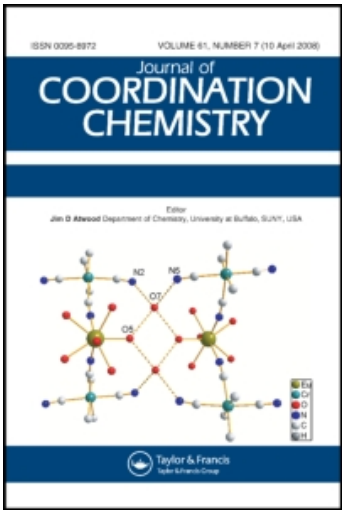


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of orthopalladated complexes of 4-chloro benzoylmethylene triphenylphosphorane and their application in Suzuki cross-coupling

Kazem Karami[a]
[a] Department of Chemistry, Isfahan University of Technology, Isfahan 84156/83111, Islamic Republic of Iran

First published on: 14 September 2010

To cite this Article Karami, Kazem(2010) 'Synthesis and characterization of orthopalladated complexes of 4-chloro benzoylmethylene triphenylphosphorane and their application in Suzuki cross-coupling', Journal of Coordination Chemistry, 63: 20, 3688 — 3696, First published on: 14 September 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.515213
URL: http://dx.doi.org/10.1080/00958972.2010.515213

Journal of Coordination Chemistry
Vol. 63, No. 20, 20 October 2010, 3688–3696

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of orthopalladated complexes of 4-chloro benzoylmethylene triphenylphosphorane and their application in Suzuki cross-coupling

KAZEM KARAMI*

Department of Chemistry, Isfahan University of Technology, Isfahan 84156/83111, Islamic Republic of Iran

(*Received 16 February 2010; in final form 2 July 2010*)

Orthopalladated binuclear complexes (**1**) have been prepared by refluxing a mixture of the phosphorus ylide (ClBPPY) with $Pd(OAc)_2$ in CH_2Cl_2. Complex **1** reacts with ligands (L) to give (L = PPh_3 (**2**), Me_3Py (**3**)). Cyclopalladated complexes are highly efficient catalysts for the Suzuki reactions of aryl bromide with aryl boronic acid. The monomeric complexes **2** and **3** are more active than the dimer **1**. Palladium mirror was observed, indicating the involvement of classic Pd(0)/Pd(II) catalytic cycle using these cyclopalladated complexes. The coupling of aryl bromide with aryl boronic acid gave the desired biphenyl congeners in good to excellent yields. We tested the various bases, finding that inorganic bases work better than organic ones.

Keywords: Cyclopalladation; Phosphorus ylide; Catalyst; Suzuki reaction

1. Introduction

The synthesis of cyclopalladated complexes has attracted attention due to their potential applications in organic synthesis, homogeneous catalysis, photochemistry, optical resolution, design of new metallomesogenes, antitumor drugs, etc. [1, 2]; various examples of their uses as homogeneous catalyses or building blocks in macromolecular chemistry have been published [3–5]. Furthermore, palladium derivatives have been widely used in organic synthesis for formation of carbon–carbon and carbon–heteroatom bonds [6–10] because of their versatility, compatibility with most functional groups and relatively low toxicity [11, 12].

The Suzuki reaction has found widespread use in organic synthesis [13]. The traditional Suzuki reaction uses P- and N-ligand-based palladium catalysts and much attention has been paid to improve the Suzuki reaction by designing new ligands [14]. Arylboronic acid used in Suzuki coupling reactions is largely unaffected by the presence of water and commercially available in laboratory scale [13]. Suzuki couplings are also

*Email: karami@cc.iut.ac.ir

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.515213

important for the synthesis of functionalized materials and supported catalysts, e.g., for the immobilization of organometallic complexes onto heterogeneous supports [15]. Aryl bromides couple efficiently with arylboronic acids. Suzuki or similar types of reactions have not been carried out with an aziridine ring present in the molecule [16]. Almost any Pd(II) or Pd(0) derivative, usually associated with phosphine, substituted with electron-withdrawing groups, gives high turnover numbers [17]. This reaction usually takes 1–24 h, urging us to reduce the time of this reaction [13–30]. In this study, synthesis and characterization of orthopalladated complexes **1–3** and their application in the Suzuki reaction were investigated. Complex **1** was prepared by reacting the phosphorus ylide (ClBPPY = 4-chloro benzoylmethyene triphenylphosphorane) with $Pd(OAc)_2$. Mononuclear complexes **2** and **3** were prepared by reactions of **1** with L to give ($L = PPh_3$ **2**), Me_3Py (2,4,6-trimethylpyridine) **3**, respectively. Herein, we report a highly efficient palladium-catalyzed Suzuki cross-coupling [14].

