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Water-soluble *cis*-[(NHC)PdBr$_2$(TPPTS)] catalysts and their applications in Suzuki–Miyaura coupling of aryl chlorides

Hayati Türkmen*, Levent Pelit, Bekir Çetinkaya

Department of Chemistry, Ege University, 35100 Bornova-Izmir, Turkey

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ABSTRACT

New palladium(II) complexes (**2**), bearing NHC/TPPTS ligands, (NHC = benzimidazol-2-ylidene; TPPTS = triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt) have been prepared and characterized by elemental analyses and spectroscopic methods. Their ability to catalyze the Suzuki–Miyaura reaction in neat water has been studied at 100 °C. Very high activities have been observed in the coupling of phenylboronic acid with aryl chlorides in the presence of 1% of the catalyst. We have compared the electronic properties of *cis*-[PdBr$_2$(NHC)(TPPTS)] with the related complexes, [PdX$_2$(NHC)]$_2$ and [*trans*-PdBr$_2$(NHC)(pdca)] (pdca = pyridine-2,6-dicarboxyic acid) (**3**) via three different techniques: cyclic voltammetry, thermogravimetric analysis and ^{13}C NMR spectroscopy.

1. Introduction

Since 1979 the Suzuki–Miyaura coupling reaction has been employed for the synthesis of functionalised biaryls which constitute important building blocks for various chemicals such as pharmaceuticals, herbicides and intermediates for material chemistry [1]. A variety of Pd(0) and Pd(II) catalysts promote these couplings, and these catalysts are usually complexes which contain phosphorus ligands [2]. Recently much attention has been paid to develop milder and operationally more simple procedures for these coupling reactions. Some important developments include the use of palladacycles [3,4], pincer palladium catalysts [5], electron-rich phosphines [6,7] and β-oximinato(phosphanyl)palladium complexes and their immobilized versions [8]. More recently, NHC ligands have been able to challenge the widely used tertiary phosphines as popular ligands for this process [9–11]. Mixed-ligand complexes of the type [PdX$_2$(NHC)L] (L = phosphine, pyridine, 3-chloropyridine, pyridine-2,6-dicarboxylic acid), in comparison to those of their bis(NHC) analogues, have been reported to give superior activity [12–14]. The NHC ligands offer several advantages. For example, NHC ligands are more electron-donating and generally form stronger bonds to the metal than phosphine ligands, resulting in a reduced tendency to dissociate. Thus, replacement of phosphines by NHC ligands can provide some significant improvements over conventional phosphine bearing analogues. Herrmann and others [15–22] have developed a series of mixed Pd(II) complexes bearing NHC/PR$_3$ ligands for C–C bond formation. The high efficiency of these complexes in comparison to [PdX$_2$(NHC)$_2$] or [PdX$_2$(PR$_3$)$_2$] has been attributed to ready dissociation of PR$_3$ from the Pd atom to allow formation of a coordinatively unsaturated metal centre and the strong electron-donating ability of the NHC ligand.

On the other hand, there has been a long-standing interest in aqueous-phase, palladium-catalyzed cross-coupling reactions [23–36]. Water is an attractive replacement for traditional organic solvents because it is inexpensive, nontoxic, and nonflammable. In addition, the use of water-soluble catalysts in aqueous/biphasic mixtures combines the advantages of homogeneous and heterogeneous catalysis, *i.e.*, separation of the organic products from the catalysts, high activity and selectivity under mild conditions. This goal has led to the development of new hydrophilic ligands and derived complexes. Water-solubility is generally achievable by introduction of functionalities such as $-SO_3^-$, COO^-, NR_4^+ into the ligands and their incorporation into the organometallic catalysts. In this context, a few sulfonated imidazol(in)ium salts have been synthesized and applied successfully in the aqueous phase Suzuki–Miyaura coupling reactions of aryl halides [37–39]. Naturally, one could anticipate that this concept would also operate with hydrophilic phosphines such as TPPTS, because PPh$_3$ and TPPTS have the same structural motif.

In view of the high reactivity of the mixed (NHC)/PR$_3$ palladium(II) complexes we envisioned that a benzimidazole based NHC and TPPTS combination would be effective in the coupling reactions of aryl chlorides under mild conditions in water. TPPTS has

* Corresponding author.
E-mail address: hayatiturkmen@hotmail.com (H. Türkmen).

