ORGANOMETALLICS

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Hybrid Thiophosphoryl−Benzothiazole Palladium SCN-Pincer Complexes: Synthesis and Effect of Structure Modifications on Catalytic Performance in the Suzuki Cross-Coupling

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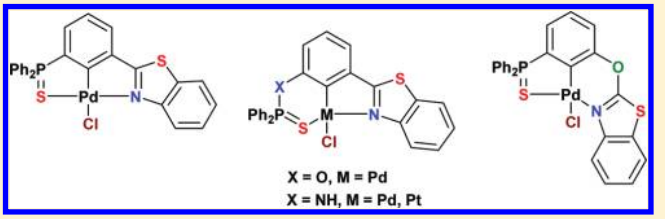
Supporting Information

ABSTRACT: The novel hybrid pincer-type ligands **3**, **6**, **9**, and **11**, bearing, as donating sites, a thiophosphoryl group and an imine moiety of the benzothiazole ring bound either directly to the central benzene core or attached to the latter one via O or NH linkers, undergo direct cyclopalladation at the C(2) position of the central benzene core in reaction with $(PhCN)_2PdCl_2$ (MeCN or PhCN as a solvent, 80−120 °C) to afford 5,5- and 5,6-membered κ^3-SCN-palladium pincer complexes **12**−**15** in good to high yields. Direct cycloplatination with the related platinum precursor was successful only in the case of *N*-[3-(1,3-benzothiazol-2-yl)phenyl]-*P*,*P*-diphenylthiophosphinic acid amide **9**. The Pd(II) complexes **12**−**15** were found to be highly active (pre)catalysts for the Suzuki cross-coupling of a range of electronically varied aryl bromides with phenylboronic acid. The most active complex, **14a**, also promoted efficiently the coupling of chloroacetophenone, ranking among the best pincer complexes suggested for this reaction.



INTRODUCTION

Palladium-catalyzed cross-coupling reactions have greatly improved the possibilities for chemists to create sophisticated chemicals, and it is not surprising that the Nobel Prize in Chemistry in 2010 was awarded to R. F. Heck, E. Negishi, and A. Suzuki, who developed this area of organic synthesis. Nevertheless, among a plethora of palladium-catalyzed cross-couplings the Suzuki reaction, which represents the coupling of an aryl halide with an organoboron reactant and is perceived to be one of the most powerful methods for $C_{aryl}-C_{aryl}$ bond construction, occupies a special place.[1,2] An utmost interest that this reaction has acquired for both academic and industrial purposes is explained by easy handling of the boron precursors (stability and nontoxicity), relatively mild reaction conditions, tolerance to a wide range of functionalities, and facility of workup. One of the main challenges in this reaction still pertains to the use of less reactive but cheaper and available aryl chlorides instead of bromo- and iodoarenes, relatively easily introduced to this cross-coupling under the catalytic action of a wide range of organopalladium species. According to the literature data, very good results for the coupling of chloroarenes were achieved using different monopalladacycles or, more precisely, their adducts with trivalent phosphorus derivatives.[3] In this respect, application of *pincer complexes* (including nonsymmetrical ones),[4−6] i.e., those having two fused metallacycles resulting from stabilization of a metal−carbon bond by two ancillary coordinating arms, could avoid the use of any additional ligand. Noteworthy, the best results for coupling of chloroarenes were achieved (but mainly the Heck reaction) just with phosphorus-containing pincer complexes or with palladacycles modified by carbenes. That was related to the extra stability provided by these ligands toward the low-ligated catalytically active Pd(0) species involved in catalytic cycle.[5] A literature survey has revealed a few pincer palladium complexes **I**−**VIII** (Figure 1) that displayed catalytic activity when aryl chlorides were used as substrates.[6b,e,f,7−11] Concerning the structures of these palladacycles, one may note that most of them bear at least one P(III)-donating moiety (phosphinite, aminophosphine, or phosphine). A high catalytic efficiency of the only divergent NCN complex **VII**[6f] apparently stems from the hemilabile coordination of the ligand that facilitates generation of active Pd(0) species.

Directed by our interest in unsymmetrical pincer complexes with organothiophosphorus ligands, we have elaborated several palladium pincer systems and thoroughly explored their catalytic performance in the Suzuki reaction as an appropriate activity evaluation benchmark (Figure 2). Thus, starting from 5,5-membered SCS′ thiocarbamoyl−thiophosphoryl palladacycles **IX**[12] we showed in principle an ability of pincer complexes with a P═S coordinating arm to promote the Suzuki cross-coupling of

Received: October 25, 2010
Published: May 04, 2011

bromoarenes with phenylboronic acid. Further developed hybrid palladium pincer complexes **X**−**XII**[13−15] with two fused metallacyles of unequal sizes were found to be more active than compounds **IX**. At the same time, SCN palladacycles **XII** bearing two coordination sites of completely different nature with a soft sulfur and hard nitrogen donor atoms appeared to have the highest catalytic activity in this range and even promoted the Suzuki cross-coupling of aryl chlorides with $PhB(OH)_2$, although the yield of a biphenyl product was only about 20%.[15]

Encouraged by these preliminary findings, we intended to design a new hybrid pincer system of SCN type combining a thiophosphoryl moiety with a bulky imine functionality, incorporated, for example, into a benzothiazole fragment. The choice of such heterocyclic moiety was dictated in particular by a convenient synthetic transformation of previously elaborated hybrid thioamide ligands, e.g., as those in complexes **IX** and **XI**, or their precursors into the corresponding benzothiazole derivatives via oxidative cyclization. Moreover, monocyclic benzothiazole-based palladium complexes were shown to possess high catalytic activity in various chemical processes, including Heck vinylation of aryl iodides,[16] and, in addition, a symmetrical NCN-pincer platinum complex with a (bis)benzothiazolylbenzene ligand exhibited valuable luminescent properties.[17] Moreover, adjusting the position of additional linkers between the donor groups and a central benzene core could result in hybrid 5,6-membered pincer complexes with either an imine- or thiophosphoryl-containing six-membered metallacycle. Such a structure variation would provide the possibility of deeper insight into the influence of structural modifications on the catalytic activity of SCN-pincer complexes. Of particular interest is the opportunity to estimate whether O−P═S and NH−P═S derivatives could compete with the above-mentioned phosphinite (**I**, **II**, **VI**, **VIII**)- and (amino)phosphine (**III**−**V**)-based pincer complexes, especially as organothiophosphorus(V) derivatives are much easier to handle.

Herein, we report on the convenient synthetic approach to a series of novel hybrid pincer ligands having thiophosphoryl and benzothiazole coordinating arms that are either directly bound to the central benzene ring or connected with it via an additional linker and their 5,5- and 5,6-memebered palladium SCN-pincer complexes. These complexes were proved to be excellent (pre)catalysts for the Suzuki cross-coupling of aryl bromides and showed, to the best of our knowledge, second-place activity among pincer complexes in the reaction with activated aryl chlorides implied in terms of a combination of the reaction time, conversion, and catalyst loading. Some mechanistic aspects of the catalytic processes are discussed.

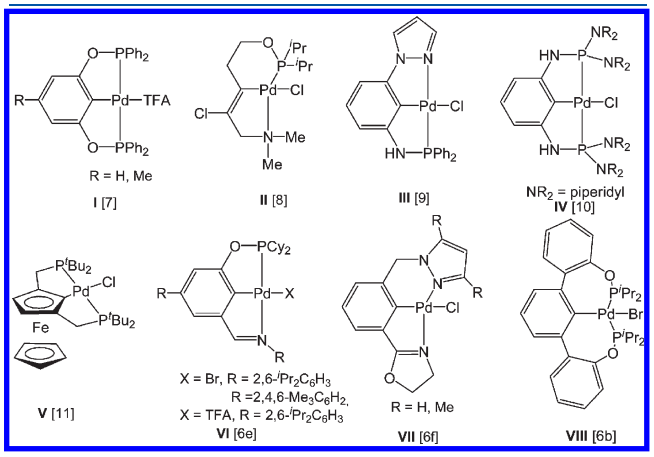


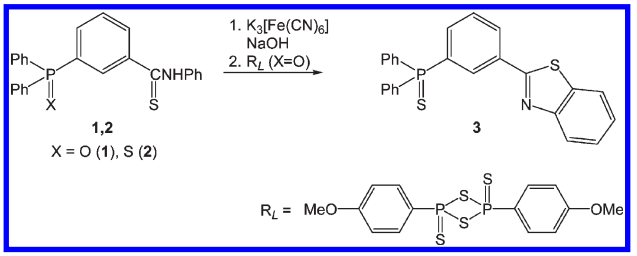
Figure 1. Pincer complexes promoting the Suzuki cross-coupling of chloroarenes with phenylboronic acid.

RESULTS AND DISCUSSION

Synthesis of Ligands. The first ligand of this series with thiophosphoryl and benzothiazole coordinating arms directly bound to the central benzene ring was obtained by the oxidative cyclization[18] of secondary *N*-arylthioamides **1** or **2** (previously used in the synthesis of complex **IX**[12]), having either a phosphoryl or a thiophosphoryl group, under the action of potassium ferricyanide in aqueous sodium hydroxide (the Jacobson synthesis). Evidently, harnessing of the phosphoryl-substituted thioamide **1** (X = O, method A) as a precursor in the synthesis of **3** required one more thionation step, whereas its *S*,*S*-analogue **2** (X = S, method B) provided the desired ligand in 54% yield in only one step while retaining the P═S moiety (Scheme 1).

To obtain the pincer ligands with a thiophosphoryl arm "elongated" with −O− and −NH− bridges, we devised a synthetic approach based on thiophosphorylation of *meta*-benzothiazole-substituted phenol and aniline as suitable precursors, respectively. Therefore, the oxidative cyclization of 3-methoxy-*N*-phenylbenzenecarbothioamide **4**[14] with $K_3[Fe(CN)_6]$ followed by demethylation afforded phenol predecessor **5**, while the one-pot condensation of 3-nitrobenzoic acid chloride generated *in situ* and aminothiophenol followed by reduction of the

Scheme 1. Synthesis of 2-[3-(Diphenylthiophosphoryl)-phenyl]-1,3-benzothiazole, 3



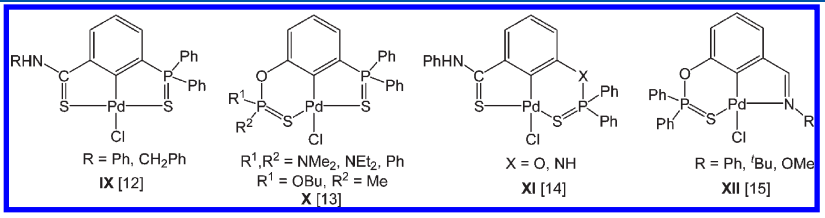
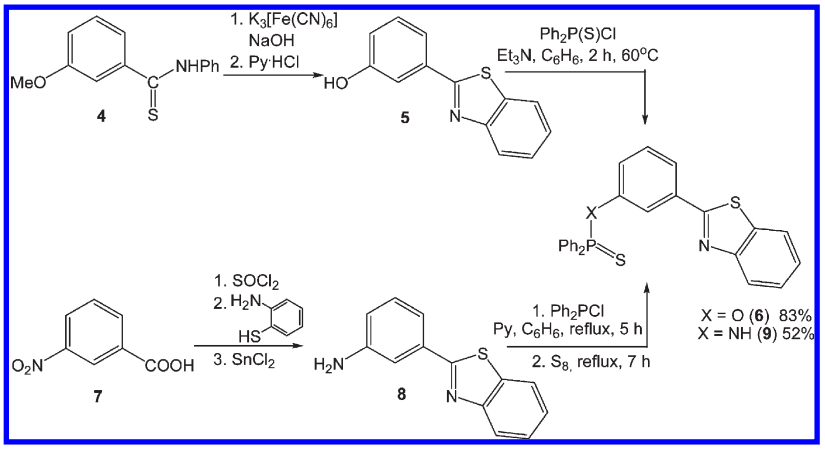


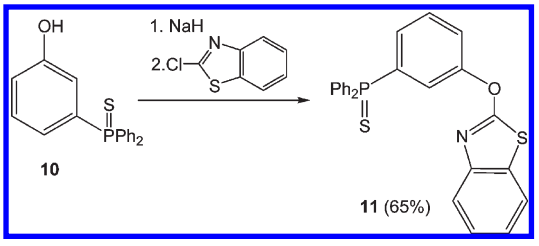
Figure 2. Hybrid pincer complexes with a thiophosphoryl coordinating arm promoting the Suzuki cross-coupling of bromoarenes with phenylboronic acid.

dx.doi.org/10.1021/om101012r |*Organometallics* 2011, 30, 2920–2932

Scheme 2. Synthesis of Thiophosphoryloxy- and Thiophosphorylamino-Substituted SCN-Pincer Ligands 6 and 9 with Benzothiazole Moieties



Scheme 3. Synthesis of 2-[3-(Diphenylthiophosphoryl)-phenoxy]-1,3-benzothiazole, 11



nitro group with tin(II) chloride provided the corresponding aniline **8** (Scheme 2). Further (thio)phosphorylations under appropriate conditions depending on the substrate nature gave the desired ligands **6** and **9** in good yields.

