



Some aspects of palladium and rhodium catalysis for synthesis of silylethers from Si–H bond

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Abstract

A mild air-stable catalyst from palladium complex having nitrogen as donor ligand for Si–O bond formation is described. A series of mono and disubstituted silyethers are prepared in near quantitative yield from the catalytic reactions of Pd(TMEDA)Cl₂ (TMEDA: *N,N,N,N*-tetramethylethylenediamine) with different silanes (such as triphenylsilane, triethylsilane, diphenylsilane and methylphenylsilane) and alcohols. The different isomers of naphthalenediols on reactions with triethylsilane or with triphenylsilane gets converted to give disubstituted product by catalytic amount of Pd(TMEDA)Cl₂. The advantages and disadvantages of this catalyst over RhCl(PPh₃)₃ as catalyst for similar reactions is discussed. The catalytic reaction of RhCl(PPh₃)₃ with diphenylsilane in stepwise manner forms Si–O and Si–S bond through reductive coupling with 1,4-naphthoquinone followed by the reaction with benzenethiol.

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Keywords: Silylethers; Pd-catalysts; *N,N,N,N*-Tetramethylethylenediamine; Wilkinson's catalyst; Silanes

1. Introduction

The use of palladium catalyst in organic synthesis is indispensable [1,2]. The catalytic ability of palladium complexes in silicon–carbon bond formation reaction such as for hydrosilylation has been extensively studied [3,4]. Among the different chemistry involving transformations at the silicon center, the silicon oxygen bond forming reactions is important. The siloxanes are used for making plastic materials as well as for alcohol protection [5–9]. The plastic recycling by transition metal catalyst is also an important process that has concern to the environment [10,11]. The siloxy cope rearrangement of *syn*-aldol products is also powerful synthetic tool [12]. The catalytic behavior of

palladium complexes towards reductive coupling reactions between alcohol and silane [13–16] as well as rearrangement of silylethers [17] are known but the synthetic utilities of them is not explored in details. We report here the versatility of a palladium(II) catalyst for Si–O bond forming reactions under aerobic condition.

The search of air-stable transition metal catalysts are desirable; as the siloxanes are abundant in nature and their formation takes place under aerobic conditions. Although silanes do not have direct relevance to natural processes but their involvement in such processes should not be ignored. The hydrolytic cleavage of silicide that leads to the formation of siloxane under ambient condition, has every possibility to pass through Si–H bond cleavage. For example the hydrolytic reaction of calcium silicide gives oligomeric silanes [18]. On the other hand, “silico–mesoxalic acid” is a class of compound having formula (Si₃O₆H₄)_n formed from

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the reaction of moist air on Si_3Cl_8 has Si–H bond [18]. There is also another aspect that requires clear attention is that the Si–O bond activation by transition metal catalysts to prepare Si–C bond; thus there is a need of selection of palladium catalyst for Si–O bond formation [19–21] that would prevent further cleavage of a Si–O bond.

2. Experimental

The $\text{Pd}(\text{COD})\text{Cl}_2$ were prepared by literature procedure [22]. For $\text{Pd}(\text{TMEDA})\text{Cl}_2$, $\text{Pd}(\text{TEEDA})\text{Cl}_2$,

$\text{Pd}(\text{DED})\text{Cl}_2$ analogous procedure as followed to the $\text{Pd}(\text{COD})\text{Cl}_2$ was followed.

2.1. A typical experimental procedure to prepare silylether by palladium(II) catalyst

To a solution containing silane (1 mmol) and alcohol (5 mmol) in toluene (2 cm^3) the palladium catalysts (0.01 mmol) was suspended. The reaction mixture was allowed to stir for the specified time at the temperature given in Table 1. The black precipitate obtained was discarded after extracting the reaction mixture with hexane (20 cm^3). In most of the reactions, the

Table 1
The Si–O bond formation on silane by $\text{Pd}(\text{TMEDA})\text{Cl}_2^a$