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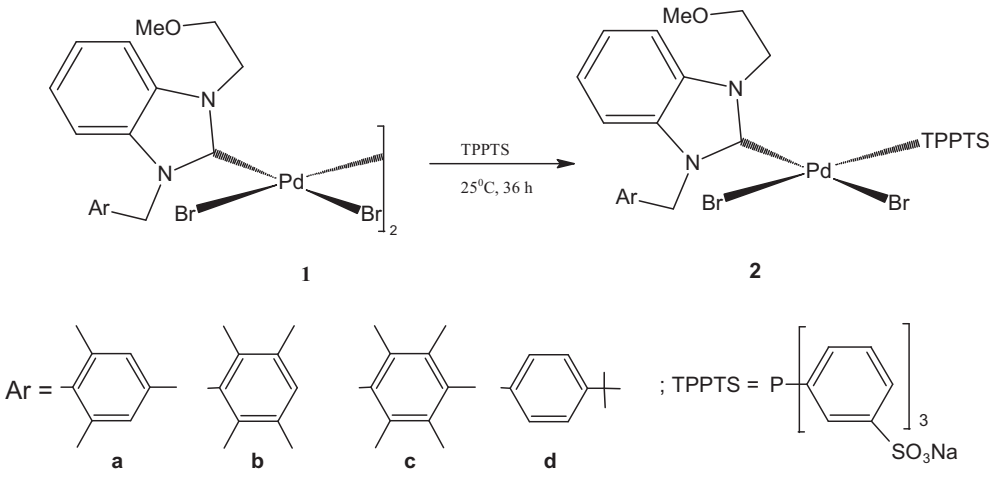


Scheme 1. Reagents and conditions: $P(PhSO_3Na)_3$, DMSO, RT, 36 h.

been selected as the ligand to enforce solubility of the catalyst in water because it is commercially available and is one of the most common hydrophilic phosphines employed in the development of active water-soluble metal catalysts. Although, the cone angle value of TPPTS (145°) was found to be the same as PPh_3, the electron-donating ability of TPPTS is slightly less than PPh_3 as determined by the CO frequency of *trans*-[RhCl(CO)L_2] [40].

2. Results and discussion

Synthesis and characterization of complexes. Dimeric Pd(II) complexes, bearing one NHC per metal centre and two bridging bromides, readily available from $Pd(OAc)_2$ and NHC precursors, can react with nucleophiles such as PPh_3 [19]. Similarly, cleavage of the dimer **1** with 2 equiv. of commercially available TPPTS in DMSO at RT after 36 h stirring afforded *cis*-[$PdBr_2$(NHC)(TPPTS)], **2(a–d)** (Scheme 1). All compounds are soluble in water and DMSO and they are stable in the solid state and in solution. Their identity was established by analytical and NMR data, and, in addition, thermal gravimetric analysis (TGA) and cyclic voltammetry (CV) were applied to the complexes **1c**, **2c**, **3c**.

^{13}C $\{^1H\}$ NMR signals of the Pd–C_{carb} of **2** (*ä* 173.9–174.3) were observed to shift slightly to lower field as compared to their signals in the PPh_3 complexes. This might be due to the more electron-poor Pd(II) centre because of the TPPTS ligand's electron density. The presence of TPPTS is clearly demonstrated by ^{31}P NMR spectroscopy, where one signal corresponding to the *cis* configuration was observed at *ä* ≈ 27 ppm, the signal of free TPPTS (*ä* −4.8 ppm) shifted downfield ∼35 ppm [41]. As both *cis* and *trans* isomers of palladium complexes of types [PdX_2(NHC)L] [15–22] and [PdX_2(NHC)$_2$] [42,43] are known, we wondered if initially a *trans* isomer formed. Thus, in a separate experiment, we terminated the cleavage reaction of **1c** with TPPTS after 30 min and the obtained product was monitored by ^{31}P NMR spectroscopy. Fig. 1 depicts the time-dependent ^{31}P NMR spectra in the range of 0–100 ppm recorded in d_6-DMSO at room temperature. Indeed, the predominant species after 0.5 h is *trans*-**2c** (19.91 ppm), which slowly isomerizes to *cis*-**2c** (26.99 ppm) with a 30% conversion after 16 h. However, after standing 36 h the *trans*-**2c** has transformed into *cis*-**2c** exclusively. The isomerization reaction is much faster when monitored at 80 °C. The assignments of the resonances in the ^{31}P NMR spectra could be achieved by comparison with the related data of PPh_3 and the general observation that for a particular phosphine ligand, the *P* value of the *trans*-isomer is up field from that of the *cis*-isomer [44]. The *trans*-complex is kinetically controlled, whereas the *cis*-isomer is thermodynamically the more favored [45].

2.1. Thermogravimetric analyses (TGA)

The thermal behavior of the complexes (**1c**–**4c**) was investigated using thermogravimetric analysis (TGA) Fig. 2. The dimeric complex (**1c**) decomposes in one step which was observed to be in a temperature range between 350 °C and 400 °C with a total mass loss of 36%. Similar to **1c**, **3c** decomposes in a one step process, but at a lower temperature. For comparison, we have included *cis*-dibromo[*N*-(pentamethylbenzyl)-*N*-(2-methoxyethyl)benzimidazol-2-ylidene] (triphenylphosphine)palladium(II), **4c** [19]. The higher thermal stability of **2c** may be attributed to the ionic nature of TPPTS ligand.