Finally, to introduce an oxygen bridge between the benzothiazole heterocycle and benzene core, the reaction of the sodium salt of thiophosphoryl-substituted phenol **10**[13] with 2-chlorobenzothiazole was used (Scheme 3).

The structures of the ligands obtained were unambiguously confirmed by multinuclear NMR (^{31}P, ^{1}H, ^{13}C) and IR spectroscopy data. Thus, the ^{31}P NMR spectra of **3** and **11** show singlet signals at ca. 42 ppm characteristic for phosphine sulfides, while the phosphorus resonances for **6** and **9** are observed at 83 and 53 ppm, respectively, i.e., the regions typical for the signals of P atoms of thiophosphoryloxy and thiophosphorylamino groups. The presence of several phenyl rings in the molecules of compounds **3**, **6**, **9**, and **11** complicates the interpretation of the ^{1}H NMR spectra in the region of aromatic proton signals; however, all the carbon resonances in the ^{13}C NMR spectra can be easily identified (see Experimental Section). Moreover, in the IR spectra of all the ligands one may note the absorption bands at 628−649 cm^{-1} corresponding to the P═S bond stretching vibrations. The molecular structure of compound **3** was also elucidated by X-ray diffraction analysis (Figure 3). According to the results, the geometric parameters of the thiophosphorylbenzene moiety in **3** are very close to those in 3-diphenylthiophosphoryloxy(amino)benzoic acid thioamides, i.e., free ligands of complexes **XI**.[14] The major difference in their molecular geometries concerns the disposition of the C−S functionality

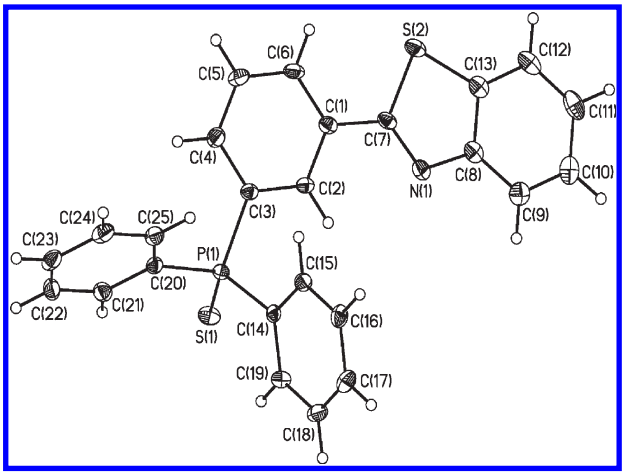


Figure 3. General view of ligand **3** in a representation of atoms by thermal ellipsoids (p = 50%).

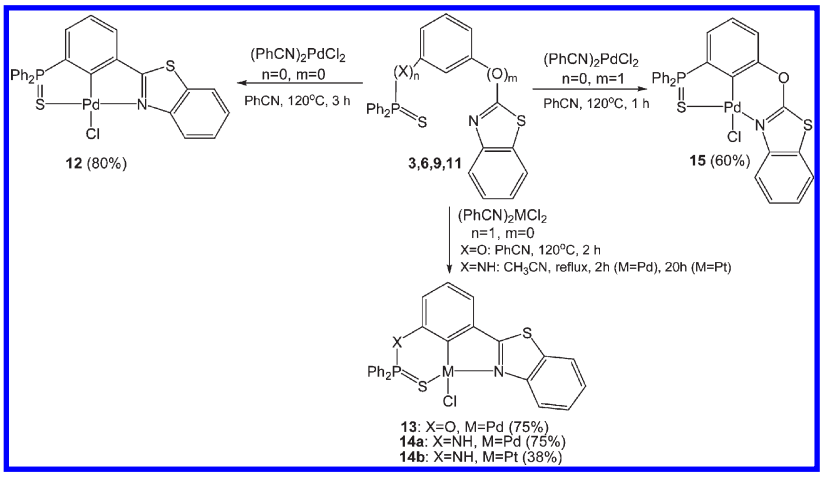
relative to the benzene core: in ligand **3** it deviates in the same direction as the P═S group (the pseudotorsion angle SPCS′ is 99.0(1)°) with an angle between the benzothiazole ring and central benzene core of 7.5(1)°, while in the above thiophosphoryl−thioamide analogues these groups deviate in opposite directions from the benzene core.

Synthesis and Characterization of Pincer Complexes. In reaction with $(PhCN)_2PdCl_2$, ligands **3**, **6**, **9**, and **11** underwent direct cyclopalladation at the C(2) position of the central benzene ring, providing the corresponding 5,5- or 5,6-membered SCN-pincer complexes **12**−**15** in good to high yields (60−89%) (Scheme 4). The most reactive thiophosphorylamino-substituted derivative, **9**, afforded palladacycle **14a** in 89% yield upon refluxing in acetonitrile for 2 h. At the same time, substantially higher temperature (heating in benzonitrile at 120 °C for 1−3 h) was required to accomplish cyclopalladation of the other ligands **3**, **6**, and **11**. In attempting to perform cycloplatination of the synthesized compounds with the related platinum precursor, we managed to obtain only complex **14b** having a NH-P═S coordination arm, with a yield not exceeding 40%.

Complexes **12**−**15** are yellow crystalline solids, air and moisture stable in the solid state. Moreover, palladium

dx.doi.org/10.1021/om101012r |*Organometallics* 2011, 30, 2920–2932

Scheme 4. Synthesis of SCN-Pincer Complexes 12−15 Having Thiophosphoryl and Benzothiazole Coordinating Arms



thiophosphoryl−benzothiazole pincer complexes are characterized with rather high thermal stability and do not undergo decomposition up to ∼250 °C, while the decomposition point for platinum complex **14b** is essentially lower (180 °C).

The structures of the complexes obtained were assigned on the basis of ^{31}P, ^{1}H, and ^{13}C NMR and IR spectroscopy. The signals of phosphorus atoms of **12** and **15** in the ^{31}P NMR spectra appeared to be strongly deshielded ($\Delta\delta$ = 22 and 15 ppm, respectively) upon complexation of phosphine sulfide moieties. Similarly, the phosphorus resonances of OPS and NHPS groups in **13** and **14** are shifted by ∼7 ppm compared to the signals of free ligands, indicating the coordination of the metal ion by these fragments, although the direction of shifting is opposite to that of **12** and **15**. The integral intensities of the proton signals in the ^{1}H NMR spectra of **12**−**15** are reduced by 1H, confirming the occurrence of metalation. In the ^{13}C NMR spectra of **14a**, the signal of the C2 atom, at which the metalation occurred, is characterized with the greatest downfield shift (16 ppm) and an increase in $^{3}J_{CP}$ (by ∼2 Hz), although the resonances of other carbon atoms (e.g., C1 and C7) are also indicative of the complex formation (see Experimental Section). A lower frequency shift of the absorption bands corresponding to ν(P═S) compared to those of the free ligands provides additional evidence for the coordination of the metal ion by these groups.

Furthermore, the structures of complexes **12** (crystallosolvate with 0.5·CH_2Cl_2), **13**, and **15** (crystallosolvate with CH_2Cl_2) were unambiguously confirmed by the single-crystal X-ray diffraction study. In all cases, the palladium atom appeared to be bonded with the nitrogen atom of the benzothiazole moiety (Figures 4−6); such a behavior has been already reported for the Pt(II) pincer complexes of bis(benzothiazolyl)benzene.[17]

The geometrical parameters of the palladacycles involving the PS and NC functionalities are different, although lie within the ranges observed earlier for similar systems.[12,14,15] In particular, the five-membered NC ring (5NC) in **12** is planar within 0.02 Å, like those in the above-mentioned platinum complex with bis(benzothiazolyl)benzene;[17] a similar ring in **13** is a flattened envelope with the C(2) atom deviating by 0.16(1) Å. The conformation of the 5PS palladacycles in **12** and **15** is an envelope with the S(1) atom deviating by 0.58(1) and 0.89(1) Å, respectively. For comparison, this deviation in the case of

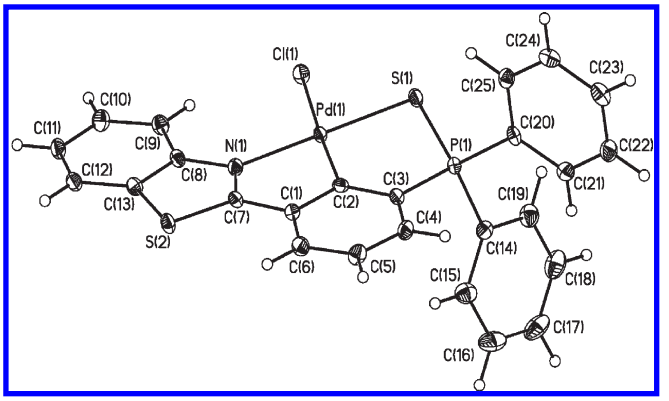


Figure 4. General view of complex **12** in a representation of atoms by thermal ellipsoids (p = 50%). The interatomic distances Pd−X (Å) are Pd(1)−N(1) 2.0970(19), Pd(1)−C(2) 1.968(2), Pd(1)−Cl(1) 2.3986(6), Pd(1)−S(1) 2.2930(6).

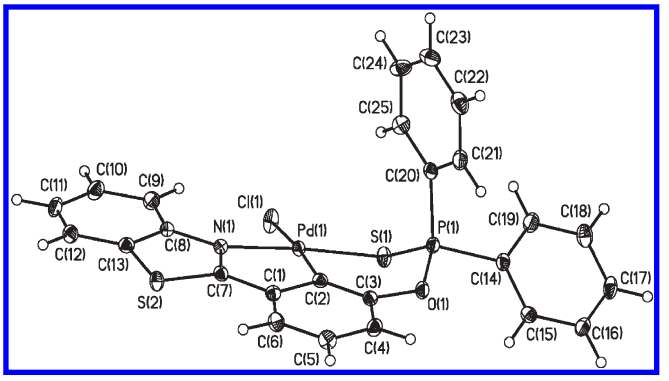


Figure 5. General view of complex **13** in a representation of atoms by thermal ellipsoids (p = 50%). The interatomic distances Pd−X (Å) are Pd(1)−N(1) 2.0780(13), Pd(1)−C(2) 2.0187(16), Pd(1)−Cl(1) 2.3987(5), Pd(1)−S(1) 2.2879(5).