2. Experimental

2.1. *Material and physical measurements*

All reagents were obtained from commercial sources and used without purification. We used analytical TLC. Gas chromatographic analyses were performed with an FID detector and a 30 m column HP-5. ^{1}H-NMR and $^{31}P\{^1H\}$-NMR spectra at 300 K were obtained in $CDCl_3$ using a 500 MHz Bruker spectrometer operating at 500.13 MHz for ^{1}H-NMR and 161.97 MHz for $^{31}P\{^1H\}$-NMR. Chemical shifts (δ) are reported relative to internal TMS and external 85% phosphoric acid. Melting points were measured on a Gallenhamp 9B 3707 F apparatus. C, H, and N elemental analyses were performed using a PE 2400 series analyzer. IR spectra were recorded on a FT-IR JASCO 680 spectrophotometer using KBr pellets.

2.2. *Synthesis of ClBPPY*

The ligand ClBPPY (4-chloro benzoyl methylene triphenyl phosphorane) was synthesized by published methods [31–33].

2.3. *Synthesis of 1*

$Pd(OAc)_2$ (0.0469 g, 0.2 mmol) was added to a solution of ClBPPY (0.0819 g, 0.2 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was refluxed for 24 h. The solvent was then evaporated and the yellow solid was dissolved in MeOH (10 mL) and anhydrous NaCl (0.0342 g or 0.6 mmol) was added. A pale yellow solid precipitated immediately. The reaction mixture was stirred for 12 h at room temperature (RT) and the resulting suspension was filtered. The yellow solid was washed with H_2O (5 mL), MeOH (10 mL), and Et_2O (15 mL) and air dried to produce **1**. Yield (0.234 g, 40%); Anal. Calcd for $C_{52}H_{38}O_2Cl_4P_2Pd_2$: C, 56.19; H, 3.45. Found: C, 56.21; H, 3.38. IR (KBr, cm^{-1}): ν 841 (C–P), 1643 (CO); ^{1}H-NMR (500 MHz, ppm, $CDCl_3$): $\delta = 4.81$ (s, CHP, minor): 4.91 (d, CHP, major, $^2J_{PH} = 2.7$ Hz), 6.54–6.58 (m, H3 + H4, C_6H_4, major + minor), 7.23–7.50

(m, H6, major + minor, Ph + C_6H_4, major + minor), 7.88–8.08 (m, H*o*, PPh_3, major + minor); $^{31}P\{^1H\}$-NMR ($CDCl_3$, ppm): $\delta = 18.97$ (major), 19.41 (minor).