2.2. Cyclic voltammetry of compounds (*1c*, *2c*, *3c*)

Cyclic voltammograms for processes involving complexes under study are presented in Fig. 3. All complexes exhibit similar voltammetric features. Complex **1c** was reduced in the two waves at about

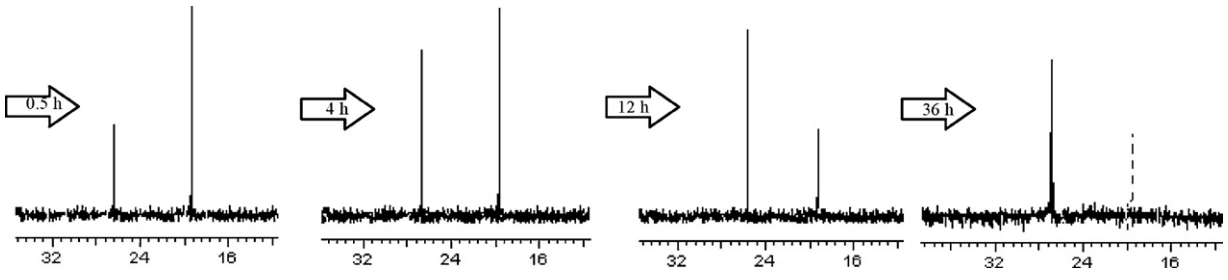


Fig. 1. Time-dependent ^{31}P NMR spectra showing the *trans–cis* isomerization of a mixed NHC-phosphine complex, **2c**.

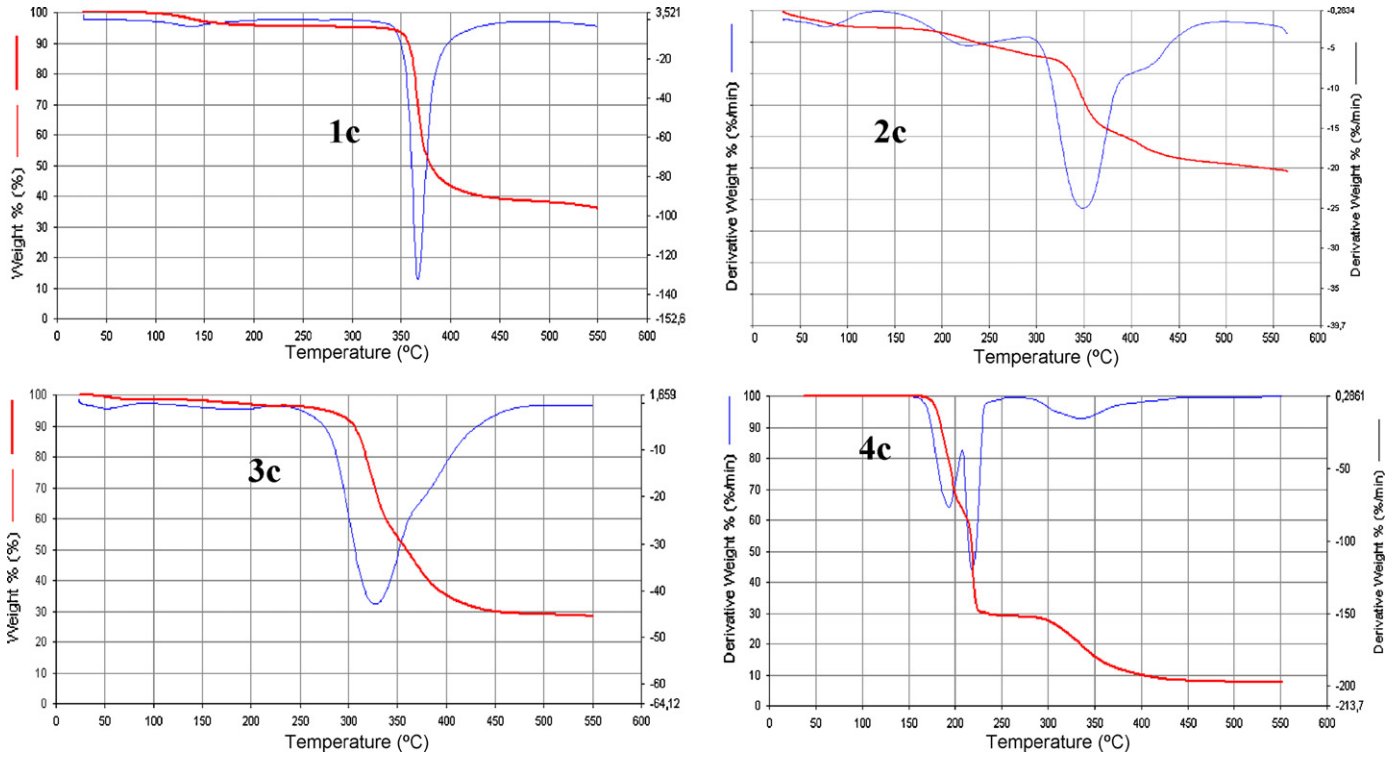


Fig. 2. The TGA and DTG curves of complexes (**1c**–**4c**).