SCS′-pincer complexes **IX**[12] is 0.24−0.28 Å. The six-membered rings in **13** and **15** are in a half-chair (PS cycle with the S(1) and P(1) atoms deviating by 0.38(1) and −0.53(1) Å) or a twist (NC cycle with the N(1) and C(7) atoms deviating by 0.92(1) and

0.69(1) Å) conformation, respectively. It should be mentioned that in the palladium complex with a similar (pyridine-based) 6NC fragment[19] the corresponding N and C atoms deviate by 0.97−0.98 and 0.73−0.79 Å, whereas in the case of the aliphatic NC substituent these deviations are even more pronounced (see, e.g., ref 20). Therefore, the benzothiazole group makes the corresponding NC palladacycle moiety less flexible, although affecting only slightly the binding with the second functionality. The latter is also reflected in the coordination polyhedron of the palladium atom. In all cases, the Pd(1) atom is characterized by a distorted square-planar configuration with folding along the S(1)···N(1) line. The C(2)Pd(1)Cl(1) angles, dihedral angles between the Pd(1)C(2)S(1)N(1) and Pd(1)Cl(1)S(1)N(1) planes, and deviations of the chlorine atoms—the parameters describing this distortion of the square-planar configuration—vary in the narrow ranges of 171.3(1)−176.3(1)°, 3.7(1)−10.2 (1)°, and 0.15(1)−0.43(1) Å, respectively; these values are typical for 5,5- and 5,6-membered pincer palladium complexes.[12,14,15]

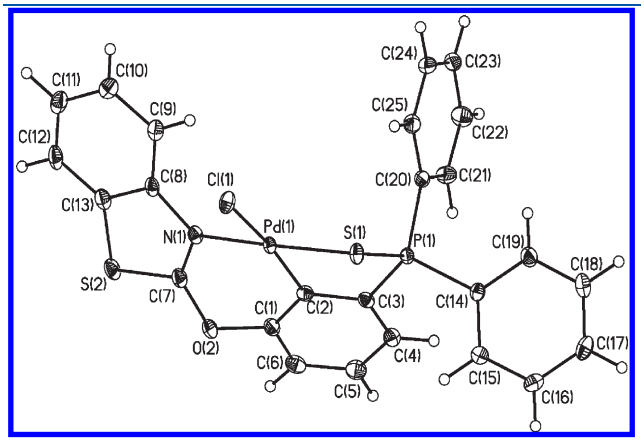


Figure 6. General view of complex **15** in a representation of atoms by thermal ellipsoids (p = 50%). The interatomic distances Pd−X (Å) are Pd(1)−N(1) 2.0644(13), Pd(1)−C(2) 1.9858(16), Pd(1)−Cl(1) 2.3946(4), Pd(1)−S(1) 2.3154(4).

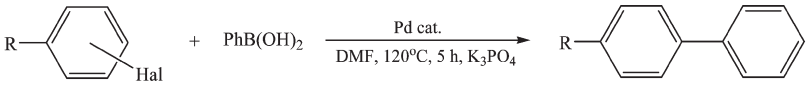
The supramolecular organizations of complexes **12**, **13**, and **15** are completely different, partly owing to the presence of solvated dichloromethane in the crystals of **12** and **15**. Thus, pincer molecules in **12** form infinite chains via rather strong S(1)···S(2) interaction (S···S 3.299(2) Å). These associates are held together by a weaker $\pi\cdots\pi$ interaction between the benzothiazole moiety and the benzene core (C···C 3.389(3) Å) and a number of C−H···Cl and C−H···π contacts. There is also a very weak C−H···Pd contact (Pd···C 3.569(2) Å) involving the dichloromethane molecule. The molecules of complex **13** are assembled into a 3D framework by means of C−H···π, C−H···S, and C−H···Cl interactions. In **15**, in addition to these three types of contacts, C═S···Cl (S···Cl 3.357(2) Å) and $\pi\cdots\pi$ (the smallest C···C distance between two benzothiazole cycles is 3.345(3) Å) interactions are observed between the molecules of the complex. The latter are assembled with the solvate dichloromethane molecules by Cl(dichloromethane)···π(benzothiazole) (Cl···S 3.309(2) Å), C−H···π, and C−H···Cl contacts.

Catalytic Studies. Similar to the other palladium pincer complexes **IX**−**XII** with hybrid thiophosphorylated ligands, complexes **12**−**15** were tested as (pre)catalysts for the Suzuki−Miyaura cross-coupling of aryl halides with phenylboronic acid. For correct comparison of the catalytic activities of complexes both within the present series and with **IX**−**XII**, all the experiments were carried out under the same conditions—heating in DMF at 120 °C using K_3PO_4 as a base—the system suggested for the symmetrical SCS-pincer complex having sulfide coordinating arms[3c] and successfully adopted for SCS′ and SCN thiophosphoryl-based palladacycles **IX**−**XII**.

Several aryl halides were efficiently subjected to the coupling reaction, and the results are summarized in Table 1. For each particular complex (**12**, **13**, **14a**, **15**), the normal dependence on the electronic properties of the substituent R (R = C(O)Me, OMe, NMe_2) at the aryl bromide was observed.[21]

For a set period of time (5 h), all the palladacycles under investigation afforded the complete conversion of easy-to-couple substrate 4-bromoacetophenone, being used in 1 mol %, and the catalyst loading could be diminished to 0.1 and 0.01 mol %

Table 1. Thiophosphoryl−Benzothiazole Pincer Palladium Complex-Catalyzed Suzuki Cross-Couplings



			Pd cat./conversion, %[a]			
entry	aryl halide	cat load. (mol %)	**12**	**13**	**14a**	**15**
1	4-bromoacetophenone	1	100	100	100	100
2	4-bromoacetophenone	0.1	100	100	100	100
3	4-bromoacetophenone	0.01	74	95.5	100	100
4	4-bromoanisole	1	97	98.5	99	61(55)
5	4-bromoanisole	0.1	92(88)	100(92)	99.5(86)	81(62)
6	4-bromoanisole	0.01	77	92	98	92(84)
7	4-bromo-*N*,*N*-dimethylaniline	1	61	39	53	40
8	4-bromo-*N*,*N*-dimethylaniline	0.1	2	26	53	32
9	4-chloroacetophenone	0.1	0	25	93	49
10	2-chloroacetophenone	0.1	0	13	29	3

[a] Yields in brackets refer to the reactions performed with Bu_4NBr additive.

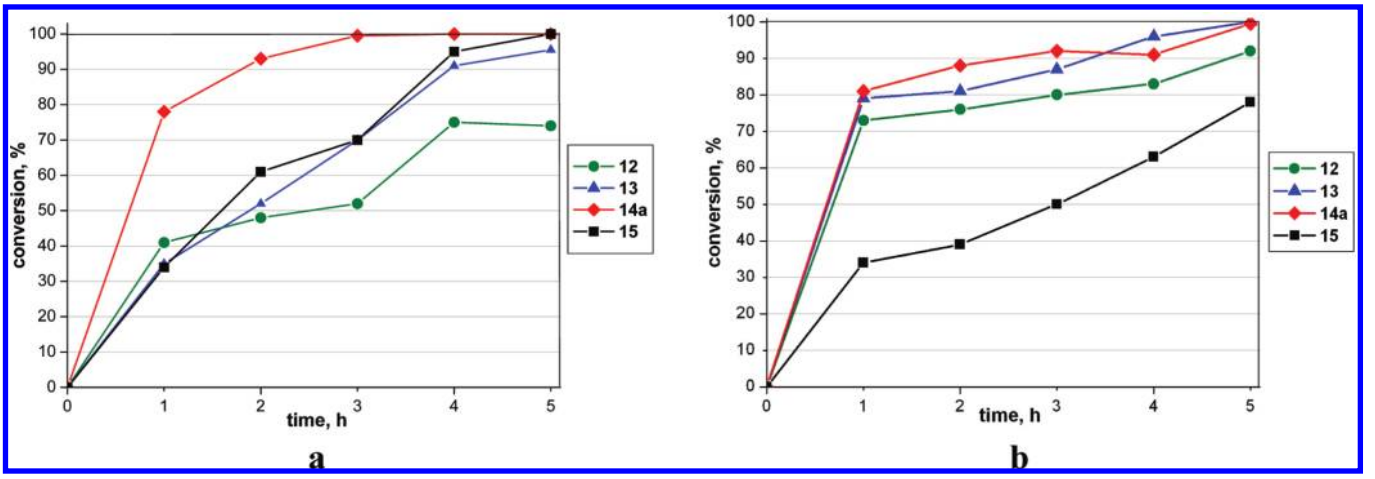


Figure 7. Plots of conversion vs time for the couplings of 4-bromoacetophenone (a) (cat. loading 0.01 mol %) and 4-bromoanisole (b) (cat. loading 0.1 mol %) catalyzed by complexes **12**−**15**.

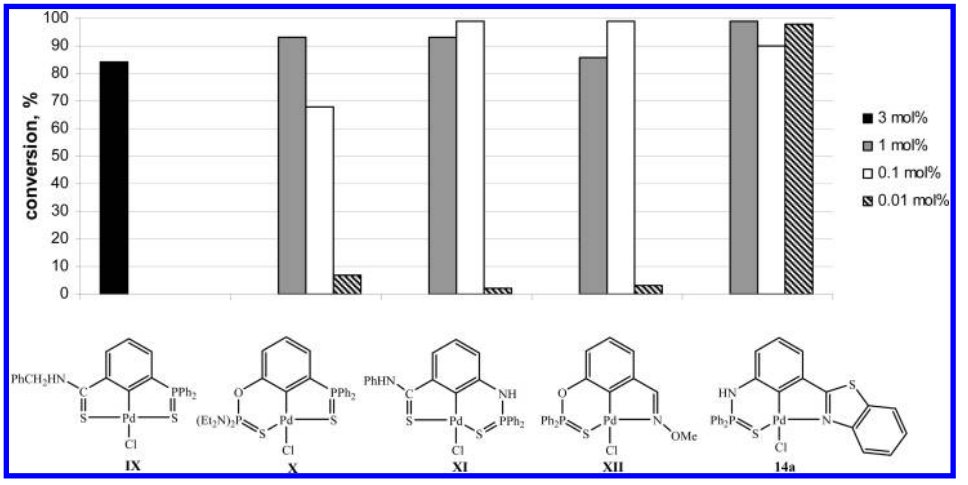


Figure 8. Catalytic activity of SCS′ and SCN thiophosphoryl-containing pincer palladium complexes in the cross-coupling of 4-bromoanisole and phenylboronic acid.

retaining the close yields (Table 1, entries 1−3). Nevertheless, further reduction in the catalyst amount (to 0.001 mol %) led to a drop in the conversion to only several percent. Good to excellent yields (77−98%) were achieved for the coupling of 4-bromoanisole at a very low (0.01 mol %) catalyst loading (Table 1, entries 4−6), although its further reduction afforded no coupling. In reaction with the less active 4-bromo-*N*,*N*-dimethylaniline, the yields of the corresponding biaryl product for a catalyst loading of 1 mol % ranged from 39% to 61%, which is reasonably good for such an electronically deactivated substrate (Table 1, entry 7). However, upon a 10-fold reduction of the catalyst amount, a moderate level of conversion (53%) was retained only for complex **14a**, appearing to be the most active one, while 5,5-membered SCN palladacycle **12** was almost inactive (Table 1, entry 8). Note that in some cases the activity at the lower catalyst loading of 0.1−0.01 mol % was somewhat higher than that when 1 mol % of a catalyst was used. Apparently, if the complexes serve as a reservoir of catalytically active Pd(0) particles, at high level of catalyst loading these colloid particles may stick together (Ostwald ripening), resulting in a decrease in their effective surface area and thereby catalytic activity. In any case, the activity passes the maximum at 0.1−0.01 mol % loading and later on steeply decreases. The maximum position depends on the ligand structure and starting substrate, and, for example, for complex **15** the activity in the coupling of 4-bromoanisole increased with a decrease of the catalyst loading. In general, in couplings of bromoarenes under these conditions no pronounced difference was observed in the catalytic performances of complexes **13**, **14a**, and **15**, with 5- and 6-membered fused metallacycles, whereas their 5,5-membered counterpart **12** was somewhat less active, excluding the reaction with 4-bromoanisole, in which activity of complex **12** was higher than that of complex **15**.

