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Inorganic Chemistry Communications



journal homepage: www.elsevier.com/locate/inoche

Solvent-free direct cyclopalladation of sulfides on silica gel

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ARTICLE INFO

Article history: Received 28 June 2012 Accepted 29 September 2012 Available online 5 October 2012

Keywords: C,S-palladacycle S,C,S-palladacycle Reactions on silica gel Cyclopalladation of sulfides

ABSTRACT

Direct cyclopalladation of benzyl methyl sulfide, benzyl phenyl sulfide and 1,3-bis(methylthiomethyl)benzene using $Pd(OAc)_2$ can be accomplished using silica gel instead of a solvent. The yields of the corresponding cyclopalladated complexes in these green transformations are very similar to those obtained using conventional solvent conditions. The X-ray crystallographic data for *trans*-Pd(HL)₂Cl₂ (HL=benzyl methyl sulfide) are reported.

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Solvent-free synthesis of organic compounds and coordination complexes is a well-known area of research [1-4] that is becoming more important due to environmental concerns. When at least one of the reagents is liquid, sometimes it is possible to use that chemical as both a reactant and a solvent, e.g. in preparation of acid halides from the corresponding carboxylic acids using excess SOCl₂. However, this approach is limited to certain reactions and cannot be considered environmentally friendly. When both reagents are solid, their grinding can result in the formation of the corresponding products [4]. However, this so-called mechanochemical approach has been applied to a limited scope of reactions usually occurring at room temperature [1,4]. In another solvent-free methodology, a solid absorbent, such as silica gel or aluminum oxide, is used as a reaction medium [2,3,5-7]. While organic transformations on silica gel with or without solvents are well documented, solvent-free preparations of organometallic compounds are very rare [8,9]. It is noteworthy that there have been sporadic reports on the preparation of organometallic complexes on silica gel or aluminum oxide in the presence of a solvent [10–12]. Recently, our group described preparation of C,N- and C,P-cyclopalladated complexes (CPCs) by direct cyclopalladation using either Pd(OAc)₂ or Na₂PdCl₄ on silica gel applying solvents on the purification step only [13–15]. In this communication, we report the extension of this methodology to the synthesis of C,S- and S,C, S-types of palladacycles from sulfides.

Benzyl methyl sulfide **1a** was used in our study for determination of the best conditions for cyclopalladation of sulfur-containing preligands on silica gel. Previously, several groups have unsuccessfully attempted preparation of the corresponding palladacycle from this preligand using Li₂PdCl₄ or Na₂PdCl₄ in refluxing MeOH [16–18]. When $Pd(OAc)_2$ in acetic acid was used, cyclopalladation of sulfide **1a** occurred at 90 °C in 30 min [19]. After treatment with LiCl, the corresponding dimeric CPC **2a** was isolated in 72% yield [19]. Solvent-free reactions of sulfide **1** with Na₂PdCl₄ on silica gel were performed in a 1:1 ratio of the reagents using room temperature, 50, 80 and 110 °C. The reaction time was varied from 1 to 72 h. In all experiments with Na₂PdCl₄, only the coordination complex Pd(HL)₂Cl₂ (**3a**, HL=**1a**) was isolated. The highest quantitative yield of **3a** was obtained in the room temperature reaction on SiO₂ after 18 h of stirring. When Na₂PdCl₄ was replaced by Pd(OAc)₂, cyclopalladation of sulfide **1a** occurred at 50 °C to afford CPC **2a** in 52% (Scheme 1 and Table 1, entry 1). The yield of complex **2a** was improved by adding the weak base NaOAc [20] and increasing the time of the reactions (Table 1, entries 2–5) [21]. Elevating the temperature to 80 °C led to a decreased yield of the CPC (entry 6).

In all reactions with $Pd(OAc)_2$ after treatment with LiCl, the corresponding coordination complex **3a** was isolated as well. The structures of complexes **2a** and **3a** were confirmed by ¹H and ¹³C{¹H} NMR spectroscopy as well as by comparing spectroscopic data and melting points of these compounds with those reported earlier [17,19]. The structure and trans geometry of the coordination complex in its solid state were proven by X-ray crystallographic analysis (Fig. 1) [22].

Next, cyclopalladation of benzyl phenyl sulfide (**1b**) on SiO₂ was studied (Scheme 1 and Table 1, entries 7–9). The best yield (50%) of the corresponding CPC (**2b**) was obtained in the reaction with $Pd(OAc)_2$ at 65 °C for 24 h (entry 8). For comparison, the same yield of **2b** was achieved in the only reported successful palladation of this sulfide [$Pd(OAc)_2$, acetic acid, 90 °C, 1 h] [23]. Similar to sulfide **1a**, in all reactions with **1b**, the coordination complex **3b** [24] was isolated as well (entries 7–9). Structures of the cyclopalladated and coordination complexes **2b** and **3b** were confirmed by ¹H and ¹³C{¹H} NMR spectra.

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^{1387-7003/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.inoche.2012.09.029



Scheme 1. Cyclopalladation of sulfides 1a,b on SiO₂.