2.4. *Synthesis of 2*

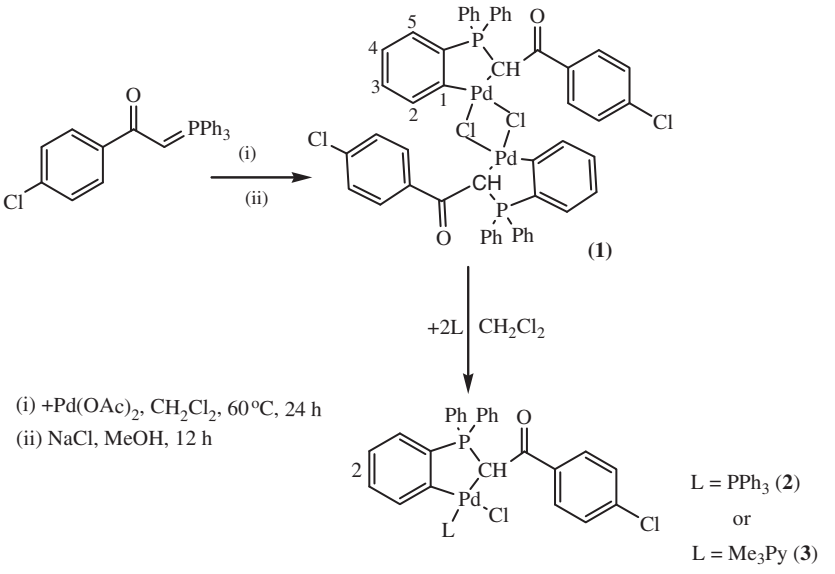
To a suspension of [Pd(μ-Cl){*C,C*-{CH[P(C_6H_4-2)Ph_2][C(O)C_6H_4Cl-4}}]$_2$ (0.19 mmol) in CH_2Cl_2 (15 mL), PPh_3 (0.38 mmol) was added. The initial yellow suspension gradually dissolved, and after 1 h stirring at RT, the resulting solution was filtered over a Celite pad to remove any residual insoluble solid. The clear solution was evaporated to dryness, and the treatment of the residue with Et_2O (30 mL) gave **2** as a yellow solid. Yield (0.127 g, 9.2%); Anal. Calcd for $C_{44}H_{34}Cl_2OP_2Pd$: C, 64.6; H, 4.19. Found: C, 65.4; H, 4.0. IR (KBr, cm^{-1}): ν 839 (C–P), 1618 (CO); ^{1}H-NMR (500 MHz, $CDCl_3$, ppm); $\delta = 5.40$ (s, 1H, CHP), 6.55 (s, 2H, C_6H_4), 6.90 (m, 1H, C_6H_4), 7.15–7.17 (m, 6H, H*m*, PPh_3), 7.18–7.24 (m, 9H, H*o* + H*p*, PPh_3), 7.30–7.31 (m, 5H, H*m*, PPh_2, H*m* + (PhCO) + 1H C_6H_4), 7.45–7.59 (m, 4H, H*m* + H*p* + H*p*, PPh_2), 7.60–7.66 (m, 2H, H*o*, PPh_2), 8.02 (m, 2H, H*o*, PPh_2), 8.29 (m, 2H, H*o*, PPh_2), 8.31 (d, 2H, H*o*, PhCO, $^3J_{HH} = 7.1$). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 15.09 (s, 1P, CHP), 32.14 (s, 1P, Pd–PPh_3).

2.5. *Synthesis of 3*

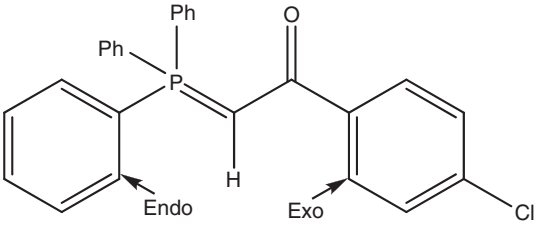
To a solution of [Pd(μ-Cl){*C,C*-{CH[P(C_6H_4-2)Ph_2][C(O)C_6H_4Cl-4}}]$_2$ (0.044 g, 40.7 mmol) in CH_2Cl_2 (10 mL), Me_3Py (200 μL, 81.5 mmol) was added, and the solution was stirred for 30 min at RT. After 1 h, the solvent was evaporated to dryness and the residue was treated with cold *n*-hexane (15 mL) to give **3** as yellow solid. Yield (0.0185 g, 34.4%); Anal. Calcd for $C_{34}H_{30}Cl_2NO_1PPd$: C, 60.33; H, 4.47; N, 2.07. Found: C, 60.45; H, 4.39; N, 2.13; IR (KBr, cm^{-1}); ν 845 (C–P), 1600 (C=N) 1621 (CO), ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): $\delta = 2.03$ (s, 3H, Me), 2.23 (s, 3H, Me), 2.88 (s, 3H, Me), 5.14 (d, 1H, CHP, $^2J_{HP} = 4.9$ Hz), 6.14 (d, 1H, C_6H_4, $^3J_{HH} = 7$ Hz), 6.69 (s, 1H, C_6H_4), 6.90 (m, 2H, C_6H_4), 7.06 (t, 2H, H*p*, PPh_2, $^3J_{HH} = 8.6$ Hz), 7.12 (m, 1H, py), 7.47 (t, 2H, H*m*, PhCO), 7.55–7.62 (m, 4H, H*m*, PPh_2), 7.86 (m, 2H, H*p*, PPh_2), 8.22 (dd, 2H, H*o*, PPh_2, $^3J_{HH} = 6$ Hz), 8.53 (dd, 2H, H*o*, PPh_2, $^3J_{HH} = 5.8$ Hz), $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 18.95$ (s, 1P, CHP).