The kinetic studies performed for coupling of 4-bromoacetophenone (catalyst loading of 0.01 mol %, Figure 7a) revealed that complex **14a** was more active than the other thiophosphoryl−benzothiazole palladacycles and provided >90% conversion for 2 h (for complete conversion 3 h was required). The 5,6-membered O-bridged complexes **13** and **15** possessed an activity similar to each other and gave similar conversion levels of >90% already in ∼4 h. At the same time, in the reaction catalyzed by complex **12**, slightly higher conversion was observed over 1 h compared with those provided by complexes **13** and **15**, but in

dx.doi.org/10.1021/om101012r |*Organometallics* 2011, 30, 2920–2932

Table 2. Pincer Complexes Catalyzing the Suzuki Cross-Coupling of 4-Chloroacetophenone

cat. (load.)	reaction conditions	conversion, %	time, h	ref
I[a] (0.1 mol %)	THF, K_2CO_3, 130 °C	67	18	7
II (1 mol %)	dioxane, CsF, 130 °C	74	27	8
III (2 mol %)	H_2O, K_2CO_3, 150 °C	77	4	9
IV (0.01 mol %)	toluene, K_3PO_4, 100 °C	92	1.5	10
V[a] (0.1 mol %)	toluene, K_2CO_3, 110 °C	88	18	11
VI (1 mol %)	dioxane, Cs_2CO_3, 100 °C	58	18	6e
VII (1 mol %)	DMF, K_3PO_4, 130 °C	99	12	6f
VIII[b] (1 mol %)	dioxane, Cs_2CO_3, 100 °C	89	20	6b
14a (0.1 mol %)	DMF, K_3PO_4, 120 °C	93	5	this study

[a] 4-Chloronitrobenzene was used as a substrate. [b] Chlorobenzene was used as a substrate.

time the level of activity became lower. This fact may be explained by the similar induction periods for these three complexes, which nevertheless provided different catalytically active species. The corresponding kinetic experiments in the case of 4-bromoanisole (catalyst loading of 0.1 mol % was chosen to provide higher conversions, Figure 7b) have revealed comparable kinetic traces for complexes **12**, **13**, and **14a**, with insignificantly higher catalytic activity of the latter one, while complex **15** stood out against a general tendency of its analogues and demonstrated lower catalytic efficacy and an increased induction period. Evidently, in this case the release of catalytically active species is rather slow. Indeed, as may be seen from Table 1 (entries 4−6), the catalytic activity of **15** increases as the catalyst loading is gradually reduced from 1 to 0.01 mol %. Such (pre)catalyst behavior may be associated with the Ostwald ripening of catalytically active Pd(0) colloid particles at higher concentrations of a complex, leading in turn to their growth and decrease in their surface area, which may cause a drop in the total catalytic activity (see above).

To compare the catalytic activities of a panel of thiophosphoryl-based pincer complexes of different types, Figure 8 outlines the results obtained for the model cross-coupling reaction of 4-bromoanisole using the most catalytically active representatives among each series of palladacycles **IX**−**XII** and **12**−**15** (the data correspond to the reactions performed over 5 h). Note that reactions promoted by complexes **IX**, **X**, and **XII** were performed in the presence of tetrabutylammonium bromide, a salt known to stabilize palladium nanoparticles,[10] and in the absence of Bu_4NBr an approximately 10−15% decrease in the yield of the final biaryl product was observed. In contrast, Bu_4NBr slightly inhibited the reaction with participation of thiophosphoryl−thiocarbamoyl- and thiophosphoryl−benzothiazole-based pincer complexes **XI**[14] and **12**−**15** (Table 1, entries 4−6 for the representative complex **15**), respectively.

As is easy to see, 5,5-membered SCS′ thiocarbamoyl−thiophosphoryl pincer complex **IX** did not provide a complete conversion of this particular substrate, even being used at 3 mol %. Showing the best catalytic activity among bis(thiophosphorylated) derivatives **X**, the complex bearing diethylamino groups at the phosphorus atom of the O−P═S moiety displayed the same level of activity even when used at 1 mol %. However, its activity decreased to 68% as the catalyst loading was reduced to 0.1 mol %, while 5,6-membered SCS′ complex **XI** as well as SCN palladacyle **XII**, based on thiophosphoryloxy−benzaldoxime, retained a high level of activity even at a low catalyst loading (0.1 mol %). Nevertheless, the yields of the biaryl product went down practically to zero as the amount of the aforesaid complexes (**IX**−**XI**) was decreased to 0.01 mol %. At the same time, SCN-pincer complexes **12**−**15**, with a benzothiazole ring, afforded almost complete conversion of 4-bromoanisole even when used at 0.01 mol %, substantially surpassing in activity the other pincer complexes with a thiophosphoryl coordinating arm.

Moreover, SCN palladium complex **14a** efficiently promoted the Suzuki cross-coupling of 4-chloroacetophenone with phenylboronic acid, providing 93% conversion at 0.1 mol % catalyst loading (Table 1, entry 9). The other 5,6-membered thiophosphoryl−benzothiazole palladacycles **13** and **15** also manifested activity in this reaction but were inferior to complex **14a**, and the yields of the biphenyl product did not exceed 50% (entry 9). Employing complexes **13**, **14a**, and **15**, poor yields were achieved in the reactions of more sterically hindered 2-chloroacetophenone (entry 10). It should be emphasized that complex **12**, having two five-membered metallacycles, showed no activity for the coupling of these aryl chlorides.

At this point, a comparison in terms of catalytic efficiency can be performed between the most active complex of this study, **14a**, and the other pincer complexes known to catalyze the Suzuki cross-coupling of aryl chlorides with phenylboronic acid (Table 2). A few points should be taken into consideration. To promote the reaction of activated chloroacetophenone (or another activated aryl chloride, 4-chloronitrobenzene) using pincer complexes **I**−**VIII** and **14a**, high temperatures (100−150 °C) were required in all cases. The reaction times, in that range of temperature, varied in a wide range (1.5−27 h), although generally exceeded 12 h. The typical catalyst loading was fairly high, 1−2 mol %. Hence, considering the data of Table 2 one can conclude that from the standpoint of the catalyst loading (0.1 mol %), reaction time (5 h), and conversion (93%), complex **14a** ranks second among all pincer palladacycles catalyzing the Suzuki cross-coupling of activated aryl chlorides reported to date.

According to the ^{31}P NMR monitoring of a complex's destiny after the catalytic cycle (representative reaction was the coupling of 4-bromoacetophenone and phenylboronic acid at 1 mol % catalyst loading), palladacycles **12**−**15** undergo at least partial decomposition over the process. Thus, in the case of a catalytic system based on complex **12**, the ^{31} P NMR spectrum of the reaction mixture demonstrated two singlets at ca. 30 and 26 ppm in a 4:1 ratio. Presumably, they pertain to the metalated (30 ppm) and nonmetalated (26 ppm) phosphoryl-containing derivatives (e.g., the chemical shift of the intermediate 2-[3-(diphenylphosphoryl)phenyl]-1,3-benzothiazole is equal to 26.87 ppm) that may result from the oxidation of the P═S group and thermally induced demetalation of the starting complex under the reaction conditions. Note that both these signals were observed also in the spectrum of the reaction mixture comprised of 4-bromoacetophenone, K_3PO_4, and 1 mol % **12** in the absence of phenylboronic acid, after heating in DMF for 30 min and, therefore, may be formed under the action of a base. The ^{31}P NMR spectrum of the reaction catalyzed by complex **13** showed solely the signals at 25.8 and 15.2 ppm in a 1.5:1 ratio, which were assigned to the products of O−P bond hydrolysis and P═S group oxidation, i.e., $Ph_2P(S)OH$ and $Ph_2P(O)OH$.[22] This allows one to assume the decomposition of the ligand structure. The phosphorus spectra registered after the reactions catalyzed by pincer complexes **14a** and **15** demonstrated signals with chemical shifts being very close to those of free ligands (at 50.6

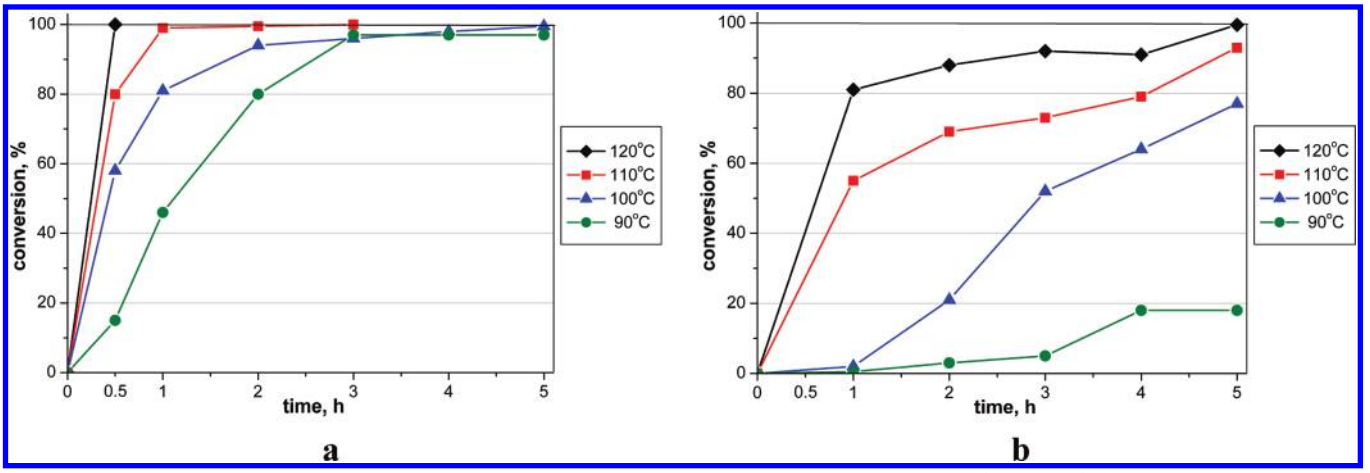


Figure 9. Temperature-varied plots of conversion vs time for the catalytic system based on complex **14a** (0.1 mol %) (coupling of 4-bromoacetophenone (a) and 4-bromoanisole (b) with $PhB(OH)_2$).

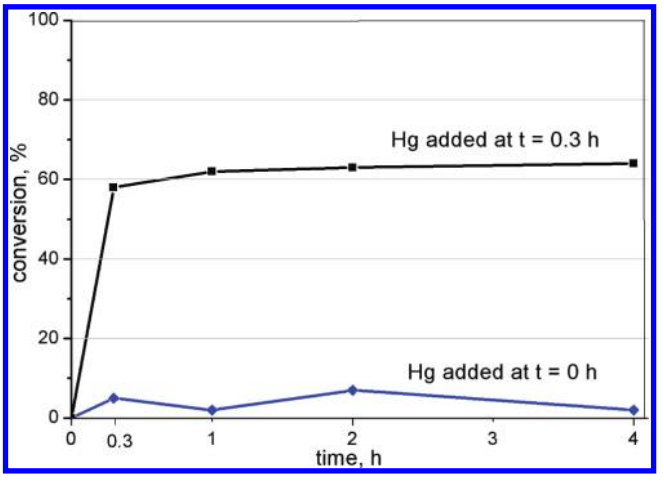


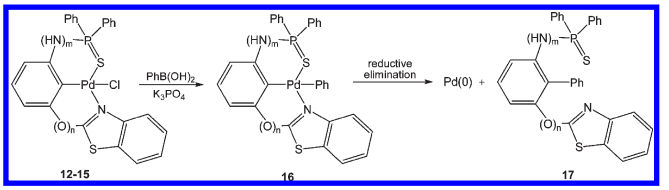
Figure 10. Conversion of 4-bromoacetophenone as a function of time in the Suzuki coupling with 0.1 mol % of complex **14a** in the presence of Hg(0).

and 43.0 ppm, respectively), hence suggesting the rupture of the Pd−C bonds.

