After overnight stirring and removal of all volatiles a white solid material was isolated. A shift of the ^{31}P NMR signal from −3.8 ppm for **2** to 31.9 ppm for **8** was observed. Furthermore, in the ^1H NMR spectra the resonance of the NMe_2 protons was unaffected. This indicated that the amine substituents were not involved in coordination, leading to the conclusion that [AuCl(PPh_2–(NC(H)N))] (**8**, Scheme 3) was formed selectively.

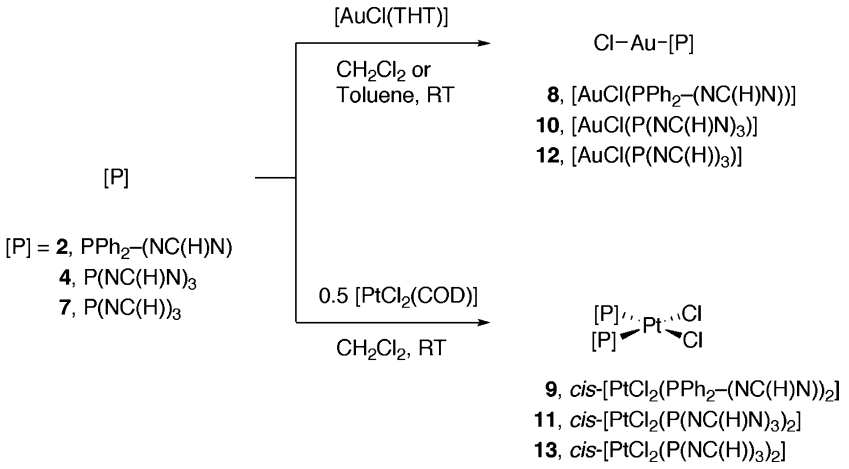
In a parallel experiment, two equivalents of **2** were reacted with [$PtCl_2$(COD)] in CH_2Cl_2 to afford the product as a light yellow oil (Scheme 3). The ^{31}P NMR spectrum of **9** in $CDCl_3$ showed a sharp resonance at 15.0 ppm with a coupling constant of $^1J(^{195}Pt–^{31}P) = 3660$ Hz, pointing to **9** being a *cis*-complex. These data are in concert with those found for the corresponding complex *cis*-[$PtCl_2(PPh_3)_2$], obtained by reaction of PPh_3 with [$PtCl_2$(COD)] (^{31}P NMR: $\delta = 14.4$ ppm, $^1J(^{195}Pt–^{31}P) = 3674$ Hz) [11]. The possible other isomer, having a *trans*-geometry, was not observed. In the ^1H NMR spectrum of **9**, no significant shift is observed for the NMe_2-protons indicating again that no interaction between nitrogen and platinum takes place. Therefore, we conclude that *cis*-Pt complex **9** is formed selectively.

$P(NC(H)N)_3$ (**4**) was subjected to the same coordination experiments (Scheme 3), using toluene as solvent for the preparation of Au(I) complex **10**. ^1H and ^{31}P NMR analysis of **10** provided evidence for selective phosphane coordination. By reaction of **4** with [$PtCl_2$(COD)], *cis*-[$PtCl_2(P(NC(H)N)_3)_2$] (**11**; ^{31}P NMR: $\delta = 14.7$ ppm, $^1J(^{195}Pt–^{31}P) = 3661$ Hz) was obtained. Apparently, functionalization of all three aryl rings at the 3- and 5-positions does not impose sufficient steric strain on the complex to hamper the formation of a *cis*-complex. In the ^1H NMR spectra of these complexes no additional interactions of the amine substituents with Au(I) or Pt(II) were observed, which follows the expected preference of Au(I) and Pt(II) for coordination to the softer phosphorus site over the binding to hard tertiary amine donor sites.

$P(NC(H))_3$ (**7**) was reacted with [AuCl(THT)] in toluene to afford the corresponding Au(I) complex [AuCl($P(NC(H))_3$)] (**12**) in high yield. Similar to the results for complexes **8** and **10**, the CH_2NMe_2 substituents in **12** did not interact with Au(I) (cf. ^1H and ^{31}P NMR spectra). Reaction of **7** with [$PtCl_2$(COD)] resulted in quantitative formation of *cis*-[$PtCl_2(P(NC(H))_3)_2$] (**13**; ^{31}P NMR: $\delta = 13.5$ ppm, $^1J(^{195}Pt–^{31}P) = 3677$ Hz) (Scheme 3).

2.2. Structures of [AuCl(PPh_2–(NC(H)N))] (8) and [AuCl($P(NC(H))_3$)] (12)

Colorless single crystals of **8**, suitable for X-ray diffraction, were obtained via recrystallization from a pentane/CH_2Cl_2 (3/1, v/v) mixture, while colorless single crystals of **12** were prepared by slow evaporation of a C_6D_6



Scheme 3. Preparation of Au(I) complexes **8**, **10**, and **12** and *cis*-Pt(II) complexes **9**, **11**, and **13**.

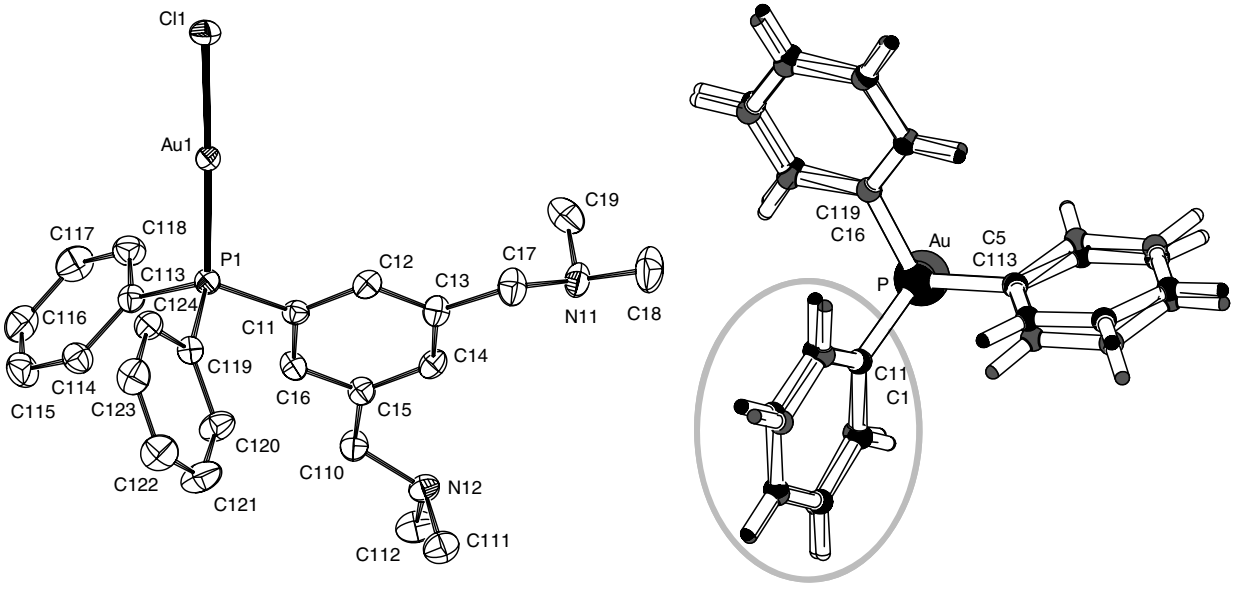


Fig. 2. Displacement ellipsoid plot (50% probability) of one of the two independent molecules of [AuCl(PPh_2–(NC(H)N))] (**8**) (hydrogen atoms are omitted for clarity) and a quaternion fit of both the triphenylphosphane-gold chloride fragments of [AuCl(PPh_2–(NC(H)N))] (**8**, gray C-atoms) and [AuCl(PPh_3)] (black C-atoms), seen along the P–Au bond. The (NC(H)N)-fragment (C11–C16) is marked with a gray circle.