2.6. *General procedure for the Suzuki coupling reaction*

Typical experimental procedure was carried out for the Suzuki cross-coupling reaction in air. A reaction tube equipped with a stirbar was charged with aryl bromide (0.5 mmol), aryl boronic acid (0.75 mmol), solvent (6 mL), and bases (1.5 mmol). The mixture was heated for 1 h under reflux (80°C), then filtered with silica gel, and the filtrate was examined by TLC. If conversion was not completed, we used GC. The solvent was evaporated under reduced pressure to provide a white solid; the pure product was prepared *via* dissolving the white solid and again precipitating with dichloromethane and *n*-hexane and drying under reduced pressure.



Scheme 1. The Synthesis of orthopalladated complexes (**1**–**3**).



Scheme 2. Regioselective positions (exo and endo) in α-keto-phosphorus ylides.

3. Results and discussion

The α-ketostabilized ylide ClBPPY was synthesized using published methods [31–33]. Treatment of ClBPPY with $Pd(OAc)_2$ (1 : 1) in refluxing CH_2Cl_2, and further reaction of the dimeric acetato-bridge intermediates with excess NaCl in methanol gave **1** as a yellow solid (scheme 1).

ClBPPY may undergo C–H activation at the phenyl ring of the benzoyl fragment and the phenyl ring of the phosphine (scheme 2) [34]. In all reported cases [4, 34], the phenylic C–H bonds of the phosphine are easily activated. In these ylides, phenyl rings of the PPh_3 are more electron rich than the benzoyl unit, suggesting an electrophilic mechanism for aromatic substitution. The carbonyl actually behaves as a strong deactivating group. For **1**–**3**, metalation can be considered *endo* metalation since the P–Cα bond belongs to the palladacycle.

Metalation of the stabilized ylides takes place at phenyls of PPh_3, in spite of the presence of an inactivating chloro at the benzoyl ring (schemes 1 and 2). This has been established through spectroscopic characterization of **2** and **3**.

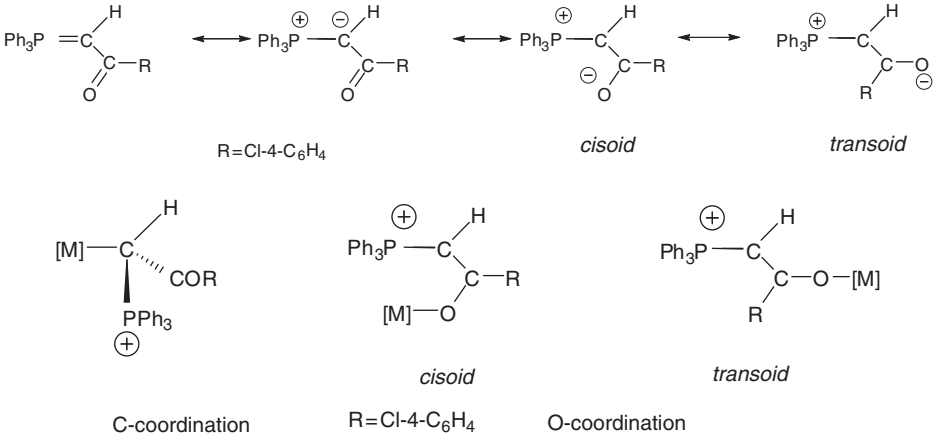


Figure 1. Resonance forms of α-keto-phosphorus ylides.

