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Suzuki–Miyaura and Hiyama reactions catalyzed by orthopalladated triarylphosphite complexes

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ABSTRACT

Orthometallated, dimeric, and monomeric palladium complexes with triphenylphoshito ligands and square-planar complexes of the type $PdCl_2[P(OR)_3]_2$ (where R=Ph, *m*-MeC_6H_4, *o*-MeC_6H_4, C_6H_3-2,4-$^t Bu_2$) were applied in the Suzuki–Miyaura and the Hiyama reactions leading to the same product, 2-Mebiphenyl. The desired product was obtained in high yield in reactions performed in ethane-1,2-diol with Cs_2CO_3 as a base. The optimized procedure was also applied to the synthesis of other biphenyl derivatives, and in most cases the Suzuki–Miyaura procedure led to higher yields of the product.

1. Introduction

The Suzuki–Miyaura and Hiyama reactions present two powerful methodologies that can be used for the generation of new C–C bonds, particularly in the synthesis of non-symmetrical biaryls, which are important materials for the production of polymers, agrochemicals, pharmaceutical intermediates, bioactive molecules, and electronic materials.[1–4] The Suzuki–Miyaura cross-coupling is a reaction of aryl or vinyl boronic acid with aryl halide, whereas in the Hiyama reaction various organosilanes are used as substrates instead of the organoboronic acid (Fig. 1).

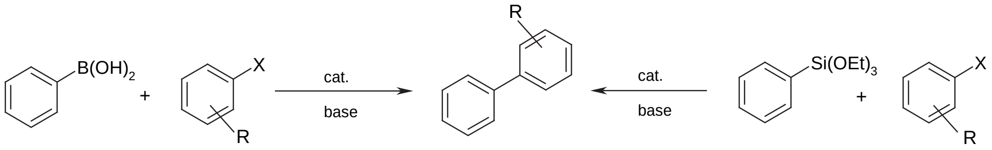

Fig. 1. Scheme of Suzuki–Miyaura and Hiyama coupling reactions.

The Suzuki–Miyaura reaction is the better studied and the more widely used reaction, although it is known to have some drawbacks that can result in additional costs, such as the limited solubility of reagents in some solvents or the difficult synthesis and purification of arylboronic acids.[5–7] For this reason, the application of cheap, non-toxic, and environmentally friendly silicon compounds as alternative reagents for C–C cross-coupling using the Hiyama procedure has been attracting increasing interest.[1,4,8] What is crucial for the success of the Hiyama coupling is the activation of the Si–C bond, which is usually achieved by generating pentacoordinated silicates in the presence of a fluoride ion originating from TBAF (tetrabutylammonium fluoride) or TASF (Tris(dimethylamino)sulfonium difluorotrimethylsilicate).[9–11] However, fluoride-free Hiyama cross-coupling reactions performed with NaOH as a base have also been described by several researchers.[12–15]

In any catalytic system, a very important role is played by the proper selection of the catalyst, which should offer high activity, selectivity, and stability under the reaction conditions. Soluble palladium compounds containing phosphorus ligands have been widely used in C–C cross-coupling reactions because of their facile synthesis and structural versatility.[16,17] In this context, palladium complexes with triphenylphosphito ligands of the type $PdCl_2[P(OR)_3]_2$ can be considered as good candidates, as has already been demonstrated for

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the Sonogashira[18] and methoxycarbonylation[19,20] reactions. Dimers containing an orthometallated Pd–C bond, formed by a phosphito or phosphinito ligand, have been successfully tested in the Suzuki[21–23] and Heck[24] couplings. In the class of phosphito-orthopalladates, a dimer with a bulky tris(2,4-di-^{t}butylphenyl) phosphite has been explored the most thoroughly. In particular, it has been shown to be an excellent precatalyst for the Suzuki–Miyaura coupling of both 4-bromoacetophenone and a more challenging, electronically deactivated substrate: 4-bromoanisole.[21–23] In reactions with PCy$_3$, the dimeric palladacycle formed an extremely active catalyst for the Suzuki coupling of 4-chloroanisole with 4-tolylboronic acid characterized by TONs of 1,000,000 after 2 h.[25]

Palladacycles formed from phosphito ligands have so far not been tested in the Hiyama process, which can be considered as an alternative to the Suzuki–Miyaura reaction method of biphenyl derivative preparation. Therefore, we undertook a study to compare the activity of palladium complexes with different triphenylphosphito ligands in the Suzuki–Miyaura and the Hiyama reactions leading to the same product, 2-Mebiphenyl. Additionally, by selecting monomeric PdCl$_2$[P(OR)$_3$]$_2$-type complexes and orthometallated dimers and monomers for our investigations, we wanted to elucidate a possible effect of the Pd–C bond on catalytic activity. It was expected that an optimized procedure developed during these studies would also be applicable to the synthesis of other biphenyl compounds.

