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Transcyclopalladation on silica gel

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ABSTRACT

A possibility of transcyclopalladation on silica gel was shown using reactions of acetato- and chloro-bridged dimeric cyclopalladated complexes derived from *N*,*N*-dimethylbenzylamine with benzyl methyl sulfide, benzyl phenyl sulfide, benzyldiphenylphosphine, 8-methylquinoline and 1,3-bis(methylthiomethyl)benzene in the presence of equimolar amount of CF_3CO_2H. The reaction provided the corresponding *C*,*S*-, *C*,*N*-, *C*,*P*- and *S*,*C*,*S*-palladacycles in 39–65% yield.

1. Introduction

Organic synthesis on silica gel using solvents on the purification step only is a well-known practice [1,2]. Interest in such reactions can be explained by a number of factors. First, use of silica gel instead of potentially harmful solvents results in the reduction of pollution. Secondly, for a number of organic transformations performed on silica gel and other absorbents, product yields are at least as high as those obtained under conventional conditions [1–4]. In some cases, reactions on silica gel require milder conditions [5]. It was also shown that the products' regio- and stereochemistry can be different from that observed for compounds obtained using traditional solvent conditions [2].

In contrast, the preparation of organometallic derivatives on SiO_2 [6,7] or Al_2O_3 [8] is rather limited due to the fact that these absorbents contain water and compounds with a carbon-metal bond are usually moisture-sensitive. Our group's research is focused on the synthesis of new cyclopalladated complexes (CPCs) and their applications. One direction is the preparation of CPCs on silica gel. Recently, we reported a general procedure for the preparation of *C*,*N*- and *C*,*P*-palladacycles – including those containing aromatic (sp^2)C–Pd, benzylic (sp^3)C–Pd and aliphatic (sp^3)C–Pd bonds – on silica gel [9–12]. The reported preparations were based on direct cyclopalladation of the corresponding preligands with $Pd(OAc)_2$ or Na_2PdCl_4.

Another method for synthesis of CPCs is transcyclopalladation, which is also known as cyclopalladated ligand exchange [13]. In transcyclopalladation, a preligand (**A**) reacts with a dimeric CPC (**B**) to form a new dimeric CPC (**C**) and a free preligand (**D**, Scheme 1). The dimeric CPC **B** acts as a source of Pd(II). The reaction is reversible and apparently is governed by the difference in thermodynamic stabilities of the starting and final palladacycles [14,15]. For the series of aryl-substituted *N*,*N*-dialkylbenzylamines, it was shown that, in D_3CO_2D–$CHCl_3$ solutions, the equilibrium favors the CPC derived from a more electron-rich ligand, e.g. 3,4-dimethoxy *vs.* 4-nitro-substituted derivative [14]. However, in acetic acid, a strong thermodynamic preference was observed for the palladacycles derived from electron-poor ligands [14].

To the best of our knowledge, all known transpalladation reactions have been carried out in solvents. At least in some cases, a newly formed CPC precipitates from a reaction mixture, so the relative solubility of two CPCs can also be considered a contributing factor determining the equilibrium position of the ligand exchange reaction in solution [16,17]. In the present study, we report the preparation of CPCs using transcyclopalladation on silica gel using solvents for purification only.

2. Results and discussion

For our study, we chose cyclopalladated acetato- and chloro-bridged dimeric complexes **1a,b** as the Pd(II) sources. These derivatives of *N*,*N*-dimethylbenzylamine are common starting CPCs in transpalladations [18,19] and, according to Ceder and co-workers they are among the less thermodynamically stable CPCs [20]. Benzyl methyl sulfide (**2**) was selected as a model preligand to determine whether transpalladation on SiO_2 is plausible and, if so, the best conditions for the transformation. Sulfide **2** is a commercially available air stable compound. It readily undergoes cyclopalladation using $Pd(OAc)_2$ in acetic acid for 30 min at either

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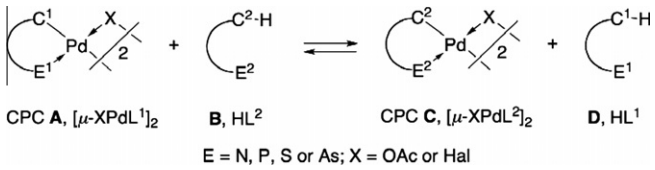


Scheme 1. General scheme for cyclopalladation.

