



Palladium (II) complexes with the unsymmetrical H-spirophosphorane ligand HP(OCMe₂CMe₂O)(OCH₂CMe₂NH): Synthesis, structural and catalytic studies

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ABSTRACT

We have investigated the reactivity of the unsymmetrical H-spirophosphorane (HSP) ligand HP(OCMe₂CMe₂O)(OCH₂CMe₂NH) **1** towards different palladium(II) precursors and synthesised the mononuclear complexes [PdCl₂{P(OCMe₂CMe₂O)OCH₂CMe₂NH₂}] **2** and [PdCl(C₃H₅){P(OCMe₂CMe₂O)OCH₂CMe₂NH₂}] **3**. The structural features of the compounds are characterised by spectroscopic methods as well as single crystal X-ray diffraction studies. The complexes are shown to be remarkably active precatalysts for the Heck and Hiyama cross-coupling reactions. The products of the C–C bond formation reactions were obtained with high conversion and stereoselectivity. Mechanistic studies of the Heck reaction reveal that, besides homogenous precatalysts, also heterogeneous Pd(0) nanoparticles are involved in the catalytic process.

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1. Introduction

Heterofunctionalised, bidentate P,E ligands (E = N, O) constitute an important, widely utilised group of ligands in transition metal chemistry. The vast majority of these compounds comprise heteroditopic phosphines, where the phosphorus is the soft donor, and the hard donor is either a nitrogen or oxygen atom. Less attention has been paid to mixed bidentate phosphites. Albeit phosphite ligands in particular P,N heterodonors, have demonstrated to be an effective ligands for asymmetric catalytic reactions such as allylic alkylation and Heck cross-coupling reactions [1]. Therefore we believe that construction of new mixed P,N ligands that can be easily synthesised from starting material is of great importance. For this purpose H-spirophosphoranes, capable of P,N- or P,O-coordination seem to be particularly useful because of their easy designing. Recently palladium complexes incorporating H-spirophosphorane (HSP) ligands have emerged as efficient catalyst precursors for Heck cross-coupling reactions [2]. The reported results show that the H-spirophosphorane palladium complex [PdCl(μ-Cl){P(OCMe₂CMe₂O)OCMe₂CMe₂OH}]₂ has proved to be a very good catalyst for the reaction of aryl bromide with *n*-butyl acrylate, while the complex [PdCl₂{P(OCH₂CMe₂NH)OCH₂CMe₂NH₂}] shows high activity in the cross-coupling of aryl bromide

not only with *n*-butyl acrylate but also with substituted styrenes. Moreover, the catalyst turns out to be highly effective in the Hiyama coupling reaction of functionalised styrylsilanes with bromobenzene [3]. The outstanding features of H-spirophosphoranes, such as facile synthetic accessibility [4,5] and ambidentate electronic properties (π -acceptor ability of the phosphorus atom along with σ -donor ability of the nitrogen atom), make them attractive for the construction of new palladium precursors suitable for catalytic processes [6]. Given our interest in the coordination abilities of H-spirophosphoranes, we were curious to investigate how fine-tuning inside the ligand molecule could influence catalytic activity.

As a part of our continuing research on the chemistry of H-spirophosphorane ligands, we report on the syntheses of unsymmetrical spirophosphorane palladium complexes, an exploration of their reactivity and application as precatalysts in the Heck and Hiyama coupling reactions.

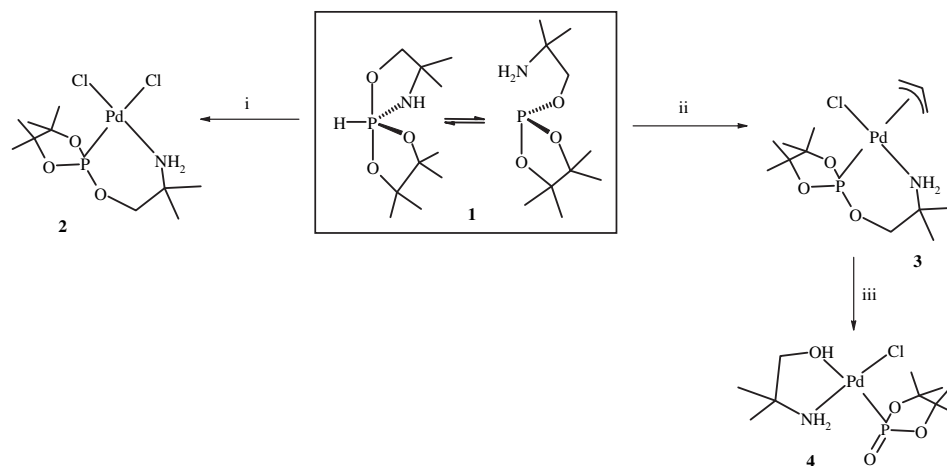
2. Results and discussion

2.1. Synthesis and spectroscopic characterisation

The unsymmetrical H-spirophosphorane ligand HP(OCMe₂CMe₂O)(OCH₂CMe₂NH) **1** was prepared by one-pot synthesis in two stages (eqs. (1) and (2)). It was obtained from equimolar amounts of pinacol and 2-amino-2-methyl-1-propanol in the presence of one equivalent of hexamethylphosphorous triamide P(NMe₂)₃. Pinacol

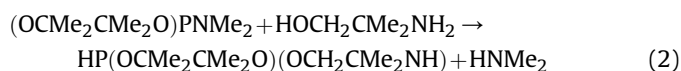
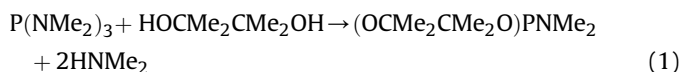
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Scheme 1. (i) $[\text{PdCl}_2(\text{cod})]$, dichloromethane; (ii) $[\text{Pd}(\text{m-Cl})(\text{C}_3\text{H}_5)_2]$, toluene; (iii) dichloromethane, $+\text{H}_2\text{O}$, $-\text{C}_3\text{H}_6$.

was the precursor of choice for the first stage, which proceeded smoothly to give $(\text{OCMe}_2\text{CMe}_2\text{O})\text{PNMe}_2$, whereas the use of aminoalcohol in the second step prevented the undesirable symmetrical product $\text{HP}(\text{OCH}_2\text{CMe}_2\text{NH})_2$ from arising in the system. Although some spectroscopic data for **1** are already known (^{31}P NMR) [7], there has been no information about the molecular and crystal structure determination. Therefore, we present the stereochemistry of **1** and, additionally, a detailed instrumental analysis.