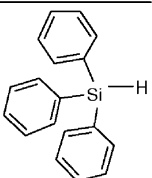
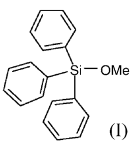
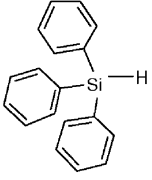
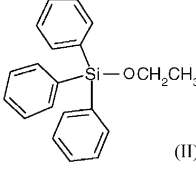
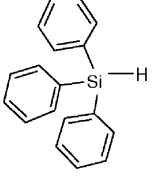
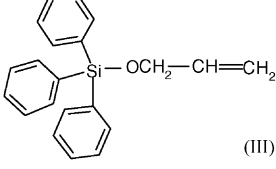
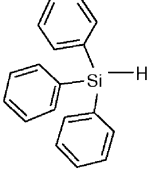
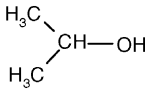
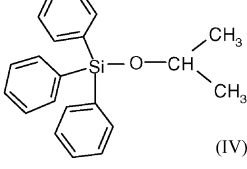
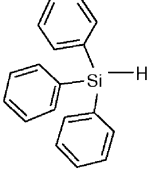
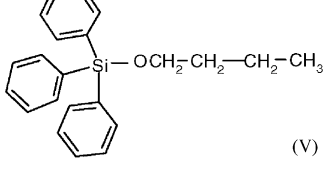
Number	Substrate	Alcohol	Product	Reaction condition (isolated yield (%))
1		CH_3OH		$40^\circ\text{C}/2\text{ h}$ (93)
2		$\text{CH}_3\text{CH}_2\text{OH}$		$40^\circ\text{C}/2\text{ h}$ (90)
3		$\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{OH}$		$40^\circ\text{C}/1.5\text{ h}$ (92)
4				$40^\circ\text{C}/1.5\text{ h}$ (92)
5		$\text{H}_3-\text{H}_2\text{C}-\text{H}_2\text{C}-\text{CH}_2-\text{OH}$		$40^\circ\text{C}/3\text{ h}$ (80)

Table 1 (Continued)

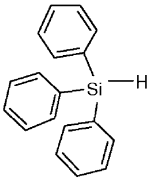
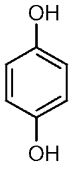
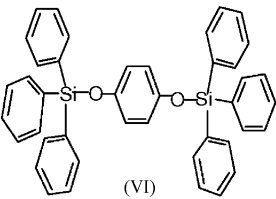
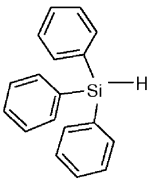
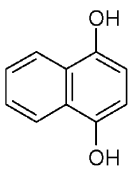
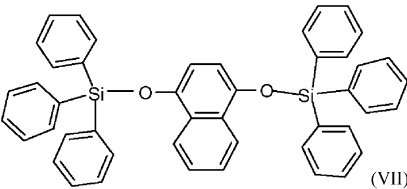
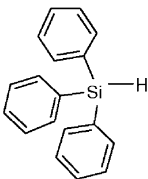
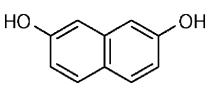
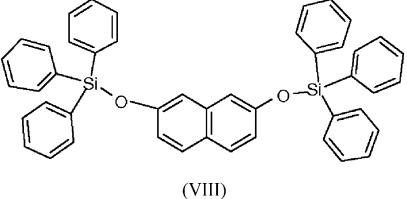
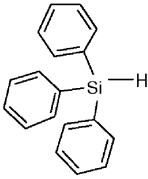
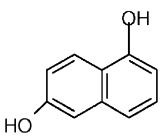
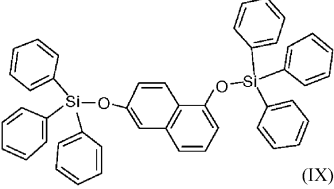
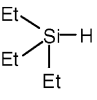
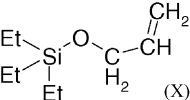
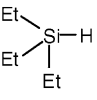
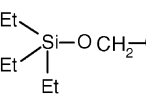