90 or 118 °C followed by treatment with LiCl to afford CPC **3** in 72% or 80% yield, respectively [17,21]. Our recent study showed that this preligand also reacts with $Pd(OAc)_2$ on SiO_2 to give **3b** in good yields [12]. To the best of our knowledge, transcyclopalladation of sulfide **2** has never been reported. It is noteworthy that only three sulfur-containing compounds, $(4\text{-}MeOC_6H_4)_2C{=}S$, $(Me_2N)_2C{=}S$ and $1,3\text{-}(MeSCH_2)_2C_6H_4$, have been successfully transcyclopalladated in solution; the source of Pd(II) in those reactions was CPC **1b** [17].

In our experiments, complex **1a** (or **1b**), sulfide **2**, and silica gel were thoroughly mixed. Then this dry mixture was stirred for 24–96 h either at rt or a higher temperature. In the end of all reactions with the acetato-bridged CPC **1a**, the silica gel mixture was washed with acetone and LiCl was added at rt to convert the acetato-bridged CPC to its μ-Cl-analog **3**. Depending on the conditions used, three products were isolated in different ratios: the desired CPC **3**, compound **4** and the coordination complex $Pd(\mathbf{2})_2Cl_2$ (Scheme 2 and Table 1). The best yield of CPC **3** was 61% (Table 1, entry 8). The structures of all complexes were confirmed by ^1H and $^{13}C\{^1H\}$ NMR data as well as by comparison of their melting points and R_f values with the reference samples obtained by known procedures.

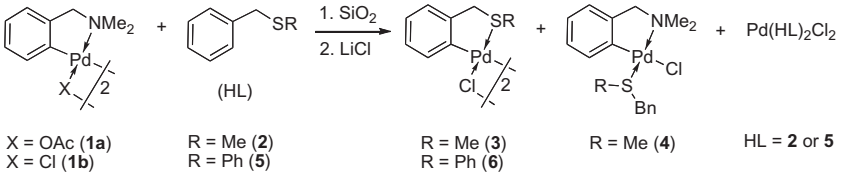
Transcyclopalladation of sulfide **2** required high temperature, 80–100 °C. The reaction occurred slowly: the optimal time appears to be 24 h. Along with the two reagents and SiO_2, CF_3CO_2H was added in some experiments. Ryabov and Yatsimirsky, who first reported transcyclopalladation [13], and other researchers [22] long believed that these reactions require the presence of a carboxylic acid such as acetic or trifluoroacetic acid. Later, Dunina's group showed that transcyclopalladations may occur in aprotic solvents without the addition of acetic or another carboxylic acid [23]. In our experiments, reactions without CF_3CO_2H did not provide even traces of CPC **3**.

To determine whether the size of the silica gel affects the reaction, two adsorbents with larger particle sizes, 100–230 and 35–60 mesh, have been tested in addition to the 230–400 mesh (entries 8–10). Experiments with different samples of silica gel gave similar results, although the reaction carried out on silica gel with the size of 100–230 mesh afforded a slightly higher yield of CPC **3**, 61%.

To show that transcyclopalladation on silica gel without using a solvent is not limited to only one substrate, other preligands have been tested as well. Benzyl phenyl sulfide (**5**) is a similar preligand to sulfide **2** and was, therefore, expected to react in a comparable manner. Akin to compound **2**, only the coordination complex $Pd(HL)Cl_2$ was produced in solution when sulfide **5** was reacted with Na_2PdCl_4 [24]. There has only been one report of the successful cyclopalladation of this preligand to form CPC **6** in 50% yield, in which the authors used $Pd(OAc)_2$ in acetic acid at 90 °C for 1 h [25]. No studies on transcyclopalladation of sulfide **5** have been reported.

We found that benzyl phenyl sulfide **5** undergoes transcyclopalladation on silica gel using CPC **1a** at 80 °C in the presence of equimolar amount of CF_3CO_2H furnishing CPC **6** in 56% (Scheme 2 and entry 1 in Table 2). Increasing the temperature to 100 °C resulted in quick decomposition of the reaction mixture with appearance of Pd black (entry 2).