Selected reactions of sulfides **1a** and **1b** with $Pd(OAc)_2$ on SiO_2 .

Table 1

Entry	Ligand	Base	Temp. (°C)	Time, h	Yield of 2a,b , %	Yield of 3a,b (%)
1	1a	None	50	18	52	18
2	1a	NaOAc	50	18	61	15
3	1a	None	50	120	63	14
4	1a	NaOAc	50	120	67	16
5	1a	None	50	168	81	12
6	1a	NaOAc	80	48	45	12
7	1b	NaOAc	50	120	31	26
8	1b	NaOAc	65	24	50	40
9	1b	NaOAc	80	18	42	16

It is important to note that mixing sulfides **1a** and **1b** with $Pd(OAc)_2$ in a 1:1 molar ratio and heating the resulting mixtures without solvent nor silica gel at 50 °C for 18 h resulted in the formation of a very dark viscous matter, which did not contain the corresponding cyclopalladated complexes according to analytical TLC.

We also expanded our solvent-free methodology to the metalation of 1,3-bis(methylthiomethyl)benzene **4**, which can give a pincer-type CPC. In the only report of the successful direct cyclopalladation of this preligand, the reaction with Pd(OAc)₂ followed by treatment with LiCl furnished the *S*,*C*,*S*-pincer complex **5** "in less than 10% yield" [19]. Similarly, in the reaction on SiO₂, disulfide **4** reacted with Pd(OAc)₂ followed by ligand metathesis with LiCl to afford 8% yield of CPC **5** (50 °C, 120 h; Scheme 2). Increasing the temperature to 80 °C did not improve the yield of the pincer complex. The structure of compound **5** was confirmed by comparing ¹H and ¹³C{¹H} MMR spectra with those reported earlier [19]. No other complexes were identified in these transformations.

In summary, it was demonstrated that direct cyclopalladation of sulfides can occur on silica gel using $Pd(OAc)_2$ without using solvents. Isolated yields of the sulfide-derived CPCs synthesized in the reactions on silica gel were very similar to those obtained in solutions. Compared to the corresponding reactions using acetic acid as the solvent, metalation of the sulfides on silica gel occurred at lower temperatures, but required a much longer reaction time. To get reproducible results in reactions on silica gel, efficient stirring was essential.

Acknowledgment

The authors acknowledge financial support from ND EPSCoR through NSF grant No. EPS-0-0184442. The Doctoral Dissertation Assistantship to V.A.S. was provided by ND EPSCoR through NSF grant No. EPS-0184442. The authors would like to thank Dr. Victor G.



Fig. 1. Molecular structure of trans-3a.



Young and the University of Minnesota X-Ray Crystallographic Laboratory for the data obtained for complex **3a**.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.09.029.

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- [21] Typical procedure and data complex **2a**: Preligand **1a** (0.0214 mg, 0.155 mmol), Pd(OAc)₂ (0.0328 mg, 0.146 mmol), SiO₂ (0.0544 mg; 375 mg per 1 mmol of preligand; 100-230 mesh) and a stirring bar were added to a small round-bottom flask and the components were vigorously mixed using spatula for ca. 1 min. The flask was fitted with a rubber septum and a 1-mL syringe packed with CaCl₂ and then was immersed in a preheated oil bath. After stirring at 50 °C for 168 h, the mixture was transferred onto a glass filter and washed with acetone (3 $\times\,5$ mL). LiCl (0.025 g, 0.60 mmol) was added to the filtrate, and the resulting mixture was stirred overnight. The crude product was purified using preparative TLC (silica gel, benzene). Complex 2a was isolated as a yellow solid in 81% yield along with 12% of complex 3a, which appeared as an orange solid. Mp 140 °C (decomp.); $R_{\rm f}$ 0.62 (10:1 benzene–acetone). ¹H NMR (CDCl₃, δ , ppm): 2.21 (s, 3H,), 3.92 (d, J=14.6 Hz, 1H, CH^A), 4.28 (d, J=14.6 Hz, 1H CH^B), 6.91 (m, 1H, H3 arom), 6.98 (d, J=5.0 Hz, 2H, H4 and H5), 7.41 (d, J=5.0 Hz, 2H, H6). ¹³C NMR (CDCl₃, δ , ppm): 23.4 (SCH₃), 47.3 (CH₂S), 123.6 (C4 arom), 125.3 (C3 arom), 126.2 (C5 arom), 135.6 (C6 arom), 146.9 (C2 arom), 148.1 (C-Pd).
- [22] Crystallographic data for complex *trans-3a* have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 888235. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk). Selected bond lengths (Å): Pd-Cl 2.2982(4), Pd–S 2.3205(4), S-C(8) 1.8050(18), S-C(7) 1.8237(17), C(1)-C(2) 1.386(2). Selected bond angles [°]: Cl'-Pd-Cl and S-Pd-S' 180.000(17), Cl'-Pd-S and Cl'-Pd-S' 98.819(16), Cl-Pd-S and Cl'-Pd-S' 94.181(16).
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