2. Results and discussion

Three types of complexes employed in these studies as catalyst precursors are shown in Fig. 2. The first group contains square-planar PdCl$_2$[P(OR)$_3$]$_2$ complexes, in which phosphito ligands are coordinated to palladium via typical Pd–P bonds (**1**). The second group consists of dimeric complexes with orthometallated, chelating phosphito ligands forming Pd–C and Pd–P bonds (**2**). In the third group of complexes, both types of phosphito ligands are present, namely an orthometallated and an mono-coordinated one (**3**).

Table 1
Results of Suzuki–Miyaura reaction in ionic liquids with catalyst **1a**

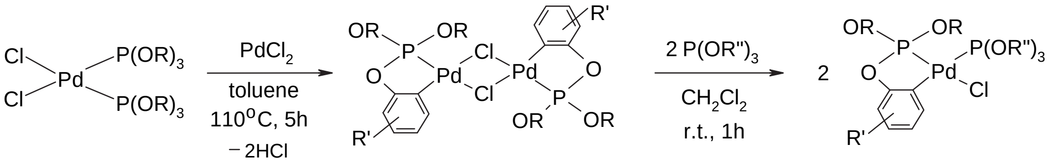
Solvent (cm^3)	Base	Time [h]	Temp [°C]	Yield [%][a]
[emim][EtSO$_4$]	Cs$_2$CO$_3$	2	80	6
[emim][EtSO$_4$]/*i*-PrOH (1:0.5)	Cs$_2$CO$_3$	2	80	14
[emim][EtSO$_4$]/H$_2$O (1:0.5)	Cs$_2$CO$_3$	2	80	24
[emim][EtSO$_4$]/H$_2$O (1:0.5)	Cs$_2$CO$_3$	2	110	37
[emim][EtSO$_4$]/H$_2$O (1:0.5)	Na$_2$CO$_3$	2	110	41
[emim][EtSO$_4$]/H$_2$O (1:0.5)	NaHCO$_3$	2	110	57
H$_2$O	NaHCO$_3$	2	80	20
H$_2$O[b]	NaHCO	2	110	21
[bmim][BF$_4$]	NaHCO$_3$	2	110	3
[bmim][BF$_4$]	NEt$_3$	2	110	34
[bmim][BF$_4$]	KOH	4	110	15
[bmim][BF$_4$]	NBu$_4$F	1	110	9
[bmim][BF$_4$]	Na$_2$CO$_3$	1	110	4
[bmim][BF$_4$]	Cs$_2$CO$_3$	1	110	1
[bmim][BF$_4$]/H$_2$O (1:0.5)	K$_2$CO$_3$	2	80	21
[bmim][BF$_4$]/H$_2$O (1:0.5)	Cs$_2$CO$_3$	2	110	33
[bmim][BF$_4$]/H$_2$O (1:0.5)	Na$_2$CO$_3$	1	110	37
[bmim][BF$_4$]/H$_2$O (1:0.5)	NaHCO$_3$	2	80	29
[bmim][BF$_4$]/H$_2$O (1:0.5)	NaHCO$_3$	2	110	58
[bmim][BF$_4$]/H$_2$O[c] (1:0.5)	NaHCO$_3$	2	110	80
[bmim][BF$_4$]/H$_2$O[b] (1:0.5)	NaHCO$_3$	2	110	86
[bmim][BF$_4$]/Ethane-1,2-diol (2:1)	K$_2$CO$_3$	2	80	7
[bmim][BF$_4$]/Ethane-1,2-diol/H$_2$O (2:1:2)	K$_2$CO$_3$	2	80	9
[bmim][BF$_4$]/Ethane-1,2-diol/H$_2$O (0.25:1:0.25)	K$_2$CO$_3$	2	80	14
[bmim][BF$_4$]/Ethane-1,2-diol (2:1)	NaHCO$_3$	2	80	57
[bmim][BF$_4$]/Ethane-1,2-diol (1:1)	NaHCO$_3$	2	80	66
[bmim][BF$_4$]/Ethane-1,2-diol (0.5:1)	NaHCO$_3$	2	80	75
[bmim][BF$_4$]/Ethane-1,2-diol (0.25:1)	NaHCO$_3$	2	80	77
[bmim][BF$_4$]/Ethane-1,2-diol/H$_2$O (1:1:1)	NaHCO$_3$	2	80	46
[bmim][BF$_4$]/Ethane-1,2-diol/H$_2$O (0.5:1:0.5)	NaHCO$_3$	2	80	53
[bmim][BF$_4$]/Ethane-1,2-diol/H$_2$O (0.25:1:0.25)	NaHCO$_3$	2	80	68
Ethane-1,2-diol	NaHCO$_3$	2	80	96