The next preligand tested was benzyldiphenylphosphine **7**. The results of the selected experiments with this phosphine are presented in Scheme 3 and Table 3. The highest yield of CPC **8** in our experiments was 39%, which is higher than 21% reported by Ryabov for the same reaction performed in a mixture of $CHCl_3$ and CH_3CO_2H at rt for four days [26]. For comparison, Lohner et al. obtained the crude complex **7** in 90% yield in the transcyclopalladation of phosphine **7** with CPC **1b** in toluene in the presence of CF_3CO_2H at reflux for 2 h [27]. It is noteworthy that reactions of phosphine **7** with **1a** or **1b** on SiO_2 without acid or with the weaker acetic acid provided only complex **9**. Reactions at the temperatures below 100 °C did not give CPC **8**, while keeping the reaction mixtures at 100 °C for more than a few hours resulted in decomposition.



Scheme 2. Preparation of *C,S*-palladacycles using transcyclopalladation on silica gel.

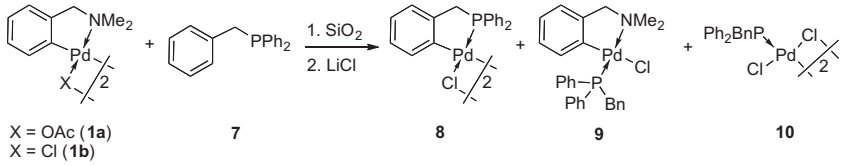
Table 1
Reactions of sulfide **2** with CPCs **1a**,**b**.

Entry	Pd(II) source	Acid	SiO_2 size (mash)	Temp. (°C)	Time (H)	Yield of 3 (%)[b]	Yield of **4** (%)	Yield of $Pd(\mathbf{2})_2Cl_2$ (%)
1	**1b**		230–400	rt	24		99	
2	**1b**		230–400	78	96		72	
3	**1a**		230–400	70	96		79	
4[a]	**1a**	CF_3CO_2H	230–400	50	24	26	15	18
5	**1a**	CF_3CO_2H	230–400	80	24	34	49	1
6	**1a**	CF_3CO_2H	230–400	80	48	46	35	
7	**1a**	CF_3CO_2H	230–400	100	24	54	24	
8	**1a**	CF_3CO_2H	100–230	100	24	61	17	
9	**1a**	CF_3CO_2H	100–230	80	24	46	24	
10	**1a**	CF_3CO_2H	35–60	80	24	51	40	
11	**1a**	CF_3CO_2H	no SiO_2	80	24	50	26	

[a] The amount of silica gel was doubled.
[b] Here and later, yields of all compounds are given after chromatographic purification and, as a rule, are averages of two or more trials.

Table 2
Reactions of sulfide **5** with CPC **1a** on silica gel

Entry	Pd(II) source	Acid	Acid (mesh)	Temp (°C)	Time (h)	Yield of **6** (%)
1	**1a**	CF_3CO_2H	230–400	80	24	56
2	**1a**	CF_3CO_2H	230–400	100	<1	7
3	**1a**	CF_3CO_2H	no SiO_2	80	24	36



Scheme 3. Use of phosphine **7** in transcyclopalladation reactions on silica gel.

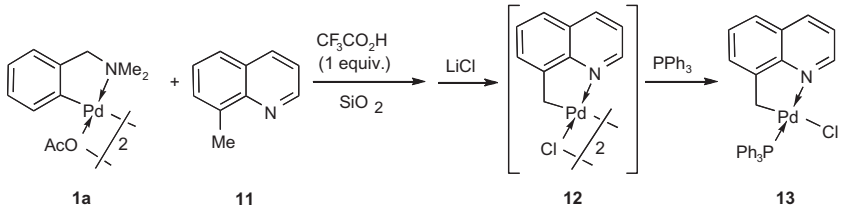
Table 3
Reactions of phosphine **7** with CPCs **1a**,**b**.