Characterization of **1–3** follows the expected patterns: (1) the carbonyl stretch appears in the IR spectra around 1505 cm^{-1}; (2) the methine proton appears in the ^{1}H-NMR spectra as a doublet with a large $^2J_{PH}$ coupling constant (around 25 Hz); and (3) the $^{31}P\{^1H\}$-NMR spectra show a single peak in each case at about 16 ppm. All these are typical for carbonyl-stabilized ylides.

3.1. *Infrared spectra*

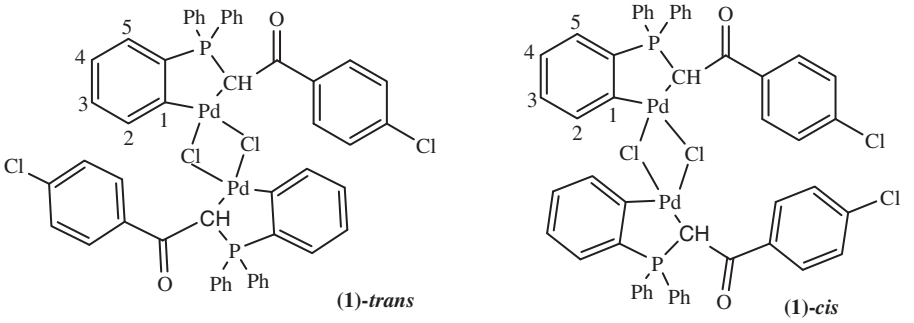
FT-IR spectra of ClBPPY show a strong peak at 1505 cm^{-1} due to carbonyl stretching. This band appears at a lower energy level compared to that found in phosphonium salts due to charge delocalization present in such compounds (figure 1).

C-coordination of the ylide leads to an increase in ν(CO) while for O-coordination a lowering in ν(CO) is expected, relative to the free ylides [35]. IR spectra of **1–3** show a strong absorption at 1618–1643 cm^{-1}, shifted to higher frequency with respect to the starting ylides, meaning that the ylides are C-bonded to palladium [35, 36]. This positive shift for ν_{CO} in the complexes indicates that the ylide is C-coordinated to Pd(II) (figure 1). The ν(P–C) are also diagnostic of the coordination at 878 cm^{-1} in the parent ylide (ClBPPY) and shift to lower frequencies for the complexes 841 (**1**), 839 (**2**), and 845 (**3**) cm^{-1}, suggesting some removal of electron density of the P–C bands.

3.2. *NMR spectra*

^{1}H-NMR for **1** shows very broad signals that cannot be easily assigned. Nevertheless, in the aromatic region of the spectrum, there are signals corresponding to orthometalated and non-orthometalated aryl rings. The components of the mixture (*cis* and *trans*) cannot be separated by fractional crystallization or by chromatography, although reactivity shows that the orthometalated complex **1** is the main component (scheme 1). This mixture of **1** can be used as starting material to synthesize derivatives.

In the ^{1}H-NMR spectrum of **1**, signals due to the methinic proton were broad (minor) or broad doublet (major). The presence of two chiral carbon centers (forming



Scheme 3. Geometric isomers for complex **1**.

diastereoisomers) in *cis* or *trans* **1** was confirmed using the ^{1}H-NMR spectra with broad signals of unequal populations for the CH and PCH groups. The ^{1}H-NMR spectra show that *cis* and *trans* complexes are obtained as two diastereoisomers. The $^{31}P\{^{1}H\}$-NMR spectra of **1** shows two sets of single peaks at 18.97 (major) and 19.41 (minor), which are shifted to a field lower than the parent ylide (16 ppm), in good agreement with the C-bonding of the ylides. The presence of two lines of different intensity on each spectrum originates from the presence of two geometric isomers for **1** (scheme 3). The metalation of a phenyl group of the PPh_3 unit is evident from the ^{1}H-NMR spectra of **1** since the resonances of the C–C(O)Ph fragment can still be observed, while the expected 6 : 3 : 6 pattern of the H*o* : H*p* : H*m* protons of PPh_3 disappears. A new pattern of signals of intensity 1 : 1 : 1 : 1 : 4 : 2 : 4 is observed, partially overlapped due to the presence of the two diastereoisomers [35, 37].

