Russian Chemical Bulletin, International Edition, Vol. 63, No. 10, pp. 2305—2308, October, 2014

Palladium(II) aminoiminophosphoranate complexes as cross-coupling catalysts*

T. A. Peganova,[a] A. M. Kalsin,[a]★ N. A. Ustynyuk,[a] and A. A. Vasil′ev[b]★

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 6471. E-mail: kalsin@ineos.ac.ru
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5328. E-mail: vasiliev@ioc.ac.ru

The Tsuji—Trost reaction between diethyl malonate and allyl acetate catalyzed by palladium(II) NPN-aminoiminophosphoranate complexes yields mono- and diallylation products in the ratios depending on the complex used. The Suzuki—Miyaura cross-coupling of 4-bromoacetophenone with phenylboronic acid catalyzed by these palladium complexes proceeds with 66—99.5% conversions.

Key words: palladium(II) aminoiminophosphoranate complexes, cross-coupling catalysts, Tsuji—Trost reaction, Suzuki cross-coupling.

In recent years, transition metal complexes with heteronuclear chelate NNN- (triazenide), NCN- (amidinate), and NPN- (aminoiminophosphoranate) ligands are topical in organometallic and coordination chemistry[1] due to ongoing search for innovative catalysts for cross-coupling applications. In this regard, the chemistry and catalytic properties of amidinate complexes are more studied[2] in contrast to complexes bearing aminophosphoranate moieties as heteronuclear (NPN) ligands. However, the latter attracts more and more attention due to their promising applications as precatalysts in a number of transformations of alkenes: cyclopropanation,[3] aziridination,[4] polymerization,[5] and oligomerization.[6] These works deal mostly with NPN-complexes of chromium, copper and nickel. Until 2009, the data on the synthesis of palladium and platinum NPN complexes were limited to only two examples, *i.e.*, ethylene-platinum complex $Cl(\eta^2-C_2H_4)Pt[Me_2P(NMe)_2]$[7] and allylpalladium complex $(\eta^3-C_3H_5)Pd[(Me_3Si)_2NP(CH_2CH=CH_2)(NSiMe_3)_2]$.[5a] In 2009, we synthesized a series of platinum and palladium NPN complexes with different auxiliary ligands $[\{Ph_2P(NC_6H_4Pr^i-p)_2\}ML_x]$ (L_x = PPh_3, Cl; NPN; C_2H_4, Cl).[8] It was found that NPN ligand has a zwitterionic structure $R_2P^+(NR'^-)_2$. Later, the molecular and electronic structure of the NPN complexes was evaluated on the example of allylpalladium and allylplatinum complexes $[\{Ph_2P(NC_6H_4R-p)_2\}M(\eta^3-C_3H_5)]$ (R = Pr^i, Me, OMe, COOEt) by X-ray diffraction and DFT calculations.[9,**] It should be noted that NPN ligands are strong σ and π donors[10] and thus can be used for the stabilization of electron-deficient organometallic complexes. Consequently, the evaluation of the catalytic activity of transition metal complexes with NPN ligands is a great challenge of the modern organic chemistry.

In the present work, we describe the catalytic performance of three recently synthesized palladium(II) NPN-complexes in the Tsuji—Trost allylation[1a,11,12] and the Suzuki—Miyaura cross-coupling.[13,14]

Results and Discussion

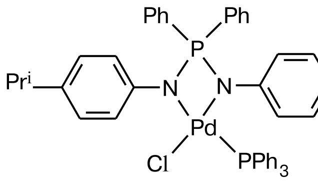
We studied catalytic activity of palladium NPN complexes **1—3** differing in the auxiliary ligands and the aryl substituents at the nitrogen atoms. Compounds **1—3** were earlier synthesized[8,9] in our research group. Their complete structure elucidation was performed by spectroscopy, microanalysis, and X-ray diffraction. In compounds **1—3**, the palladium atom is in the 2+ oxidation state and the phosphorus atom has an azaphosphorane nature and is not involved in the coordination with metal.

---

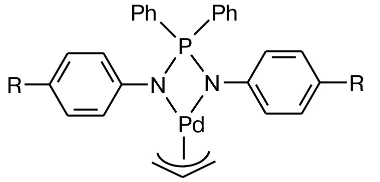
[*] Dedicated to Academician of the Russian Academy of Sciences Yu. N. Bubnov on the occasion of his 80th birthday and the 60th anniversary of the foundation of A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

[**] T. A. Peganova, M. G. Peterleitner, P. V. Petrovskii, K. A. Lyssenko, I. V. Fedyanin, O. V. Gusev, A. M. Kalsin, *Eur. J. Inorg. Chem.* (in press).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2305—2308, October, 2014.