Furthermore, we detected the downfield shifted signals at 58.3, 62.2, and 94.7 ppm in the ^{31}P NMR spectra of the reaction mixtures after a catalytic process for palladacycles **12**, **15**, and **14a**, respectively. The first two values fall within the region typical for the metalated P═S-coordinated derivatives (which may also possess monopalladacyclic nature), while the latter one is likely to correspond to the pincer-type complex with a P(III) coordinating arm (compare, e.g., with the phosphorus resonance of PCN-pincer complex **III**[9] at 91.3 ppm).

Note that in the catalysis of cross-coupling reactions for the pincer systems, both symmetric and unsymmetrical, two alternative mechanisms including Pd(II)/Pd(0) and Pd(II)/Pd(IV)[23] catalytic cycles were suggested. The decomposition of palladacycles **12**−**15** over the catalytic cycle in combination with the observation of palladium black formation (particularly but not exclusively in the case of complex **13**) allow proposing that they serve as precatalysts of zerovalent low-ligated palladium, and the described catalytic transformations apparently include a Pd(0)−Pd(II) catalytic cycle. The abrupt decrease in the catalytic efficiency of these complexes at very low concentrations

Scheme 5. Suppositional Way of Generation of Pd(0) Species



(0.001 mol %) is also in good agreement with the proposal of the Pd(0) nature of true catalysts.[24]

The kinetic studies performed with the representative complex **14a** (0.1 mol %) at different temperatures (the temperature was gradually reduced by 10 degrees from 120 to 90 °C) using both 4-bromoacetophenone and 4-bromoanisole as a starting substrate (Figure 9) revealed that the system under consideration is characterized by sigmoidal kinetics, and an induction period, necessary for the starting pincer complex to generate catalytically active species, becomes especially apparent below 100 °C. This strongly indicates that pincer complex **14a** serves as a (pre)-catalyst rather than a true catalyst. Furthermore, in addition to the above-mentioned kinetic experiments, these data indicated that at this catalyst loading complete conversion in reaction with 4-bromoacetophenone at 120 °C was achieved in only 0.5 h.

Moreover, the lack of activity of complexes **12**−**14** in the presence of excess of Hg(0), which has no poisoning effect on molecular homogeneous organometallic complexes containing metals in high oxidation states that are tightly bound by protective ligands,[25,26] provides additional evidence that these systems are susceptible to decomposition under reaction conditions to form soluble Pd(0) species, as shown in Figure 10 for the representative reaction catalyzed by complex **14a**. In brief, when Hg(0) was added to the reaction mixtures at time 0 or 20 min, the reaction stopped at the conversion level of 2% and 38−42%, 2% and 63−66%, 5% and 58−64%, and 1% and 55% (three to four measurements up to t = 4 h) for the catalytic systems based on complexes **12**, **13**, **14a**, and **15**, respectively.

But how can such active species be generated? The ^{31}P NMR spectrum of the reaction mixture containing only 4-bromoacetophenone (i.e., those free of phenylboronic acid and K_3PO_4)

dx.doi.org/10.1021/om101012r |*Organometallics* 2011, 30, 2920–2932

and complex **14a** (1 mol %) revealed no changes in the chemical shift of the latter one after heating for 30 min. Therefore, complexes **13**−**15** apparently generate the catalytically active Pd(0) species by the reductive elimination of the *ortho*-metalated species with an aryl group introduced by phenylboronic acid (Scheme 5). In this case, the signals observed in the ^{31}P NMR spectra of the reaction mixtures after complete catalytic cycle with chemical shifts close to those of free ligands may relate to the products **17** of the reductive elimination of L−Pd−Ph intermediates **16**, which differ from the starting ligands **9** and **11** by an additional phenyl ring at the C2 position of the central benzene core. It should be noted that such a mechanism of the formation of catalytically active species in the Suzuki cross-coupling promoted by palladacycles has already been suggested in the literature for both CN- and CP-monopalladacycles[3d,27] and 5,5-membered symmetrical PCP-pincer complexes,[26] where the product of transmetalation, i.e., the L−Pd−Ph complex, was isolated and structurally characterized. Nevertheless, in the latter case the experimental results in total were indicative of a Pd(II)−Pd(IV) catalytic cycle, and no further reductive elimination with liberation of biaryls was observed. In the case of SCN-pincer complexes **12**−**14** the hemilabile coordination may facilitate such reductive elimination by more feasible, than in the case of strongly bound P(III) moieties, decoordination of weakly bonded ancillary arms in order to achieve *ortho*-mutual disposition of two leaving phenyl fragments. Indeed, according to the ^{31}P NMR monitoring, heating of complex **15** with 3 equiv of phenylboronic acid and 4.5 equiv of K_3PO_4 in DMF at 120 °C for 1 h leads to the main two components that answer to the phosphorus signals at 57.5 and 43.0 ppm. The first one obviously corresponds to the unreacted starting pincer complex, while the second one is unambiguously not the free ligand (proven by the addition of compound **11** as an internal standard) and is tentatively assigned to the biaryl **17**.[27]

Despite all the data supporting the Pd(II)/Pd(0) catalytic cycle for complexes **12**−**15**, at least for 5,5-membered complex **12** the alternative Pd(II)/Pd(IV) mechanism cannot be entirely disclaimed as a minor parallel process. First of all, unlike the other SCN thiophosphoryl−benzothiazole pincer complexes, it does not contain a rather weakly bonded six-membered metallacycle to make feasible the reductive elimination of intermediate **16**. Similar to ref 26, in this case a further scenario may comprise the reaction with ArBr to give Pd(IV) species followed by catalyst recovery after elimination of biaryl. The partial retaining of catalytic activity in the Hg(0) poisoning experiment could be a reasonable argument for this hypothesis. Furthermore, it cannot be completely excluded that Hg(0) interferes with catalysis in a way other than killing the true heterogeneous catalyst.

In conclusion it should be noted that the main disparity in the activities of complexes tested consists in the performances of 5,5-membered complex **12** and its counterparts **13**−**15**. Obviously, the lower activity of compound **12** may be explained by its higher stability, leading to a slower generation of the catalytically active species. In this respect, the hemilabile properties of pincer complexes **13**−**15**, having five- and rather weakly bonded six-membered fused metallacycles, apparently serve as a factor for their higher activity.

CONCLUSIONS

To summarize the results presented, we have elaborated the synthetic approaches to novel types of NCS-pincer ligands having a thiophosphoryl group and a benzothiazole imine moiety as coordination sites. Direct cyclometalation of these ligands afforded 5,5- and 5,6-membered pincer palladium complexes and a 5,6-membered pincer platinum one in the case of the ligand having a thiophosphorylamino moiety. The palladacycles derived were proved to be excellent (pre)catalysts for the Suzuki cross-coupling of electronically varied bromoarenes, while 5,6-membered pincer complex **14a**, with a thiophosphorylamino group, also efficiently promoted the reaction with chloroacetophenone, ranking among the best pincer (pre)catalysts suggested for this reaction.

EXPERIMENTAL SECTION

If not noted otherwise, all manipulations were carried out without taking precautions to exclude air and moisture. Benzene was distilled over sodium/benzophenone ketyl, and acetonitrile was distilled from P_2O_5. 3-(Diphenylphosphoryl)-*N*-phenylbenzamide,[12] 3-(diphenylphosphoryl)-*N*-phenylbenzenecarbothioamide, **1**,[28] 3-(diphenylthiophosphoryl)-*N*-phenylbenzenecarbothioamide, **2**,[12] 3-methoxy-*N*-phenylbenzenecarbothioamide, **4**,[14] 2-(3-methoxyphenyl)-1,3-benzothiazole,[18] 3-amino-*N*-phenylbenzamide,[29] $Ph_2P(S)Cl$,[30] 3-(diphenylthiophosphoryl)phenol, **10**,[13] 2-(3-nitrophenyl)benzothiazole, and the corresponding amino derivative **8** (for both compounds see ref 31) were obtained according to literature procedures. All other chemicals and solvents were used as purchased.

NMR spectra were recorded on Bruker Avance-300 and Bruker Avance-400 spectrometers, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H and ^{13}C) or externally to H_3PO_4 (^{31}P). The ^{13}C NMR spectra were registered using the *J*MODECHO mode; the signals for the C atoms bearing odd and even numbers of protons have opposite polarities. The numeration for carbon atoms of the central benzene ring in the descriptions of the ^{13}C spectral data is in agreement with IUPAC nomenclature used for the ligand **3**. The same principle of numbering was used to describe the solid-state molecular structures characterized by X-ray crystallography.

Flash chromatography was carried out using Merck silica gel 60 (230−400 mesh ASTM). IR spectra were recorded on a Magna-IR750 Fourier spectrometer (Nicolet), resolution 2 cm^{-1}, 128 scans. The assignment of absorption bands in the IR spectra was made according to ref 32. Melting points were determined with a MPA 120 EZ-Melt automated melting point apparatus and are uncorrected.

Synthesis of Ligands. *2-[3-(Diphenylthiophosphoryl)phenyl]-1,3-benzothiazole,* ***3****. Method A.* To a suspension of 3-(diphenylphosphoryl)-*N*-phenylbenzenecarbothioamide (**1**) (1.8 g, 4.4 mmol) in 1 mL of ethanol was added a 30% aqueous solution of NaOH (3.3 mL). Then the mixture was diluted with water to reach a final concentration of NaOH of 10%. Aliquots of this mixture (0.5 mL) were added at one-minute intervals to a stirred solution of $K_3[Fe(CN)_6]$ (5.73 g, 17.4 mmol) in water (20 mL) at 80 °C. The reaction mixture was heated at 80 °C for 30 min. After cooling to room temperature, the resulting precipitate was filtered, rinsed with water, and dried *in vacuo* to afford 1.2 g of 2-[3-(diphenylphosphoryl)phenyl]-1,3-benzothiazole as a white, crystalline solid. Yield: 67%. Mp: 165.0−167.1 °C (benzene). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ 26.87 ppm. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.37−7.77 (m, 14H), 7.91 (d, 1H, H(C6), $^3J_{HH}$ = 7.8 Hz), 8.07 (d, 1H, H(C12), $^3J_{HH}$ = 8.2 Hz), 8.35 (d, 1H, H(C9), $^3J_{HH}$ = 7.8 Hz), 8.41 (d, 1H, H(C2), $^3J_{HP}$ = 12.3 Hz). Anal. Calcd for $C_{25}H_{18}NOPS$: C, 72.98; H, 4.40; N, 3.40. Found: C, 73.14; H, 4.39; N, 3.27.