solution of this complex. The unit cell of **8** contains two independent molecules that differ slightly in torsion angles of the aryl fragments with respect to the P–Au bond (one of the two independent molecules is shown in Fig. 2). The PPh_2–(NC(H)N) ligand is coordinated to the Au-center *trans* to the chloride ion and the three aryl fragments have a propeller-like arrangement. Secondary interactions or intermolecular close-contacts are not observed, which indicates that the CH_2NMe_2 substituents are free. Comparison of the obtained molecular structure of **8** with the previously reported structure of [AuCl(PPh_3)] [12] shows a striking similarity (Table 1). A quaternion fit of both triphenylphosphane-gold chloride fragments of these complexes underlines this equivalence (Fig. 2) [12]. Only slight differences in the interatomic distances, bond angles, and torsion angles are observed, which indicates that the presence of the single 3,5-bis[(dimethylamino)methyl] substitution pattern in **8** leaves the primary structure of the [AuCl(PPh_2Ar)] scaffold unaffected.

The structure of **12** in the solid state shows a propeller-shaped complex having a diagonally coordinated gold center and an exact, crystallographic threefold rotation axis about the P–Au–Cl-axis (P–Au–Cl: 180° by symmetry) (Fig. 3). Again, no interactions between the dimethylamino

Table 1
Selected interatomic distances and angles of [AuCl(PPh_2–(NC(H)N))] (**8**),[a] [AuCl($P(NC(H))_3$)] (**12**), and [AuCl(PPh_3)] [12]

[AuCl(PPh_2(N(H)CN))] (**8**)		[AuCl($P(NC(H))_3$)] (**12**)		[AuCl(PPh_3)]	
Bond lengths (Å)					
Au1–Cl1	2.2789(6)	Au1–Cl1	2.272(2)	Au1–Cl1	2.278
Au1–P1	2.2289(6)	Au1–P1	2.231(2)	Au1–P1	2.233
P1–C11	1.810(2)	P1–C1	1.814(2)	P1–C1	1.799
P1–C119	1.811(3)			P1–C5	1.788
P1–C113	1.821(2)			P1–C16	1.858
Angles (°)					
P1–Au1–Cl1	178.34(2)	P1–Au1–Cl1	180	P1–Au1–Cl1	179.71
Au1–P1–C11	114.57(8)	Au1–P1–C1	112.00(10)	Au1–P1–C1	114.72
Au1–P1–C119	112.88(8)			Au1–P1–C5	112.41
Au1–P1–C113	111.61(8)			Au1–P1–C16	113.66
C113–P1–C11	104.20(11)	C1–P1–C1a	106.82(11)	C16–P1–C1	103.00
C119–P1–C11	106.41(11)			C5–P1–C1	106.60
C113–P1–C119	106.46(14)			C16–P1–C5	105.56
Torsion (°)					
Au1–P1–C11–C12	36.3(2)	Au1–P1–C1–C6	−39.8	Au1–P1–C5–C6	38.78
Au1–P1–C113–C118	53.8(2)			Au1–P1–C16–C4	58.16
Au1–P1–C119-C124	26.7(2)			Au1–P1–C1–C15	29.88

[a] Only one of the two independent molecules is considered.

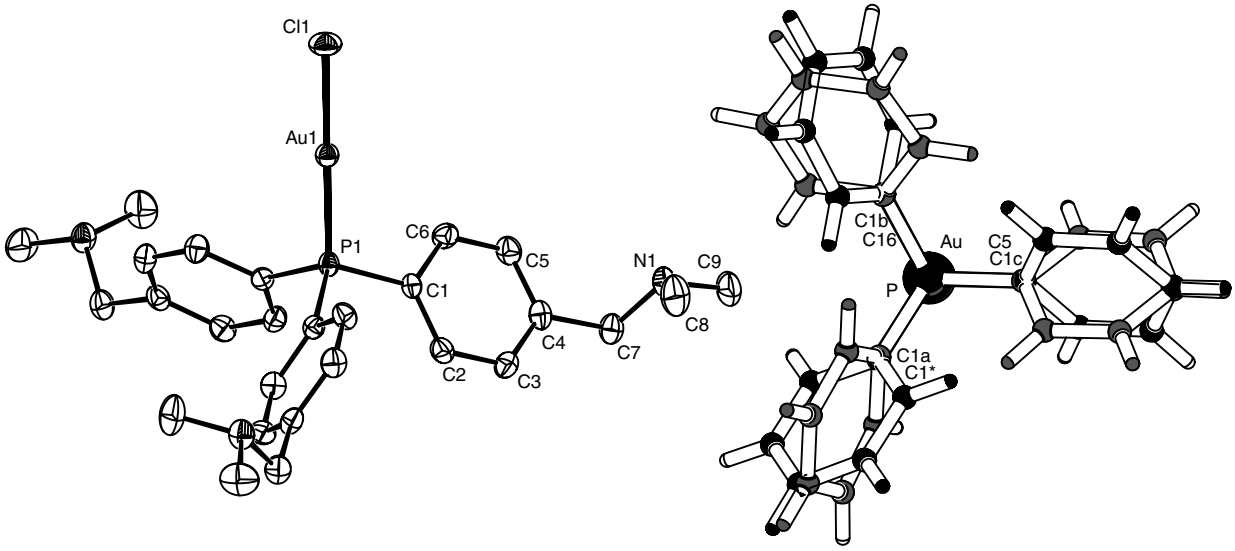
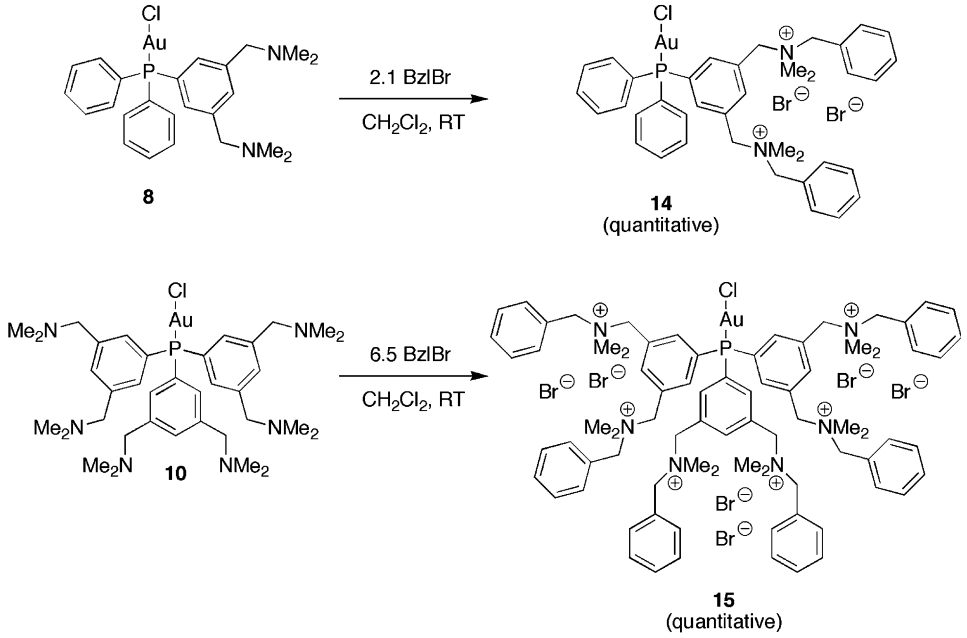


Fig. 3. Displacement ellipsoid plot (50% probability) of [AuCl(P(NC(H))$_3$)] (**12**) (hydrogen atoms are omitted for clarity) and a quaternion fit of both the triphenylphosphane-gold chloride fragments of [AuCl(P(NC(H))$_3$)] (**12**, gray C-atoms; C1a, C1b, C1c) and [AuCl(PPh$_3$)] (black C-atoms; C1*, C5, C16), seen along the P–Au bond.