+350 mV and −165 mV respectively. In the reverse scan, two anodic much lower current intensity waves were observed at +85 mV and +560 mV respectively. This is indicative of irreversible processes, which may be related to slow electron transfer to Pd(II) (electrochemical irreversibility) or to instability of the reduced species of Pd(II) (chemical irreversibility) or to both of them. Considering the well known redox properties of palladium, the observed cathodic peaks can be attributed to the reduction of Pd(II) to Pd(0).

Two reversible reduction peaks were also observed for **3c** at 0 mV, followed by a second one of much higher current intensity at −420 mV. Upon scan inversion, two oxidation waves were detected at −2 mV and −335 mV respectively. Similarly two reversible reduction waves were observed at about −350 mV and −525 mV for **2c**. Two oxidation waves were detected on the reverse scan at −325 mV and −560 mV respectively.

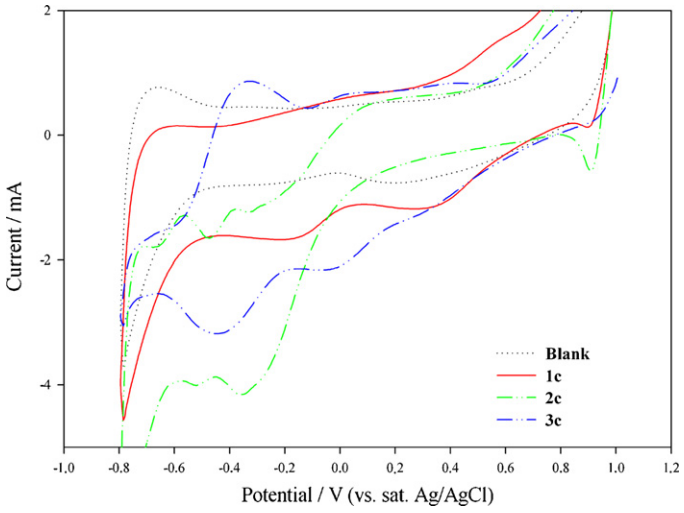


Fig. 3. Cyclic voltammogram of 1 mM complex (**1c**–**3c**) in a solution of water–acetonitrile mixture (1:1, v/v) at room temperature vs. Ag/AgCl reference electrode (scan rate: 100 mV/s).

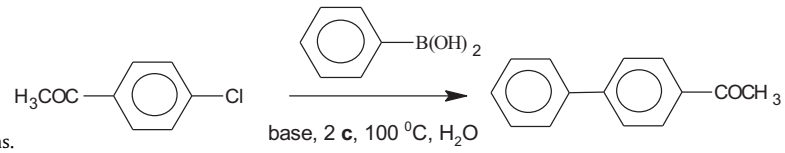
These oxidation waves characterized the complex generated by the reduction of the initial complexes. An interesting aspect about the voltammetric behavior of the complexes (**2c**, **3c**) is the presence of two peaks, though of dissimilar height. This indicates the presence of different species in solution, most likely due to the substitution of the Cl^- anions bound to the metal with coordinating solvent molecules.

The ease of reduction of palladium(II) complexes investigated here has been in the order **1c** > **3c** > **2c**. The reduction wave of **1c** was shifted to a more negative potential by substitution with TPPTS and pdca by about 700 mV and 350 mV respectively. From the reduction potentials of the palladium(II) complexes, one observes that, for a given ligand, the introduction of TPPTS onto the Pd(II) complexes resulted in more negative potentials [46,47]. The reduction potential of the complex is related to the charge density on metal. Thus, stronger electron-donor ligands will form Pd(II) complexes with a smaller positive charge density on the metal. As a result the reduction potential will shift to more negative values. The reduction potential of the complexes show that the TPPTS is a greater electron donor than other ligands and consequently the Pd(II) ligated by TPPTS ligands is less easily reduced than complexes ligated by bromide and pdca. As a result the TPPTS ligand increased the catalytic activity of Pd(II) complexes. These results were also in good agreement with catalytic tests.

