ChemPubSoc Europe

DOI: 10.1002/ejic.201700823

EurJIC European Journal of Inorganic Chemistry

Full Paper

Palladium–Sulfur Catalysts

Mercaptoaryl-Oxazoline Complexes of Palladium and Their High Activities as Catalysts for Suzuki–Miyaura Coupling Reactions in Water

Christof Holzer,[a,b] Antoine Dupé,[a] Lydia M. Peschel,[a] Ferdinand Belaj,[a] and Nadia C. Mösch-Zanetti*[a]

Abstract: The synthesis, spectroscopic characterization, and catalytic activities of a series of Pd^{II} complexes bearing the monoanionic, bidentate ligand 2-(2-thiophenyl)-4,4-dimethyloxazoline (S-Phoz) are reported. These complexes were used as precatalysts for Suzuki–Miyaura coupling reactions under aqueous conditions. The dimers $[\{PdX(S\text{-}Phoz)\}_2]$ (X = Cl, Br, I; **1**–**3**) were treated with the N-heterocyclic carbene (NHC) ligand 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) to afford the mononuclear complexes [PdX(S-Phoz)(IMes)] (X = Cl, Br, I; **4**–**6**). The σ-donor/π-acceptor complexes $[PdCl(S\text{-}Phoz)(EPh_3)]$ (E = P, As, Sb; **7**–**9**) were synthesized to evaluate the influence of a second donor ligand on the catalytic activity. Within the [PdCl(S-Phoz)L] series, the activity trend for L follows the trend PPh_3 > IMes ≈ $AsPh_3$ > $SbPh_3$. The sulfur-bridged dinuclear complexes **1**–**3** are highly active for the benchmark coupling of *p*-bromoacetophenone with phenylboronic acid and exhibit turnover frequencies (TOFs) of up to 16000 h^{-1}. DFT and G_0W_0 calculations were performed to rationalize the facile reduction and, hence, excellent activities of the dinuclear complexes.

Introduction

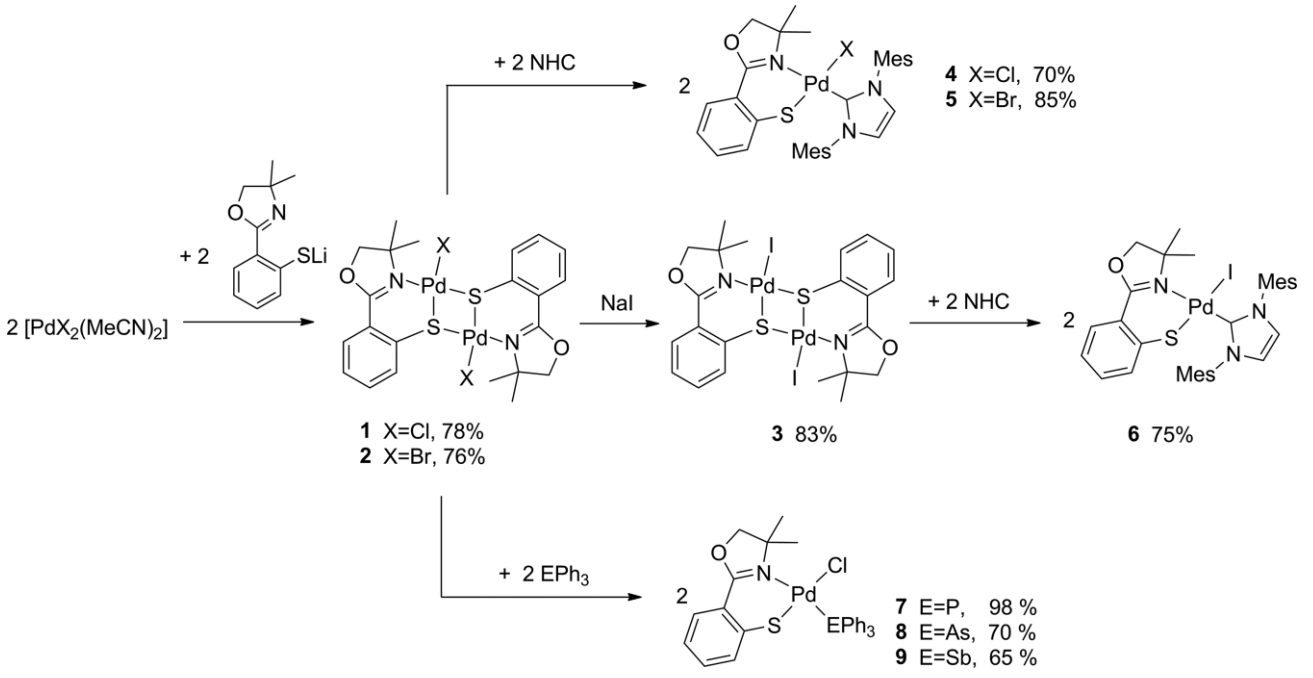
The discovery of the $[Pd(PPh_3)_4]$-catalyzed cross-coupling reaction of phenylboronic acid with haloarenes by Miyaura, Yanagi, and Suzuki in 1981[1] led to the development of numerous palladium catalytic systems for the cross-coupling of sp^2-hybridized aromatic carbon atoms and boronic acids. These systems are used in industrial syntheses to produce a wide variety of products, including pharmaceuticals.[2] The two most prominent ligand systems for these Pd-catalyzed reactions are phosphines and N-heterocyclic carbenes (NHCs),[3] which enable stereoelectronic fine-tuning at the metal center. Hence, low catalyst loadings and high yields can be achieved, even for demanding substrates such as aryl chlorides.[4,5] To design more eco-friendly and cheaper processes, the use of water as the solvent for Suzuki–Miyaura coupling (SMC) was investigated extensively.[6] To overcome the poor solubility of the catalysts and reactants in H_2O, various methods were developed, for example, sulfonation of the ligand,[7] the use of cyclodextrin-substituted catalysts,[8,9] high reaction temperatures, and the addition of phase-transfer catalysts.[8,10]