1

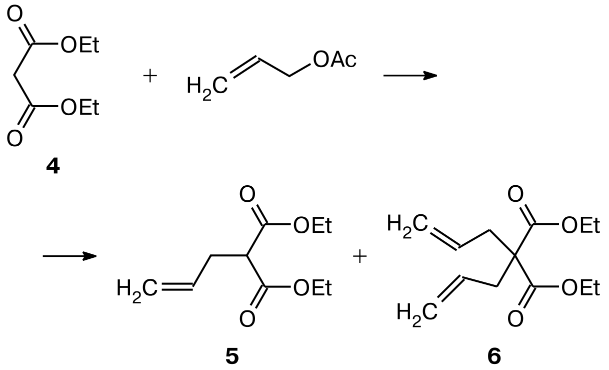


2, 3

R = OMe (**2**), COOEt (**3**)

The Tsuji—Trost reaction of diethyl malonate (**4**) with allyl acetate was performed at room temperature under phase transfer conditions in DMF using K_2CO_3 as a base following the known procedure[12a,b] (Scheme 1, Table 1).

Scheme 1



Conditions: **1**, **2** or **3** (2 mol.%), K_2CO_3, DMF, 20 °C, 15 h.

Compound **1** turned to be the most efficient catalyst among the tested complexes. It provides complete conversion of substrate **4** to give diallyl derivative **6** as a major product. On using complexes **2** and **3**, the major product is monoallyl derivative **5**, while diallylation does not occur to any significant extent and the conversion of malonate **4** was incomplete. Complex **3** bearing electron-withdrawing substituents is more active than complex **2**. Note that complex **2** can be regarded as a catalyst for selective monoallylation of diethyl malonate. The attempted prenylation of malonate **4** with less active sterically hindered prenyl acetate in the presence of complexes **1**—**3** failed (*cf.* Ref. 12a).

It should be noted that the use of the conventional phosphine- or diamidophophite-based Pd^0 catalysts in the absence of unfavorable factors gives rise to diallyl derivative **6**.[12a,d] In our case, complexes **2** and **3** show a lower catalytic performance than complex **1**. Indeed, the π allylpalladium complexes are the intermediates of the Tsuji—Trost reaction.[1a,11] We suggest that true catalysts in this reaction is the Pd^0-based complexes generated *via* the reduction of precatalysts **1**—**3** under reaction conditions. Since thiphenylphosphine unit favors the stabilization of these Pd^0 complexes, complex **1** shows the stronger catalytic effect.

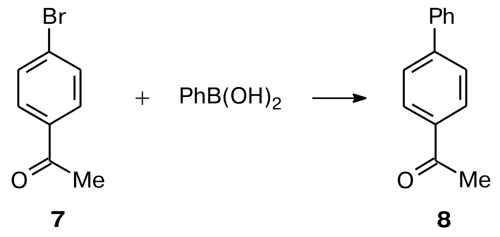
Table 1. Palladium catalyzed Tsuji—Trost allylation of diethyl malonate **4** with allyl acetate

Catalyst	Reaction mixture composition* (%)		
	4	**5**	**6**
1	0	22	78
2	23	77	0
3	1	91	8

* GC data.

Compounds **1**—**3** were also studied as catalysts for Suzuki—Miyaura cross-coupling[13,14] of highly reactive 4-bromoacetophenone (**7**) with phenylboronic acid. The reaction was carried out under typical aqueous Suzuki—Miyaura conditions[15] in 1,2-dimethoxyethane in the presence of Na_2CO_3 as a base (Scheme 2). This procedure accommodates a wide range of bromo- and iodoarenes as well as arylboronic acids. In our reactions catalyzed by complex **1**, the yield of biaryl **8** was almost quantitative; however, on going to complexes **2** and **3** the conversions of bromide **7** were noteably below 100%. In all cases, the precipitation of palladium black is observed indicating cessation of the reaction. This fact suggests both the decomposition of complexes **1**—**3** and the absence of the species capable of palladium stabilizing in the reaction media. Thus, compounds of the type of complexes **1**—**3** though being able to catalyze the Suzuki—Miyaura cross-couplings cannot be regarded as powerful catalysts.