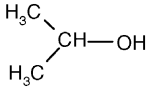
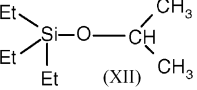
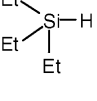
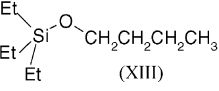
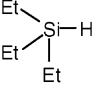
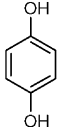
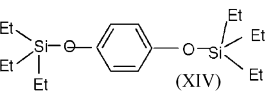
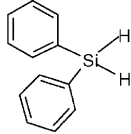
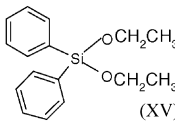
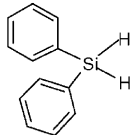
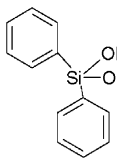
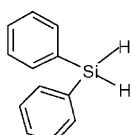
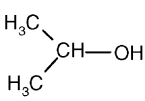
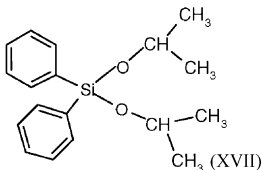
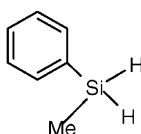
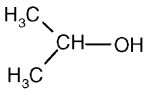
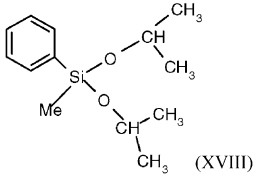
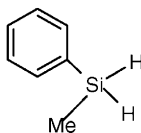

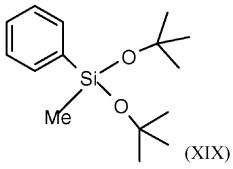
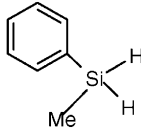
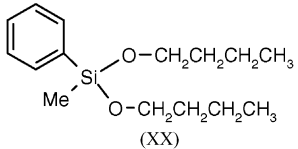
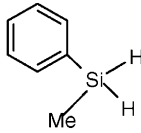
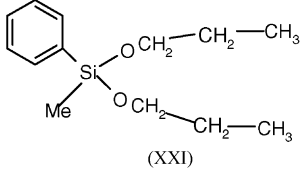
Number	Substrate	Alcohol	Product	Reaction condition (isolated yield (%))
6			 (VI)	45 °C/2h (85)
7			 (VII)	50 °C/5h (50)
8			 (VIII)	50 °C/2h (30)
9			 (IX)	60 °C/2h (67)
10		$\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{OH}$	 (X)	45 °C/1.5h (80)
11		$\text{CH}_3\text{CH}_2\text{OH}$	 (XI)	45 °C/1.5 h (85)
12			 (XII)	45 °C/1.5h (70)
13		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	 (XIII)	45 °C/1.5h (82)
14			 (XIV)	40 °C/1h (56)

Table 1 (Continued)

Number	Substrate	Alcohol	Product	Reaction condition (isolated yield (%))
15		CH ₃ CH ₂ OH	 (XV)	RT/1.5 h (50)
16		CH ₃ OH	 (XVI)	RT/1.5 h (50)
17			 (XVII)	RT/1.5 h (35)
18			 (XVIII)	RT/1.5 h (80)
19			 (XIX)	RT/1.5 h (57)
20		CH ₃ CH ₂ CH ₂ CH ₂ OH	 (XX)	RT/1.5 h (30)
21		CH ₃ CH ₂ CH ₂ OH	 (XXI)	RT/1.5 h (40)

^a 1 mol% catalyst was used in each cases.

reactions were quantitative in product formation; thus the products were obtained by removing the solvent under reduced pressure. Wherever required the products were purified by column chromatography. Wherever possible the purity of the products were checked by gas chromatography by using FID detector with a SE-30 column, otherwise relied on the purity based on the TLC. The products were further characterised by recording their elemental analysis, IR, ^1H and ^{13}C NMR spectra and also mass spectra in specific cases and compared with the literature [9,12].