Having established our expertise in the coordination of the 2-(2-thiophenyl)-4,4-dimethyloxazoline (S-Phoz) ligand with group 6 and 10 metals,[11,12] we recognized the potential of our previously reported Pd–(S-Phoz) system for Suzuki–Miyaura couplings in water. In agreement with the hard and soft acids and bases (HSAB) principle, Pd–S bonds are strong, as this interaction is seen as a soft-acid, soft-base bond, which is believed to be beneficial under the usually harsh conditions applied during SMC in water. Numerous Pd catalysts bearing thiolate or thioether ligands, phosphine or NHC ligands, or both catalyze SMC reactions,[13–15] some of them in water.[16–18] The latter are active at elevated temperatures (≥100 °C) or with catalyst loadings of 0.1–1 mol-%; therefore, possible improvements could be made. Thus, the established stabilities of palladium thiophenolate complexes under the aqueous, basic conditions and elevated temperatures necessary for green Suzuki–Miyaura couplings is a good starting point for the search for new sulfur-based cross-coupling catalysts that could exhibit higher catalytic activities.

Results and Discussion

The halide complexes of the type $[\{PdX(S\text{-}Phoz)\}_2]$ (X = Cl, **1**; Br, **2**; I, **3**) were prepared as shown in Scheme 1. Through the procedure previously reported by our group, the reaction of $[PdX_2(MeCN)_2]$ (X = Cl, Br) and LiS-Phoz[12] in acetonitrile under reflux allowed the isolation of yellow-orange **1** and orange **2**, respectively, as microcrystalline powders in very good yields.[11] The corresponding orange-red iodido complex $[\{PdI(S\text{-}Phoz)\}_2]$ (**3**) was prepared in a Finkelstein-type reaction by stirring an acetone solution of **1** and a 25-fold excess of NaI at 40 °C for 6 h.

[a] *Institute of Chemistry, University of Graz, Schubertstraße 1, 8010 Graz, Austria*
E-mail: nadia.moesch@uni-graz.at
[b] *Institute of Physical Chemistry, Karlsruher Institut für Technologie, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany*
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.201700823.



Scheme 1. Synthesis of palladium complexes **1**–**9**. Mes = 2,4,6-trimethylphenyl (mesityl).

The palladium dimers **1**–**3** were subjected to the coordination of additional donor ligands. The bulky σ-donor ligand 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) was treated with 0.5 equiv. of the Pd dimers **1**–**3** in toluene at room temp. to yield the corresponding cleavage products [PdX(S-Phoz)(IMes)] (X = Cl, Br, I; **4**–**6**, Scheme 1). The reactions were apparent as the insoluble starting materials were consumed slowly to yield yellow to orange solutions. The products were obtained as yellow (**4**), yellow-orange (**5**), and orange (**6**) crystals after recrystallization from benzene. In addition, [{PdCl(S-Phoz)}$_2$] (**1**) was cleaved with stoichiometric amounts of the series of group 15 donor ligands PPh_3, $AsPh_3$, and $SbPh_3$ in $CHCl_3$ at room temp. to afford [PdCl(S-Phoz)(EPh_3)] (E = P, As, Sb; **7**–**9**). Again, the slow reactions were apparent as the insoluble **1** was consumed slowly to yield orange-red **7**,[11] red **8**, and deep red **9**. Recrystallization from benzene afforded the desired complexes as microcrystalline powders.