Reaction conditions: catalyst **1a**, 1mol%; [PhB(OH)$_2$] 1.5 mmol; [2-bromotoluene] 1 mmol; [base] 2 mmol.

[a] Conversion to the coupled product determined by GC.

[b] Catalyst **2b**.

[c] Catalyst **2a**.



1a R = C$_6$H$_5$
1b R = *m*-MeC$_6$H$_4$
1c R = *o*-MeC$_6$H$_4$
1d R = 2,4-*t*Bu$_2$C$_6$H$_3$

2a R = C$_6$H$_5$, R' = H
2b R = *m*-MeC$_6$H$_4$, R' = *m*-Me
2c R = 2,4-*t*Bu$_2$C$_6$H$_3$, R' = 2,4-*t*Bu$_2$

3a R = C$_6$H$_5$, R' = H
R" = P(OPh)$_3$
3b R = C$_6$H$_5$, R' = H
R" = P(O-*m*-MeC$_6$H$_4$)$_3$
3c R = C$_6$H$_5$, R' = H
R" = P(O-*o*-MeC$_6$H$_4$)$_3$
3d R = 2,4-*t*Bu$_2$C$_6$H$_3$,
R' = 2,4-*t*Bu$_2$, R" = P(OPh)$_3$

Fig. 2. Palladium triarylphosphite complexes used as catalysts.

In the first step of our studies, we investigated the effect of the solvent in the Suzuki–Miyaura reaction with special emphasis on the application of ionic liquids. It had been found before that palladium complexes with phosphito ligands exhibited high catalytic activity in the Sonogashira reaction in an ionic liquid environment. The results of screening experiments, performed with **1a** as the catalyst precursor with various bases and ionic liquids, are gathered in Table 1.

Two ionic liquids were selected, and in both cases the yield of the product was rather low, ca. 10% only. Exceptionally, in [bmim]BF$_4$ with NEt$_3$ as a base, 34% of 2-Mebiphenyl was obtained. An improvement in the reaction yield was noted when water was added as a co-solvent to the reaction. For example, in a mixture of [emim][EtSO$_4$] and H$_2$O, 24% of 2-Mebiphenyl was formed at 80 °C and as much as 57% at 110 °C. Similarly, in a [bmim]BF$_4$/H$_2$O mixture, 21–29% of the product was obtained at 80 °C and 33–58% at 110 °C. In the same solvent mixture, quite satisfactory yields, 80 and 86%, were obtained using orthometallated complexes **2a** and **2b**, respectively, at 110 °C.

When ethane-1,2-diol was used instead of water as a second solvent together with an ionic liquid, better results were obtained with **1a** already at 80 °C. Under such conditions, a yield of 73–77% was obtained, depending on the [[bmim]BF$_4$]:[ethane-1,2-diol] ratio. However, when water was added to this mixture as a third solvent, the catalytic results were slightly poorer than in the two component mixtures. Thus, the Suzuki–Miyaura reaction can be successfully performed in [emim][EtSO$_4$]/H$_2$O, [bmim]BF$_4$/H$_2$O, or [bmim]BF$_4$/ethane-1,2-diol mixtures. Better results were obtained when ethane-1,2-diol was used instead of water together with an ionic liquid. However, the highest yield, 96%, was recorded in ethane-1,2-diol alone, which consequently was used as the solvent in further experiments performed according to Fig. 3, in which the Suzuki–Miyaura and Hiyama reactions were considered as alternative pathways affording the same product, 2-Mebiphenyl.

