Immobilized Sonogashira catalyst systems: new insights by multinuclear HRMAS NMR studies†

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Received 1st October 2010, Accepted 7th December 2010
DOI: 10.1039/c0cc04194g

A new chelate phosphine linker and its Pd and Cu complexes have been synthesized and immobilized. The solvent impact on these immobilized species, their mobility, and coordination preferences have been studied in situ by HRMAS (High-Resolution Magic Angle Spinning) NMR. The catalyst recycling characteristics match the HRMAS results.

Metal catalyzed carbon–carbon bond forming reactions have dominated homogeneous catalysis over the last decade. One of the most widely used catalytic reactions is the Sonogashira coupling of aryl halides with acetylenes, which is catalyzed by a Pd(0)/Cu(I) system. However, detailed mechanistic studies remain scarce. In homogeneous solution, mechanistic studies are complicated by the presence of many different species, and it is often unclear whether palladium catalyzed reactions are achieved by tethered molecular entities, or metallic Cu nanoparticles, or molecular Pd species in solution that form during the reaction. Catalyst immobilization helps to disentangle the different components and effects. Furthermore, tethering the catalyst system to a solid support such as silica offers the advantage that, under the right conditions, the catalysts can easily be removed from the reaction mixture and recycled many times. In this contribution, we will demonstrate that the line-narrowing HRMAS technique can provide valuable insights into structures of surface-bound linkers and catalysts and especially processes taking place at the liquid/solid interface.

The chelate ligand 1 (Scheme 1) has been synthesized in high yields by reacting (EtO)3Si(CH2)3NH2 with paraformaldehyde and HPh2. This synthesis is very versatile and applicable to aryl amines and other phosphines HPR (R = alkyl, aryl). Ligand 1 readily coordinates to a Pd center to form 2 (Scheme 1). A single crystal X-ray structure (Fig. 1) shows that 2 is nearly square planar at the metal center, the interplanar angle between the two selected planes Cl1/Cl2/Pd1 and P1/P2/Pd1 amounts to only 7.74(4). A strong pyramidalization at the nitrogen atom is indicated by a deviation of N1 by 0.469(3) Å out of the plane from its neighbouring carbon atoms.

The Cu component of the Sonogashira catalyst, 4i, can be generated on silica by treating I with [(Ph3P)2CuNCMe]BF4 (Scheme 1). The PPh3 and PPh2 31P HRMAS signals of 4i are found at 5.7 and −17.8 ppm, with the expected intensity ratio of 1 : 2. In contrast to the immobilized Pd component 2i, for 4i the 31P HRMAS spectra in different solvents (Fig. 2) reveal different views (DCM inclusion and H atoms omitted for clarity).

Scheme 1 Synthesis of Pd complex 2 and 1i–4i.

Fig. 1 Single crystal X-ray structure of Pd complex 2. Two different views (DCM inclusion and H atoms omitted for clarity).

† CCDC 795029. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc04194g
that some polar solvents, such as dioxane, are able to replace the PPh₃ ligand at the Cu center, and the signal of uncoordinated PPh₃ can be seen in the corresponding spectra at about –6 ppm. This result reflects the tendency of Cu phosphine complexes to exchange ligands rapidly in solution. However, this important involvement of the solvents has not been considered in detail previously with respect to possible leaching of the catalyst component from the support, or when contemplating the different activities of the catalyst in various solvents (see below). Therefore, in addition to classical CP/MAS, HRMAS measurements are an indispensable tool for probing the interactions of catalyst precursors with the corresponding solvents prior to catalysis.

Fortunately, in spite of the potential exchange of the PPh₃ ligand by a solvent molecule, the Cu component of the Sonogashira catalyst system does not show substantial leaching tendencies when immobilized by a phosphine chelate linker. However, the Pd component is known to leach substantially. Therefore, in order to check the coordinating strength of ligand 1 for the Pd complex, we sought to compare it with a thiol linker that is recognized as a strong transition metal scavenger. The modified silica 5i (Scheme 2) has been obtained using (MeO)₃Si(CH₂)₃SH (5) under the standard immobilization conditions. Reaction of 5i with Cl₂Pd(NCPh₃)₂ leads to 6i (Scheme 2, structure according to ref. 5a). 5i and 6i are missing the ³¹P probe for checking the completion of the coordination, but ¹³C HRMAS spectra can successfully be applied instead (Fig. 3).