Scheme 2



Catalyst	Yield of **8** (%)
1	99.5
2	66
3	86

Conditions: **1**, **2** or **3** (3 mol.%), Na_2CO_3, 1,2-dimethoxyethane, water, 90 °C, 6 h.

In summary, we first examined the catalytic efficiency of Pd^{II} aminoiminophosphoranate complexes in the Tsuji—Trost allylation and Suzuki—Miyaura cross-coupling reactions. The moderate product yields can be explained by the fact that these reactions should be favored by the Pd^0-based catalytic systems containing ligands effectively stabilizing the palladium intermediates in the solutions. However, the obtained results are of interest for fundamental understanding of the cross-coupling processes. Finally, the possibility of raising the efficiency of complexes **1**—**3** by their use in combination with other stabilizing ligands cannot be excluded.

Experimental

GC analyses with flame ionization detection were performed with a Chrom-5 chromatograph (the injector and detector temperatures were 250 °C), capillary column (0.2×25000 mm) with SE-30; the thermostat temperature was programmed as follows: 120→230 °C for the allylation of diethyl malonate or 150→250 °C for the cross-coupling of 4-bromoacetophenone with phenylboronic acid, heating rate of 10—15 deg min^{-1}, carrier gas was nitrogen. The composition of the mixtures was calculated using a normalization method. The solvents were distilled prior to use. Commercially available reagents were used as purchased. Complexes **1**—**3** were synthesized by the known procedures.[8,9]

Diethyl 2-allylmalonate (5) and diethyl 2,2-diallylmalonate (6). A Schlenk tube equipped with a magnetic stirring bar and a rubber septum was charged with diethyl malonate **4** (80 mg, 0.5 mmol) and DMF (1 mL). The mixture was evacuated/refilled three times with argon. Then complex **1**, **2** or **3** (0.01 mmol) was added and the mixture was stirred for 5 min. Allyl acetate (125 mg, 1.25 mmol, ~0.15 mL) was added. After 10 min stirring, freshly powdered K_2CO_3 (207 mg, 1.5 mmol) was added. After each opening, the flack was evacuated and refilled with argon. The mixture was stirred at ~20 °C for 15 h. The aliquot of the reaction mixture was treated with water, extracted with diethyl ether, and analyzed by GC. The GC chromatograms contained only peaks of compounds **4**—**6**. It was suggested that under mild reaction conditions compounds **4**—**6** did not undergo resinification and cleavage of the ester groups; therefore, the conversion of the starting compound **4** was considered equal to the yields of the products **5** and **6**. The retention times for compounds **5** and **6** coincided with τ_{ret} of the reference samples, whose structures were earlier confirmed in the similar reactions.[12a,d] The compositions of the reaction mixtures obtained using different catalysts are given in Table 1.

4-Acetylbiphenyl (8). The reactions were carried out in a two-neck flask equipped with a rubber septum and a condenser connected to a vacuum line. According to the earlier described procedure,[15] complex **1**, **2** or **3** (0.015 mmol) was added to a deaerated solution of 4-bromoacetophenone **7** (100 mg, 0.5 mmol) in 1,2-dimethoxyethane (2 mL) and the mixture was stirred for 30—40 min under argon. Phenylboronic acid was added (67 mg, 0.55 mmol) and the mixture was carefully evacuated/refilled two-times with argon. Then, a freshly prepared deaerated solution of Na_2CO_3 (0.27 g) in water (1.5 mL) was added *via* syringe. Heating the reaction mixture to reflux caused the precipitation of palladium black. The mixture was refluxed for 6 h, cooled, diluted with water, and extracted with toluene. After drying with $CaCl_2$, the extracts were analyzed by GC. The GC chromatograms contained predominantly peaks of compounds **7** and **8** (the retention times coincided with the retention times of the reference samples). In some cases, small amounts of biphenyl (the product of homocoupling of phenylboronic acid, which was discarded on GC data calculations) were detected. It was assumed that compounds **7** and **8** are chemically stable and do not undergo resinification upon reaction, therefore, the yield of compound **8** was considered equal to the conversion of the starting compound **7** (see Scheme 2).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 14-03-00345 and 08-03-00086).