Table 2
Effect of catalyst **2b** concentration in Suzuki–Miyaura reaction

2b [mol %]	Time [min]	Yield[a] [%]	TON	TOF/h^{-1}
1	5	80	80	964
1	10	97	97	582
1	15	99	99	396
1	20	100	100	300
0.1	30	73	730	1460
0.1	120	86	860	430
0.05	120	73	1460	730
0.01	120	59	5900	2950

Reaction conditions: catalyst **2b**; [PhB(OH)$_2$] 1.5 mmol; [2-bromotoluene] 1 mmol; [Cs$_2$CO$_3$] 2 mmol; solvent: ethane-1,2-diol, 2.5 cm^3; 80 °C.

[a] Conversion to the coupled product determined by GC.

Preliminary studies of the effect of the base on the course of both reactions were performed for one of the selected complexes **2b**. As shown in Fig. 4, in the Suzuki–Miyaura reaction the kind of base has practically no effect on the reaction yield, which is close to 100% in almost all cases. Only NEt$_3$ gave a poorer result, 57% of 2-Mebiphenyl. In contrast, the Hiyama reaction exhibited strong sensitivity to the kind of base present in the system, with the highest yield, 100%, being obtained with K$_3$PO$_4$ and NaOH. Cs$_2$CO$_3$ also afforded a good result of 89% yield. Like in the case of the Suzuki–Miyaura reaction, the lowest yield, 17%, was obtained in the presence of NEt$_3$. Interestingly, with a fluoride donor, namely [Bu$_4$N]F, only 42% of 2-Mebiphenyl was formed in the Hiyama reaction. Thus, there is no advantage gained from the presence of a fluoride co-catalyst in the system, and consequently further reactions were performed without that additive.

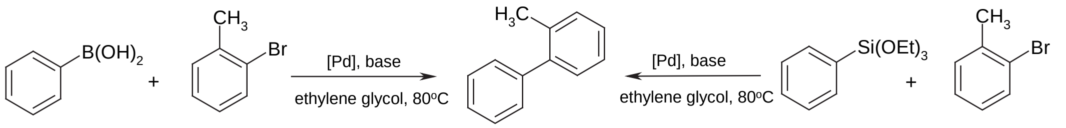


Fig. 3. Suzuki–Miyaura and Hiyama reactions under studies.

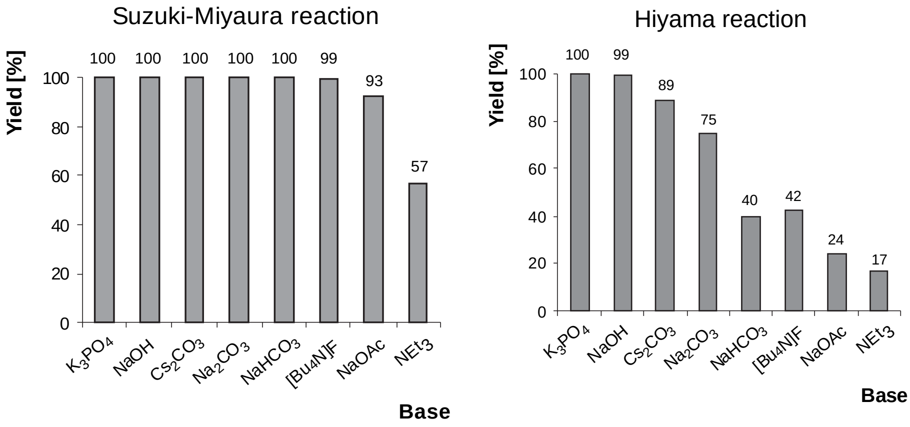


Fig. 4. Effect of base on the yield (GC determined) of 2-methylbiphenyl in Suzuki–Miyaura and Hiyama reactions with catalyst **2b** (1 mol %) in ethane-1,2-diol at 80 °C.

The effect of palladium concentration was also investigated. Catalyst **2b** was applied in the Suzuki–Miyaura reaction in amounts ranging from 0.01 to 1 mol %. The reaction proceeded smoothly at 80 °C, as shown by the data in Table 2. Using the obtained results, we calculated the TON and TOF values, which reached a maximum of 5900 and 2950, respectively (Table 2). Table 2 also provides kinetic data that make it possible to follow the rate of the Suzuki–Miyaura reaction with catalyst **2b**. It can be seen that 97% of the product was formed after just 10 min, and 100% yield was achieved after 15 min.