Since many of the compounds are known and their spectroscopic data are compared with compound prepared by literature procedure [23–26] analytical data for only few illustrative examples are given (for compound number please refer to Table 1).

Compound **I**: ^1H NMR (CDCl_3): 7.4–7.7(m, 15H) 3.7 δ (s, 3H); ^{13}C NMR (CDCl_3): 135.5, 135.0, 130.2, 127.9, 51 δ ; IR(KBr): 3300(bw), 3098(w), 3068(w), 2875(w), 2800(w), 1650(w), 1475(s), 1230(w), 1125(s), 1100(s), 780(w), 760(w), 750(s), 735(s), 705(s), 535(s). Elemental analysis: calcd. for $\text{C}_{19}\text{H}_{18}\text{OSi}$, calcd. C, 78.62, H, 6.2, found C, 78.49, H, 6.02.

Compound **II**: ^1H NMR (CDCl_3): 7.6–7.64(m, 6H) 7.34–7.46(m, 9H); 3.87 (q, $J = 10\text{ Hz}$, 2H); 1.21(t, $J = 10\text{ Hz}$, 3H); ^{13}C NMR (CDCl_3): 135.4, 135.0, 130.1, 127.9, 60, 20; IR(KBr): 3069(bm), 1588(w), 1487(w), 1423(s), 1119(s), 836(s), 708(s), 511(s) cm^{-1} . Elemental analysis: calcd. for $\text{C}_{20}\text{H}_{20}\text{OSi}$, calcd. C, 78.95, H, 6.62, found C, 78.98, H, 6.29.

Compound **IX**: mp = 106 °C; IR(KBr): 3339(b), 3067(w), 3057, 3026(w), 1674(s), 1587(s), 1495(m), 1464(m), 1438(s), 1387(m), 1341(m), 1305(s), 1269(m), 1234(m), 1126(s), 1085(m), 1008(w), 1003(w), 906(s), 860(m), 844(m), 773(m), 747(m), 716(s), 583(w), 517(s); ^1H NMR (CDCl_3): 7.3 δ –7.7 δ (m); Mass (m/e) 676, 521, 443, 259, 199, 181, 105.

Compound **X**: mp = 135 °C; IR(KBr): 3349(bw), 3067(w), 3042(w), 1505(m), 1433(s), 1259(w); ^1H NMR (CDCl_3): 7.3 δ –7.7 δ (m); IR(KBr): 1213(w), 1121(s), 967(w), 921(w), 839(w), 701(s), 506(s); Mass (m/e) 676, 599, 521, 457, 379, 259, 207, 199, 181, 165, 136, 105.

Compound **XI**: mp = 52 °C; ^1H NMR (CDCl_3): 7.8–7.1(m, 34H), 6.5(m, 2H); IR(KBr): 3303(bm), 3067(m), 3047(m), 3021(w), 1628(w), 1592(w), 1587(w), 1428(s), 1362(m), 1264(m), 1228(m), 1116(s), 972(w), 911(m), 839(m), 747(m), 701(s), 511(s); Mass (m/e) 676, 599, 521, 443, 259, 199, 181, 165, 105.

2.2. Reaction of diphenylsilane 1,4-naphthoquinone catalysed by $\text{RhCl}(\text{PPh}_3)_3$

To a solution of $\text{RhCl}(\text{PPh}_3)_3$ (10 mg, 0.01 mmol) in toluene (2 cm^3) 1,4-naphthoquinone was added with stirring. After dissolution of the 1,4-naphthoquinone, diphenylsilane (372 mg, 2.0 mmol) was added at one portion and the reaction mixture was allowed to stir at room temperature for 4 h. A colloidal solution was observed, which turns into a homogeneous solution, this process was accompanied by evolution of hydrogen. After the reaction is complete, to the reaction mixture hexane (30 cm^3) was added and the catalyst was thus precipitated. The filtrate on evaporation under reduced pressure gave the product **XXII** exclusively (590 mg, 99%). ^1H NMR (benzene- d_6): 8.56(dd, $J = 18$, 10 Hz, 2H), 7.75–7.69(m, 8H), 7.25(dd, $J = 18$, 10 Hz, 2H), 7.18–7.00(m, 12H), 6.74(s, 2H), 5.98(s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 146.0., 134.5, 130.5, 133.0, 128.1, 128.0, 124.9, 122.4 111.3; IR (neat) 3050(w), 2150(vs), 1610(w), 1590(m), 1510(s), 1460(w), 1430(w), 1390(w), 1240(bs), 1030(s), 1015(s), 1090(s), 940(bs), 820(s). Elemental analysis: calcd. for $\text{C}_{34}\text{H}_{28}\text{O}_2\text{Si}_2$: C, 77.86, H, 5.34, found C, 77.33, H, 5.45.