2.3. Suzuki–Miyaura coupling

The water-soluble complexes (**2**) were assessed for their activity in the Suzuki–Miyaura coupling by studying the reaction of phenylboronic acid with activated and non activated aryl chlorides in neat water. We adopted reaction conditions that have been used previously and *trans*-[$PdBr_2$(NHC)(pdc)] (pdca = pyridine-2,6-dicarboxylic acid) complexes were also included into these studies for the sake of comparison [13]. A mixture of phenylboronic acid

Table 1



Screening of bases and reaction conditions.

Entry	**2c** [Pd]%	Bases	Time	Yield (%)
1	1	KOH	4	99
2	0.1	KOH	4	78
3	0.01	KOH	4	40
4	0.001	KOH	4	10
5	1	NaOH	4	79
6	1	K_2CO_3	4	67
7	1	K_3PO_4	4	54
8	1	Et_3N	4	58
9	1	KOH	2	67
10	1	KOH	0.5	34
11	1	KOH	4	54[a]

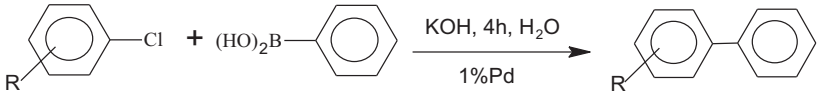
[a] Reaction temperature was set to 80 °C.

(1.2 equiv), aryl chloride (1.0 equiv) KOH (2.0 equiv), and 1 mol% catalyst was heated at 100 °C for 4 h. The coupling products, insoluble in water, were simply filtered off and washed with water. We have not experienced purification problems caused by the dechlorinated side-products or the excess of phenylboronic acid.

We surveyed the effect of bases, the catalyst loading and reaction times on the cross-coupling reaction between 4-chloroacetophenone and phenylboronic acid using complex **2c** as a palladium source. As shown in Table 1, among organic and inorganic bases examined, it has been found that KOH is the most efficient (entry 1), other bases, such as NaOH, K_2CO_3, K_3PO_4 and Et_3N were slightly less efficient (entries 5–8), but 4-acetyldiphenyl was still formed in moderate GC yields. When the palladium loading decreased from 1% to 0.1%, a slightly lower GC yield was obtained (entry 2).

Compared to the *trans*-[$PdBr_2$(NHC)(pda)] catalyst reported previously, the activity of the *cis*-[$PdBr_2$(NHC)(TPPTS)] complex in Suzuki coupling reactions is significantly improved. The reaction of *p*-chloroacetophenone and phenylboronic acid (Table 2, entry 3) gave good yields. Although optimization studies have been not

Table 2
The Suzuki coupling reaction of aryl chlorides with phenylboronic acid.

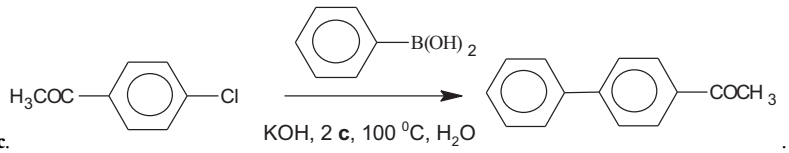


Entry	Complex	Aryl chloride	Conversion (%)	Yield (%)[a]
1	**2a**	4-Chloroacetophenone	100	94(93)
2	**2b**	"	100	94(91)
3	**2c**	"	100	99(93)
4	**2d**	"	99	93
5	**2a**	4-Chlorotoluene	99	85(89)
6	**2b**	"	98	83(85)
7	**2c**	"	95	90(89)
8	**2d**	"	96	80
9	**2a**	4-Chloroanisole	87	82(87)
10	**2b**	"	81	78(85)
11	**2c**	"	87	88(88)
12	**2d**	"	82	80
13	**2a**	4-Chlorobenzaldehyde	91	79(91)
14	**2b**	"	94	80(88)
15	**2c**	"	99	89(92)
16	**2d**	"	85	78
17	**2a**	2-Chloroanisole	90	70
18	**2b**	"	83	73
19	**2c**	"	89	81
20	**2d**	"	86	72
21	**2a**	1-Chloro-4-nitrobenzene	93	89
22	**2b**	"	90	85
23	**2c**	"	95	93
24	**2d**	"	88	82
25	**2a**	4-Chlorobenzonitrile	89	83
26	**2b**	"	90	85
27	**2c**	"	92	88
28	**2d**	"	88	85
29	**2a**	2-Chloro-p-xylene	58	42
30	**2b**	"	55	40
31	**2c**	"	60	45
32	**2d**	"	56	39

[a] The yields shown in parentheses were taken from Ref. [13].

Table 3

Recyclic of catalyst **2c**.



Entry	Yield (%)	Trial	Yield (%)[a]
1	99(99)	4	83(48)
2	94(67)	5	72(41)
3	88(63)	6	54(30)

[a] The yields shown in parentheses were taken from Ref. [13].

carried out, these compare with the use of activated aryl chlorides under identical conditions (entries 5–20), to give moderate to excellent yields of unsymmetrical biaryls. The similar reactivity trends with our previous report is in agreement with the stronger donating ability of alkyl substituents, making the donor atoms more electron-rich.