A mixture of the above 2-[3-(diphenylphosphoryl)phenyl]-1,3-benzothiazole (0.65 g, 1.6 mmol) and the Lawesson reagent (2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione, 0.32 g,

0.8 mmol) was refluxed in xylene (20 mL) for 12 h. After cooling to room temperature, the mixture was washed with a 20% aqueous solution of Na_2CO_3 and water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was recrystallized from EtOAc to give 0.4 g of **3** as a white solid. Yield: 59%. Mp: 173.1−174.2 °C (EtOAc). ^{31}P NMR (161.98 MHz, DMSO-d_6): δ 42.35 ppm. ^{1}H NMR (DMSO-d_6): δ 7.47−7.51 (m, 1H), 7.54−7.69 (m, 7H), 7.73−7.78 (m, 6H), 8.08 (d, 1H, H(C12), $^3J_{HH}$ = 8.0 Hz), 8.17 (d, 1H, H(C9), $^3J_{HH}$ = 7.6 Hz), 8.29−8.31 (m, 1H), 8.51 (d, 1H, H(C2), $^3J_{HP}$ = 14.1 Hz). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$/DMSO-d_6): δ 121.89 (s, C9), 122.98 (s, C12), 125.49 (s, C11), 126.40 (s, C10), 128.58 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 12.6 Hz), 129.37 (d, C2, $^2J_{CP}$ = 12.1 Hz), 130.15 (d, C5, $^3J_{CP}$ = 15.9 Hz), 130.21 (s, C6), 131.68 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 10.4 Hz), 131.75 (s, *p*-C in P(S)Ph_2), 131.84 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 85.1 Hz), 133.41 (d, C1, $^3J_{CP}$ = 12.6 Hz), 133.78 (d, C4, $^2J_{CP}$ = 9.9 Hz), 134.01 (d, C3, $^1J_{CP}$ = 84.0 Hz), 134.48 (s, C13), 153.40 (s, C8), 165.73 (s, C7). IR (KBr, ν/cm^{-1}): 495(w), 515(s), 614(m), 628(m) (ν(P═S)), 641(m), 659(m), 680(m), 696(s), 714(s), 725(m), 742(m), 754(m), 787(w), 999(m), 1098(s), 1234(w), 1312(m), 1409(m), 1435(s), 1457(w), 1478(m), 1507(w) (ν(C═N)), 1585(w), 1700(w), 3051(w). Anal. Calcd for $C_{25}H_{18}NPS_2$: C, 70.23; H, 4.24; N, 3.28. Found: C, 70.19; H, 4.17; N, 3.23.

Method B. Analogous to the first stage of method A, the reaction of 3-(diphenylthiophosphoryl)-*N*-phenylbenzenecarbothioamide (**2**) (1.5 g, 3.5 mmol) with $K_3[Fe(CN)_6]$ (4.6 g,14.0 mmol) led to compound **3** (0.8 g, 54% yield).

3-(1,3-Benzothiazol-2-yl)phenol, ***5***. A mixture of 2-(3-methoxyphenyl)-1,3-benzothiazole (2.2 g, 9.1 mmol) and pyridine hydrochloride (3.2 g, 27.7 mmol) was heated under stirring at 180−190 °C (oil bath) for 3 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2, washed with water, and dried over anhydrous Na_2SO_4. After separation of Na_2SO_4, the filtrate was half-evaporated to afford precipitation of the crude product, which then was recrystallized from $CHCl_3$. Yield: 1.2 g (58%). Mp: 161.9−164.2 °C (compare with 161−163 °C in ref 33).

O-[3-(1,3-Benzothiazol-2-yl)phenyl]diphenylthiophosphinate, ***6***. A solution of $Ph_2P(S)Cl$ (0.9 g, 3.6 mmol) in benzene (5 mL) was slowly added dropwise to a mixture of **5** (0.8 g, 3.6 mmol) and Et_3N (0.5 mL, 3.6 mmol) in 20 mL of C_6H_6. The resulting reaction mixture was stirred at 60 °C for 2 h and left overnight. The reaction mixture was filtered, and the filtrate was evaporated to dryness, crystallized from diethyl ether, purified by flash chromatography (eluent CH_2Cl_2), and recrystallized from EtOAc to give 1.3 g of **7** as a white solid. Yield: 83%. Mp: 148.4−149.6 °C (EtOAc). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ 82.98 ppm. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.19 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 7.32−7.40 (m, 2H), 7.45−7.55 (m, 7H), 7.77 (d, 1H, H(C2), $^4J_{HP}$ = 1.8 Hz), 7.83−7.89 (m, 2H), 7.97−8.05 (m, 5H). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 120.67 (d, C2, $^3J_{CP}$ = 5.1 Hz), 121.46 (s, C9), 123.15 (s, C12), 123.71 (d, C5, $^4J_{CP}$ = 1.1 Hz), 123.79 (d, C4, $^3J_{CP}$ = 4.7 Hz), 125.18 (s, C11), 126.19 (s, C10), 128.44 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 13.4 Hz), 129.73 (s, C6), 131.26 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 11.6 Hz), 132.11 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 3.3 Hz), 133.79 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 110.8 Hz), 134.79 (s, C13), 134.90 (s, C1), 150.88 (d, C3, $^2J_{CP}$ = 8.4 Hz), 153.80 (s, C8), 166.63 (s, C7). IR (KBr, ν/cm^{-1}): 491(m), 506(s), 640(m) (ν(P═S)), 687(m), 717(m), 728(s), 757(m), 791(m), 846(m), 857(m), 893(m), 910(s), 1107(m), 1161(m), 1174(m) 1238(m), 1254(m), 1313(w), 1436(s), 1463(w), 1505(m) (ν(C═N)), 1580(m), 1605(w), 3028(w), 3051(w), 3064(w). Anal. Calcd for $C_{25}H_{18}NOPS_2$: C, 67.70; H, 4.09; N, 3.16. Found: C, 67.71; H, 4.09; N, 3.21.

N-[3-(1,3-Benzothiazol-2-yl)phenyl]-P,P-diphenylthiophosphinic Acid Amide, ***9***. A solution of Ph_2PCl (1.3 g, 5.9 mmol) in 15 mL of benzene was slowly dropwise added to a suspension of **8** (1.3 g, 5.8 mmol) and pyridine (0.55 mL, 5.8 mmol) in 35 mL of C_6H_6 under an argon atmosphere. The reaction mixture was refluxed for 5 h and, after addition of sulfur (0.22 g, 6.9 mmol), continued to reflux for a further 7 h. After cooling to room temperature, the resultant mixture was filtered; the filtrate was washed with 5% aq. HCl and water, dried over Na_2SO_4, and evaporated to dryness. The resulting residue was recrystallized from benzene to afford 1.93 g of **9** as a white solid. Mp: 169.4−172.4 °C (C_6H_6). Yield: 52%. ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$): δ 52.61 ppm. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 5.22 (d, 1H, NH, $^3J_{HP}$ = 6.0 Hz), 7.13−7.15 (m, 1H, H_{Ar}), 7.22−7.25 (m, 1H, H_{Ar}), 7.35−7.38 (m, 1H, H_{Ar}), 7.45−7.55 (m, 7H, H_{Ar}), 7.60 (d, 1H, H(C6), $^3J_{HH}$ = 7.4 Hz), 7.65 (br s, 1H, H(C2)), 7.86 (d, 1H, H(C12), $^3J_{HH}$ = 7.9 Hz), 8.00−8.06 (m, 5H, *o*-H in P(S)Ph_2+H(C9)). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 117.80 (d, C2, $^3J_{CP}$ = 7.6 Hz), 120.76 (s, C6), 120.91 (d, C4, $^3J_{CP}$ = 6.2 Hz), 121.48 (s, C9), 122.81 (s, C12), 125.21 (s, C11), 126.30 (s, C10), 128.64 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 13.1 Hz), 129.59 (s, C5), 131.45 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 11.8 Hz), 131.11 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 2.1 Hz), 133.04 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 103.8 Hz), 133.73 (s, C13), 134.55 (s, C1), 140.99 (s, C3), 153.09 (s, C8), 167.83 (s, C7). IR (KBr, ν/cm^{-1}): 483(w), 510(m), 613(m) and 629(m) (both ν(P═S)), 690(m), 717(s), 753(m), 936(s), 1018(w), 1105(m), 1197(w), 1260(w), 1279(w), 1304(m), 1372(w), 1437(s), 1463(m), 1486(s), 1510(m) (ν(C═N)), 1589(m), 1606(m), 2922(w), 3055(w), 3201(m). Anal. Calcd for $C_{25}H_{19}N_2PS_2$: C, 67.85; H, 4.32; N, 6.33. Found: C, 67.69; H, 4.25; N, 6.21.

2-[3-(Diphenylthiophosphoryl)phenoxy]-1,3-benzothiazole, ***11***. A mixture of 2-chloro-1,3-benzothiazole (0.7 g, 4 mmol) and sodium phenolate prepared from 3-(diphenylthiophosphoryl)phenol **10** (0.6 g, 1.9 mmol) and a 60% dispersion of NaH in mineral oil (0.09 g, 1.9 mmol) in 15 mL of xylene was refluxed for 20 h and allowed to cool. After evaporation of the reaction mixture, the resulting residue was dissolved in Et_2O and filtered. The ether filtrate was evaporated to dryness, and the resulting residue was recrystallized from a EtOAc−hexane mixture (1:2) to give 0.56 g of **11** as a white, crystalline solid. Yield: 65%. Mp: 127.3−129.8 °C (EtOAc−hexane (1:2)). ^{31}P NMR (161.98 MHz, DMSO-d_6): δ 41.87 ppm. ^{1}H NMR (DMSO-d_6): δ 7.35 (m, 1H), 7.45 (m, 1H), 7.57−7.76 (m, 15H), 7.97 (d, 1H, H(C9), $^3J_{HH}$ = 8.0 Hz). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 121.24 (s, C9), 121.64 (s, C12), 123.44 (d, C6, $^4J_{CP}$ = 2.6 Hz), 124.11 (d, C2, $^2J_{CP}$ = 11.7 Hz), 124.21 (s, C11), 126.23 (s, C10), 128.52 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 12.7 Hz), 129.62 (d, C4, $^2J_{CP}$ = 10.1 Hz), 130.08 (d, C5, $^3J_{CP}$ = 14.0 Hz), 131.66 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 2.9 Hz), 132.14 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 10.8 Hz), 132.19 (s, C13), 132.24 (d, C3, $^1J_{CP}$ = 85.7 Hz), 135.37 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 84.1 Hz), 148.65 (s, C8), 154.21 (d, C1, $^3J_{CP}$ = 16.6 Hz), 170.80 (s, C7). IR (KBr, ν/cm^{-1}): 515(m), 633(w) and 649(m) (both ν(P═S)), 693(m), 717(m), 751(m), 764(w), 1098(m), 1210(m), 1229(s), 1247(m), 1411(m), 1439(s), 1529(s) (ν(C═N)), 1580(w), 1599(w), 3054(w). Anal. Calcd for $C_{25}H_{18}NOPS_2$: C, 67.70; H, 4.09; N, 3.16. Found: C, 67.05; H, 3.93; N, 2.83.

Synthesis of Pincer Complexes. *General Procedure (complexes* ***12****,* ***13****, and* ***15****).* A solution of $(PhCN)_2PdCl_2$ (77 mg, 0.2 mmol) and the corresponding ligand **3**, **6**, or **11** (0.2 mmol) in 4 mL of benzonitrile was heated at 120 °C for 3, 2, and 1 h, respectively, and allowed to cool. The resulting mixture was diluted with CH_2Cl_2 (12 mL) and filtered. After evaporation of dichloromethane, 15 mL of diethyl ether was added. The desired precipitated product was collected by filtration, washed with Et_2O (15 mL), and dried in air. When the compound **11** was used as a starting ligand, to precipitate the desired pincer product, diethyl ether was added directly to the benzonitrile reaction mixture.