Entry	Pd(II) source	Acid	SiO_2 size (mesh)	Temp. (°C)	Time (h)	Yield of **8** (%)	Yield of **9** (%)	Yield of **10** (%)
1	**1b**	CF_3CO_2H	100–230	120	1	39		15
2	**1a**	CF_3CO_2H	120–400	120	1		>90	
3	**1a**	CF_3CO_2H	120–400	120	2	26		traces
4	**1b**	–	100-230	120	1		>90	

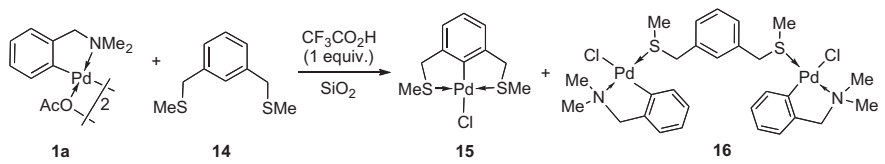
8-Methylquinoline (**11**) was chosen as the next substrate because of the possibility of forming a benzylic (sp^3)C–Pd bond in the product. Hartwell et al. described the direct cyclopalladation of **11** in MeOH/H_2O at rt, but no yield was reported [28]. Starting from CPC **1b** in a CH_3CO_2H–$CHCl_3$ mixture at 50 °C for 24 h, Ryabov et al. obtained CPC **12** in 64% yield [13], which was then increased to 95% using CPC **1a** (60 °C, 12 h in CH_3CO_2H) [29]. In our experiment, 8-methylquinoline **11** reacted with complex **1a** at 100 °C for 48 h followed by treatment with LiCl at rt (Scheme 4). The crude product was quite insoluble in common solvents, so it was mixed with PPh_3 in order to get the more soluble cyclopalladated adduct **13**. After the purification using chromatography, complex **13** was obtained in 46% yield. The melting point of the synthesized compound **13** matched the one reported previously [30]. The ^1H and DEPT NMR spectra of the complex confirmed conversion of the methyl group to the methylene fragment.

We were also interested in whether preligands leading to pincer complexes could be transcyclopalladated on silica gel. 1,3-Bis(methylthiomethyl)benzene (**14**) was selected for the study because this preligand provides only one CPC of the *S*,*C*,*S*-pincer type (**15**) [17] out of the two possible (second probable CPC arises from double palladation of the ligand resulting in the 1,2,4,5-tetrasubstituted aromatic ring). Transcyclopalladation of disulfide **14** in CH_3CO_2H–C_6H_6 at reflux for 2.5 h was reported to give 97% yield of CPC **15**, while the direct cyclopalladation of this preligand afforded less than 10% yield (no conditions were given) [17]. In our experiments, compound **14** underwent transcyclopalladation on SiO_2 using CPC **1a** at 80 °C to give 65% yield of the pincer complex **15** (Scheme 5). The yield of the reaction, which was repeated several times, was very sensitive to stirring; in the majority of the experiments, the coordination complex **16** was isolated as well. The structure of the new compound **16** was supported by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and its composition was confirmed by elemental analysis.

To the best of our knowledge, no examples of preparation of palladacycles with a non-benzylic (sp^3)C–Pd bond using transcyclopalladation in solution have been reported. To test if CPCs with a non-benzylic (sp^3)C–Pd bond can be formed as a result of



Scheme 4. Transcyclopalladation of 8-methylquinoline **11** on silica gel.



Scheme 5. Preparation of *S*,*C*,*S*-pincer CPC **15** using transcyclopalladation on silica gel.

cyclopalladated ligand exchange on SiO_2, 2-*tert*-butyl-4,4-dimethyl-2-oxazoline (**17**) was reacted with CPC **1a**. This oxazoline was chosen because we recently published our data on the successful direct metalation of this preligand with $Pd(OAc)_2$ on silica gel [10] and the sample of the desired CPC was available to us. After stirring a mixture of heterocycle **17**, CPC **1a** and CF_3CO_2H in a 2:1:2 ratio on SiO_2 at 80 °C for 24 h, the ^1H NMR spectrum of the reaction mixture as well as the analytical TLC plate showed no indication of the CPC formation.