2.4. Catalyst recycling

We examined the possibility of reusing the catalyst **2c** for the Suzuki–Miyaura reaction of 4-chloroacetophenone and phenylboronic acid and the reactions were conducted under the same conditions. After the first reaction, the solid product was separated by filtration (99% yield). To the filtrate containing **2c** fresh substrates, KOH and sufficient distilled water were added to bring the volume to 5.0 mL. The yields for the 2nd, 3rd and 4th cycles were 94%, 88% and 83% respectively (Table 3). The catalyst **2c** appears to be reusable for 6 cycles for the reaction of 4-chloroacetophenone; however, on the sixth cycle the yield dropped to 54%.

3. Conclusion

The coordination of sulfonated phosphine (*m*-TPPTS) to the $PdBr_2$(NHC) fragment affords stable and water-soluble complexes which are initially *trans*-isomers. However, they convert into thermodynamically more stable *cis*-isomers in polar solutions. The *cis*-isomer is active towards the Suzuki–Miyaura coupling of phenylboronic acid and chloroarenes in water at 100 °C. Advantages of the reaction protocol are: (i) ease of catalyst-product separation; (ii) ability for recycling for at least four runs. Thus, this process is ecologically and economically acceptable. Further catalytic applications of novel NHC ligands with TPPTS in water are currently being investigated.

4. Experimental

4.1. General procedures

The complexes **1**, **3c** and **4c** were prepared according to the literature methods [13,19]. NMR spectra were recorded at 297 K on a Varian Mercury AS 400 at 400 MHz (^{1}H), 100.56 MHz (^{13}C), 161.87 MHz (^{31}P). Elemental analyses were carried out by the analytical service of TUBITAK with a Carlo Erba Strumentazione Model 1106 apparatus. The yields of C–C coupling products were determined using GC and NMR. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained using a Perkin–Elmer Pyris 6 analyzer in the range 50–600 °C in alumina crucibles under nitrogen (flux rate: 20 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1} using alumina as reference.

4.2. General procedure for the preparation **2**; cleavage of the dimer **1** with TPPTS

A sample of **1** (0.5 mmol) and triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt, TPPTS (1.0 mmol) were dissolved in 10 mL of dimethyl sulfoxide. The mixture was stirred at ambient temperature for 36 h. The volume of the solution was reduced to *ca* 5 mL in vacuo. Diethyl ether (10 mL) was added to the solution to obtain a bright cream precipitate which was collected by filtration, washed with 10 mL of diethyl ether, and dried in vacuo.

2a: Yield: 0.52 g, 93.0%. ^{1}H NMR (400 MHz, DMSO): *ä* TPPTS-*H*: 7.93 (d, 1H, *J* = 1.9 Hz); 7.83 (d, 1H, *J* = 1.9 Hz); 7.71 (d, 1H, *J* = 1.2 Hz,); 7.61 (b, 2H), 7.50 (b, 2H), 7.37 (m, 3H); 7.26 (b, 2H, *J* = 1.2 Hz), 7.14 (t, 1H, *J* = 1.8 Hz, Ar–H), 7.06 (t, 1H, *J* = 1.9 Hz, Ar–H), 6.91 (s, 2H, $CH_2C_6H_2(CH_3)_3$), 6.91 (d, 1H, *J* = 2.0 Hz, Ar–H), 6.23 (d, 1H, *J* = 2.0 Hz, Ar–H), 5.72 (d, 1H, *J* = 2.2 Hz, $CH_2C_6H_2(CH_3)_3$), 5. 26 (d, 1H, *J* = 2.1 Hz, $CH_2C_6H_2(CH_3)_3$), 5.15 (d, 1H, *J* = 2.2 Hz, $CH_2C_6H_2(CH_3)_3$), 4.57, 4.99 (d, 1H, *J* = 2.2 Hz, $CH_2C_6H_2(CH_3)_3$), 4.64 (m, 2H, $NCH_2CH_2OCH_3$), 3.96, 3.87 (b, 2H, $NCH_2CH_2OCH_3$), 2.54 (s, 3H, $NCH_2CH_2OCH_3$), 2.50 (s, 3H, $CH_2C_6H_2(CH_3)_3$), 2.26 (s, 6H, $CH_2C_6H_2(CH_3)_3$). ^{13}C NMR (100 MHz, DMSO): *ä* 173.9 (C–Pd), 147.1, 135.3, 135.0, 134.6, 134.4, 133.8, 132.7, 129.7, 129.4, 128.8, 128.7, 128.6, 123.4, 122.8, 112.3, 110.9 (Ar–C, TPPTS-C, $C_6H_2(CH_3)_3$), 70.6 ($NCH_2CH_2OCH_3$), 58.9 ($NCH_2CH_2OCH_3$), 51.3 ($CH_2C_6H_2(CH_3)_3$), 48.8 ($NCH_2CH_2OCH_3$), 20.7, 16.7 ($CH_2C_6H_2(CH_3)_3$). ^{31}P NMR (162.0 Hz, DMSO): *ä* 27.1. Anal. Calc. for $C_{38}H_{36}Br_2N_2Na_3O_{10}PPdS_3$ (M = 1143.07) C 39.93, H 3.17, N 2.45. Found C 40.01, H 3.13, N 2.39%.