References

1. (a) B. M. Trost, D. L. van Vranken, *Chem. Rev.*, 1996, **96**, 395; (b) M. Witt, H. W. Roesky, *Chem. Rev.*, 1994, **94**, 1163; (c) V. G. Gibson, S. K. Spitzmesser, *Chem. Rev.* 2003, **103**, 283.
2. (a) J. Barker, M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219; (b) F. T. Edelmann, *Coord. Chem. Rev.,* 1994, **137**, 403; (c) H. Nagashima, H. Kondo, T. Hayashida, Y. Yamaguchi, M. Gondo, S. Masuda, K. Miyazaki, K. Matsubara, K. Kirchner, *Coord. Chem. Rev.*, 2003, **245**, 177; (d) D. A. Kissounko, M. V. Zabalov, G. P. Brusova, D. A. Lemenovskii, *Russ. Chem. Rev.*, 2006, **75**, 351.
3. (a) B. F. Straub, P. Hofmann, *Angew. Chem., Int. Ed.*, 2001, **40**, 1288; (b) B. F. Straub, I. Gruber, F. Rominger, P. Hofmann, *J. Organomet. Chem.*, 2003, **684**, 124; (c) B. F. Straub, F. Rominger, P. Hofmann, *Organometallics*, 2000, **19**, 4305.
4. N. Nebra, C. Lescot, P. Dauban, S. Mallet-Ladeira, B. Martin-Vaca, D. Bourissou, *Eur. J. Org. Chem.*, 2013, 984.
5. (a) W. Keim, R. Appel, A. Storeck, C. Kruger, R. Goddard, *Angew. Chem., Int. Ed.*, 1981, **20**, 116; (b) V. M. Mohring, G. Fink, *Angew. Chem., Int. Ed.*, 1985, **24**, 1001; (c) R. Schubbe, K. Angermund, G. Fink, G. Goddard, *Macromol. Chem. Phys.*, 1995, **196**, 467; (d) R. L. Stapleton, J. Chai, N. J. Taylor, S. Collins, *Organometallics*, 2006, **25**, 2514; (e) S. Collins, T. Ziegler, *Organometallics*, 2007, **26**, 6612; (f) R. Vollmerhaus, P. Shao, N. J. Taylor, S. Collins, *Organometallics*, 1999, **18**, 2731; (g) R. Tomaszewski, R. Vollmerhaus, A. Al-Humydi, Q. Wang, N. J. Taylor, S. Collins, *Can. J. Chem.*, 2006, **84**, 214; (h) S. Li, D. Cui, D. Li, Z. Hou, *Organometallics*, 2009, **28**, 4814.
6. (a) K. Albahily, V. Fomitcheva, S. Gambarotta, I. Korobkov, M. Murugesu, S. I. Gorelsky, *J. Am. Chem. Soc.*, 2011, **133**, 6380; (b) K. Albahily, Y. Shaikh, E. Sebastiao, S. Gambarotta, I. Korobkov, S. I. Gorelsky, *J. Am. Chem. Soc.*, 2011, **133**, 6388; (c) K. Albahily, S. Licciulli, S. Gambarotta, I. Korobkov, R. Chevalier, K. Schuhen, R. Duchateau, *Organometallics*, 2011, **30**, 3346; (d) K. Albahily, V. Fomitcheva, Y. Shaikh, E. Sebastiao, S. I. Gorelsky, S. Gambarotta, I. Korobkov, R. Duchateau, *Organometallics*, 2011, **30**, 4201.
7. O. J. Scherer, A. Nahrstedt, *Angew. Chem., Int. Ed.*, 1979, **18**, 234.
8. T. A. Peganova, A. V. Valyaeva, A. M. Kalsin, P. V. Petrovskii, A. O. Borissova, K. A. Lyssenko, N. A. Ustynyuk, *Organometallics*, 2009, **28**, 3021.