To compare the efficiency of the Suzuki–Miyaura and the Hiyama reactions as alternative procedures for the preparation of 2-Mebiphenyl, we studied the effect of temperature on the reaction course. Temperature change in the range from 40 °C to 140 °C affects the yield of Suzuki–Miyaura reaction only slightly. At a temperature as low as 40 °C, a high yield of the product, 97%, was obtained after 2 h with **2b**, which is a very promising result. The Hiyama procedure seems to be more dependent on temperature: the best result, 89% yield, was achieved at 80 °C. That is also the only temperature at which results obtained using both methods were comparable (Fig. 5).

All of the complexes studied exhibited excellent activity in the Suzuki–Miyaura reaction performed in ethane-1,2-diol with Cs$_2$CO$_3$ as a base (Fig. 6). Under the same conditions, the yield of the Hiyama cross-coupling was slightly lower, with the lowest value, 60%, for complex **1c** and the highest one, 91%, for **3d**.

When NaHCO$_3$ was used instead of Cs$_2$CO$_3$, the yield of 2-Mebiphenyl in the Suzuki–Miyaura reaction varied from 65% (**1d**) to 100% (**1c**, **2b**, **2c**, **3d**). The Hiyama cross-coupling afforded poorer results, ranging from 40% for **2b** to 74% for **3d**, with the average yield being close to 41% (Fig. 7).

The low yield of the Hiyama cross-coupling obtained in the presence of NaHCO$_3$ could be rationalized in the light of results of base screening shown in Fig. 4. Consequently, it was expected that K$_3$PO$_4$ and NaOH should enhance the yield of Hiyama product compared with NaHCO$_3$. Indeed, as shown in Fig. 8, yields of 2-Mebiphenyl exceeding 70% were obtained in all reactions performed with these bases. In the series of catalysts tested, the best was the orthometallated complex **2b**, although more than 80% of the product was also formed when the other orthometallated complexes were used, whether dimeric (**2a**,**c**) or monomeric (**3b**–**c**). The monomeric

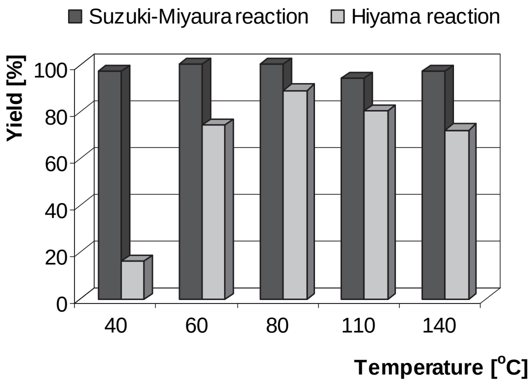


Fig. 5. Effect of temperature on the yield (GC determined) of 2-methylbiphenyl in Suzuki–Miyaura and Hiyama reactions with catalyst **2b** (Cs_2CO_3 as a base, ethane-1,2-diol as a solvent).

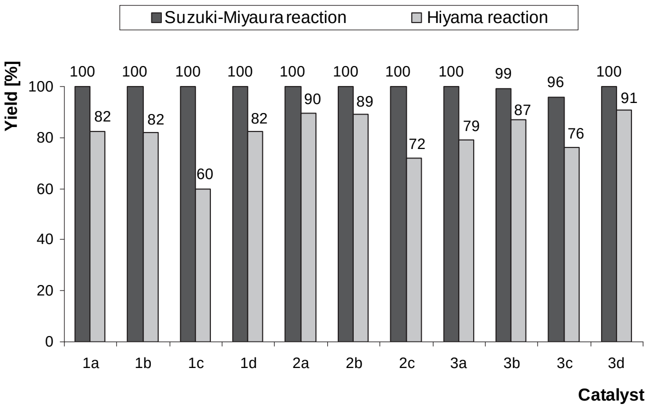


Fig. 6. Yield (GC determined) of 2-methylbiphenyl obtained in Suzuki–Miyaura and Hiyama reactions in ethane-1,2-diol at 80 °C with Cs_2CO_3 as a base.