2b: Yield: 0.46 g, 81.0%. ^{1}H NMR (400 MHz, DMSO): *ä* TPPTS-*H*: 7.92 (d, 1H, *J* = 2.0 Hz), 7.80 (d, 1H, *J* = 1.9 Hz); 7.66 (d, 1H, *J* = 1.9 Hz); 7.19–6.93 (b, 12H, Ar–H, $CH_2C_6H(CH_3)_4$), 6.65 (b, 1H, Ar–H), 6.31 (b, 1H, Ar–H), 5.54 (b, ^{1}H, $CH_2C_6H(CH_3)_4$), 5.11 (b, 1H, $CH_2C_6H(CH_3)_4$), 4.63 (b, 1H, $NCH_2CH_2OCH_3$), 4.34 (b, 1H, $NCH_2CH_2OCH_3$), 3.84 (b, 2H, $NCH_2CH_2OCH_3$), 2.50 (s, 3H, $NCH_2CH_2OCH_3$), 2.43 (s, 6H, $CH_2C_6H(CH_3)_4$), 2.30 (s, 6H, $CH_2C_6H(CH_3)_4$). ^{13}C NMR (100 MHz, DMSO): *ä* 174.3 (C–Pd), 149.1, 149.0, 148.9, 136.7, 135.4, 134.7, 133.4, 133.2, 132.9, 132.4, 132.3, 132.2, 129.9, 129.6, 129.5, 129.2, 129.1, 127.2, 123.6, 123.1, 112.8, 110.7 (Ar–C, TPPTS-C, $C_6H(CH_3)_4$), 70.6 ($NCH_2CH_2OCH_3$), 58.8 ($NCH_2CH_2OCH_3$), 51.7 ($CH_2C_6H(CH_3)_4$), 48.6 ($NCH_2CH_2OCH_3$), 17.8, 17.3 ($CH_2C_6H(CH_3)_4$). ^{31}P NMR (162.0 Hz, DMSO): *ä* 26.9. Anal. Calc. for $C_{39}H_{38}Br_2N_2Na_3O_{10}PPdS_3$ (M = 1157.09) C 40.48, H 3.31, N 2.42. Found C 40.41, H 3.27, N 2.49%.

2c: Yield: 0.49 g, 84.0%. ^{1}H NMR (400 MHz, DMSO): *ä* TPPTS-*H*: 7.96–7.84 (m, 2H), 7.71–7.56 (m, 10H), 7.34 (d, 1H, *J* = 1.9 Hz, Ar–H), 7.06 (t, 1H, *J* = 1.9 Hz, Ar–H), 6.78 (t, 1H, *J* = 2 Hz, Ar–H), 6.18 (d, 1H, *J* = 1.9 Hz, Ar–H), 5.62 (d, 1H, *J* = 2.1 Hz, $CH_2C_6(CH_3)_5$), 5.19 (d, 1H, *J* = 2.2 Hz, $CH_2C_6(CH_3)_5$), 4.57 (m, 2H, $NCH_2CH_2OCH_3$), 3.85, 3.80 (b, 2H, $NCH_2CH_2OCH_3$), 2.49 (s, 3H, $NCH_2CH_2OCH_3$), 2.40 (s, 6H, $CH_2C_6(CH_3)_5$), 2.32 (s, 6H, $CH_2C_6(CH_3)_5$), 2.24 (s, 3H, $CH_2C_6(CH_3)_5$). ^{13}C NMR (100 MHz, DMSO): *ä* 174.3 (C–Pd), 149.1, 149.0, 148.9, 136.6, 135.4, 134.7, 133.4, 133.2, 132.9, 132.4, 132.1, 132.0, 129.9, 129.6, 129.4, 129.2, 129.1, 127.2, 123.6, 123.0, 112.8, 110.8 (Ar–C, TPPTS-C, $C_6(CH_3)_5$), 70.5 ($NCH_2CH_2OCH_3$), 58.8

($NCH_2CH_2OCH_3$), 51.7 ($CH_2C_6(CH_3)_5$), 48.6 ($NCH_2CH_2OCH_3$), 17.8, 17.3, 16.7 ($CH_2C_6(CH_3)_5$). ^{31}P NMR (162.0 Hz, DMSO): *ä* 26.9. Anal. Calc. for $C_{40}H_{40}Br_2N_2Na_3O_{10}PPdS_3$ (M = 1171.12) C 41.02, H 3.44, N 2.39. Found C 41.12, H 3.50, N 2.33%.