9. A. M. Kalsin, T. A. Peganova, A. V. Valyaeva, K. A. Lyssenko, *9th Congr. Organomet. Chem. of the Ital. Chem. Soc. COGICO 9* (Firenze, June 8—11, 2010), Firenze, P18.
10. P. J. Bailey, K. J. Grant, S. Parsons, *Organometallics*, 1998, **17**, 551.
11. (a) B. M. Trost, *Acc. Chem. Res.*, 1980, **13**, 385; (b) U. Kazmaier, M. Pohlman, in *Metal-Catalyzed Cross-Coupling Reactions*, Eds A. de Meijere, F. Diedrich, Wiley-VCH, Weinheim, 2004, p. 531.
12. (a) A. A. Vasil´ev, S. E. Lyubimov, E. P. Serebryakov, V. A. Davankov, M. I. Struchkova, S. G. Zlotin, *Russ. Chem. Bull.* (*Int. Ed.*), 2010, **59**, 605 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2010, 592]; (b) A. A. Vasil´ev, S. E. Lyubimov, E. P. Serebryakov, V. A. Davankov, S. G. Zlotin, *Mendeleev Commun.*, 2012, **22**, 39; (c) A. A. Vasil´ev, I. V. Kuchurov, S. G. Zlotin, *Mendeleev Commun.*, 2013, **23**, 84; (d) A. A. Vasil´ev, S. G. Zlotin, *Mendeleev Commun.*, 2014, **24**, 23; (e) K. N. Gavrilov, I. V. Chuchelkin, S. V. Zheglov, A. A. Shiryaev, O. V. Potapova, I. M. Novikov, *Russ. Chem. Bull.* (*Int. Ed.*), 2012, **61**, 1925 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2012, 1910]; (f) K. N. Gavrilov, I. M. Novikov, I. V. Chuchelkin, S. V. Zheglov, M. S. Levkina, A. N. Volov, I. A. Zamilatskov, *Russ. Chem. Bull.* (*Int. Ed.*), 2013, **62**, 2628 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2013, 2628].
13. (a) N. Miyaura, A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (b) A. Suzuki, in *Metal-Catalyzed Cross-Coupling Reactions*, Eds F. Diederich, P. J. Stang, Wiley-VCH, Weinheim, 1998, p. 49; (c) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron*, 2002, **58**, 9633; (d) R. F. Bellina, A. Carpita, R. Rossi, *Synthesis*, 2004, 2419; (e) R. Martin, S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461; (f) F. Alonso, I. P. Beletskaya, M. Yus, *Tetrahedron*, 2008, **64**, 3047; (g) J. M. Serrano-Becerra, D. Morales-Morales, *Curr. Org. Synth.*, 2009, **6**, 169.
14. (a) A. A. Vasil´ev, V. Yu. Aleksenko, D. V. Aleksanyan, V. A. Kozlov, *Mendeleev Commun.*, 2013, **23**, 344; (b) A. Yu. Kryukov, S. Yu. Davydov, I. M. Izvol´skii, E. G. Rakov, N. V. Abramova, V. I. Sokolov, *Mendeleev Commun.*, 2012, **22**, 237; (c) I. M. Aladzheva, O. V. Bykhovskaya, Yu. V. Nelyubina, Z. S. Klemenkova, O. I. Artyushin, P. V. Petrovskii, A. A. Vasil´ev, I. L. Odinets, *Inorg. Chim. Acta*, 2013, **395**, 203; (d) V. A. Kozlov, D. V. Aleksanyan, Yu. V. Nelyubina, K. A. Lyssenko, P. V. Petrovskii, A. A. Vasil´ev, I. L. Odinets, *Organometallics*, 2011, **30**, 2920; (e) Yu. V. Ioni, S. E. Lyubimov, A. A. Korlyukov, M. Yu. Antipin, V. A. Davankov, S. P. Gubin, *Russ. Chem. Bull.* (*Int. Ed.*), 2012, **61**, 1825 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2012, 1810]; (f) L. A. Bulygina, N. S. Khrushcheva, S. M. Peregudova, V. I. Sokolov, *Russ. Chem. Bull.* (*Int. Ed.*), 2012, **61**, 1998 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2012, 1980]; (g) V. V. Ermolaev, D. M. Arkhipova, L. Sh. Nigmatullina, I. Kh. Rizvanov, V. A. Milyukov, O. G. Sinyashin, *Russ. Chem. Bull.* (*Int. Ed.*), 2013, **62**, 657 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2013, 656]; (h) A. A. Vasil´ev, M. I. Struchkova, A. B. Sheremetev, F. S. Levinson, R. V. Varganov, K. A. Lyssenko, *Russ. Chem. Bull.* (*Int. Ed.*), 2011, **60**, 2306 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2011, 2262].
15. (a) N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.*, 1981, **11**, 513; (b) B. I. Alo, A. Kandil, P. A. Patil, M. J. Sharp, M. A. Siddiqui, V. Snieckus, *J. Org. Chem.*, 1991, **56**, 3763; (c) S. I. Sviridov, A. A. Vasil´ev, N. L. Sergovskaya, M. V. Chirskaya, S. V. Shorshnev, *Tetrahedron*, 2006, **62**, 2639.

Received June 6, 2014;
in revised form July 7, 2014