All of the obtained complexes are stable towards air and moisture and can be stored for several months without apparent decomposition. Compound **1** is only sparingly soluble in CH_2Cl_2, $CHCl_3$, and 1,2-dichlorethane and insoluble in other organic solvents including benzene, toluene, and acetonitrile. The solubility of **2** is even lower, and **3** is practically insoluble in chlorinated solvents. All three complexes are insoluble in water. The cleavage of the dimers improves the solubility significantly. Complexes **4**–**9** are soluble in chlorinated solvents as well as polar nonchlorinated and aromatic solvents. Within the three general structures [{PdX(S-Phoz)}$_2$] (**1**–**3**), [PdX(S-Phoz)(IMes)] (**4**–**6**), and [PdCl(S-Phoz)(EPh_3)] (**7**–**9**), the ^{1}H NMR spectra and, if they could be obtained, ^{13}C NMR spectra indicate high structural similarities. The ^{1}H NMR spectra of **1**–**3** are characterized by significantly broadened resonances for the CH_2 protons of the oxazoline moiety, and the signal broadening has been attributed to dynamic behavior in solution. Owing to the inherent low solubilities of **2** and **3**, their ^{1}H NMR spectra could only be obtained with increased scan numbers. No ^{13}C NMR resonances could be detected after 4000 scans. The ^{1}H NMR spectra of **4**–**6** are characterized by four sharp methyl singlets for the mesitylene and dimethyloxazoline moieties as well as the signal of the imidazolium (N–CH=CH–N) protons, which interestingly resonate as a singlet at δ = 6.2 ppm. The attenuated total reflectance (ATR) IR spectra exhibited pronounced C=N bands at $\tilde{\nu}$ = at 1607 (**1**), 1611 (**2**), 1611 (**3**), 1610 (**4**), 1612 (**5**), 1614 (**6**), 1615 (**7**), 1610 (**8**), and 1612 cm^{-1} (**9**). The molecular structures of **4**–**6** were elucidated through XRD, which confirmed the suggested [PdX(S-Phoz)(IMes)] structures (vide infra). The molecular structures of [{PdCl(S-Phoz)}$_2$] (**1**) and [PdCl(S-Phoz)(PPh_3)] (**7**) were obtained previously,[11] and analogous structures are proposed for **2**/**3** and **8**/**9** owing to their pronounced similarities.

Molecular Structures

The molecular structures of the IMes complexes **4**–**6** were determined by X-ray diffraction analyses. Suitable single crystals were obtained by the slow evaporation of saturated benzene solutions at room temperature, and the molecular structures are shown in Figure 1. Selected bond lengths and angles are presented in Table 1, and the crystallographic details are listed in Table 2 and the Supporting Information.

All [PdX(S-Phoz)(IMes)] (X = Cl, Br, I; **4**–**6**) complexes feature distorted square-planar Pd^{II} centers, the first coordination spheres of which contain one bidentate S-Phoz ligand, the carbene moiety of the IMes ligand, and the respective halide ligand. The distortion from ideal square-planar geometry increases from Cl to I, and the respective τ_4 values[19] are 0.037 (**4**), 0.061

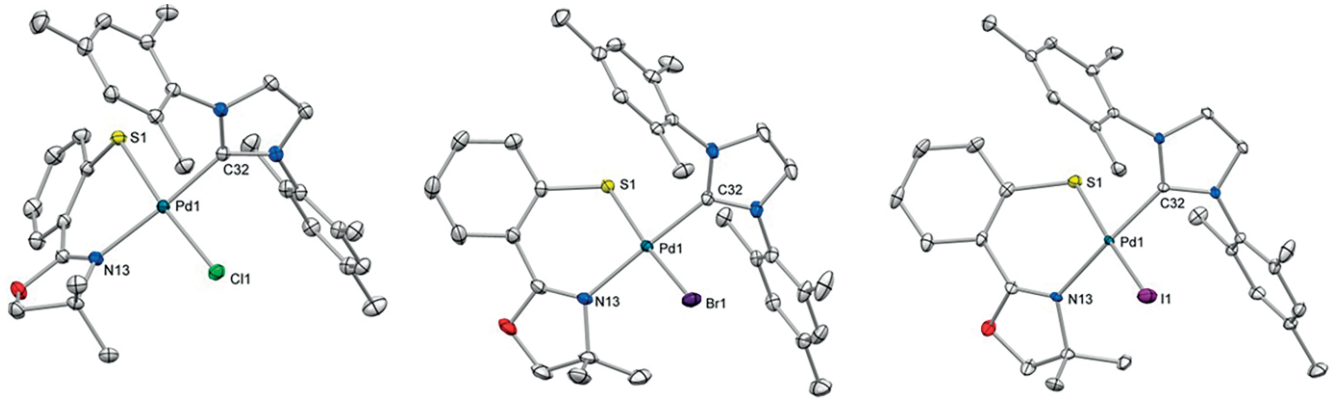


Figure 1. Molecular structures of [PdX(S-Phoz)(IMes)] (X = Cl, Br, I; **4**–**6**). Probability ellipsoids are drawn at the 50 % level, hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for [PdX(S-Phoz)(IMes)] (**4**–**6**).

	4, X = Cl	**5**, X = Br	**6** X = I
Pd1–X1	2.3559(3)	2.4793(2)	2.6380(3)
Pd1–N13	2.0946(9)	2.1125(13)	2.112(2)
Pd1–S1	2.2706(3)	2.2784(4)	2.2967(7)
Pd1–C32	1.9794(10)	1.9853(16)	1.989(3)
S1–Pd1–X1	174.739(10)	170.96(3)	170.808(19)
C32–Pd1–N13	175.95(4)	173.75(6)	171.40(9)
C32–Pd1–X1	87.08(3)	86.37(5)	87.32(7)
N13–Pd1–X1	95.49(2)	96.28(4)	97.43(6)
N13–Pd1–S1	89.75(2)	89.84(4)	88.72(7)
C32–Pd1–S1	87.70(3)	88.22(5)	87.47(8)

(**5**), and 0.071 (**6**). As expected, the Pd1–X1 bond length increases significantly from Cl to I from 2.3559(3) to 2.6380(3) Å. The Pd–N13 and Pd–S1 bond lengths follow this trend but are less pronounced, whereas the Pd–C32 bond lengths remain largely uninfluenced. All of the observed bond lengths and angles are within the ranges for previously reported [PdX(imidazolidine)] compounds[18,20] and compounds with [PdXSNC] cores.[21]