The ^{1}H- and ^{31}P-NMR spectra of **2** are in agreement with the proposed structures. ^{1}H-NMR and $^{31}P\{^{1}H\}$-NMR signals for the PCH were shifted downfield as compared to those in the free ylides, presumably due to inductive effects of the metal center. The $^{2}J_{PH}$ value for mononuclear **2** and **3** was smaller than those in the free ylides and phosphonium salts; such behavior has been observed in other C-coordinated carbonyl-stabilized phosphorus ylide complexes because the hybridization changes in the ylidic carbon (sp^2 to sp^3) in the C-coordination mode [38].

In all cases, the $[C_6H_4PPh_2CH]$ unit remains C,C-bonded to Pd, even if the reaction is performed in the presence of an excess of ligand. Complex **2** shows the PPh_3-bonded *trans* to the ylide C, in accord with the data obtained from the $^{31}P\{^{1}H\}$-NMR spectra and their comparison with related arrangements [39, 40].

^{1}H-NMR spectra of **2** and **3** show the expected resonances for all of the groups present in these molecules with no unusual features. The $^{31}P\{^{1}H\}$-NMR spectra of **2** at RT show a singlet at 15 ppm attributed to the CHP of ylide and a singlet at 32 ppm assigned to PPh_3. Both ^{1}H- and $^{31}P\{^{1}H\}$-NMR spectra show the presence of a single isomer. The $^{31}P\{^{1}H\}$-NMR spectra of **3** show a singlet at 18.95 ppm attributed to CHP. The ^{1}H-NMR spectra of **3** show one doublet at 5.14 ppm attributed to CHP.

^{1}H-NMR spectra show the resonance attributed to the H_6 of the C_6H_4 shifted strongly upfield appearing at 6.58 (**2**). This is also observed in other complexes [36, 40]; the reason for this shift is the anisotropic shielding of this proton due to the *cis* pyridine [40, 41].

Table 1. Data obtained from Suzuki cross-coupling in different conditions.

Catalyst	mmol%	Base	Solvent	Time (min)	Conversion	Yield (%)
1	0.5	Na_2CO_3	MeOH	60	20	17
1	1	Na_2CO_3	MeOH	60	32	32
1	1.5	Na_2CO_3	MeOH	60	30	29
1	2	Na_2CO_3	MeOH	60	57	53
1	2.5	Na_2CO_3	MeOH	60	78	76
2	0.5	Na_2CO_3	MeOH	60	91	90
2	1	Na_2CO_3	MeOH	60	96	94
2	1.5	Na_2CO_3	MeOH	60	100	100
2	2	Na_2CO_3	MeOH	60	100	100
2	2.5	Na_2CO_3	MeOH	60	100	100
2	1	K_2CO_3	MeOH	60	100	100
2	1	Cs_2CO_3	MeOH	60	100	97
2	1	NaOAc	MeOH	60	Trace	Trace
2	1	Et_3N	MeOH	60	57	51
2	1	K_2CO_3	THF	60	Trace	Trace
2	1	K_2CO_3	DMF	60	46	46
2	1	K_2CO_3	$C_6H_5CH_3$	60	Trace	Trace
2	1	K_2CO_3	CH_3CN	60	74	73
2	1	K_2CO_3	MeOH	30	100	100
2	1	K_2CO_3	MeOH	25	100	100
2	1	K_2CO_3	MeOH	20	100	100
2	1	K_2CO_3	MeOH	15	100	100
2	1	K_2CO_3	MeOH	10	100	96
3	0.5	Na_2CO_3	MeOH	60	Trace	Trace
3	1	Na_2CO_3	MeOH	60	Trace	Trace
3	1.5	Na_2CO_3	MeOH	60	10	8
3	2	Na_2CO_3	MeOH	60	18	17
3	2.5	Na_2CO_3	MeOH	60	40	37

3.3. *Catalytic study*

Initially, the Suzuki cross-coupling (figure 1) reactions of aryl bromides with aryl boronic acid were screened with various catalysts, bases, and solvents (table 1). The initial conditions were 60 min at 75°C, and we optimized them by changing bases and solvents. We used **3** and observed that it is not suitable for this reaction (table 1). In using **2**, we observed a very good effect (table 1). Hoping the dimer can increase the yield by having two active sites, we tested **1** with good results, but not as good as for **2**, perhaps due to lower polarity of the dimer. The observed palladium mirror indicated formation of Pd(0) during the reaction, although there is no report on palladium mirror formation in Suzuki reactions catalyzed by cyclopalladated complexes.