2d: Yield: 0.49 g, 84.0%. ^{1}H NMR (400 MHz, DMSO): *ä* TPPTS-*H*: 7.96–7.84 (m, 2H), 7.71–7.56 (m, 10H), 7.34 (d, 1H, *J* = 1.9 Hz, Ar–H), 7.06 (t, 1H, *J* = 1.9 Hz, Ar–H), 6.78 (t, 1H, *J* = 2 Hz, Ar–H), 6.18 (d, 1H, *J* = 1.9 Hz, Ar–H), 5.62 (d, 1H, *J* = 2.1 Hz, $CH_2C_6(CH_3)_5$), 5.19 (d, 1H, *J* = 2.2 Hz, $CH_2C_6(CH_3)_5$), 4.57 (m, 2H, $NCH_2CH_2OCH_3$), 3.85, 3.80 (b, 2H, $NCH_2CH_2OCH_3$), 2.49 (s, 3H, $NCH_2CH_2OCH_3$), 2.40 (s, 6H, $CH_2C_6(CH_3)_5$), 2.32 (s, 6H, $CH_2C_6(CH_3)_5$), 2.24 (s, 3H, $CH_2C_6(CH_3)_5$). ^{13}C NMR (100 MHz, DMSO): *ä* 174.2 (C–Pd), 149.1, 149.0, 148.9, 136.6, 135.4, 134.7, 133.4, 133.2, 132.9, 132.4, 132.1, 132.0, 129.9, 129.6, 129.4, 129.2, 129.1, 127.2, 123.6, 123.0, 112.8, 110.8 (Ar–C, TPPTS-C, $C_6(CH_3)_5$), 70.5 ($NCH_2CH_2OCH_3$), 58.8 ($NCH_2CH_2OCH_3$), 51.7 ($CH_2C_6(CH_3)_5$), 48.6 ($NCH_2CH_2OCH_3$), 17.8, 17.3, 16.7 ($CH_2C_6(CH_3)_5$). ^{31}P NMR (162.0 Hz, DMSO): *ä* 26.9. Anal. Calc. for $C_{40}H_{40}Br_2N_2Na_3O_{10}PPdS_3$ (M = 1171.12) C 41.02, H 3.44, N 2.39. Found C 41.12, H 3.50, N 2.33%.

4.3. General procedure for the Suzuki coupling reactions

A two-necked 25 mL flask fitted with a reflux condenser was charged with aryl chlorides (1.0 mmol), 2 mmol KOH, phenylboronic acid (1.5 mmol), *diethyleneglycol-di-n-butylether* (0.6 mmol, internal standard), 1.0% **2a**–**d** in 6 mL of H_2O was added. The flask was placed in a preheated oil bath (100 °C) under air atmosphere, temperature 100 °C, and 4 h. The conversion was monitored by gas chromatography following filtration or extractions with CH_2Cl_2. Yields were determined by gas chromatography for an average of two runs.

4.4. Recycling of catalyst

The flask was charged with catalyst **2c**, 4-chloroacetophenone (1.0 mmol), 2 mmol KOH, phenylboronic acid (1.5 mmol), and *diethyleneglycol-di-n-butylether* (0.6 mmol, internal standard). The reaction was carried out in water at 100 °C. After cooling to room temperature, the organic products were removed by filtration. The aqueous phase was then transferred to a new reaction flask for next cycle. Yields were determined by gas chromatography for an average of two runs.

4.5. Electrochemical measurements

All reagents used in this work were of analytical grade and all solutions were prepared using ultra pure water supplied from a Milli-Q purification system (18.2 MΩ cm, Millipore System Inc.). The electrochemical measurements were performed in a conventional three-electrode electrochemical cell using a Palmsence electrochemical analyzer interfaced with a PC. A platinum wire served as a counter electrode, and the reference electrode is saturated Ag/AgCl. A stationary platinum disk was used as a working electrode. Cyclic voltammetric measurements were obtained with sweeping from +1000 to −800 mV at 100 mV/s scan rate.

The electrochemical behavior of Pd(II) complexes (**1c**–**3c**) was analyzed by cyclic voltammetry in 1 mM acetonitrile–water mixture (1:1, v/v) solutions of the complexes (**1c**–**3c**) containing 0.05 M KCl supporting electrolyte. All electrolyte solutions were purged by high purity argon for 5 min prior to any measurements at room temperature.

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