2.3. Reaction of **XXII** with thiophenol

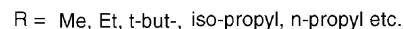
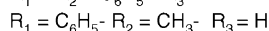
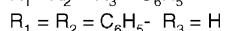
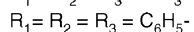
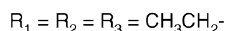
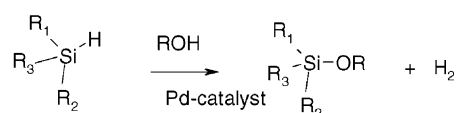
To a solution of **XXII** (330 mg, 1.0 mmol) and thiophenol in toluene (2 cm^3) $\text{RhCl}(\text{PPh}_3)_3$ (10 mg, 0.1 mmol) was added. The reaction mixture was allowed to stir at room temperature under inert atmosphere for 16 h. To the reaction mixture hexane (30 cm^3) was added and the catalyst was removed by filtration. On removal of solvent under reduced pressure gave the corresponding silyl thioether **XXIII** as light yellow oil (98%). ^1H NMR (CDCl_3): 8.05(m, 2H), 7.90(m, 4H), 7.70–7.25(m, 20H), 7.10–6.95(m, 4H), 6.90–6.85(m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3):

145.0, 135.2, 134.8, 132.6, 130.7, 128.3, 128.1, 127.9, 127.0, 126.8, 122.2, 120.4, 112.8; IR (neat) 3050(m), 1620(vw), 1590(s), 1480(m), 1460(s), 1430(s), 1390(s), 1260(s), 1230(s), 1110(s), 1090(s), 1020(m), 900(s), 820(bs), 740(s). Elemental analysis: calcd. for $C_{46}H_{36}O_2Si_2S_2$: C, 74.59, H, 4.86, found C, 74.62, H, 5.56.

3. Results and discussion

A few palladium complexes having bidentate ligands such as *N,N,N,N*-tetramethylethylenediamine

enylsilane, triethylsilane with various alcohols is catalysed by *N,N,N,N*-tetramethylethylenediamine palladium(II) chloride. These siloxyethers can be prepared in quantitative yield by palladium complex catalysed reactions. The reaction is not only applicable to ordinary alcohols but also applicable to diols. In this regard, we had earlier demonstrated the capability of oligomerisation of dihydrosilanes with benzene diols and quinones [13,14]. The naphthalendiols easily get converted to the corresponding silylether on treatment with monohydrosilanes. The reaction of different silanes with varieties of alcohols is



(1)

(TMEDA), *N,N,N,N*-tetraethylethylenediamine (TEEDA), *N,N*-diethylethylenediamine (DED), 1,4-cyclooctadiene (COD) to act as spectator ligand (Fig. 1) were tested for their catalytic ability for Si–H bond activation.