We tested bases that are usually used for Suzuki coupling [1–13] (table 1) and compared the results with those of Na_2CO_3, showing that inorganic bases work better than organic bases with K_2CO_3 the best. Cs_2CO_3 is often reported as the best base for Suzuki coupling [1–13], but with **2**, K_2CO_3 was better. We also tested the solvent effect on this reaction. Toluene is the most used solvent in Suzuki coupling; however, it was not a good candidate in this reaction. MeOH gives the best result.

With these optimized conditions, we optimized the reaction time showing that 10–15 min are sufficient.

According to these results, the optimum concentration of **2** was 1 mol%. The base plays a crucial role in the rate and the product distribution of the Suzuki coupling reactions.

The remarkable difference in the catalytic activity shown by **2** and **3** must result from the triphenylphosphine, which is the main difference in their structures. Based on a simple steric argument, the efficiency of **2** may be expected to be higher than that of **3** due to the bigger cone angle present at triphenylphoshine *versus* a 4-picoline center. We assume that **2** is easier to reduce to the active Pd(0) species compared with the corresponding **3** under the same conditions. The *in situ* generated Pd(0) species were probably the active catalysts.

4. Conclusion

In this study, the synthesis and characterization of orthopalladated complexes **1**–**3** of phosphorus ylides have been investigated. Cyclopalladated complexes of phosphorus ylides (**1**–**3**) are active catalysts for Suzuki reactions. Complex **2** was efficient for coupling of aryl bromide with aryl boronic acid giving biphenyl in good to excellent yields.

Acknowledgments

The author thanks the Isfahan University of Technology (IUT) Research Council and Center of Excellence in Sensor and Green Chemistry (IUT) for supporting this study.

References

[1] V. Rietling, C. Sirlin, M. Pfeffer. *Chem. Rev.*, **102**, 1731 (2002).
[2] D. Aguilar, M.A. Aragues, R. Bielsa, E. Serrano, T. Soler, R. Navarro, E.P. Urriolabeitia. *J. Organomet. Chem.*, **693**, 417 (2008).
[3] F. Lopez-Ortiz. *Curr. Org. Synth.*, **3**, 187 (2006).
[4] L.R. Falvello, S. Fernandez, C. Larraz, R. Llusar, R. Navarro, E.P. Urriolabeitia. *Organometallics*, **20**, 1424 (2001).
[5] E. Ruba, K. Mereiter, R. Schmid, K. Kerchner, E. Bustelo, M.C. Puerta, P. Valerga. *Organometallics*, **21**, 2912 (2002).
[6] J.M. O'Connor, K.D. Bunker. *J. Organomet. Chem.*, **671**, 1 (2003).
[7] K. Onitsuka, M. Nishii, Y. Matsushima, S. Takahashi. *Organometallics*, **23**, 5630 (2004).
[8] W. Petz, C. Kutschera, B. Neumuller. *Organometallics*, **24**, 5038 (2005).
[9] E. Serrano, C. Valles, J.J. Carbo, A. Lledos, T. Soler, R. Navarro, E.P. Urriolabeitia. *Organometallics*, **25**, 4653 (2006).
[10] Y. Canac, S. Conejero, M. Soleilhavoup, B. Donnadieu, G. Bertrand. *J. Am. Chem. Soc.*, **128**, 459 (2006).
[11] A. Kawachi, T. Yoshioka, Y. Yamamoto. *Organometallics*, **25**, 2390 (2006).
[12] J. Vicente, M.T. Chicote, M.C. Lagunas, P.G. Jones, E. Bembenek. *Organometallics*, **13**, 1243 (1994).
[13] T.Z. Nichele, C. Favero, A.L. Monteiro. *Catal. Commun.*, **10**, 693 (2009).
[14] C. Pan, M. Liu, L. Zhang, H. Wu, J. Ding, J. Cheng. *Catal. Commun.*, **9**, 508 (2008).
[15] J. Schwarz, V.P.W. Böhm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber. *Chem. Eur. J.*, **6**, 1773 (2000).
[16] D.J. Lapinsky, S.C. Bergmeier. *Tetrahedron Lett.*, **42**, 8583 (2001).
[17] D. Zim, A.L. Monteiro, J. Dupont. *Tetrahedron Lett.*, **41**, 8199 (2000).
[18] H. Li, Y. Wu, W. Yan. *Organomet. Chem.*, **691**, 5688 (2006).
[19] B. Basu, P. Das, M.H. Bhuiyan, S. Jha. *Tetrahedron Lett.*, **44**, 3817 (2003).
[20] H.-S. Wang, Y.-C. Wang, Y.-M. Pan, S.-L. Zhao, Z.-F. Chen. *Tetrahedron Lett.*, **49**, 2634 (2008).