Analytically most indicative are the SCH₂ carbon signals, which prove that all thiol linkers are bound to the metal center. On coordinating the thiol to Pd, the SCH₂ carbon resonance shifts from about 29 to 25 ppm (Fig. 3), and the line becomes broader due to the restricted mobility enforced by the chelate formation. This also accounts for the broadening of the other CH₂ resonances on going from 5i to 6i. Due to the high spectral resolution, two sorts of OMe groups can be distinguished, the surface-bound (OMe’) and residual methoxy groups (OMe) at the silane.

Fig. 3 ¹³C HRMAS spectra (high power decoupling, 2 s pulse delay, acetone-d₆) of 5i (bottom) and 6i (top). * Denotes the CH₃ signal of residual toluene.

Mixing batches of 5i and 2i and stirring them in acetone overnight resulted in the top ³¹P spectrum in Fig. 4. In contrast to our expectation, no traces of the uncoordinated phosphine 1i with its ³¹P signal at about –30 ppm could be detected. However, when mixing batches of 1i and 6i the formation of 2i (Fig. 4, bottom trace) besides 1i starts immediately. Following the process in situ by ³¹P HRMAS spectroscopy, accumulating the FIDs over 3 h intervals (Fig. 4, middle section), reveals its timeline. Within 18 h practically all PdCl₂ fragments have migrated from the thiol to the chelate phosphine linkers. The process is continuous, as the signal of 1i decreases, the signal of 2i increases correspondingly. Therefore, we conclude that the chelate phosphine 1i coordinates the Pd fragment even better than the thiol linkers.

The recycling results of the Sonogashira catalyst system with the immobilized Pd component 2i and CuI added for each run corroborate the HRMAS findings regarding the solvent influence and the coordination strength of the linkers. The thiol-bound catalyst 6i, in combination with CuI, is the least active in dioxane and piperidine as solvents and produces only about 5% tolane in the first and 2% in the fourth run. The impact of the solvent on the catalyst activity of 2i is shown in Fig. 5. Dioxane propagates the most extensive leaching, which was determined to be quantitative by AAS measurements of the combined supernatants of the three runs. Offering additionally uncoordinated 1i as the Pd scavenger on the surface leads to a catalyst that can be recycled four times until most of the activity is lost. Since the formation of Pd nanoparticles could be excluded by TEM measurements, Pd is leaching from the surface, as the HRMAS spectra suggest, and acting as a molecular species in solution, in accord with results on other Pd catalysts.

This contribution demonstrates that HRMAS NMR of immobilized catalysts in different solvents can give valuable insights into the nature and timescale of processes at the solid–liquid interface.
1 This material is based upon work supported by The Welch Foundation (A-1706), the National Science Foundation (CHE-0911207), INSTRUCTION, and DFG (SFB 623).

Notes and references


10 Synthesis of the chelate phosphine ligand 1: (EtO)2Si(CH3)2NH2 (0.58 g, 2.63 mmol) is dissolved in 20 ml of toluene and (CH3)2O (0.19 g, 2.56 mmol) and Ph2PH (0.98 g, 5.26 mmol) are added. The suspension turns into a clear solution within 2 h after heating to 60 °C, and is stirred overnight at this temperature. The solvent is removed in vacuo, and a 1.40 g (2.27 mmol, yield 85%) of 1 results as a clear, viscous liquid. δH (500.1 MHz, CDCl3) 7.53–7.04 (m, Haryl), 3.76 (q, 2JHH = 7.0 Hz, OCH2), 3.63 (d, JHPh = 4.3 Hz, PCH3), 3.00 (t, 2JHH = 7.1 Hz, CH2CH3N), 1.75 (quint., 2JHH = 7.6 Hz, CH2CH2CH3), 1.57 (t, 2JHH = 7.0 Hz, CH3), 0.65 (t, 2JHH = 8.1 Hz, SiCH2); δ(13C) (125.8 MHz, CDCl3) 139.14 (d, 2JPC = 13.7 Hz, C3), 133.54 (d, 2JPC = 18.5 Hz, C2), 126.33 (d, 2JPC = 6.6 Hz, C0), 128.55 (s, C5), 59.64 (t, 2JPC = 9.0 Hz, CH2CH3N), 59.23 (dd, 2JPC = 9.3 Hz, JPC = 5.3 Hz, C1), 58.43 (s, OCH2), 20.31 (s, CH3CH2CH3).

11 Recycling characteristics of 2i in the indicated solvents. Cul and the substrates Phl and PhCCH are added for each cycle.18

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