Several reactions of mono-hydrosilanes and dihydrosilanes were carried out are listed in Table 1. The reactions of different silanes such as triphen-

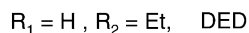
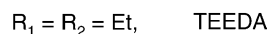
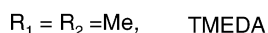
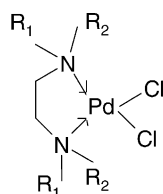
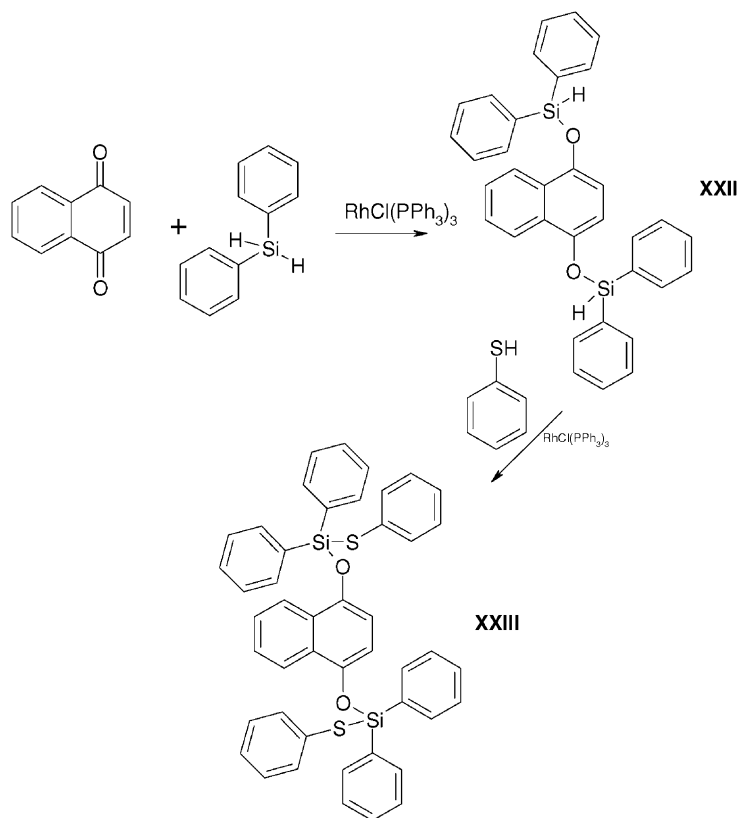


Fig. 1. Silylether formation by different catalysts.

represented by Eq. (1). The relative catalytic efficiency of the reaction between triphenylsilane with ethanol by different palladium(II) complexes were determined from controlled kinetics experiments. The relative transformation of triphenylsilane to corresponding silylether of triphenylsilane is shown in Fig. 2. The decay profile of triphenylsilane studied by gas chromatography in the above reaction was proportional to the formation of silylether; suggests no degradation of the product to form side product also that the no side reaction was occurring. The relative rate of silylether formation by different catalysts shown in Fig. 1 suggests that the Pd(COD)Cl₂ complex be the most efficient catalyst among the catalysts whose reactivity were compared. But it is observed that all the catalyst works at a catalyst: substrate ratio 1:100; but the time taken for the completion of these reactions are different. Since the nitrogen donor complexes of palladium(II) are common and non-toxic in terms of palladium phosphine complexes, we preferred to study its catalysis by palladium complexes bearing nitrogen donors. The synthetic procedure described in this article is based on the use of Pd(TMEDA)Cl₂ as catalyst in Si–O bond formation.

The advantage of this catalyst system is the stability of the complex in ordinary condition. Although the compound has poor solubility in organic solvents, these reactions takes place when the catalyst is suspended in the benzene or toluene solution containing the reactants. The reactions pass through reduction of the palladium(II) catalyst to colloidal palladium(0) state; as metallic particles can be observed at the end of the reaction. Although we have not characterised the particles formed from the reaction whose profile is shown in Fig. 2 but we have confirmed such observation in the residue obtained from the oligomerisation reaction of diphenylsilane with naphthoquinone by catalytic amount of Pd(TMEDA)Cl₂. Fig. 2 also supports involvement of palladium(0) as catalytic species as there is a lapse of time from which there is rapid dehydrogenative coupling reactions. All the reactions described here accompany hydrogen evolution.