Finally, we checked whether transcyclopalladation might occur without either a solvent or silica gel by mixing the appropriate neat reagents. A slurry of liquid sulfide **3** and solid CPC **1a** in a molar ratio of 2:1 was mixed with 2 M equiv. (10 μL) of CF_3CO_2H. The resulting mixture was heated at 80 °C for 24 h. CPC **3** was still formed in this reaction in 51% yield (Table 1, entry 11); however, the formation of Pd black was apparent and the sticky reaction mixture was almost impossible to stir. Interestingly, this obtained yield is only 11% less than the best yield using silica gel. In a similar experiment with sulfide **5**, which has the melting point of 40–45 °C, the corresponding CPC **6** was also formed, but in a lower yield of 36% (Table 2, entry 3). Therefore, in general, transcyclopalladation may occur not only without solvent but also without silica gel, particularly when the ligand to be palladated is a liquid. However, even in these cases, the use of silica gel as a reaction medium results in a better mixing of the reagents, less decomposition and higher yields. It appears that mixing two solid reagents in the presence of silica gel is much more efficient than just mixing them alone. Furthermore, one should not assume that all transcyclopalladation and palladation [9–11] reactions that are possible on SiO_2 will occur without silica gel. Attempts to heat a mixture of complex **1a** with solid $BnPh_2P$ **7** (m.p. 77–83 °C) resulted in the formation of a black sticky material insoluble in any common solvents. For comparison, we previously reported that cyclopalladation of phosphine **7** with Na_2PdCl_4 occurs on silica gel to give the corresponding CPC in 56% yield, while mixing the phosphine with the palladating agent under the same conditions without SiO_2 did not result in the formation of even traces of the desired cyclometallated complex [11].

In summary, we showed that transcyclopalladation may occur without solvent. Silica gel can be successfully used as a "green" medium for this reaction. For all substrates tested, cyclopalladation on SiO_2 required the presence of a strong acid such as CF_3CO_2H. To obtain good yields of the CPCs with aromatic (sp^2)C–Pd or benzylic (sp^3)C–Pd by transcyclopalladation on SiO_2, high temperatures (80–100 °C), long reaction times (ca. 24 h except for phosphine **7**) and efficient stirring were necessary.

3. Experimental

3.1. General methods and materials.

Purifications by preparative thin-layer chromatography (TLC) were carried out on 200 × 250 mm glass plates with an unfixed layer of Natland or Merck silica gel 60 (230–400 mesh) containing 5–10% of the Aldrich-Sigma thin-layer chromatography silica gel with fluorescent indicator. Analytical TLC was performed on Whatman silica gel 60 (F_{254}) 250 mm pre-coated plates. Compounds were visualized on TLC plates using UV light (254 nm) and iodine stain. ^1H (500 MHz) and $^{13}C\{^1H\}$ (126 MHz) as well as DEPT, COSY, and HMQC spectra were recorded on a Bruker AVANCE 500 NMR spectrometer. Chemical shifts, δ, are reported in ppm with $SiMe_4$ as an internal standard. Spin-spin coupling constants, *J*, are given in Hz. Spectra were recorded in $CDCl_3$. Acetone was distilled over $KMnO_4$. CH_2Cl_2 and $CHCl_3$ were distilled over CaH_2. Benzyl methyl sulfide **2** and benzyl phenyl sulfide **5** were purchased from Acros Organics, 8-methylquinoline **11** from Alfa Aesar and benzyldiphenylphosphine **8** from Sigma–Aldrich; all were used without purification. 1,3-Bis(methylthiomethyl)benzene **14** was synthesized according to the procedure published by Fujihara et al. [31]. 2-*tert*-4,4-Dimethyl-2-oxazoline **17** was prepared according to the procedure published by Stepanova et al. [10]. Di(μ-acetato)bis-{2-[(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}dipalladium(II) **1a** was obtained as described earlier [32].

^1H and ^{13}C NMR spectra as well as the melting points of coordination complexes $Pd(\mathbf{2})_2Cl_2$ and $Pd(\mathbf{5})_2Cl_2$ obtained in this study were identical to those reported previously [12,24,33]. NMR spectra and the melting points of coordination complex **10** isolated in this study were identical to those reported by others [34,35] and us [11].