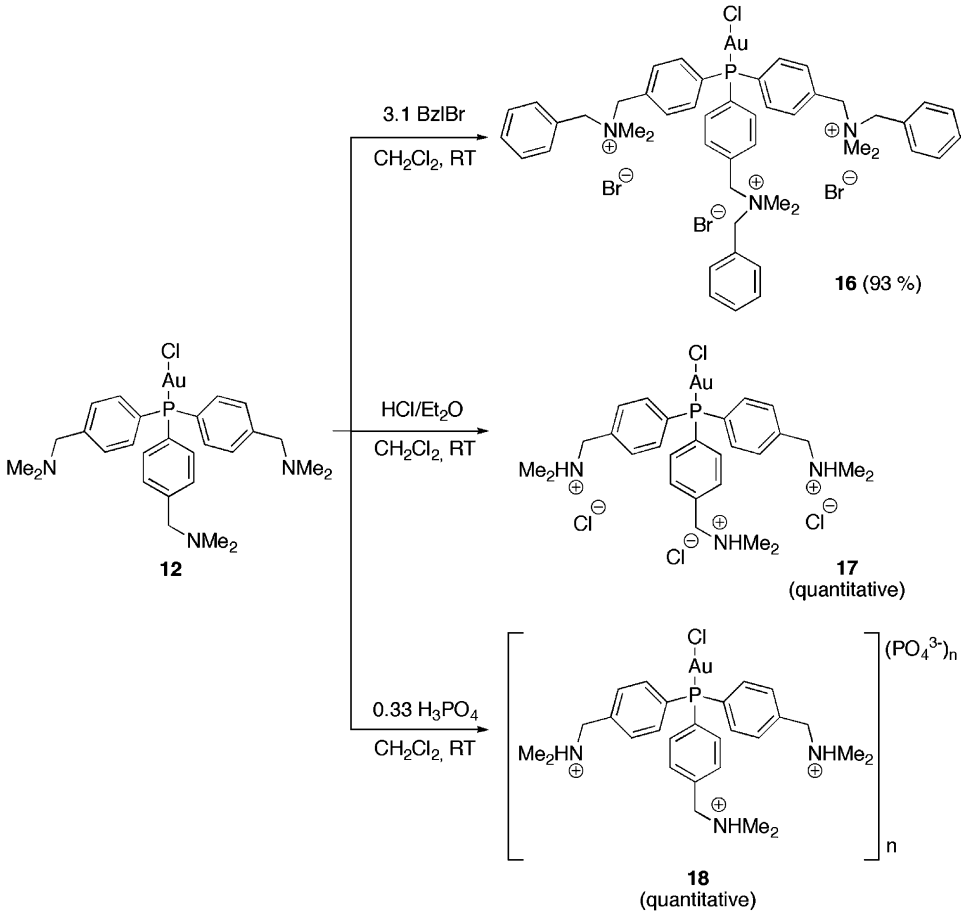
groups and the gold atom are observed. Compared to the structure of [AuCl(PPh$_3$)] the bond lengths and C–P–C angles are very similar. A quaternion fit of **12** and [AuCl(PPh$_3$)] reveals a difference in sign of the Au–P–C1–C2 torsion angles (Fig. 3), whereas the magnitude of those angles is similar.

2.3. Alkylation and protonation of *8*, *10*, and *12*

To investigate if the NC(H)N manifold in **8** and **10** is available for reaction, we chose the alkylation reaction of the amine groupings with an alkyl halide. A small excess (calculated with respect to the CH_2NMe_2 equivalents in these complexes) of benzyl bromide was added to both complexes (Scheme 4). ^{1}H and ^{31}P NMR spectroscopic analysis of these reactions showed that, in both cases, the phosphorus–gold(I) bond remains unaffected (^{31}P NMR, CD_3OD, $\delta = 36.4$ ppm for **14**, $\delta = 39.4$ ppm for **15**), and that full conversion to the *N*-per-alkylated species occurs. Interestingly, the ^{31}P NMR chemical shift for bis-functionalized **14** lies significantly more downfield compared to that of hexa-functionalized **15**. The solubility of both these



Scheme 4. Reaction of **8** and **10** with benzyl bromide to afford 3,5-bis-ammonium-substituted triarylphosphane gold(I) chloride complexes **14** and **15**, respectively.



Scheme 5. Reaction of **12** with benzyl bromide, HCl, and H_3PO_4.

alkylated complexes changes dramatically from soluble in chlorinated organic solvents to soluble only in polar solvents like MeOH and EtOH.

[AuCl(P(NC(H))$_3$)] (**12**) was also reacted with a small excess of benzyl bromide (Scheme 5), affording the tris-ammonium salt **16** selectively, as was confirmed by ^{1}H and ^{31}P NMR data. The ^{31}P NMR shift for **16** (CD_3OD, $\delta = 39.3$ ppm) is very similar to that of **15** (CD_3OD, $\delta = 39.4$ ppm), despite the differences in substitution pattern (4-mono compared to 3,5-bis) and in number of ammonium groups (3 compared to 6). Reaction of a small excess of HCl in Et_2O with **12** dissolved in CH_2Cl_2 resulted in the formation of a white precipitate (**17**, Scheme 5). The product was highly hygroscopic and soluble in H_2O. In the ^{1}H NMR spectrum, the signal corresponding to the NMe_2 fragment shifts from 1.95 (in C_6D_6) to 2.7 ppm (in D_2O) upon protonation, while the ^{31}P NMR spectrum confirmed the phosphane-gold complexation (D_2O, $\delta = 33.0$ ppm). Upon dropwise addition of a solution of H_3PO_4 in acetone to **12**, dissolved in CH_2Cl_2, a white precipitate slowly formed. The ^{31}P NMR spectrum of the product in D_2O, in which it is slightly soluble, showed two clear, but relatively broad signals, representing the *P*–Au ($\delta = 29.7$) and PO_4^{3-} ($\delta = -0.1$ ppm) phosphorus atoms. Based on the low solubility of **18** in water as well as the broad signals in ^{31}P NMR, we assume that a polymeric network was formed rather than a tricationic triarylphosphane structure with discrete, separate entities (Scheme 5).

3. Discussion

This report presents the synthesis and coordination chemistry of 4-mono and 3,5-bis[(dimethylamino)methyl]-phenylphosphanes. The NMR spectra of these aminophosphane ligands show no signs of N → P interactions (cf. Fig. 1(a) and (b)). This can be explained by the substitution pattern, which imposes inter- rather than energetically more favorable intramolecular coordination [6,7].