Various isomers of naphthalenediols were difunctionalised with triphenylsilane gave the corresponding disilyloxyethers. The dihydrosilanes are also as effective as the monohydrosilanes for Si–O bond formation under catalytic condition. The reaction of diphenylsilane and methylphenylsilane with different alcohols lead to disilyloxyethers in near quantitative yield. However, the reaction of diphenylsilane with alcohol in 1:1 molar ratio has not given the desired monosilylether and it was found that under aerobic condition such reactions leads to siloxyether through reaction with water as the products in such cases are highly hygroscopic. The literature suggests that the monosilylated ether of diphenylsilane can be prepared by using RhCl(PPh₃)₃ as a catalyst [26]. In palladium catalysed reaction, we could not isolate any monosilylated ether from diphenylsilane as well as methylphenylsilane in pure form. However, we have found that the product of monosilylated ether of 1,4-dihydroxynaphthalene with diphenylsilane could be prepared



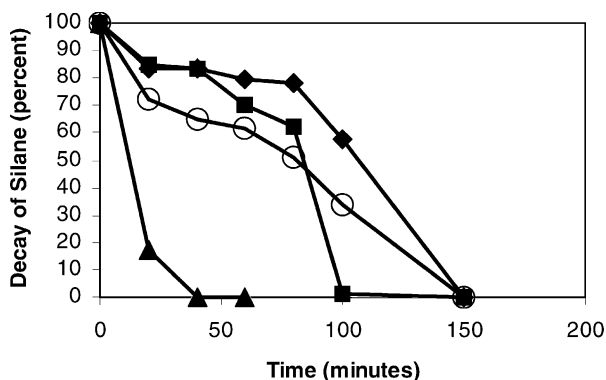


Fig. 2. The change of concentration of triphenylsilane (0.13 mmol) on reaction with ethanol (3 cm³) at 10 °C in the presence of 1 mol% of (A) Pd(TMEDA)Cl₂, (B) Pd(DED)Cl₂, (C) Pd(COD)Cl₂, (D) Pd(TEEDA)Cl₂.

by alternative route using Wilkinson's catalyst (Eq. (2)). However, for this purpose a reductive coupling reaction of 1,4-naphthoquinone with diphenylsilane in the presence of catalytic amount of Rh(PPh₃)₃Cl was used (Eq. (2)). This reaction is also of interest as it can provide a new synthon for further functionalisation and also provide an insight to the feasibility of synthesis of analogous monosilyl ether. In this case exclusive product **XXII** could be formed and isolated in quantitative yield as single product. The advantage of the RhCl(PPh₃)₃ catalysed reaction is that the compound **XXII** could be further functionalised. For example to show the formation of Si–O bond as well as Si–S bond formation; the monosilylether **XXII** was isolated and further reacted with thiophenol obtain corresponding thioether **XXIII** in quantitative yield. In our earlier report, we had demonstrated that the reactivity of two hydrogens in diphenylsilane could be distinguished in the RhCl(PPh₃)₃ catalysed reaction of diphenylsilane with benzenethiol and the Si–H bond could be substituted in sequential manner [27–29]. However, the reaction of 1,4-naphthoquinone with diphenylsilane involves different route as it involves processes such as reductive Si–O bond formation followed by aromatisation [7]. Nevertheless, the RhCl(PPh₃)₃ catalysed reaction gives the complementary monosilylated product that could not be prepared from the reaction of 1,4-naphthalenediol with diphenylsilane in the presence of Pd(II)-catalysts.

In conclusion a simple air-stable palladium catalytic system for functionalisation of silane is de-

scribed, along with the comparison of this catalyst over Wilkinson's catalyst.

4. Synopsis

A mild air-stable catalyst of palladium complex having nitrogen donor ligand for Si–O bond formation is described. A series of mono and disubstituted silyethers are prepared in near quantitative yield from the catalytic reactions of Pd(TMEDA)Cl₂ (TMEDA: *N,N,N,N*-tetramethylethylenediamine) with different silanes (such as triphenylsilane, triethylsilane, diphenylsilane and methylphenylsilane) and alcohols. The different isomers of naphthalenediols on reactions with triethylsilane or with triphenylsilane gets converted to give disubstituted product by catalytic amount of Pd(TMEDA)Cl₂. The advantages and disadvantages of this catalyst over RhCl(PPh₃)₃ as catalyst for similar reactions is discussed. The catalytic reaction of RhCl(PPh₃)₃ with diphenylsilane in stepwise manner forms Si–O and Si–S bond through reductive coupling with 1,4-naphthoquinone followed by the reaction with benzenethiol.