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** at room temperature exhibits two resonances, at $\delta = -49.21$ ppm and $\delta = 148.45$ ppm, due to the presence of two tautomeric penta- and tri-coordinated forms of phosphorus atom. The presence of a P–H bond was manifested not only in the ^{31}P NMR spectrum but also in ^1H NMR as a doublet at 7.49 ppm with $^1J(\text{P-H}) = 772.5$ Hz. Besides the resonances assigned to the proton at the phosphorus atom, the ^1H NMR spectrum exhibited signals for the NH proton: a doublet at $\delta = 2.78$ ppm, and signals assigned to CH_2 protons: two multiplets at $\delta = 3.54$ ppm and $\delta = 3.57$ ppm assigned to equatorial and axial protons. Additionally, six singlets were detected in the aliphatic resonance range, attributed to six unequal methyl protons. The presence of P–H and N–H

groups found reflection in infrared spectra. Absorption bands for appropriate stretching frequencies are present at $\nu(\text{P-H}) = 2362$ cm^{-1} and $\nu(\text{N-H}) = 3350$ cm^{-1} respectively.

Complexation reactions of ligand **1** were carried out with the use of two palladium precursors: $[\text{PdCl}_2(\text{cod})]$ (cod = 1,5-cyclooctadiene) and $[\text{Pd}(\mu\text{-Cl})(\text{C}_3\text{H}_5)_2]$ (Scheme 1). An equimolar reaction of **1** with appropriate precursors gave rise to the mononuclear chelating complexes $[\text{PdCl}_2\{\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})\text{OCH}_2\text{CMe}_2\text{NH}_2\}]$ **2** (i) and $[\text{PdCl}(\text{C}_3\text{H}_5)\{\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})\text{OCH}_2\text{CMe}_2\text{NH}_2\}]$ **3** (ii) respectively. Ligand **1** coordinates in its predictable tautomeric form, *via* tricoordinated phosphorus and nitrogen atoms. Both complexes were isolated as yellow or white solids, well soluble in dichloromethane and acetonitrile. Prolonged exposure of dichloromethane solution of **3** to atmospheric moisture causes a new palladium(II) complex, $[\text{PdCl}\{\text{P}(\text{O})(\text{OCMe}_2\text{CMe}_2\text{O})\}\text{HOCH}_2\text{CMe}_2\text{NH}_2]$ **4**, to form as yellow crystals suitable for X-ray structural analysis (see Supplementary material). It is apparently formed as a result of hydrolytic cleavage of a coordinated H-spirophosphorane ligand and simultaneous loss of the allyl molecule. The presence of released propene was confirmed by means of GC–MS in an experiment performed in a tube sealed with a rubber tap. The H-spirophosphorane ligand underwent hydrolytic rupture to form 2-amino-2-methyl-propanol-1 bounded to palladium in a protonated N,O chelating mode and the phosphonate moiety $\text{P}(\text{O})(\text{OCMe}_2\text{CMe}_2\text{O})$ coordinated *via* the phosphorus atom.

The chemical compositions of **2** and **3** were ascertained by microanalytical and spectroscopic data. ^1H NMR spectra for both complexes at room temperature show first-order patterns with

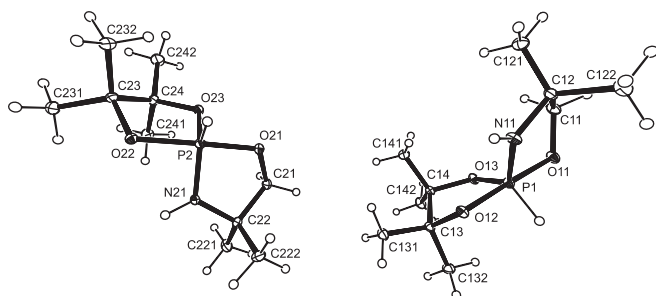


Fig. 1. Molecular structure of ligand **1**. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

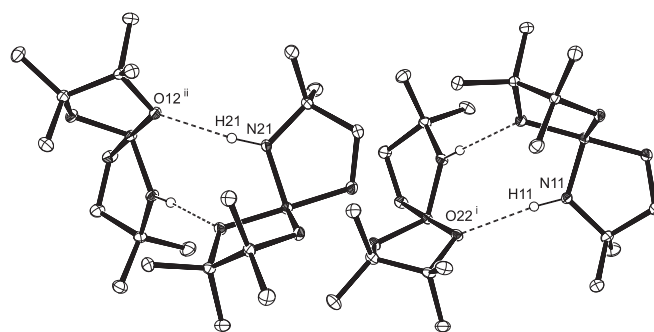


Fig. 2. Hydrogen bonds in ligand **1**. Hydrogen atoms not involved in hydrogen interactions are omitted for clarity. Symmetry codes: (i) $0.5 + x, y, 0.5 - z$; (ii) $-0.5 + x, y, 0.5 - z$.

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