Coordination of the ligands **2**, **4**, and **7** to Au(I) and Pt(II) shows that they behave as pure phosphane donor ligands towards these ions, and that the amino substituents are not involved in the coordination. This is supported by the solid state structures of the gold complexes **8** and **12**. Multiple 3,5-bis-substitution of so-called BIPHEP (2,2-bis(diarylphosphanyl)biphenyl) ligands leading to a 'meta-effect' in catalysis was reported by Pregosin et al. [13]. In that case the *meta*-substitution pattern resulted in the formation of a more rigid and slightly larger chiral pocket in the corresponding Ru-complex. In our case, the exclusive formation of *cis*-complexes in the case of the

$PtCl_2$ bisphosphane complexes **9** and **11** seems unaffected by the presence of 3,5-bis-substitution. The solid state structure of complex **8**, which is almost identical to that of the corresponding PPh_3 complex, supports this observation. Interestingly, this exclusive formation of a *cis*-platinum dichloride complex in the case of **6** is in contrast with the findings for its previously reported hexa-ammonium salts (*Dendriphos*) [8], for which increased bulk and, presumably, larger cone angles lead to the exclusive formation of the *trans*-platinum dichloride complexes [14]. The similarity of **8** and [AuCl(PPh_3)] in the solid state is in line with the observations of Dunitz, who discussed the structure of triphenylmethane and triphenylphosphane stereoisomers in the solid state [15]. Generally, such molecules will adopt slightly distorted C_3-symmetric conformations. The observed C_3-symmetric solid state feature of the 4-mono-functionalized complex **12** follows those predictions. It differs from the structure of [AuCl(PPh_3)] mainly in the sign of the Au–P–C1–C2 torsion angles, i.e., the other stereoisomer was found. In solution, the formation of a *cis*-platinum bisphosphane complex in the case of **13**, and the similarity of the ^{31}P NMR spectra of **9**, **11**, and **13** suggest that there are no significant differences in steric behavior.

The experiments with Au(I) complexes **8**, **10**, and **12** show that the phosphorus center is effectively protected by the Au–P coordination, allowing selective functionalization of the amino substituents with either an alkyl halide or an acid. The benzyl bromide salts **14**, **15**, and **16** represent coordination complexes that have a relatively high polar character (soluble in MeOH), while the HCl salt **17** is water soluble. The protonation of **12** to afford **17** demonstrates the use of the amino-'handle' in **12** for facile transfer of a gold-phosphane coordination complex to an aqueous environment. This hints at the application of these ligands in aqueous phase or phase transfer catalysis. Reaction of **12** with exactly one-third equivalent of the tri-acid H_3PO_4, in principle, could have lead to selective formation of tris-ammonium salt entities of the formula [AuCl-($P(NC(H))_3)H_3$]PO_4. In this case, however, the formation of a very poorly soluble product points to the formation of a polymeric network. This procedure provides a means for facile recovery of such gold(I) phosphane complexes from almost any solvent, by addition of a dilute solution of H_3PO_4.

4. Conclusions

The presented 3,5-bis and 4-mono(dimethylamino)-methyl-functionalized triarylphosphanes, coordinate to Au(I) and Pt(II) via selective phosphorus–metal coordination. The similarity of Au(I) complexes of these CH_2NMe_2-substituted triarylphosphanes to the parent triphenylphosphane complex is apparent from the bond lengths and C–P–C angles in the obtained crystal structures. The $PtCl_2$ complexes **11** and **13** show that in solution the 4- and the 3,5-bisfunctionalized ligands have similar structural features. Complexation to gold provides excellent protection for the phosphane center, allowing subsequent reactions of the amine functionalities with an alkyl halide or with acid. Further investigations on these compounds focus on the application of these ligands in aqueous media and on their phase transfer behavior.

5. Experimental

5.1. General

All air and moisture sensitive experiments were conducted under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents for these manipulations were dried over appropriate materials and distilled prior to use. 1-Bromo-3,5-bis[(dimethylamino)methyl]benzene (**1**) [9], tris{3,5[(dimethylamino)methyl]phenyl}phosphane oxide (**3**) [8], 1-bromo-4-[(dimethylamino)methyl]benzene (**5**) [16], [$PtCl_2$(COD)] [17], and [AuCl(THT)] [18] were prepared via the literature procedures. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 298 K on a Varian Mercury 200 MHz or a Varian Inova 300 MHz spectrometer. All ^1H and ^{13}C NMR chemical shifts are in ppm referenced to the residual solvent signal and all ^{31}P NMR chemical shifts are referenced against H_3PO_4 as external standard. MS data were collected on an Applied Biosystems Voyager System mass spectrometer (MALDI-TOF MS). ESI-MS spectra were recorded on a Micromass LC-T mass spectrometer. Elemental analyses were performed by Kolbe, Mülheim a/d Ruhr, Germany.

5.2. Synthesis

5.2.1. Synthesis of {3,5-bis[(dimethylamino)methyl]-phenyl}diphenylphosphane, (PPh_2–(NC(H)N), **2**)

To a solution of 1-bromo-3,5-bis[(dimethylamino)-methyl]benzene (**1**) (3.30 g, 11.90 mmol) in dry Et_2O (75 mL) was added dropwise *t*-BuLi (16.30 mL, 1.5 M in pentane, 24.50 mmol) at −78 °C, resulting in a beige suspension. After stirring for 30 min at −78 °C Ph_2PCl (2.40 mL, 13.20 mmol) was added and the mixture was allowed to warm to room temperature overnight. Degassed NaOH (15 mL, 4 M) was slowly added at 0 °C until pH > 10, followed by removal of all volatiles. The resulting aqueous layer was extracted with CH_2Cl_2 (3×40 mL) and to the combined organic fractions HBF_4 (2.74 mL, 54 wt% Et_2O, 23.80 mmol) was added, followed by addition of H_2O (15 mL) until a clear biphasic system was obtained. The aqueous layer was washed with CH_2Cl_2 (3×30 mL) and degassed NaOH (15 mL, 4 M) was slowly added at 0 °C until pH > 10. The product was extracted with CH_2Cl_2 (4×30 mL) and the combined organic fractions were dried over $MgSO_4$. All volatiles were evaporated in vacuo followed by Kugelrohr distillation (100 °C, 0.1–0.2 mm Hg) affording a dark yellow oil. Yield: 3.18 g (71%). ^1H NMR (C_6D_6, 300 MHz): $\delta = 7.44$ (m, 6H, ArH), 7.00 (m, 7H, ArH), 3.15 (s, 4H,

CH_2N), 1.98 (s, 12H, $N(CH_3)_2$); ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 140.19$ (d, $^3J_{PC} = 7.3$ Hz, ArC), 138.34 (d, $^1J_{PC} = 12.8$ Hz, PhC), 137.47 (d, $^1J_{PC} = 11.6$ Hz, ArC), 134.00 (d, $^2J_{PC} = 19.4$ Hz, PhC), 133.30 (d, $^2J_{PC} = 20.0$ Hz, ArC), 130.33 (ArC), 128.65 (PhC), 128.64 (d, $^3J_{PC} = 6.7$ Hz, PhC), 64.02 (s, CH_2N), 45.14 (s, $N(CH_3)_2$); ^{31}P NMR (C_6D_6, 81 MHz): $\delta = -3.84$; MALDI-TOF MS: m/z 377.38 $[M + H]^+$ (82%). Anal. Calc. for $C_{24}H_{29}N_2P$: C, 76.57; H, 7.76; N, 7.44; P, 8.23. Found: C, 76.64; H, 7.68; N, 7.36; P, 8.20%.