[2-(1,3-Benzothiazol-2-yl)-6-(diphenylthiophosphoryl)phenyl]-palladium Chloride, ***12***. Yield: 80%. Mp: >295 °C (dec). ^{31}P{^{1}H} NMR (161.98 MHz, DMSO-d_6): δ 64.17 ppm. ^{1}H NMR (400.13 MHz, DMSO-d_6): δ 7.37−7.42 (m, 1H), 7.78−7.64 (m, 3H), 7.69−7.72 (m,

Table 3. Crystal Data and Structure Refinement Parameters for 3, 12, 13, and 15

	3	12·0.5CH_2Cl_2	13	15·0.5CH_2Cl_2
empirical formula	$C_{25}H_{18}NPS_2$	$C_{51}H_{36}Cl_4N_2P_2Pd_2S_4$	$C_{25}H_{17}ClNOPPdS_2$	$C_{26}H_{19}Cl_3NOPPdS_2$
fw	427.49	1221.60	584.34	669.26
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Z	2	2	4	2
a, Å	7.1960(8)	9.6828(6)	9.9749(9)	8.8770(4)
b, Å	11.8679(13)	11.1434(6)	20.4107(19)	11.9311(5)
c, Å	13.0523(15)	12.3807(7)	11.6540(11)	13.0779(5)
α, deg	107.189(3)	71.5290(10)		84.7270(11)
β, deg	101.533(2)	82.3750(11)	108.592(2)	79.5330(10)
γ, deg	100.036(2)	69.1980(10)		71.3160(10)
V, Å^3	1010.5(2)	1184.15(12)	2248.9(4)	1289.44(9)
D_{calc} (g cm^{-1})	1.405	1.713	1.726	1.724
linear absorption, μ, cm^{-1}	3.55	12.69	12.21	12.77
F(000)	444	610	1168	668
$2\theta_{max}$, deg	58	56	58	58
reflns measd	12 072	13 105	26 543	15 418
indep reflns	5349	5685	5979	6816
obsd reflns [with $I > 2\sigma(I)$]	4131	4982	5145	6180
params	262	293	289	316
R1	0.0392	0.0277	0.0210	0.0225
wR2	0.0995	0.0678	0.0527	0.0509
GOF	1.004	1.008	1.003	1.010
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.451/−0.264	1.481/−0.986	0.508/−0.504	0.568/−1.018

4H, *m*-H in P(S)Ph_2), 7.78−7.81 (m, 2H, *p*-H in P(S)Ph_2), 7.87 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 13.6 Hz), 8.00 (d, 1H, H(C6), $^3J_{HH}$ = 7.3 Hz), 8.27 (d, 1H, H(C12), $^3J_{HH}$ = 7.8 Hz), 9.47 (d, 1H, H(C9) $^3J_{HH}$ = 8.1 Hz). IR (KBr, ν/cm^{-1}): 518(s), 601(m) (ν(P═S)), 618 (w), 692(m), 704(m), 718(m), 732(m), 748(m), 761(s), 996(w), 1038(m), 1101(m), 1272(w), 1319(w), 1394(m), 1415(m), 1434(m), 1475(w), 1511(w), 1546(m) (ν(C═N)), 1600(w), 2852(w), 2926(w), 3043(w), 3061(w). Anal. Calcd for $C_{25}H_{17}ClNPPdS_2 \cdot 0.67CH_2Cl_2$: C, 49.32; H, 2.96; N, 2.24. Found: C, 49.27; H, 2.91; N, 2.24.

{2-(1,3-Benzothiazol-2-yl)-6-[(diphenylthiophosphoryl)oxy]phenyl}-palladium Chloride, ***13***. Yield: 75%. Mp: >275 °C (dec). $^{31}P\{^1H\}$ NMR (161.98 MHz, DMSO-d_6): δ 75.22 ppm. ^1H NMR (400.13 MHz, DMSO-d_6): δ 7.34 (m, 2H), 7.50−7.60 (m, 3H), 7.65−7.70 (m, 4H), 7.75−7.77 (m, 2H), 8.06 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 13.8 Hz), 8.19 (d, 1H, H(C12), $^3J_{HH}$ = 7.6 Hz), 9.58 (d, 1H, H(C9), $^3J_{HH}$ = 8.5 Hz). IR (KBr, ν/cm^{-1}): 492(m), 515(m), 633(m) (ν(P═S)), 692(s), 719(s), 756(s), 782(w), 798(w), 952(s), 962(m), 1106(s), 1119(s), 1164(m), 1198(s), 1270(m), 1298(m), 1412(m), 1435(m), 1446(w), 1457(w), 1488(w) (ν(C═N)), 1580(w), 2854(w), 2925(w), 3081(w), 3438(w). Anal. Calcd for $C_{25}H_{17}ClNOPPdS_2$: C, 51.38; H, 2.93; N, 2.40. Found: C, 51.10; H, 2.73; N, 2.34.

[2-(1,3-Benzothiazol-2-yloxy)-6-(diphenylthiophosphoryl)phenyl]-palladium Chloride, ***15***. Yield: 60%. Mp: >249 °C (dec). $^{31}P\{^1H\}$ NMR (121.49 MHz, DMSO-d_6): δ 56.87 ppm. ^1H NMR (300.13 MHz, DMSO-d_6): δ 7.04−7.10 (m, 1H), 7.30−7.35 (m, 1H), 7.40−7.46 (m, 3H), 7.67−7.86 (m, 10H), 8.01−8.04 (m, 1H), 8.61−8.63 (m, 1H). IR (KBr, ν/cm^{-1}): 517(s), 562(m), 607(m) and 623(w) (both ν(P═S)), 671(m), 692(s), 707(s), 720(m), 755(s), 996(w), 1059(w), 1107(m), 1147(w), 1159(m), 1192(m), 1234(m), 1272(s), 1289(s), 1400(m), 1437(m), 1448(m), 1458(w), 1515(m) (ν(C═N)), 1560(w), 1593(w), 2856(w), 2925(w), 3040(w), 3432(w). Anal. Calcd for $C_{25}H_{17}ClNOPPdS_2$: C, 51.38; H, 2.93; N, 2.40. Found: C, 51.11; H, 2.88; N, 2.35.

{2-(1,3-Benzothiazol-2-yl)-6-[(diphenylthiophosphoryl)amino]-phenyl}palladium Chloride, ***14a***. A solution of $(PhCN)_2PdCl_2$ (46 mg, 0.120 mmol) in 5 mL of acetonitrile was slowly dropwise added to a suspension of ligand **9** (0.120 mmol) in 5 mL of CH_3CN. The stirred reaction mixture was refluxed for 2 h. After cooling to room temperature, the resulting precipitate was filtered, washed with CH_3CN (7 mL) and Et_2O (15 mL), and dried *in vacuo* to give 62 mg of **14a** as a yellow solid. Yield: 89%. Mp: >268 °C (dec). $^{31}P\{^1H\}$ NMR (121.49 MHz, DMSO-d_6): δ 45.21 ppm. ^1H NMR (300.13 MHz, DMSO-d_6): δ 7.06 (d, 1H, H(C4), $^3J_{HH}$ = 7.8 Hz), 7.18 (m, 1H, H(C5)), 7.34 (d, 1H, H(C6), $^3J_{HH}$ = 7.3 Hz), 7.44−7.54 (m, 2H, H(C10)+H(C11)), 7.64−7.74 (m, 6H, *p*- and *m*-H in P(S)Ph_2), 7.81−7.88 (m, 4H, *o*-H in P(S)Ph_2), 8.12 (d, 1H, H(C12), $^3J_{HH}$ = 7.5 Hz), 9.22 (d, 1H, NH, $^2J_{HP}$ = 5.7 Hz), 9.49 (d, 1H, H(C9), $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR (125.76 MHz, DMSO-d_6): δ 120.32 (s, C9), 121.91 (d, C4, $^3J_{CP}$ = 9.6 Hz), 122.38 (s, C6), 123.02 (s, C12), 125.57 (s, C11), 126.39 (s, C5), 126.50 (s, C10), 128.55 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 99.8 Hz), 128.99 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 11.5 Hz), 130.53 (s, C13), 131.83 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 11.5 Hz), 133.19 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 3.8 Hz), 134.34 (d, C2, $^3J_{CP}$ = 9.6 Hz), 141.99 (s, C1), 142.14 (s, C3), 150.65 (s, C8), 178.13 (s, C7). IR (KBr, ν/cm^{-1}): 512(m), 606(m) (ν(P═S)), 623(m), 690(m), 710(s), 724(m), 754(m), 760(m), 951(m), 1115(m), 1273(m), 1303(m), 1373(s), 1427(m), 1435(m), 1458(m), 1491(w) (ν(C═N)), 1575(w), 2922(w), 3095(w), 3142(m), 3430(w). Anal. Calcd for $C_{25}H_{18}ClN_2PPdS_2$: C, 51.47; H, 3.11; N, 4.80. Found: C, 51.34; H, 3.13; N, 4.91.

{2-(1,3-Benzothiazol-2-yl)-6-[(diphenylthiophosphoryl)amino]-phenyl}platinum Chloride, ***14b***. A solution of $(PhCN)_2PtCl_2$ (53 mg, 0.112 mmol) and ligand **9** (50 mg, 0.112 mmol) in 15 mL of CH_3CN was refluxed for 20 h. The resulting precipitate was filtered and recrystallized from a DMSO−Et_2O (1:3) mixture to give 29 mg of **14b** as a yellow, crystalline solid. Yield: 38%. Mp: >180 °C (dec). $^{31}P\{^1H\}$ NMR (121.49 MHz, DMSO-d_6): δ 42.09($^2J_{PPt}$= 65.7 Hz) ppm. ^1H NMR

(300.13 MHz, DMSO-d_6): δ 7.06 (d, 1H, HC(4), $^3J_{HH}$ = 7.5 Hz), 7.20 (m, 1H, H(C5)), 7.42 (d, 1H, HC(6), $^3J_{HH}$ = 7.3 Hz), 7.50−7.62 (m, 2H, H(C10)+H(C11)), 7.67−7.80 (m, 6H, *p*- and *m*-H in P(S)Ph_2), 7.88 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 13.7 Hz), 8.18 (d, 1H, H(C12), $^3J_{HH}$ = 8.0 Hz), 9.22 (d, 1H, NH, $^2J_{HP}$ = 7.5 Hz), 9.73 (d, 1H, H(C9) $^3J_{HH}$ = 8.2 Hz). IR (KBr, ν/cm^{-1}): 513(m), 605(m) (ν(P═S)), 623(w), 685(m), 710(s), 724(w), 747(m), 753(m), 955(m), 1023(w), 1101(m), 1115(m), 1274(m), 1297(m), 1305(m), 1372(s), 1424(m), 1435(m), 1458(m), 1484(w) (ν(C═N)), 1580(w), 2924(w), 3098(w), 3174(m), 3438(m). Anal. Calcd for $C_{25}H_{18}ClN_2PPtS_2$: C, 44.68; H, 2.70; N, 4.17. Found: C, 44.60; H, 2.87; N, 4.02.

Catalytic Experiments. In a typical experiment a solution of 0.25 mmol of aryl halide, 0.375 mmol of $PhB(OH)_2$, 0.5 mmol of K_3PO_4, and the mentioned amount of the corresponding palladium complex (used as titrated solutions in DMF) in 1 mL of DMF was heated at the corresponding temperature (ordinarily at 120 °C) for 5 h. For kinetic experiments the time was varied from 30 min up to 5 h. After cooling, the reaction mixture was treated with water (3−4 mL), extracted with benzene, and analyzed by GC. Hg(0) poisoning experiments were performed according to ref 34 with 300 equiv of Hg relative to the metal complex. Hg was added at either t = 0 or 20 min to the reaction mixture.

X-ray Crystallography. Single crystals were grown by recrystallization of **3** from a CH_2Cl_2−EtOH (1:3) solution, slow diffusion of ethanol into a DMSO solution of **12**, and slow diffusion of pentane into CH_2Cl_2 solutions of **13** and **15**. All diffraction data were collected on a Bruker SMART APEX II CCD diffractometer [λ(Mo Kα) = 0.71072 Å, ω-scans] at 100 K. The substantial redundancy in data allows the empirical absorption correction to be made with the SADABS program (Sheldrick, G. M., SADABS; University of Gottingen, 1996) using multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic−isotropic approximation. All calculations were performed with the SHELXTL software package (SHELXTL, version 6.1; Bruker AXS Inc.: Madison, WI, 2005). Crystal data and structure refinement parameters are listed in Table 3.

■ ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The authors are grateful to the Russian Foundation for Basic Research (grant 08-03-00508) for financial support.

■ REFERENCES

(1) For reviews on the Suzuki−Miyaura cross-coupling, see: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (c) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. (d) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633. (e) Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *248*, 2283. (f) Bellina, F.; Carpita, A.; Rossi, R. *Synthesis* **2004**, 2419. (g) Barder, T. E.; Walker, Sh. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685. (h) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442. (i) Franzen, R.; Xu, Y. *Can. J. Chem.* **2005**, *83*, 266. (j) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133. (k) Alonso, F.; Beletskaya, I. P.; Yus, M. *Tetrahedron* **2008**, *64*, 3047, and references therein.

(2) For some recent advances in application of Suzuki cross-coupling, see: (a) Molander, G. A.; Gormisky, P. E.; Sandrock, D. L. *J. Org. Chem.* **2008**, *73*, 2052. (b) Tan, Ch. G.; Grass, R. N. *Chem. Commun.* **2008**, 4297. (c) Davies, C. J.; Gregory, A.; Griffith, P.; Perkins, T.; Singh, K.; Solan, G. A. *Tetrahedron* **2008**, *64*, 9857. (d) Smith, A. E.; Clapham, K. M.; Batsanov, A. S.; Bryce, M. R.; Tarbit, B. *Eur. J. Org. Chem.* **2008**, 1458. (e) Roulland, E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3762. (f) Kylmala, T.; Kuuloja, N.; Xu, Y.; Rissanen, K.; Franzen, R. *Eur. J. Org. Chem.* **2008**, 4019. (g) Burzicki, G.; Voisin-Chiret, A. S.; Sopkovà-de Oliveira Santos, J.; Rault, S. *Tetrahedron* **2009**, *65*, 5413. (h) Grimm, J. B.; Wilson, K. J.; Witter, D. J. *J. Org. Chem.* **2009**, *74*, 6390. (i) Kabri, Y.; Gellis, A.; Vanelle, P. *Eur. J. Org. Chem.* **2009**, 4059. (j) Filatov, M. A.; Guilard, R.; Harvey, P. D. *Org. Lett.* **2010**, *12*, 196. (k) Bergin, E.; Hughes, D. L.; Richards, Ch. J. *Tetrahedron: Asymmetry* **2010**, *21*, 1619. (l) Knappke, Ch. E. I.; von Wangelin, A. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 3568. (m) Liu, T.-P.; Xing, Ch.-H.; Hu, Q.-Sh. *Angew. Chem., Int. Ed.* **2010**, *49*, 2909. (n) Afonso, A.; Roses, C.; Planas, M.; Feliu, L. *Eur. J. Org. Chem.* **2010**, 1461.

(3) (a) Botella, L.; Najera, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 179. (b) Alonso, D. A.; Najera, C.; Pacheco, M. C. *J. Org. Chem.* **2002**, *67*, 5588. (c) Zim, D.; Gruber, A. S.; Ebeling, G.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2000**, *2*, 2881. (d) Bedford, R. B.; Cazin, C. S. J. *Chem. Commun.* **2001**, 1540. (e) Bedford, R. B.; Cazin, C. S. J.; Hazelwood, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 4120. (f) Schnyder, A.; Indolese, A. F.; Studer, M.; Blaser, H. U. *Angew. Chem., Int. Ed.* **2002**, *41*, 3668. (g) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E.; Albisson, D. A.; Draper, S. M.; Scully, P. N.; Coles, S. J.; Hursthouse, M. B. *Chem.−Eur. J.* **2003**, *9*, 3216. (h) Navarro, O.; Kelly, R. A.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194.

(4) For reviews on catalytic properties of pincer complexes, see: (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (b) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (c) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (d) Morales-Morales, D. *Rev. Soc. Quím. Méx.* **2004**, *48*, 338. (e) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. (f) Moreno, I.; SanMartin, R.; Ines, B.; Churruca, F.; Dominguez, E. *Inorg. Chim. Acta* **2009**, *363*, 1903. (g) Moreno, I.; SanMartin, R.; Ines, B.; Herrero, M. T.; Domínguez, E. *Curr. Org. Chem.* **2009**, *13*, 878. (h) Morales-Morales, D. *Curr. Org. Synth.* **2009**, *6*, 169.

(5) Morales-Morales, D.; Jensen, C. M., Eds. *The Chemistry of Pincer Compounds*; Elsevier: New York, 2007.

(6) For recent examples of application of pincer complexes for the Suzuki−Miyaura cross-coupling, see: (a) Zhang, B.-Sh.; Wang, Ch.; Gong, J.-F.; Song, M.-P. *J. Organomet. Chem.* **2009**, *694*, 2555. (b) Lipke, M. C.; Woloszynek, R. A.; Ma, L.; Protasiewicz, J. D. *Organometallics* **2009**, *29*, 188. (c) Solano-Prado, M. A.; Estudiante-Negrete, F.; Morales-Morales, D. *Polyhedron* **2010**, *29*, 592. (d) Hurtado, J.; Ibanez, A.; Rojas, R.; Valderrama, M. *Inorg. Chem. Commun.* **2010**, *13*, 1025. (e) Yorke, J.; Sanford, J.; Decken, A.; Xia, A. *Inorg. Chim. Acta* **2010**, *363*, 961. (f) Hao, X.-Q.; Wang, Y.-N.; Liu, J.-R.; Wang, K.-L.; Gong, J.-F.; Song, M.-P. *J. Organomet. Chem.* **2010**, *695*, 82. (g) Serrano-Becerra, J. M.; Hernández-Ortega, S.; Morales-Morales, D. *Inorg. Chim. Acta* **2010**, *363*, 1306.

(7) Bedford, R. B.; Draper, S. M.; Scully, P. N.; Welch, S. L. *New J. Chem.* **2000**, *24*, 745.

(8) (a) Rosa, G. R.; Ebeling, G.; Dupont, J.; Monteiro, A. L. *Synthesis* **2003**, *18*, 2894. (b) Rosa, G. R.; Rosa, C. H.; Rominger, F.; Dupont, J.; Monteiro, A. L. *Inorg. Chim. Acta* **2006**, *359*, 1947.

(9) (a) Ines, B.; SanMartin, R.; Churruca, F.; Dominquez, E.; Urtiga, M. K.; Arriortua, M. I. *Organometallics* **2008**, *27*, 2833. (b) Ines, B.; Moreno, I.; SanMartin, R.; Dominquez, E. *J. Org. Chem.* **2008**, *73*, 8448.

(10) Bolliger, J. L.; Blacque, O.; Frech, C. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6514.

(11) Sheloumov, A. M.; Tundo, P.; Dolgushin, F. M.; Koridze, A. A. *Eur. J. Inorg. Chem.* **2008**, 572.

(12) Kozlov, V. A.; Aleksanyan, D. V.; Nelyubina, Yu. V.; Lyssenko, K. A.; Gutsul, E. I.; Puntus, L. N.; Vasil'ev, A. A.; Petrovskii, P. V.; Odinets, I. L. *Organometallics* **2008**, *27*, 4062.

(13) Kozlov, V. A.; Aleksanyan, D. V.; Nelyubina, Yu. V.; Lyssenko, K. A.; Gutsul, E. I.; Vasil'ev, A. A.; Petrovskii, P. V.; Odinets, I. L. *Dalton Trans.* **2009**, 8657.

(14) Aleksanyan, D. V.; Kozlov, V. A.; Nelyubina, Y. V.; Lyssenko, K. A.; Puntus, L. N.; Gutsul, E. I.; Shepel, N. E.; Vasil'ev, A. A.; Petrovskii, P. V.; Odinets, I. L. *Dalton Trans.* **2011**, *40*, 1535.
(15) Kozlov, V. A.; Aleksanyan, D. V.; Nelyubina, Yu. V.; Lyssenko, K. A.; Vasil'ev, A. A.; Petrovskii, P. V.; Odinets, I. L. *Organometallics* **2010**, *29*, 2054.
(16) (a) Gai, X.; Grigg, R.; Collard, S.; Muir, J. E. *Chem. Commun.* **2000**, 1765. (b) Grigg, R.; Khamnaen, T.; Rajviroongit, Sh.; Sridharana, V. *Tetrahedron Lett.* **2002**, *43*, 2601. (c) Gai, X.; Grigg, R.; Koppen, I.; Marchbank, J.; Sridharan, V. *Tetrahedron Lett.* **2003**, *44*, 7445. (d) Gai, X.; Grigg, R.; Ramzan, M. I.; Sridharan, V.; Collard, S.; Muir, J. E. *Chem. Commun.* **2000**, 2053.
(17) Okamoto, K.; Kanbara, T.; Yamamoto, T.; Wada, A. *Organometallics* **2006**, *25*, 4026.
(18) Stevens, M. F. G.; McCall, C. J.; Lelieveld, P.; Alexander, P.; Richter, A.; Daviess, D. E. *J. Med. Chem.* **1994**, *37*, 1689.
(19) Yoon, M. S.; Ryu, D.; Kim, J.; Ahn, K. H. *Organometallics* **2006**, *25*, 2409.
(20) Vicente, J.; Abad, J. A.; Lopez-Saez, M.-J.; Jones, P. G. *Organometallics* **2006**, *25*, 1851.
(21) In the Suzuki reaction usually no side products are observed. Indeed, in the reactions catalyzed by complexes **12**−**15**, no products of homocoupling were detected at any significant level according to the GC data, so conversion of the starting aryl halide was perceived to conform with the yield of a biphenyl product.
(22) Such a pathway of (pre)catalyst decomposition was previously observed for another type of pincer palladacycle having a coordinated O−P═S moiety, that is, thiophosphoryloxy−thiophosphoryl palladium pincer complexes **X**.
(23) (a) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. (b) Morales-Morales, D.; Redon, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619. (c) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161. (d) Aydin, J.; Larsson, J. M.; Selander, N.; Szab, K. J. *Org. Lett.* **2009**, *11*, 2852.
(24) Bumagin, N. A.; Bykov, V. V.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1990**, *315*, 1133.[*Dokl. Chem. (Engl. Transl.)*, **1990**, *315*, 354].
(25) (a) Widegren, J. A.; Finke, R. G. J. *Mol. Catal. A: Chem.* **2003**, *198*, 317. (b) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609. (c) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884. (d) Tsuji, Y.; Fujihara, T. *Inorg. Chem.* **2007**, *46*, 1895. (e) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161.
(26) (a) Gerber, R.; Blacque, O.; Frech, Ch. M. *ChemCatChem.* **2009**, *1*, 393. (b) Olsson, D.; Wendt, O. F. *J. Organomet. Chem.* **2009**, *694*, 3112.
(27) Bedford, R. B.; Welch, S. L. *Chem. Commun.* **2001**, 129.
(28) Compound **1** was synthesized using the general procedure reported in ref 18. The yield of the product was 65%, and physicochemical characteristics were identical to those previously reported by us.[12]
(29) Rivier, H.; Zeltner, J. *Helv. Chim. Acta* **1937**, *20*, 691.
(30) Johnes, I. B.; DiPietro, H. R. *J. Org. Chem.* **1964**, *29*, 1970.
(31) Stevens, M. F. G.; Shi, D.-F.; Castro, A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 83.
(32) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1975.
(33) Mukhopadhyay, Ch.; Datta, A. *J. Heterocycl. Chem.* **2009**, *46*, 91.
(34) Weddle, K. S.; Aiken, J. D.; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653.