3.2. General procedure

Using a syringe (if the preligand was liquid) or a spatula (if solid), the preligand, e.g., benzyl methyl sulfide **2** (0.0176 g, 0.127 mmol), was placed in a small round-bottomed flask. Then SiO_2 (230–400 mesh, 0.0909 g; 750 mg per mmol of the preligand) and di-(μ-acetato)bis-{2-[(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}dipalladium(II) **1a** (0.0361 g, 0.0602 mmol) were added to the flask and the components were vigorously mixed with a spatula until the mixture attained a homogenous color. A magnetic stir bar was added and the flask was capped with a septum and immersed in a preheated oil bath. A syringe was then used to add trifluoroacetic acid (10 μL, 0.14 mmol) dropwise through the septum directly onto the reaction mixture. A $CaCl_2$-filled syringe was poked through the septum and the reaction mixture (which looked like a dry uniform powder) was set to stir. In the end of the reaction, the product was washed from SiO_2 using acetone (5 × 3 mL) into a round-bottomed flask containing LiCl (0.0103 g, 0.243 mmol). The reaction mixture was then stirred overnight at rt. The solvent was then removed and the obtained solid residue was purified using preparative TLC (SiO_2, 10:1 benzene–acetone or another eluent).

3.2.1. Di-(μ-chloro)bis-[2-(methylthiomethyl)phenyl-*C*,*S*]dipalladium(II) (**3**)

The general procedure was followed for this reaction, with the following reagents and amounts: benzyl methyl sulfide **2** (0.0230 g, 0.166 mmol), SiO_2 (100–230 mesh, 0.1247 g), di-(μ-acetato)bis-{2-[(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}dipalladium(II) **1a** (0.0503 g, 0.0839 mmol), trifluoroacetic acid (15 μL, 0.20 mmol), and LiCl (0.0175 g, 0.410 mmol). The oil bath was preheated to 80 °C and the reaction mixture was allowed to stir for 24 h. When the acid was added, the color of the reaction mixture immediately turned from light to darker yellow. Complex **3** was isolated in 61% yield (0.0144 g) using preparative TLC in CH_2Cl_2. R_f 0.62 (benzene–acetone 10:1); m.p. 140 °C (decomposed). NMR data matched those reported [17] for complex **3** earlier.

3.2.2. Chloro-{2-[(N,N-dimethylamino)methyl]phenyl-C,N}(benzyl methyl sulfide-S)palladium(II) (**4**)

This coordination complex was isolated in every transpalladation reaction involving preligand **2**. Complex **4** was also obtained in quantitative yield using the following procedure described above with the following exceptions. Benzyl methyl sulfide **2** (0.0079 g, 0.057 mmol) and SiO_2 (0.0429 g) were mixed with di-(μ-chloro)bis-{2-[(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}dipalladium(II) (**1b**) (0.0157 g, 0.0284 mmol) instead of CPC **1a** and no trifluoroacetic acid was added. No oil bath was used because the reaction mixture was stirred at room temperature for 24 h. The crude coordination complex was a very light yellow solid (0.0231 g, 97.5% yield). R_f 0.40 (10:1 benzene–acetone); m.p.

146 °C (decomp.). ^{1}H NMR data ($CDCl_3$, δ): 2.48 (s, 3H, SCH_3), 2.88 (s, 6H, NCH_3), 3.96 (s, 2H, SCH_2), 4.32 (s, 2H, NCH_2), 6.94 (t, 1H, H(5) of C_6H_4Pd), 7.00 (t, 2H, H(3,4) of C_6H_4Pd), 7.15 (d, 1H, J = 5, H(6) of C_6H_4Pd), 7.30 (d, 1H, J = 5, p-H of C_6H_5), 7.33 (t, 2H, m-H of C_6H_5), 7.47 (d, 2H, J = 5, o-H of C_6H_5); $^{13}C\{^1H\}$ NMR data ($CDCl_3$, δ): 29.7 (SCH_3), 44.0 (SCH_2), 52.5 (NCH_3), 74.0 (NCH_2), 122.7 (C(4) of C_6H_4Pd), 125.3 (C(3) of C_6H_4Pd), 126.0 (C(5) of C_6H_4Pd), 128.5 (p-C of C_6H_5), 129.1 (m-C of C_6H_5), 130.3 (o-C of C_6H_5), 133.0 (C(6) of C_6H_4Pd), 135.0 (C(1) of C_6H_5), 147.5 (C(2) of C_6H_4Pd), 148.5 (C(1) of C_6H_4Pd).