5.2.2. General procedure for the reduction of (dimethylamino)methyl-substituted triarylphosphane oxides

$HSiCl_3$ (10 equiv.) and NEt_3 (10 equiv.) were added to a solution of the phosphane oxide in dry C_6H_6 and the mixture was heated to reflux temperature for 2 h. After cooling to room temperature, the mixture was neutralized by dropwise addition of a saturated aqueous solution of $NaHCO_3$ and the organic layer was removed in vacuo. The aqueous layer was extracted twice with CH_2Cl_2 and the combined organic fractions were dried on Mg_2SO_4, filtered, and evaporated to dryness, affording the pure phosphane as a light yellow sticky solid.

5.2.3. Synthesis of tri{3,5-bis[(dimethylamino)methyl]-phenyl}phosphane ($P(NC(H)N)_3$, **4**)

Starting from **3** (1.37 g, 2.21 mmol) in dry C_6H_6 (40 mL) by addition of $HSiCl_3$ (2.2 mL, 21.7 mmol) and NEt_3 (3.1 mL, 22.1 mmol). Yield: 0.85 g (64%). ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 7.24$ (s, 3H, ArH), 7.08 (dd, 6H, $^3J_{PH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz, ArH), 3.30 (s, 12H, CH_2N), 2.14 (s, 36H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 138.98$ (d, $^3J_{PC} = 6.7$ Hz, ArC), 137.39 (d, $^2J_{PC} = 11.6$ Hz, ArC), 133.56 (d, $^1J_{PC} = 14.6$ Hz, ArC), 130.71 (ArC), 64.21 (CH_2N), 45.60 ($N(CH_3)_2$); ^{31}P NMR ($CDCl_3$, 81 MHz): $\delta = -5.44$ (s); MALDI-TOF MS: m/z 605.66 $[M + H]^+$ (100%). Anal. Calc. for $C_{36}H_{57}N_6P$: C, 71.49; H, 9.50; N, 13.89; P, 5.12. Found: C, 71.37; H, 9.43; N, 13.72; P, 5.08%.

5.2.4. Synthesis of tri{4-[(dimethylamino)methyl]-phenyl}phosphane oxide ($P(O)(NC(H))_3$, **6**)

t-BuLi (30.21 mL, 1.5 M in pentane, 45.31 mmol) was added dropwise to a solution of 1-bromo-4-(dimethylamino)methylbenzene (**7**; 4.85 g, 22.65 mmol) in dry Et_2O (40 mL) at −78 °C and the resulting light brown suspension was stirred for 45 min. PBr_3 (0.71 mL, 7.55 mmol) was added dropwise and the mixture was allowed to warm up to room temperature over 16 h. H_2O (40 mL) was added carefully and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic fractions were dried over Mg_2SO_4, filtered and evaporated to dryness. Kugelrohr distillation at 100 °C (0.1–0.2 mm Hg) was applied for 2 h, after which the product was dissolved in THF (50 mL) and H_2O_2 (0.20 mL, 35% in H_2O) was added. The mixture was stirred for 2 h, NaOH (50 mL, 1M) was added and all volatiles were removed in vacuo. The resulting aqueous mixture was extracted with CH_2Cl_2 (2 × 50 mL) and the combined organic layers were dried on Mg_2SO_4, filtered and evaporated to dryness. The product was obtained as a white microcrystalline solid by precipitation from Et_2O. Yield: 2.41 g (71%). ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.43$ (dd, $^3J_{HH} = 11.4$ Hz, $^3J_{PH} = 8.2$ Hz, 6H, ArH), 7.22 (dd, $^3J_{HH} = 7.6$ Hz, $^4J_{PH} = 2.4$ Hz, 6H, ArH), 3.09 (s, 6H, CH_2N), 1.95 (s, 18H, $N(CH_3)_2$); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 143.34$ (d, $^3J_{PC} = 3.0$ Hz, ArC), 134.17 (ArC), 132.33 (d, $^2J_{PC} = 10.2$ Hz, ArC), 128.78 (d, $^1J_{PC} = 11.7$ Hz, ArC), 63.90 (s, CH_2N), 45.34 ($N(CH_3)_2$); ^{31}P NMR (C_6D_6, 81 MHz): $\delta = 25.56$; MALDI-TOF MS: m/z 450.40 $[M + H]^+$ (100%). Anal. Calc. for $C_{27}H_{36}N_3OP$: C, 72.13; H, 8.07; N, 9.35; P, 6.89. Found: C, 71.96; H, 7.93; N, 9.27; P, 6.75%.

5.2.5. Synthesis of tri{4-[(dimethylamino)methyl]phenyl}-phosphane ($P(NC(H))_3$, **7**)

Starting from **6** (1.20 g, 2.67 mmol) in dry C_6H_6 (40 mL) by addition of $HSiCl_3$ (2.71 mL, 26.8 mmol) and NEt_3 (3.75 mL, 26.8 mmol). Yield: 1.11 g (96%). ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 7.26$, 7.24 (overlapping doublets, 12H, ArH), 3.40 (s, 6H, CH_2N), 2.22 (s, 18H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 139.73$ (ArC), 136.09 (d, $^3J_{PC} = 9{,}7$ Hz, ArC), 133.81 (d, $^2J_{PC} = 19{,}9$ Hz, ArC), 129.21 (d, $^1J_{PC} = 21.2$ Hz, ArC), 64.37 (CH_2N), 45.74 ($N(CH_3)_2$); ^{31}P NMR ($CDCl_3$, 81 MHz): $\delta = -6.16$; MALDI-TOF MS: m/z 434.47 $[M + H]^+$ (100%). Anal. Calc. for $C_{27}H_{36}N_3P$: C, 74.80; H, 8.37; N, 9.69; P, 7.14. Found: C, 74.67; H, 8.32; N, 9.74; P, 7.19%.

5.2.6. Synthesis of [AuCl(PPh_2–(NC(H)N))] (**8**)

A solution of PPh_2–(NC(H)N) (**2**; 114.0 mg, 0.30 mmol) in CH_2Cl_2 (20 mL) was slowly added to a solution of [AuCl(THT)] (87.0 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 16 h at room temperature protected from sunlight. All volatiles were evaporated in vacuo affording a light yellow oil. Yield: 0.17 g (93%). Colorless crystals, suitable for X-ray diffraction, were obtained by addition of pentane (20 mL) to a solution of **6** in CH_2Cl_2 (10 mL) after overnight standing at room temperature. ^1H NMR (C_6D_6, 300 MHz): $\delta = 7.57$ (s, 1H, ArH), 7.49 (d, 2H, $^3J_{PH} = 9.9$ Hz, ArH), 7.38 (dd, 4H, $^3J_{HH} = 11.7$ Hz, $^4J_{PH} = 4.2$ Hz, ArH), 6.99 (m, 6H, ArH), 3.09 (s, 4H, CH_2N), 1.96 (s, 12H, $N(CH_3)_2$); ^{13}C NMR (C_6D_6, 75 MHz) $\delta = 141.09$ (d, $^3J_{PC} = 11.0$ Hz, ArC), 134.17 (d, $^2J_{PC} = 14.0$ Hz, PhC), 133.16 (d, $^2J_{PC} = 15.2$ Hz, ArC), 132.41 (ArC), 131.25 (d, $^1J_{PC} = 50.3$ Hz, PhC), 131.05 (PhC), 130.57 (d, $^1J_{PC} = 47.3$ Hz, ArC), 129.05 (d, $^3J_{PC} = 11.0$ Hz, PhC), 63.47 (CH_2N), 45.08 ($N(CH_3)_2$); ^{31}P NMR (C_6D_6, 81 MHz): $\delta = 31.89$; MALDI-TOF MS: m/z 609.19 $[M + H]^+$ (100%). Anal. Calc. for $C_{24}H_{29}N_2PAuCl$: C, 47.34; H, 4.80; N, 4.60; P, 5.10. Found: C, 47.52; H, 4.76; N, 4.55; P, 5.13%.