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References

- [1] J. Tsuji (Ed.), *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, New York, 1995.
- [2] T. Hiyama, T. Kusumoto, in: B.M. Trost, I. Fleming (Eds.), *Comprehensive Organic Synthesis*, vol. 8, Pergamon Press, Oxford, 1991, p. 763.
- [3] Y. Ito, M. Sugimoto, M.J. Murakami, *J. Org. Chem.* 56 (1991) 1948.
- [4] C. Shlenk, A. Kleij, W.H. Frey, V.G. Koten, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 3445.
- [5] T.W. Greene, P.G.M. Wurtz, *Protective Groups in Organic Synthesis*, second ed., Wiley, New York, 1991.
- [6] E. Corey, E. Snides, *J. Am. Chem. Soc.* 92 (1974) 2549.
- [7] M.N. Bakola-Christanopoulou, *Appl. Organomet. Chem.* 15 (2001) 889.
- [8] M. Schellhaas, H. Waldmann, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 2056.
- [9] P.J. Kocienski, D. Enders, R. Noyori, B.M. Trost (Eds.), *Protecting Groups*, Thieme, Stuttgart, 1994, p. 28.
- [10] J. Brandrup (Ed.), *Recycling and Recovery of Plastics*, first ed., Hanser/Gardner, Munchen, 1996.
- [11] W. Kaminsky, F. Hartmann, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 331.
- [12] C. Schneider, *Synletters* (2001) 1079.
- [13] A. Purkayshtha, J.B. Baruah, *Appl. Organometal. Chem.* 14 (2000) 477.
- [14] A. Purkayshtha, J.B. Baruah, *Appl. Organometal. Chem.* 15 (2001) 1.
- [15] P.N. Reddy, B.P.S. Chauhan, T. Hayashi, M. Tanaka, *Chem. Lett.* (2000) 250.
- [16] J.A. Davies, F.R. Hartley, S.G. Murray, G. Marshall, *J. Mol. Catal.* 10 (1981) 171.
- [17] K. Tamao, G-R. Sun, A. Kawachi, *J. Am. Chem. Soc.* 117 (1995) 8043.
- [18] A.F. Wells (Ed.), *Structural Inorganic Chemistry*, fourth ed., Oxford University press, Oxford, 1979.
- [19] T. Fujii, T. Koike, A. Mori, K. Osakada, *Synletters* (2002) 298.
- [20] K. Hirabayashi, A. Mori, J. Kawashima, M. Suguro, Y. Nishihara, T. Hiyama, *J. Org. Chem.* 65 (2000) 5342.
- [21] K. Hirabayashi, A. Mori, *J. Synth. Org. Chem. Jpn.* 58 (2000) 926.
- [22] M.F. Rittig, R.M. Wing, G.R. Wiger, *J. Am. Chem. Soc.* 103 (1981) 2981.
- [23] C. Lorentz, U. Schubert, *Chem. Ber.* 128 (1995) 1267.
- [24] T.C. Bedard, J.Y. Corey, *J. Organomet. Chem.* 428 (1992) 315.
- [25] F.L. Bideau, T. Coradin, J. Henique, E. Samuel, *Chem. Commun.* (2001) 1408.
- [26] I. Ojima, T. Kogure, M. Nihonyanagi, H. Kono, S. Inaba, Y. Nagai, *Chem. Lett.* (1973) 501.
- [27] J.B. Baruah, K. Osakada, T. Yamamoto, *J. Mol. Catal.* 101 (1995) 17.
- [28] J.B. Baruah, K. Osakada, T. Yamamoto, *Organometallics* 15 (1996) 456.
- [29] J.B. Baruah, *Polyhedron* 15 (1996) 3709.