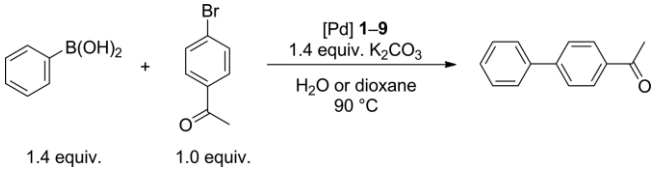
Catalytic Suzuki–Miyaura Couplings

To assess the activities of our complexes as catalysts for the Suzuki–Miyaura Coupling reaction in water, the coupling of *p*-bromoacetophenone with phenylboronic acid was investigated as a benchmark reaction (Scheme 2). In a typical catalytic run, *p*-bromoacetophenone (1 mmol) and phenylboronic acid (1.4 mmol) were reacted in the presence of K_2CO_3 (1.4 mmol) and the corresponding loading of catalyst in water (5 mL) at 90 °C. The reaction was also tested with NaOH or diisopropylamine as the base, but the best results were obtained with K_2CO_3. The results for the screening of the catalysts and the reactions conditions are presented in Table 3. To confirm the role of water in the formation of the active catalytic species, the

Table 2. Crystallographic data and structure-refinement details for **4**–**6**.

	[PdCl(S-Phoz)(IMes)] (**4**)	[PdBr(S-Phoz)(IMes)] (**5**)	[PdI(S-Phoz)(IMes)] (**6**)
Empirical formula	$C_{32}H_{36}ClN_3OPdS{\cdot}2(C_6H_6)$	$C_{32}H_{36}IN_3OPdS$	$C_{32}H_{36}BrN_3OPdS$
Crystal description	block, yellow	block, orange	block, orange
Crystal size [mm]	0.24 × 0.21 × 0.20	0.30 × 0.25 × 0.21	0.29 × 0.18 × 0.13
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $C2/c$	monoclinic, $P2_1/n$
a [Å]	15.7798(5)	15.1540(8)	12.3987(4)
b [Å]	14.5940(5)	14.7111(7)	13.8467(4)
c [Å]	17.4554(6)	27.3264(12)	17.5863(5)
β [°]	103.2628(13)	100.8295(17)	91.7953(13)
Z	4	8	4
Reflections collected/unique	65894/17222	85223/8725	39242/8803
Significant unique reflections [$I > 2\sigma(I)$]	14560	7867	7843
R(int), *R*(σ)	0.0308, 0.0273	0.0423, 0.0293	0.0272, 0.0366
Completeness to θ max [%]	99.9 (θ = 35°)	100 (θ = 30°)	99.9 (θ = 30°)
Refinement method	Full-matrix least-squares on F^2		
Data/parameters/restraints	17222/483/0	8725/373/0	8803/373/0
Goodness-of-fit on F^2	1.026	1.087	1.053
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0251	R_1 = 0.0244	R_1 = 0.0349
	wR_2 = 0.0616	wR_2 = 0.0596	wR_2 = 0.1032
R indices (all data)	R_1 = 0.0345	R_1 = 0.0288	R_1 = 0.0399
	wR_2 = 0.0668	wR_2 = 0.0612	wR_2 = 0.1080
CCDC	1532713	1532715	1532714

reactions were also tested in dioxane, but the catalysts were significantly more active in water.



Scheme 2. Cross-coupling reaction of *p*-bromoacetophenone with phenylboronic acid.

Table 3. Screening and results for the SMC of *p*-bromoacetophenone with phenylboronic acid.

Catalyst	Loading [mol-%][a]	Solvent	Time [h]	Conversion [%]	TOF [h^{-1}][b]	TON[b]
1	0.1	H_2O	24	>99	21	500
1	0.1	dioxane	24	34	7	170
1	0.01	H_2O	1.5	>99	3333	5000
1	0.01	H_2O	1	> 99	5000	5000
1	0.001	H_2O	3	96	16000	48000
2	0.1	H_2O	24	>99	21	500
2	0.1	dioxane	24	50	10	250
2	0.01	H_2O	1.5	>99	3333	5000
2	0.01	H_2O	1	>99	5000	5000
3	0.01	H_2O	1.5	88	3333	5000
3	0.01	H_2O	1	>99	5000	5000
4	0.1	H_2O	24	>99	42	1000
4	0.1	dioxane	24	61	25	610
4	0.02	H_2O	1.5	90	3000	4500
5	0.1	H_2O	24	>99	42	1000
5	0.1	dioxane	24	48	20	480
5	0.02	H_2O	1.5	93	3100	4650
6	0.02	H_2O	1.5	92	3067	4600
7	0.1	H_2O	24	>99	42	1000
7	0.1	dioxane	24	20	8	200
7	0.02	H_2O	1.5	>99	3333	5000
7	0.02	H_2O	1	94	4700	4700
8	0.02	H_2O	3	60	1000	3000
9	0.02	H_2O	3	20	333	1000

[a] Precatalyst loading. [b] Calculated per Pd center. General procedure: *p*-bromoacetophenone (1.0 mmol), phenylboronic acid (1.4 equiv.), and K_2CO_3 (1.4 equiv.) in solvent (5 mL) at 90 °C.