*5.2.7. Synthesis of cis-[$PtCl_2(PPh_2$–(NC(H)N))$_2$] (**9**)*

A solution of PPh_2–(NC(H)N) (**2**; 94.4 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) was added to a solution of [$PtCl_2$(COD)] (47.0 mg, 125 μmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 1 h at room temperature, followed by heating to reflux temperature for 15 min. CH_2Cl_2 and COD were removed in vacuo and a light yellow oil was obtained. Yield: 0.12 g (96%). ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.45$–7.08 (overlapping, 13H, ArH), 3.22 (s, 4H, CH_2N), 2.09 (s, 12H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 138.44$ (broad, ArC), 134.91 (broad, PhC), 132.85 (ArC), 130.86 (PhC), 129.73 ($^1J_{PC} = 64.5$ Hz, ArC), 128.87 (overlapping d, ArC), 128.54, 128.04 (PhC), 63.50 (CH_2N), 45.24 ($N(CH_3)_2$); ^{31}P NMR ($CDCl_3$, 81 MHz): $\delta = 15.04$ ($J_{PtP} = 3660$ Hz); MALDI-TOF MS: *m/z* 947.59 $[M - 2Cl]^+$ (100%). Anal. Calc. for $C_{48}H_{58}Cl_2N_4P_2Pt$: C, 56.58; H, 5.74; N, 5.50; P, 6.08. Found: C, 56.51; H, 5.84; N, 5.42; P, 6.04%.

*5.2.8. Synthesis of [AuCl(P(NC(H)N)$_3$)] (**10**)*

Solid [AuCl(THT)] (78.5 mg, 0.25 mmol) was added to a solution of **4** (0.15 g, 0.25 mmol) in toluene (30 mL) and the mixture was stirred for 30 min at room temperature. The resulting light yellow solution was evaporated to dryness, hexane was added and the solution was filtered. Evaporation of the hexane filtrate afforded the product as an off-white solid. Yield: 0.19 g (91%). ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.58$, 7.52 (overlapping s and d, 9H, ArH), 3.01 (s, 12H, CH_2N), 1.93 (s, 36H, $N(CH_3)_2$); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 141.17$ (d, $^3J_{PC} = 11.7$ Hz, ArC), 133.14 (d, $^2J_{PC} = 14.5$ Hz, ArC), 132.69 (s, ArC), 129.68 (d, $^1J_{PC} = 59.7$ Hz, ArC), 63.50 (CH_2N), 45.12 ($N(CH_3)_2$); ^{31}P NMR (C_6D_6, 81 MHz): $\delta = 33.42$; MALDI-TOF MS: *m/z* 835.64 $[M]^+$ (100%). Anal. Calc. for $C_{36}H_{57}AuClN_6P$: C, 51.64; H, 6.86; N, 10.04; P, 3.70. Found: C, 51.77; H, 6.89; N, 9.89; P, 3.85%.

*5.2.9. Synthesis of cis-[$PtCl_2$(P(NC(H)N)$_3$)$_2$] (**11**)*

To a solution of **4** (101.6 mg, 0.13 mmol) in dry CH_2Cl_2 was added solid [$PtCl_2$(COD)] (24.4 mg, 65.1 μmol) and the mixture was stirred for 1 h at room temperature, followed by heating to reflux temperature for 15 min. Subsequently, all volatiles were removed in vacuo, affording **11** as a light yellow solid in quantitative yield. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4$–7.2 (overlapping, 9H, ArH), 3.19 (s, 12H, C*H*$_2$N), 2.09 (s, 36H, N(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 138.29$ (broad, ArC), 134.64 (broad, ArC), 132.18 (ArC), 129.58 (d, $^1J_{PC} = 66.5$ Hz, ArC), 63.64 (CH_2N), 45.36 ($N(CH_3)_2$); ^{31}P NMR (C_6D_6, 81 MHz): $\delta = 14.66$ (t, $J_{PtP} = 3641$ Hz). MALDI-TOF MS: *m/z* 1403.92 $[M - 2Cl]^+$ (100%).

*5.2.10. Synthesis of [AuCl(P(NC(H))$_3$)] (**12**)*

Solid [AuCl(THT)] (0.45 g, 1.41 mmol) was added to a solution of **7** (0.61 g, 1.41 mmol) in dry toluene (50 mL) and the mixture was stirred for 16 h at room temperature, resulting in a dark purple solution. The crude mixture was filtered over celite and evaporated to dryness. The resulting off-white solid was purified further by precipitation from a CH_2Cl_2/hexane (1/10, v/v) mixture, resulting in a off-white solid. Yield: 0.74 g (79%). Crystals, suitable for X-ray diffraction were obtained by slow evaporation of a C_6D_6 solution of **12**. ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.3$–7.0 (m, 12H, ArH), 3.05 (s, 6H, CH_2N), 1.95 (s, 18H, $N(CH_3)_2$); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 143.89$ (ArC), 134.14 (d, $^2J_{PC} = 14.1$ Hz, ArC), 129.32 (d, $^3J_{PC} = 12.1$ Hz, ArC), 128.33 (d, $^1J_{PC} = 27.0$ Hz, ArC), 63.63 (CH_2N), 45.44 ($N(CH_3)_2$); ^{31}P NMR (C_6D_6, 81 MHz): $\delta = 32.14$; MALDI-TOF MS: *m/z* 664.61 $[M]^+$ (100%). Anal. Calc. for $C_{27}H_{36}AuClN_3P$: C, 48.69; H, 5.45; N, 6.31; P, 4.65. Found: C, 48.72; H, 5.35; N, 6.26; P, 4.58%.

*5.2.11. Synthesis of cis-[$PtCl_2$(P(NC(H))$_3$)$_2$] (**13**)*

To a solution of **7** (38.2 mg, 88.1 μmol) in dry CH_2Cl_2 (20 mL) was added a solution of [$PtCl_2$(COD)] (16.5 mg, 44.1 μmol) and the mixture was stirred for 1 h at room temperature, followed by heating to reflux temperature for 15 min. Subsequently, all volatiles were evaporated to dryness, and the solid residue was washed with hexane, affording **13** as a light yellow solid in quantitative yield. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.41$ (dd, 12H, $^3J_{HH} = 8.1$ Hz, $^2J_{PH} = 10.8$ Hz, ArH), 7.08 (d, 12H, $^3J_{HH} = 6.9$ Hz, ArH), 3.36 (s, 12H, CH_2N), 2.20 (s, 36H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 141.99$ (ArC), 135.13 (d, $^3J_{PC} = 5.4$ Hz, ArC), 128.49 (d, $^2J_{PC} = 5.8$ Hz, ArC), 128.31 (d, $^1J_{PC} = 66.5$ Hz, ArC), 63.50 (CH_2N), 45.28 ($N(CH_3)_2$); ^{31}P NMR ($CDCl_3$, 121.5 MHz): $\delta = 13.53$ (t, $J_{PtP} = 3677$ Hz); MALDI-TOF MS: *m/z* 1062.23 $[M - 2Cl]^+$. Anal. Calc. for $C_{54}H_{72}Cl_2N_6P_2Pt$: C, 57.24; H, 6.40; N, 7.42; P, 5.47. Found: C, 57.30; H, 6.33; N, 7.37; P, 5.35%.