3.2.3. Di-(μ-chloro)bis-{2-[(phenylthio)methyl]phenyl-C,S}dipalladium(II) (**6**)

The following reagents and their amounts were used for this reaction: benzyl phenyl sulfide **5** (0.0215 g, 0.107 mmol), SiO_2 (0.0767 g), μ-OAc-CPC **1a** (0.0307 g, 0.0512 mmol), trifluoroacetic acid (7 μL, 0.1 mmol), and LiCl (0.0087 g, 0.20 mmol). The oil bath was preheated to 80 °C and the reaction was set to stir for 24 h. Preparative TLC was done in CH_2Cl_2–acetone, 50:1. The yield of **6** was 0.0196 g (56%). R_f 0.80 (50:1 benzene–acetone 50:1); m.p. 125–127 °C (decomp.). Spectroscopic data for this complex matched those reported previously [25].

3.2.4. Di-(μ-chloro)bis-{2-[(diphenylphosphino)methyl]phenyl-C,P}dipalladium(II) (**8**)

The following procedure was used in place of the general procedure for this reaction: SiO_2 (0.0561 g) and di-(μ-acetato) bis-{2-[(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}dipalladium(II) **1a** (0.0222 g, 0.0370 mmol) were mixed first in a small round-bottomed flask. A stir bar was inserted and the flask, septum, and stirring spatula were all transferred to a glove box with an atmosphere of N_2. Benzyldiphenylphosphine **7** (0.020 g, 0.072 mmol) was then added to the flask and thoroughly mixed with the spatula. The reaction was allowed to stir at room temperature in the glove box. The flask was capped with the septum before being removed from the glove box and put in a preheated oil bath (100 °C) for 2 h. No $CaCl_2$-filled syringe was used in this reaction. The reaction mixture was filtered into a flask with LiCl as described in the general procedure and purified using preparative TLC in CH_2Cl_2. The first fraction consisted of the desired CPC **8** (39% yield). R_f 0.69 (CH_2Cl_2); m.p. 197–201 °C (decomposed). NMR data matched those reported [11] for complex **8** earlier.

3.2.5. Chloro-{2-[(N,N-dimethylamino)methyl]phenyl-C,N}(benzyldiphenylphosphine-P)palladium(II) (**9**)

This coordination complex was isolated as an orange solid in some reactions involving $BnPh_2P$. M.p. 181–183 °C. ^{1}H NMR data ($CDCl_3$, δ): 2.88 (s, 6H, NCH_3), 3.95 (s, 2H, NCH_2), 4.02 (d, $^2J_{P,H}$ = 12 - Hz, 2H, PCH_2), 6.35 (t, $^4J_{P,H}$ = $^3J_{H,H}$ = 7 Hz, 1H, H(5) of C_6H_4Pd), 6.40 (t, $^3J_{H,H}$ = 7 Hz, 1H, H(4) of C_6H_4Pd), 6.77 (t, $^3J_{H,H}$ = 7 Hz, 1H, H(4) of C_6H_4Pd), 6.92 (d, $^3J_{H,H}$ = 7 Hz, 1H, H(3) of C_6H_4Pd), 7.08 and 7.14 (two m, 5H, C_6H_5 of Bn), 7.31, 7.42 and 7.58 (three m, 10H, two Ph groups of $BnPh_2P$). *Anal.* Calc. for $C_{28}H_{29}ClNPPd$: C, 60.88; H, 5.29%. Found: C, 60.74; H, 5.20%.

3.2.6. Chloro[(8-quinolinyl)methyl-C,N](triphenylphosphine-P)palladium(II) (**13**)

The following reactants and their amounts were used in this reaction: 8-methylquinoline **11** (0.0215 g, 0.150 mmol), di-(μ-acetato)bis-{2-[(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}dipalladium(II) **1a** (0.0432 g, 0.0721 mmol), trifluoroacetic acid (13 μL, 0.18 mmol), 230–400 mesh SiO_2 (0.1096 g), and LiCl (0.0122 g, 0.288 mmol). The oil bath was preheated to 100 °C and the reaction was allowed to stir for 48 h before the second step with LiCl. The insoluble, yellow solid (crude complex **12**) was washed with hexane, MeOH, and DCM to remove unreacted preligand and CPC **1a**. The yield of the crude product was 0.0119 g. The compound was then reacted with triphenylphosphine (0.0129 g, 0.0492 mmol) to obtain complex **13** in 46% yield (0.0186 g). R_f 0.69 (ethyl acetate–hexane 2:1); m.p. 148–153 °C (decomp.; lit data [30] 148 °C).