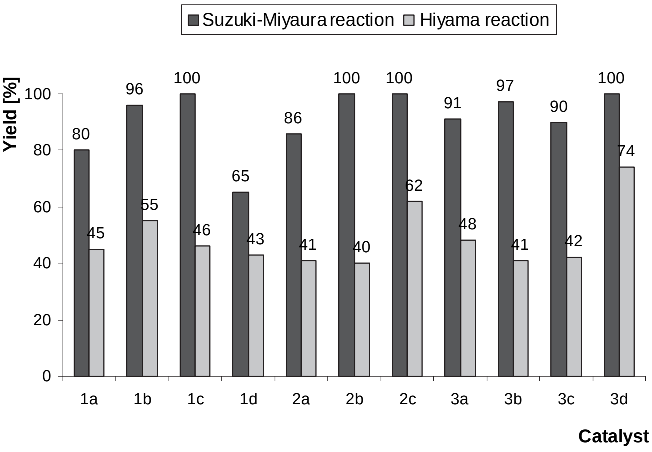


Fig. 7. Yield (GC determined) of 2-methylbiphenyl obtained in Suzuki–Miyaura and Hiyama reactions in ethane-1,2-diol at 80 °C with $NaHCO_3$ as a base.

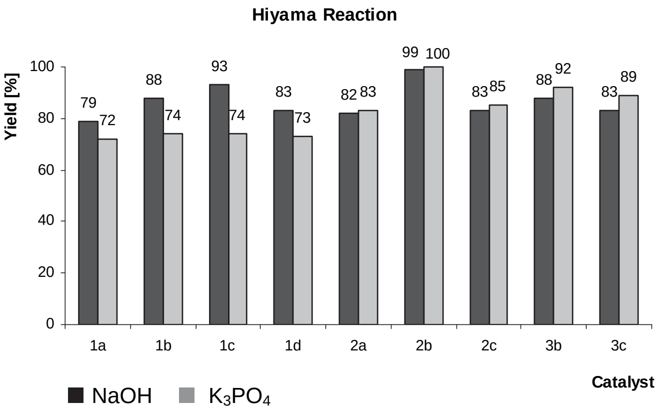


Fig. 8. Yield (GC determined) of 2-methylbiphenyl obtained in Hiyama reaction in ethane-1,2-diol at 80 °C with NaOH and K_3PO_4 as a base.

$PdCl_2[P(OR)_3]_2$ complexes (**1a**–**d**) were less productive, especially in the presence of K_3PO_4.

To explore the generality and scope of the procedures studied, reactions of different aryl bromides were carried out with complexes **1a** and **2b** under the optimal reaction conditions (Table 3).

In the Suzuki–Miyaura cross-coupling reaction of phenylboronic acid with 2-bromotoluene, 2-bromobenzaldehyde, 2-bromoacetophenone, 4-bromoacetophenone, and 1-bromonaphtalene, 100% yield of the product was obtained for both of the catalysts tested. Slightly lower yields were only noted for 4-bromoanisole: 96% for complex **2b** and 94% for complex **1a**; and for 4-bromotoluene: 90% for complex **2b** and 69% for complex **1a**. In the Hiyama reaction, the best results (100% yield) were achieved in the coupling of triethoxyphenylsilane with 2-bromobenzaldehyde. A similar high yield was obtained in reactions with 4-bromoacetophenone (93% for complex **2b** and 98% for complex **1a**), 1-bromonaphtalene (90% for complex **2b** and 78% for complex **1a**), and 4-bromoanisole (89% for complex **2b** and 87% for complex **1a**). Generally, higher yields for all of the aryl halides tested were obtained in the Suzuki–Miyaura cross-coupling with both complexes, **2b** and **1a**. When the activity of the two catalysts is compared, in most cases better results were found for the orthometallated complex **2b**.

To verify whether Suzuki–Miyaura and Hiyama reactions can be also successfully performed in other diols, catalytic experiments were performed according to Fig. 3, in 2,3-dimethyl-2,3-butanediol (pinacol) and in 1,2-propanediol (propylene glycol) (Table 4). The results obtained in Suzuki–Miyaura cross-coupling in both diols were similar to these in ethane-1,2-diol and in 1,2-propanediol up to 100% of 2-Mebiphenyl was found. In the Hiyama reaction good yields of product were obtained in 1,2-propanediol, whereas in pinacol the results were disappointing with a yield less than 1%.

3. Conclusions

We have found that $PdCl_2[P(OR)_3]_2$-type complexes and their orthopalladated derivatives, both dimeric and monomeric, are active catalyst precursors for the Suzuki–Miyaura and the Hiyama reactions in ethane-1,2-diol as solvent. All such complexes efficiently catalyze the Hiyama cross-coupling without any fluoride co-catalyst; however, the yield of the product strongly depends on the type of base used. In the optimized procedure, Cs_2CO_3 was applied.