*5.2.12. Synthesis of [AuCl(PPh_2–(NC(H)N)) · Bzl_2]Br_2 (**14**)*

To a solution of **8** (20.0 mg, 33.0 μmol) in CH_2Cl_2 (30 mL) was added dropwise benzyl bromide (0.80 mL, 0.084 M in CH_2Cl_2, 67.00 μmol). The colorless clear reaction mixture was stirred overnight after which all volatiles were removed and a white sticky residue was obtained. The pure product was obtained by precipitation from a MeOH/Et_2O mixture (1/5, v/v). Yield: 29.5 mg (94%). ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 8.3$–7.4 (m, ArH), 4.77 (s, CH_2N), 4.68 (s, C*H*$_2$Ph), 3.01 (s, $N(CH_3)_2$); ^{13}C NMR (CD_3OD, 75 MHz): $\delta = 141.03$ (ArC), 140.00 (d, $^3J_{PC} = 13.1$ Hz, ArC), 134.72 (d, $^2J_{PC} = 14.6$ Hz, PhC), 134.49 (d, $^2J_{PC} = 14.25$ Hz, ArC), 133.51 (d, $^1J_{PC} = 30.0$ Hz, ArC), 133.31, 132.69 (CH_2Ph*C*), 130.86 (PhC), 130.33 (d, $^3J_{PC} = 11.6$ Hz, PhC), 129.69 (dd, $^2J_{PC} = 11.85$ Hz, $J_{CC} = 3.3$ Hz, PhC), 128.27 (dd, $^1J_{PC} = 69.0$ Hz, $J_{CC} = 13.5$ Hz, PhC), 129.15, 127.35 (CH_2Ph*C*), 68.41 (CH_2N), 67.01 (Ph*C*H_2), 48.39 ($N(CH_3)_2$); ^{31}P NMR (CD_3OD, 81 MHz): $\delta = 36.42$;

ESI-MS: m/z 915.43 $[M - Cl]^+$ (12%), 743.15 $[M - Cl - C_7H_7Br]^+$. Anal. Calc. for $C_{38}H_{43}AuBr_2ClN_2P$: C, 47.99; H, 4.56; N, 2.95; P, 3.26. Found: C, 47.56; H, 4.64; N, 2.78; P, 3.12%.

*5.2.13. Synthesis of [AuCl(P(NC(H)N)$_3$) · Bzl$_6$]Br$_6$ (**15**)*

Benzyl bromide (27.0 μL, 0.23 mmol) was added dropwise to a solution of **10** (29.6 mg, 35.4 μmol) in CH_2Cl_2 (30 mL) and the mixture was stirred for 2 h at room temperature. All volatiles were evaporated and the excess of benzyl bromide was removed by precipitation of the product from a MeOH/Et_2O (1/3, v/v) mixture, affording a white solid in quantitative yield. ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 8.70$ (d, $^3J_{PH} = 12.0$ Hz, 6H, ArH), 8.10 (s, 3H, ArH), 7.71, 7.68, 7.52, 7.49 (m, 30H, PhH), 4.79 (s, 12H, CH_2N), 4.75 (s, 12H, PhCH_2), 3.07 (s, 36H, $N(CH_3)_2$); ^{13}C NMR (CD_3OD, 75 MHz): $\delta = 141.95$ (s, ArC), 141.30 (d, $^2J_{PC} = 14.6$ Hz, ArC), 133.51 (PhC), 132.60 (d, $^1J_{PC} = 60.4$ Hz, ArC), 130.83 (PhC), 130.71 (ArC), 129.15, 127.60 (PhC); ^{31}P NMR (CD_3OD, 81 MHz): $\delta = 39.44$; ESI-MS: m/z 1828.73 $[M - Cl]^+$, 874.99 $[M - Cl - Br]^{2+}$ (45%), 556.34 $[M - Cl - 2Br]^{3+}$ (100%). Anal. Calc. for $C_{78}H_{99}AuBr_6ClN_6P$: C, 50.27; H, 5.35; N, 4.51; P, 1.66. Found: C, 50.15; H, 5.42; N, 4.37; P, 1.70%.

*5.2.14. Synthesis of [AuCl(P(NC(H))$_3$) · Bzl$_3$]Br$_3$ (**16**)*

Benzyl bromide (0.12 mL, 1.04 mmol) was added to a solution of **12** (0.23 g, 0.34 mmol) in CH_2Cl_2 (50 mL) and the mixture was stirred for 2 h at room temperature. All volatiles were evaporated and the excess of benzyl bromide was removed by repeated precipitation of the product from a MeOH/Et_2O (1/3, v/v) mixture, affording a white solid. Yield: 0.37 g (93%). ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 8.71$ (d, $^3J_{PH} = 12.4$ Hz, 6H, ArH), 8.12 (s, 6H, ArH), 7.71, 7.68, 7.52, 7.49 (m, 15H, PhH) 4.84 (s, 6H, CH_2Ph), 4.76 (s, 6H, CH_2N), 3.07 (s, 18H, $N(CH_3)_2$); ^{13}C NMR (CD_3OD, 75 MHz): $\delta = 135.15$ (d, $^2J_{PC} = 14.3$ Hz, ArC), 134.43 (d, $^3J_{PC} = 12.0$ Hz, ArC), 133.31 (PhC), 132.13 (d, $^4J_{PC} = 2.8$ Hz, ArC), 131.17 (d, $^1J_{PC} = 59.4$ Hz, ArC), 130.88, 129.23, 127.49 (PhC), 68.45 (CH_2N), 67.38 (PhCH_2), 48.68 ($N(CH_3)_2$); ^{31}P NMR (D_2O, 81 MHz): $\delta = 39.34$; ESI-MS: m/z 1144.51 $[M - Cl]^+$ (30%), 531.78 $[M - Cl - Br]^{2+}$ (100%). Anal. Calc. for $C_{48}H_{57}AuBr_3ClN_3P$: C, 48.89; H, 4.87; N, 3.56; P, 2.63. Found: C, 48.87; H, 4.93; N, 3.39; P, 2.68%.

*5.2.15. Protonation of **12** to afford [AuCl(P(NC(H))$_3$) · H$_3$]Cl$_3$ (**17**)*

To a solution of **12** (32.2 mg, 48.3 μmol) in CH_2Cl_2 was added HCl (1 M in Et_2O, 0.1 mL). The mixture was stirred for 15 min and all volatiles were evaporated, affording **17** as a light yellow solid in quantitative yield. ^{1}H NMR (D_2O, 300 MHz): $\delta = 7.73$ (dd, 6H, $^3J_{HH} = 8.1$ Hz, $^3J_{PH} = 12.9$ Hz, ArH), 7.66 (dd, 6H, $^3J_{HH} = 8.1$ Hz, $^4J_{PH} = 2.1$ Hz, ArH), 4.42 (s, 6H, CH_2N), 2.89 (s, 18H, $N(CH_3)_2$); ^{13}C NMR (D_2O, 75 MHz): $\delta = 135.21$ (d, $^2J_{PC} = 14.3$ Hz, ArC), 133.89 (d, $^4J_{PC} = 2.7$ Hz, ArC), 131.80 (d, $^3J_{PC} = 12.2$ Hz, ArC), 129.86 (d, $^1J_{PC} = 64.5$ Hz, ArC), 60.33 (CH_2N), 42.50 (d, $J = 4.2$ Hz, $N(CH_3)_2$); ^{31}P NMR (D_2O, 121.5 MHz): $\delta = 32.97$; ESI-MS: m/z 703.42 $[M - 2Cl]^+$ (30%), 333.75 $[M - 3Cl]^{2+}$ (100%).