To compare the efficiencies of the different catalysts, the reaction time was shortened to 1.5 h, and the catalyst loading was decreased to 0.02 or 0.01 mol-% for the dinuclear complexes. Under these conditions, **1**–**3** displayed full conversions to the product, as did mononuclear complex **7** (L = PPh_3), whereas **4**–**6** bearing the IMes ligand afforded 90–93 % conversions. The reaction was again shortened to 1 h for **7**, and 94 % conversion was obtained, which is equivalent to a turnover frequency (TOF) of 4700 h^{-1}. The optimization of the reactions conditions with the highly active dimer complexes allowed us to decrease the catalyst loading to 0.001 mol-% for **1**, and 96 % conversion of *p*-bromoacetophenone to 4-acetylbiphenyl was obtained after 3 h, which corresponds to a turnover number (TON) of 48000 and a TOF of 16000 h^{-1} per palladium center. Hence, our Pd(S-Phoz) catalyst **1** shows a higher activity than those of comparable literature-known systems with anionic S-donor moieties.[14,15,17,18,22] In water, TOFs of up to 2273 h^{-1} per Pd center were reached previously with a thiolato-functionalized benzannulated NHC ligand.[17] As dimers **1**–**3** show such high activities for the SMC in water, the formation of Pd^0 species is straightforward for this type of structure. To identify the nature of the active catalytic species, mercury drop tests were performed for **1**, **3**, **6**, and **7**. This test is used to assess the formation of Pd^0 nanoparticles. Amalgamation should only deactivate heterogeneous metal particle catalysts and is not expected to occur for ligated homogeneous Pd^{II} species.[23] For the coupling reaction of *p*-bromoacetophenone with phenylboronic acid in the presence of 0.01 mol-% of **1**, **3**, **6**, or **7**, a drop of Hg^0 was added to the reaction mixture at $t = 0$. In all four tests, the catalytic activity was completely stopped, and this suggests that the active catalytic species are indeed Pd^0 nanoparticles.

The SMC reactions of other liquid and solid bromoaryls with phenylboronic acid were also investigated (Table 4). The SMC of 4-bromophenol with phenylboronic acid afforded the corresponding coupling product in quantitative yield after 2 h in the presence of 0.01 mol-% of **1**. Similar results were obtained with the dinuclear complex **3**. As Pd^0 nanoparticles are possibly the active catalytic species for these reactions, the similar activities observed for **1** and **3** with different substrates confirm that a similar process occurs for the formation of nanoparticles from these dinuclear complexes, independent of the nature of the halide ligand. As bromobenzene is a liquid and immiscible with water, 75 % conversion was obtained for the SMC of PhBr with $PhB(OH)_2$ after 3 h in the presence of 0.02 mol-% of **1** or **3** in pure water. The reaction in a 5:1 EtOH/H_2O mixture resulted in a better conversion (94 % conversion, 0.02 mol-% **1**, 3 h, 90 °C).

The catalytic activities of the series with group 15 donor ligands, that is, [PdCl(S-Phoz)(EPh_3)] (**7**–**9**), decrease in the order PPh_3 > $AsPh_3$ > $SbPh_3$. This is attributed to the enhanced σ-donor ability and stronger *trans* effect of PPh_3 compared with those of $AsPh_3$ and $SbPh_3$.[24] Although NHC ligands have repeatedly enhanced the catalytic performances of precious-metal catalysts,[25] for our Pd–S-Phoz system, the σ-donor/π-acceptor ligand PPh_3 (**7**) exhibited superior performance compared with that of its IMes counterpart (**4**). However, when we investigated the more challenging SMC of chloroacetophenone with phenylboronic acid, only the NHC-substituted complex **6** was active, and 24 % conversion of the substrate to the biaryl

Table 4. SMC reactions of various substrates with phenylboronic acid in water catalyzed by (S-Phoz)Pd complexes.

Entry	Substrate	Solvent	Catalyst (loading)	Conversion [%]	Time [h]	TON[a]/TOF[a] [h^{-1}]
1	4-bromophenol	H_2O	**1** or **3** (0.01 mol-%)	>99	2	5000/2500
2	bromobenzene	H_2O	**1** or **3** (0.02 mol-%)	75	3	1875/625
3	bromobenzene	H_2O/EtOH (5:1)	**1** (0.02 mol-%)	94	3	2350/783
4	4-chlorotoluene	H_2O/THF (25:1)	**6** (0.1 mol-%)	24	18	240/–

[a] Calculated per Pd center. General procedure: substrate (1.0 mmol), phenylboronic acid (1.4 equiv.), and K_2CO_3 (1.4 equiv.) in solvent (5 mL) at 90 °C.

product was observed after 18 h with a catalyst loading of 0.1 mol-% (Table 4, Entry 4). To achieve this conversion, a stock solution of the catalyst in tetrahydrofuran (THF) was used, and the THF was not removed before the reaction. The addition of *tert*-butyl ammonium bromide as a phase-transfer agent[5] did not improve the yield. The reaction with **7** under the same conditions afforded a conversion of less than 10 %, and catalysts **1** and **3** did not afford any product.