[21] D. Saha, K. Chattopadhyay, B.C. Ranu. *Tetrahedron Lett*., **50**, 1003 (2009).
[22] C. Dupuis, K. Adiey, L. Charruault, V. Michelet, M. Savignac, J.-P. Genet. *Tetrahedron Lett*., **42**, 6523 (2001).
[23] I.D. Kostas, A.G. Coutsolelos, G. Charalambidi, A. Skondr. *Tetrahedron Lett*., **48**, 6688 (2007).
[24] J. Gong, G. Liu, C. Du, Y. Zhu, Y. Wu. *Organomet. Chem*., **690**, 3963 (2005).
[25] Z. Weng, L.L. Koh, T.S.A. Hor. *Organomet. Chem*., **689**, 18 (2004).
[26] A. Konovets, A. Penciu, E. Framery, N. Percina, C. Goux-Henry, D. Sinou. *Tetrahedron Lett*., **46**, 3205 (2005).
[27] J.-H. Li, Q.-M. Zhu, Y.-X. Xie. *Tetrahedron*, **62**, 10888 (2006).
[28] M. Mora, C. Jimenez-Sanchidrian, J.R. Ruiz. *J. Mol. Catal. A: Chem*., **285**, 79 (2008).
[29] D. Schonfelder, O. Nuyken, R. Weberskirch. *Organomet. Chem*., **690**, 4648 (2005).
[30] M. Joshaghani, E. Faramarzi, E. Rafiee, M. Daryanavard, J. Xiao, C. Baillie. *J. Mol. Catal. A: Chem*., **259**, 35 (2006).
[31] J. Vicente, M.T. Chicote, J. Fernandez-Baeza, J.A. Cayuelas, P.G. Jones, G.M. Sheldrick, P. Espinet. *J. Chem. Soc., Dalton Trans*., 1163 (1985).
[32] F. Ramirez, S. Dershowitz. *J. Org. Chem*., **22**, 41 (1957).
[33] K. Karami. *Inorg. Chim. Acta*, **362**, 2093 (2009).
[34] J.S. Chen, A.N. Vasiliev, A.P. Panarello, J.G. Khinast. *Appl. Catal., A*, **325**, 76 (2007).
[35] D. Aguilar, M.A. Aragues, R. Bielsa, E. Serrano, R. Navarro, E.P. Urriolabeitia. *Organometallics*, **26**, 3541 (2007).
[36] H. Koezuka, G. Matsubayashi, T. Tanaka. *Inorg. Chem*., **25**, 417 (1976).
[37] R. Navarro, E.P. Urriolabeitia. *J. Chem. Soc., Dalton Trans*., 4111 (1999).
[38] J. Vicent, M.T. Chicote, M.C. Lagunas, P.G. Jones. *J. Chem. Soc., Dalton Trans*., 2579 (1991).
[39] L.R. Falvello, S. Fernandez, R. Navarro, A. Rueda, E.P. Urriolabeitia. *Organometallics*, **17**, 5887 (1998).
[40] A.J. Deeming, I.P. Rothwell, M.B. Hursthouse, L. New. *J. Chem. Soc., Dalton Trans*., 1490 (1978).
[41] M. Kalyanasundari, K. Panchanatheswaran, V. Parthasarathi, W.T. Robinson, H. Wen. *Acta Crystallogr*., **50**, 1738 (1994).