*5.2.16. Protonation of **12** to afford [AuCl(P(NC(H))$_3$) · H$_3$](PO$_4$)$_n$ (**18**)*

To a solution of **12** (50.7 mg, 76.13 μmol) in CH_2Cl_2 (15 mL) was added dropwise a solution of H_3PO_4 in acetone (1.02 mL, 2.48 mg/mL, 25.3 μmol) and the mixture was stirred for 1 h. The resulting white suspension was evaporated to dryness, affording the product as a white solid in quantitative yield. ^{1}H NMR (D_2O, 200 MHz): $\delta = 6.9$–6.6 (overlapping, 12H, ArH), 3.42 (s, 6H, CH_2N), 1.90 (s, 18H, $N(CH_3)_2$); ^{13}C NMR: solubility too low to measure; ^{31}P NMR (D_2O, 81 MHz): $\delta = 29.66$ (AuP), −0.05 (PO_4^{3-}). ESI-MS m/z 1295.84 $[2M - 2PO_4 - Cl - 4H]^+$ (100%), 666.38 $[M - PO_4 - 2H]^+$ (35%).

5.3. Crystal structure determination of **8** and **12**

X-ray intensities were collected on a Nonius KappaCCD diffractometer with rotating anode and Mo Kα radiation (graphite monochromator, $\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}. The structures were solved with automated Patterson methods [19] for **8** and with Direct Methods [20] for **12**, and refined with SHELXL-97 [21] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. The drawings, geometry calculations, and checking for higher symmetry were performed with the program PLATON [22].

*Crystal data for **8***: $C_{24}H_{29}AuClN_2P$, $F_w = 608.88$, colorless plate, $0.48 \times 0.27 \times 0.12$ mm^3, triclinic, $P\bar{1}$ (No. 2), $a = 10.8697(1)$ Å, $b = 14.0294(1)$ Å, $c = 17.6771(2)$ Å, $\alpha = 91.6520(3)°$, $\beta = 107.6593(4)°$, $\gamma = 109.7291(4)°$, $V = 2391.84(4)$ Å^3, $Z = 4$, $\rho = 1.691$ g/cm^3. 48,519 Reflections were measured. An analytical absorption correction was applied ($\mu = 6.34$ mm^{-1}, 0.13–0.64 correction range). 10,905 Reflections were unique ($R_{int} = 0.048$). 531 Parameters were refined with no restraints. R_1/wR_2 $[I > 2\sigma(I)]$: 0.0195/0.0440. R_1/wR_2 [all reflections]: 0.0246/0.0460. $S = 1.031$. Residual electron density between −0.81 and 1.00 e/Å^3.

*Crystal data for **12***: $C_{27}H_{36}AuClN_3P$, $F_w = 665.97$, colorless needle, $0.48 \times 0.12 \times 0.09$ mm^3, hexagonal, $P6_3$ (No. 173), $a = b = 13.1848(7)$ Å, $c = 9.0589(8)$ Å, $V = 1363.81(16)$ Å^3, $Z = 2$, $\rho = 1.622$ g/cm^3. 17,936 Reflections were measured. An analytical absorption correction was applied ($\mu = 5.57$ mm^{-1}, 0.38–0.66 correction range). 2088 Reflections were unique ($R_{int} = 0.037$). 102 Parameters were refined with one restraint. R_1/wR_2 $[I > 2\sigma(I)]$: 0.0139/0.0280. R_1/wR_2 [all reflections]: 0.0181/0.0289.

$S = 1.084$. Flack parameter $x = -0.026(6)$. Residual electron density between -0.26 and $0.76\ e/Å^3$.

6. Supplementary materials

CCDC-274165 (compound **8**) and 274166 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Note added in proof

Recently, single crystals were obtained for complex **13**, which turned out to be the *trans* isomer. Full details of the structure of *trans*-13 and on its structural analysis will be submitted shortly to Acta Crystallographica.

References

[1] B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1–2, VCH, Weinheim, Germany, 1996.
[2] (a) M. Karlsson, M. Johansson, C. Andersson, J. Chem. Soc., Dalton Trans. (1999) 4187;
(b) B. Cornils, W.A. Herrmann, Aqueous-phase Organometallic Chemistry: Concepts and Applications, Wiley–VCH, Weinheim, Germany, 1998.
[3] (a) For a short review on fluorous phosphanes in catalysis see: E. de Wolf, G. van Koten, B.-J. Deelman, Chem. Soc. Rev. 28 (1999) 37; Examples of this class of fluorous phosphanes: (b) S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem., Int. Ed. Engl. 36 (1997) 1628;
(c) D. Sinou, G. Pozzi, E.G. Hope, A. Stuart, Tetrahedron Lett. 40 (1999) 849;
(d) B. Richter, E. de Wolf, G. van Koten, B.-J. Deelman, J. Org. Chem. 65 (2000) 3885.
[4] See for example: (a) S.D. Walker, T.E. Barder, J.R. Martinelli, S.L. Buchwald, Angew. Chem., Int. Ed. 43 (2004) 1871;
(b) O. Niyomura, M. Tokunaga, Y. Obora, T. Iwasawa, Y. Tsuji, Angew. Chem., Int. Ed. 42 (2003) 1287.
[5] See for example: (a) M. Aránza Alonso, J.A. Casares, P. Espinet, K. Soulantica, Inorg. Chem. 42 (2003) 3856;
(b) V.F. Slagt, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Angew. Chem., Int. Ed. 40 (2001) 4271;
(c) B. Breit, W. Sache, Angew. Chem., Int. Ed. 44 (2005) 1640;
(d) N.C. Gianneschi, S.T. Nguyen, C.A. Mirkin, J. Am. Chem. Soc. 127 (2005) 1644.
[6] D.A. Atwood, A.H. Cowley, J. Ruiz, Inorg. Chim. Acta 198-200 (1992) 271.
[7] F. Carré, C. Chuit, R.J.P. Corriu, A. Mehdi, C. Reyé, J. Organomet. Chem. 529 (1997) 59.
[8] R. Kreiter, R.J.M. Klein Gebbink, G. van Koten, Tetrahedron 59 (2003) 3389.
[9] P. Steenwinkel, S.L. Stuart James, D.M. Grove, N. Veldman, A.L. Spek, G. van Koten, Chem. Eur. J. 2 (1996) 1440.
[10] M. Albrecht, G. van Koten, Angew. Chem., Int. Ed. 40 (2001) 3750.
[11] I.M. Al-Naiiar, Inorg. Chim. Acta 128 (1987) 93.
[12] Crystal structure of $ClAuPPh_3$ from CCDB (CTPPAU); Fit achieved by removal of the $CH_2N(CH_3)_2$ fragments from complex **8**, and use of the fit by click routine in PLATON [22].
[13] G. Trabesinger, A. Albinati, N. Feiken, R.W. Kunz, P.S. Pregosin, M. Tschoerner, J. Am. Chem. Soc. 119 (1997) 6315.
[14] R. Kreiter, R.J.M. Klein Gebbink, G. van Koten (in preparation).
[15] J.D. Dunitz, X-ray Analysis and the Structure of Organic Molecules, VCH, Weinheim, Germany, 1995 (chapter 10).
[16] J.H. Short, U. Biermacher, J. Pharm. Sci. 51 (1962) 881.
[17] D. Drew, J.R. Doyl, A.G. Shaver, Inorg. Synth. 13 (1972) 47.
[18] R. Uson, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 85.
[19] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
[20] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[21] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Germany, 1997.
[22] A.L. Spek, J. Appl. Cryst. 36 (2003) 7.