3.2.7. Chloro-{2,6-bis(methylthiomethyl)phenyl-S,C,S'}palladium(II) (**15**)

The general procedure was performed with the following compounds and amounts: di-(μ-acetato)bis-{2-[(*N*,*N*-dimethylamino) methyl]phenyl-*C*,*N*}dipalladium(II) **1a** (0.0197 g, 0.0329 mmol), SiO_2 (0.0505 g), 1,3-bis(methylthiomethyl)benzene **14** (0.0129 g, 0.0650 mmol), trifluoroacetic acid (5 μL, 0.07 mmol), and LiCl (0.0059 g, 0.14 mmol). The oil bath was preheated to 80 °C. Preparative TLC (25:1 CH_2Cl_2–acetone) yielded three fractions. The second fraction was the desired CPC **6**, which was isolated in an average of 65% yield as a yellow oil. R_f 0.55 (20:1 CH_2Cl_2–acetone). NMR data matched those reported [17] for complex **15** earlier.

3.2.8. Dichlorobis-{2-[(N,N-dimethylamino)methyl]phenyl-C,N}[1,3-bis(methylthiomethyl)benzene-S,S]dipalladium(II) (**16**)

The highest yield of complex **16** was obtained under the following amounts and conditions: 1,3-Bis(methylthiomethyl)benzene **14** (0.0138 g, 0.0696 mmol), SiO_2 (0.0518 g), μ-OAc-CPC **1a** (0.0205 g, 0.0342 mmol), trifluoroacetic acid (5 μL, 0.07 mmol), and LiCl (0.0063 g, 0.15 mmol). The oil bath was preheated to 80 °C and the reaction was set to stir for 60 h. Preparative TLC was done in 6:1 benzene–acetone. Two compounds were isolated: **16** as a yellow oil (0.0163 g, 65%) and CPC **15** (0.0081 g, 35%). R_f 0.41 (20:1 CH_2Cl_2–acetone); m.p. 79–81 °C (decomp.). ^{1}H NMR data ($CDCl_3$, δ): 2.44 (s, 6H, SCH_3), 2.88 (s, 12H, NCH_3), 3.96 (s, 4H, NCH_2), 4.30 (s, 4H, SCH_2), 6.92 (m, 2H, CH_{arom} of $C_6H_4CH_2NMe_2$), 6.99 (m, 4H, 2 CH_{arom} of $C_6H_4CH_2NMe_2$) 7.09 (d, J = 7.9, 2H, CH_{arom} of $C_6H_4CH_2NMe_2$), 7.32 (t, J = 7.9, 1H, 5-H of $C_6H_4(CH_2SCH_3)_2$), 7.46 (d, J = 7.9, 2H, 4-H and 6-H of $C_6H_4(CH_2SCH_3)_2$), 7.58 (s, 1H, 2-H of $C_6H_4(CH_2SCH_3)_2$); ^{13}C NMR data ($CDCl_3$, δ): 20.5 (SCH_3), 43.3 (SCH_2), 52.2 (NCH_3), 73.7 (NCH_2), 122.3 (HC_{arom} of $C_6H_4CH_2NMe_2$), 124.9 (HC_{arom} of $C_6H_4CH_2NMe_2$), 125.6 (HC_{arom} of $C_6H_4CH_2NMe_2$), 129.1 (HC_{arom} of $C_6H_4(CH_2SCH_3)_2$), 129.8 (HC_{arom} of $C_6H_4(CH_2SCH_3)_2$), 131.0 (HC_{arom} of $C_6H_4(CH_2SCH_3)_2$), 132.6 (HC_{arom} of $C_6H_4CH_2NMe_2$), 135.2 (quat. C_{arom}), 147.0 (quat. C_{arom}), 148.1 (quat. C_{arom}). *Anal.* Calc. for $C_{28}H_{38}Cl_2N_2Pd_2S_2$: C, 44.81; H, 5.10; N, 3.73%. Found: C, 44.53; H, 4.97; N, 3.67%.

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