Ab Initio Calculations of Quasiparticle States

Complexes **1**–**9** were optimized with the PBE0 hybrid functional[26] and the def2-TZVP basis set.[27] Dispersion effects on the geometry were included by employing a D3 dispersion correction with Becke–Johnson damping.[28] At the optimized geometries, single-point G_0W_0@PBE0/def2-TZVP(P) calculations were performed to determine the quasiparticle (QP) energies of **1**–**9**. To date, GW-based methods have mainly been used for the prediction of electronic structures in solid-state chemistry.[29] However, newer implementations and algorithms also allow the use of GW methods in finite molecular frameworks.[30–32] The PBE0 functional was chosen as the starting point for G_0W_0 calculations, as this combination previously yielded accurate results for quasiparticle energies.[30,33] As the quasiparticle states obtained by G_0W_0 are connected directly to the ionization potential (QP energies of occupied orbitals) and to electron-attached states (QP energies of empty orbitals), they give valuable information on how readily the compounds may be reduced or oxidized. The calculated highest occupied molecular orbitals (HOMOs) of **1**, **4**, and **7** are shown in Figure 2.

As summarized in Table 5, three groups emerge for **1**–**9**: the group with low QP HOMO and lowest unoccupied molecular orbital (LUMO) energies (**1**–**3**), the group with high QP HOMO/LUMO energies (**4**–**6**), and the one with intermediate QP HOMO/LUMO energies (**7**–**9**). Thus, the most catalytically active dinuclear complexes, **1**–**3**, have low HOMO/LUMO energies, and the G_0W_0 results suggest that these complexes are reduced with the least effort to form the active Pd^0 species under SMC reactions conditions. The HOMO/LUMO energies of the dinuclear complexes **1**–**3** are lower by ca. 1 eV compared with those of **4**–**6**, which show inferior catalytic performances. Within the groups **1**–**3** and **4**–**6**, it should be noted that the G_0W_0 calculations show similar LUMO energies for the Cl, Br, and I complexes, and this correlates with the observed similar catalytic activities within a group.

The G_0W_0 calculations also indicate that there are only subtle changes in the electronic structures of **7**–**9**. Although the catalytic performance of the PPh_3-ligated complex **7** is in good agreement with the calculated low LUMO energies, the significantly lower performances of its $AsPh_3$ and $SbPh_3$ homologues **8** and **9** cannot be explained by the information obtained from the theoretical calculations. Thus, for these complexes, we assume that the decreased catalytic efficiency is caused by the *trans* influence of the ligand in the catalytically active species (vide infra). One may also note that the HOMO–LUMO gaps of **1**–**9** are all very similar. Therefore, predictions based on these gaps alone are not expedient, and the catalytic activities of **1**–**9** in the studied reactions cannot be rationalized from them.

Overall, the study suggests that it is possible to use G_0W_0 calculations to rationalize some aspects of the catalytic performances of **1**–**9** in Suzuki–Miyaura couplings in water, in particular, the very good activities of the dinuclear complexes **1**–**3**, which are shown to be easily reduced to the Pd^0 active species. The reduction behavior of **1**–**3** was confirmed by electrochemical experiments: the cyclic voltammogram of the dinuclear complex **1** reveals an irreversible reduction at $E = -1.35$ V

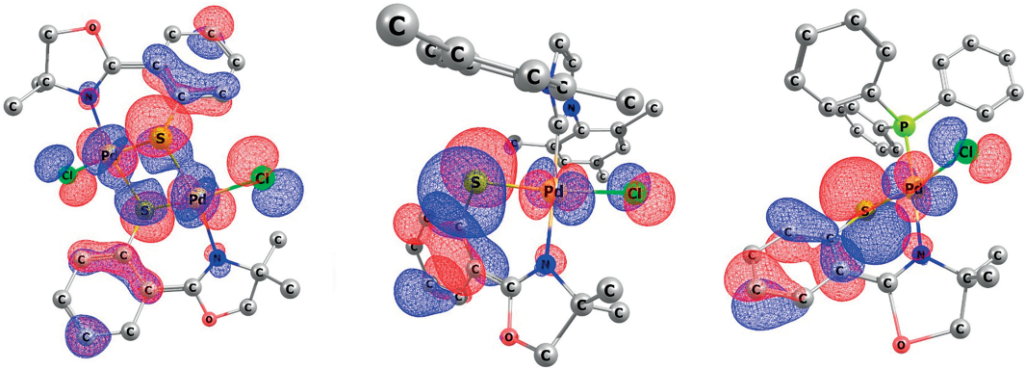


Figure 2. HOMOs of **1** (left), **4** (middle), and **7** (right) calculated at the PBE0/def2-TZVP(P) level and shown with an isovalue of 0.03. These examples represent the HOMOs of each group: high HOMO (**4**–**6**), intermediate HOMO (**7**–**9**), and low HOMO (**1**–**3**). The graphics were generated with Chemcraft 1.6.[34]

Table 5. Calculated PBE0/def2-TZVP and CC2/def2-TZVP excitation energies of the first dipole-allowed electronic excitations.