In competitive experiments, the Suzuki–Miyaura reaction was seen to be the more effective method to obtain biphenyl products than the Hiyama procedure. The most active catalyst precursors in both the Suzuki–Miyaura and the Hiyama reactions were the orthometallated complexes **2b**, **3b**,**d**.

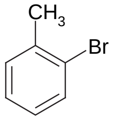
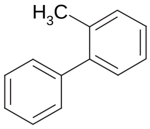
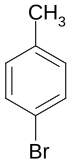
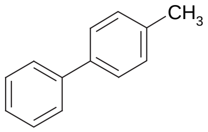
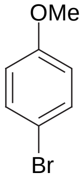
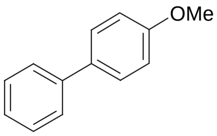
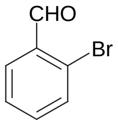
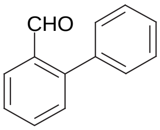
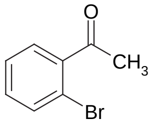
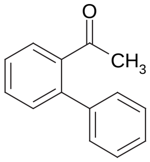
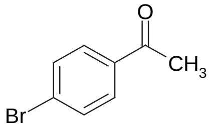
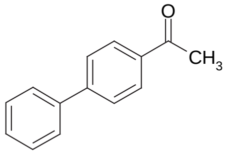
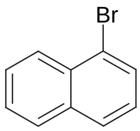
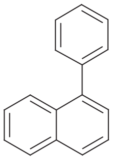
4. Experimental

4.1. General

Complexes **1a**, **1c**,[26] **1b**,[18] and **1d**,[21] **2a**, **2b**,[27] **2c**,[21] **3a**,[27] and **3d**[21] were obtained according to the literature methods. Complexes **3b** and **3c** were obtained by the same method as complex **3a**.

4.1.1. $[PdCl\{\kappa^2\text{-}P,C\text{-}P(OC_6H_4)(OC_6H_5)_2\}\{P(O\text{-}m\text{-}MeC_6H_4)_3\}]$, ***3b***. The solution of complex **2a** (0.4 g; 0.443 mmol) and $P(O\text{-}m\text{-}MeC_6H_4)_3$ ($0.41\ cm^3$; 1.33 mmol) in dichloromethane ($5\ cm^3$) was stirred in

Table 3
Reaction of various aryl halides for Suzuki-Miyaura and Hiyama reaction

Aryl halide	Catalyst	Product	Yield[a] [%]	
			Suzuki–Miyaura	Hiyama
	**1a**		100	82, 71[b], 78[c]
	2b		100	89
	**1a**		69	73
	2b		90	71
	**1a**		94	87
	2b		96	89
	**1a**		100	100
	2b		100	100
	**1a**		100	31, 15[b], 3[c], 47[d]
	2b		100	66, 44[b], 5[c], 62[d]
	**1a**		100	98
	2b		100	93
	**1a**		100	78
	2b		100	90

Reaction conditions: [Pd] 1 mol %; [aryl halide] 1 mmol; [PhB(OH)$_2$] 1.5 mmol; [PhSi(OEt)$_3$] 1.1 mmol; [Cs$_2$CO$_3$] 2 mmol; solvent: ethane-1,2-diol 2.5 cm^3; 80 °C; 2 h.

[a] Conversion to the coupled product determined by GC.

[b] With addition of 1 mmol of KF.

[c] With addition of 1 mmol of [Bu$_4$N]F.

[d] With addition of 1 mmol of KF, without Cs$_2$CO$_3$.

Table 4
Results of Suzuki–Miyaura and Hiyama reactions in 2,3-dimethyl-2,3-butanediol and in 1,2-propanediol

Catalyst	Yield[a] [%]		
	2,3-Dimethyl-2,3-butanediol	1,2-Propanediol	
	Suzuki–Miyaura	Suzuki–Miyaura	Hiyama
1a	89	97	91
2a	89	99	94
2b	89	100	93

Reaction conditions: [Pd] 1 mol %; [2-bromotoluene] 1 mmol; [PhB(OH)$_2$] 1.5 mmol; [PhSi(OEt)$_3$] 1.1 mmol; [Cs$_2$CO$_3$] 2 mmol; solvent: 2.5 cm^3; 80 °C; 2 h.

