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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, $n = 3$)

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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

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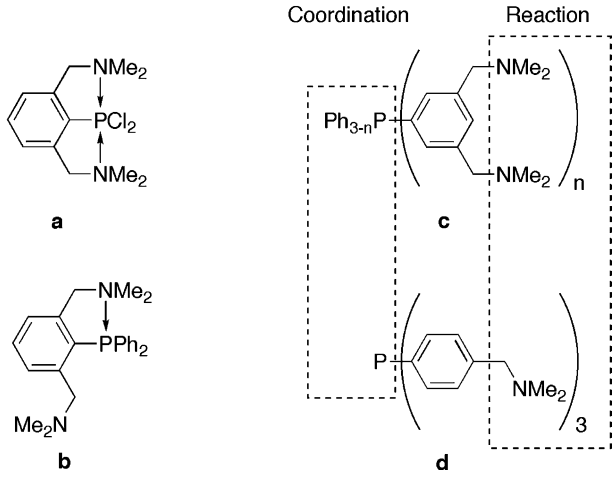


Fig. 1. Examples of (dimethylamino)methyl-substituted arylphosphanes reported by Cowley [6] (a), Corriu [7] (b), and in this report (c, d).

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.

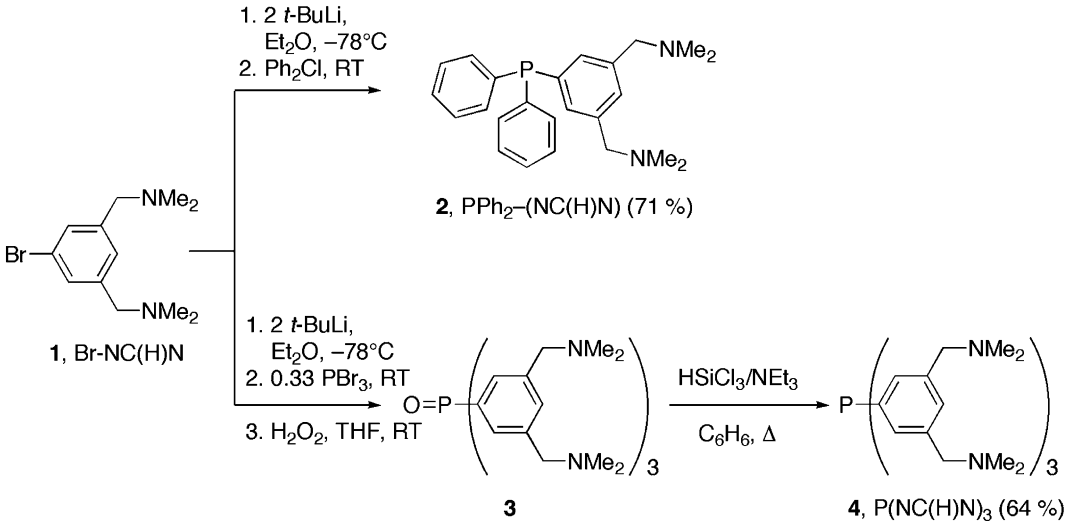
In our research, we set out to design and prepare bifunctional arylphosphanes of the general formula $PPh_{3-n}Ar_n$ (Ar = 1-$C_6H_3(CH_2NMe_2)_2$-3,5 (NC(H)N); or Ar = 1-C_6H_4-(CH_2NMe_2)-4 (NC(H))) (Fig. 1(c) and (d)) which on the one hand could function as typical triarylphosphane ligands, i.e., 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**).