Complex	1	2	3	4	5	6	7	8	9
QP HOMO [eV] (G_0W_0@PBE0)	–7.33	–7.32	–7.10	–6.27	–6.39	–6.36	–6.53	–6.50	–6.65
QP LUMO [eV] (G_0W_0@PBE0)	–0.97	–1.07	–1.07	0.20	0.05	–0.05	–0.47	–0.49	–0.63
HOMO–LUMO gap [eV]	6.36	6.25	6.03	6.47	6.44	6.31	6.06	6.01	6.02
Catalytic activity [%][a]	>99[b]	>99[b]	>99[b]	90	92	93	>99	60	20

[a] The SMC of bromoacetophenone with phenylboronic acid, 0.02 mol-% catalyst precursor, H_2O, 3 h, 90 °C. [b] 0.01 mol-% catalyst precursor.

versus Ag/Ag^+ (Figure S1), whereas measurements with the mononuclear complexes **6** and **7** did not reveal any reduction process under these conditions.

Conclusions

Nine mononuclear and dinuclear Pd^{II} compounds bearing the mercaptoaryl-oxazoline ligand S-Phoz were synthesized and characterized. The obtained complexes are active precatalysts for Suzuki–Miyaura cross-coupling reactions in aqueous media, especially the sulfur-bridged dinuclear complexes, which are highly active for the benchmark coupling of *p*-bromoacetophenone with phenylboronic acid and exhibit TOFs of up to 16000 h^{-1}. The catalytic performances of these precursors could be correlated to their electronic features, as assessed through DFT and G_0W_0 calculations as well as electrochemical measurements. Even in the absence of unequivocal elucidation of the active species, all data point to the high influence of the reducibility of the precatalyst on the catalytic activity. Thus, these easily accessible Pd–(S-Phoz) complexes provide a new entry towards more efficient catalytic systems for SMC reactions under eco-friendly conditions, for example, SMC reactions in aqueous media.

Experimental Section

General Procedures: Unless otherwise specified, all experiments were performed under atmospheric conditions with standard laboratory equipment. Solvents were dried with a Pure Solv solvent purification system. LiS-Phoz, [{PdCl(S-Phoz)}$_2$] (**1**), and [PdCl(S-Phoz)(PPh$_3$)] (**7**) were synthesized according to our previously reported protocols.[11,12] The [PdX$_2$(MeCN)$_2$] precursors and the IMes NHC ligand were synthesized according to literature procedures.[35] All other chemicals were obtained from commercial sources and used without further purification. The NMR spectra were recorded with a Bruker Avance III 300 MHz spectrometer at 25 °C. The ^{1}H and ^{13}C chemical shifts are given in ppm and were referenced to the solvent signals. The ^{31}P NMR spectra were referenced externally to 85 % H_3PO_4. The coupling constants *J* are listed in Hz. The IR spectra of solid samples were measured with a Bruker ALPHA-P Diamant ATR-FTIR spectrometer at a resolution of 2 cm^{-1}. The signals were assigned on the basis of their relative intensities as strong (s) or medium (m), and weak signals were omitted. The mass spectra were recorded with an Agilent Technologies 5975C inert XL MSD instrument by the direct insertion technique. Elemental analyses were performed at the Microanalytical Laboratory of the University of Vienna with a EuroVector EA3000 analyzer or at the Institut für Anorganische Chemie of the TU Graz with an Elementar vario EL analyzer. The GC–MS measurements were performed with an Agilent 7890A instrument with a 19091J-433 column coupled to a 5975C mass spectrometer. The electrochemical measurements were performed under an inert atmosphere in a glovebox in dry CH_2Cl_2 with a Gamry Instruments Reference 600 potentiostat and a three-electrode setup. Glassy carbon was used as the working electrode, platinum wire (99.99 %) was used as the supporting electrode, and the reference electrode was a silver wire immersed in a 0.01 M $AgNO_3$/0.1 M $NBu_4(PF_6)$ CH_3CN solution, separated by a Vycor tip. NBu_4PF_6 (0.1 M) was used as the supporting electrolyte.

Crystallographic Details: The X-ray data collection was performed with a Bruker AXS SMART APEX2 CCD diffractometer with Mo-K_α radiation (0.71073 Å) at 100 K. Further details of the structure solutions can be found in the Supporting Information.

CCDC 1532713 (for **4**), 1532714 (for **6**), and 1532715 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Procedure for Catalytic Runs: Stock solutions of the catalysts were prepared (**1**–**3** in $CHCl_3$, **4**–**9** in THF), the corresponding amount of catalyst was placed in a 10 mL round-bottom flask, and the solvent was removed. Aryl bromide (1 mmol), K_2CO_3 (0.193 g, 1.4 mmol), and phenylboronic acid (0.171 g, 1.4 mmol) were weighed into the flask, and H_2O (5 mL) was added. The reaction mixture was stirred at 90 °C for the corresponding time, and then the solution was cooled to room temperature, extracted with ethyl acetate (5 mL), and dried with $MgSO_4$. For the conversion of *p*-bromoacetophenone to 4-bromophenol, the pure product could be isolated by simple filtration. The conversions and product yields were determined by GC–MS through peak integration with mesitylene as an internal standard. For the reactions with chloroacetophenone, catalyst **6** was used without the removal of the THF.