[a] Conversion to the coupled product determined by GC.

room temperature for 1 h, after which the solvent was evaporated in vacuo and the white product was precipitated by addition of ethanol and recrystallized from the CH$_2$Cl$_2$/EtOH mixture. Yield: 0.56 g, 79%; calcd for C$_{39}$H$_{35}$ClO$_6$P$_2$Pd (%): C 58.30, H 4.39; found: C 57.96H 3.82; δ_H (500.1 MHz, CDCl$_3$) 8.18 (m, 1H, H3 orthopalladated ring), 7.04 (m, Ph), 2.22 (s, 9H, CH$_3$); δ_P (202.5 MHz, CDCl$_3$) 109.34 (d, $^2J_{PP}$=55.9 Hz, P(O-*m*-MeC$_6$H$_4$)$_3$); 128.11 (d, $^2J_{PP}$=55.9 Hz, orthopalladated phosphite).

*4.1.2. [PdCl{κ^2-P,C-P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}{P(O-o-MeC$_6$H$_4$)$_3$}], **3c**.*

The solution of complex **2a** (0.4 g; 0.443 mmol) and P(O-*o*-MeC$_6$H$_4$)$_3$ (0.41 cm^3; 1.33 mmol) in dichloromethane (5 cm^3) was stirred in room temperature for 1 h, after which the solvent was evaporated in vacuo and the white product was precipitated by addition of ethanol and recrystallized from the CH_2Cl_2/EtOH mixture. Yield: 0.7 g, 98%; calcd for $C_{39}H_{35}ClO_6P_2Pd$ (%): C 58.30, H 4.39; found: C 58.72H 3.90; δ_H (500.1 MHz, $CDCl_3$) 8.12 (m, 1H, H3 orthopalladated ring), 7.08 (m, Ph), 2.13 (s, 9H, CH_3); δ_P (202.5 MHz, $CDCl_3$): 108.02 (d, $^2J_{PP}$=56.5 Hz, P(O-*o*-$MeC_6H_4)_3$); 128.42 (d, $^2J_{PP}$=56.5 Hz, orthopalladated ring).

4.2. Catalytic reactions

The Suzuki–Miyaura and Hiyama reactions were carried out in a Schlenk tube with magnetic stirring. Reagents for Suzuki–Miyaura reaction: phenylboronic acid (0.183 g, 1.5 mmol), of 2-bromotoluene (0.118 cm^3, 1 mmol), base (2 mmol), solvent (2.5 cm^3), palladium catalyst (1 mol %). Reagents for Hiyama reaction: triethoxy(phenyl) silane (0.26 cm^3, 1.1 mmol), 2-bromotoluene (0.118 cm^3, 1 mmol), base (2 mmol), solvent (2.5 cm^3), palladium catalyst (1 mol %). Reagents introduced directly to the Schlenk tube. Next, the Schlenk tube was sealed with a rubber tap and introduced into an oil bath pre-heated to 80 °C. The reaction was carried out at 80 °C for 2 h and after this time cooled down. Organic products were separated by extraction with hexane (4 cm^3, 3 cm^3, and 3 cm^3). The combined extracts (10 cm^3) were GC-FID analyzed (Hewlett Packard 8452A) with 0.076 cm^3 of dodecane as an internal standard to determine the yield of products.

GC/MS (Hewlett Packard 8452A) was used for products identification.

MS data of biphenyl products: 4-Methylbiphenyl: 168 (100) [M^+], 167 (85) [M^+-1], 153 (20) [M^+-CH3], 152 (27), 115 (11), 82 (15). 4-Methoxybiphenyl: 184 (100) [M^+], 169 (49) [M^+-CH_3], 141 (45), 115 (38). 2-Carbaldehydebiphenyl: 182 (76) [M^+], 181 (100) [M^+-1], 152 (48), 76 (35) [Ph−1]. 4-Acethylbiphenyl: 196 (52) [M^+], 181 (100) [M^+-CH_3], 152 (54), 76 (16) [Ph−1]. 2-Acethylbiphenyl: 196 (57) [M^+], 181 (100) [M^+-CH_3], 152 (55), 76 (14) [Ph−1]. 1-Phenylnaphthalene: 204 (100) [M^+], 101 (47).

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.10.021.

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