Theoretical Calculations: The structures were optimized with the PBE0 hybrid functional and added dispersion correction with Becke–Johnson damping (D3BJ). The def2-TZVPP basis set was used in conjunction with the Stuttgart–Dresden ECP28MWB basis set for Pd.[27,36] For all other elements, def2-TZVP was used.[27] The G_0W_0[31] calculations were performed with a PBE0 reference and the def2-TZVPP basis set for all elements except hydrogen, for which def2-TZVP was used. This combination is denoted as def2-TZVP(P). For the G_0W_0 quasiparticle calculations, electrons with orbital energies below −5.0 a.u. were frozen. For **1**–**3**, the point-group symmetry of the *Ci* group was exploited in all calculations. All calculations made use of the resolution of identity (RI) approximation with the corresponding def2-TZVP(P) fitting basis sets ("cbas").[37] All calculations were performed with a local version of Turbomole 7.1.[38]

[{PdBr(S-Phoz)}$_2$] (2): [PdBr$_2$(MeCN)$_2$] (0.290 g, 0.83 mmol) was suspended in MeCN (40 mL), and the suspension was stirred under reflux. After the solid dissolved, LiS-Phoz was added (0.186 mg, 0.87 mmol), and the reaction mixture was stirred under reflux for 3 h. After the mixture cooled to room temperature, the precipitate was isolated by filtration, washed with benzene, and dried in vacuo to afford **2** in 76 % yield (0.250 g, 0.32 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86 (s, 2 H, Ar-*H*), 7.48 (br s, 4 H, Ar-*H*), 7.38 (d, *J* = 8.2 Hz, 2 H, Ar-*H*), 4.32 (s, 4 H, CH_2), 1.79 (s, 6 H, Me), 1.71 (s, 6 H, Me) ppm. ^{13}C NMR not recorded owing to low solubility. IR (ATR): $\tilde{\nu}$ = 1611 (s, C=N), 1460 (m), 1365 (s), 1322 (m), 1108 (m), 1049 (s), 953 (s), 768 (s), 737 (s), 691 (m) cm^{-1}. EI-MS: *m*/*z* = 702.5 $[M - Br]^+$. $C_{22}H_{24}Br_2N_2O_2Pd_2S_2 \cdot 0.33C_6H_6$ (785.21 + 25.77): calcd. C 35.53, H 3.23, N 3.45; found C 35.61, H 3.61, N 3.41.

[{PdI(S-Phoz)}$_2$] (3): [{PdCl(S-Phoz)}$_2$] (**1**, 0.160 g, 0.23 mmol) and NaI (25 equiv., 0.862 g, 5.75 mmol) were suspended in acetone (25 mL), and the suspension was stirred at 40 °C for 24 h. The red precipitate was isolated by filtration, washed with acetone and water, and then dried in vacuo to afford **3** in 83 % yield (0.167 g, 0.19 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86–8.94 (m, 2 H, Ar-*H*), 7.37–7.55 (m, 6 H, Ar-*H*), 4.32 (m, 4 H, CH_2), 1.72–1.80 (m, 12 H, CH_3) ppm. ^{13}C NMR not recorded owing to low solubility. IR (ATR): $\tilde{\nu}$ = 1611 (s, C=N), 1466 (m), 1374 (s), 1324 (s), 1130 (m), 1113 (m), 1050 (m), 955 (s), 765 (s), 735 (s) cm^{-1}. EI-MS: *m*/*z* = 518.1 $[M - PdI_2]^+$. $C_{22}H_{24}I_2N_2O_2Pd_2S_2$ (879.21): calcd. C 30.05, H 2.73, N 3.19, S 7.29; found C 30.07, H 2.84, N 3.11, S 6.40.

General Procedure for the Syntheses of the IMes Complexes 4–6: A 2:1 mixture of IMes and [{PdX(S-Phoz)}$_2$] (**1–3**) was dissolved in

toluene (5 mL), and the solution was stirred for 24 h at room temperature and filtered through a pad of Celite. After the removal of the solvent in vacuo, the crude product was recrystallized from benzene. Single crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of benzene at room temp.

[PdCl(S-Phoz)(IMes)] (4): [{PdCl(S-Phoz)}$_2$] (**1**, 0.095 g, 0.14 mmol) and IMes (0.085 g, 0.28 mmol) afforded **4** in 70 % yield (0.125 g, 0.19 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.60 (d, J = 8.0 Hz, 1 H, Ar-*H*), 7.32 (d, J = 9.2 Hz, 1 H), 6.90 (ddd, J = 8.9, 7.7, 1.6 Hz, 1 H, Ar-*H*), 6.78 (d, J = 9.4 Hz, 4 H, Ar-*H*), 6.74–6.67 (m, 1 H, Ar-*H*), 6.19 (s, 2 H, N–C*H*=C*H*–N) 3.15 (s, 2 H, CH_2), 2.61 (s, 6 H, Me), 2.47 (s, 6 H, Me), 2.06 (s, 6 H, Me), 1.49 (s, 6 H, Me) ppm. ^{13}C NMR (300 MHz, C_6D_6): δ = 162.83 (NCN), 162.50 (C–S), 146.55 (Ar), 130.73 (Ar), 129.73 (Ar), 129.26 (Ar), 129.02 (Ar), 128.81 (Ar), 128.20 (Ar), 127.86 (Ar), 125.33 (Ar), 123.21 (N–CH=CH–N), 121.91, 80.86 (CH_2), 70.39 (O–*C*Me$_2$), 27.25 (Me), 20.60 (Me), 19.71 (Me), 19.06 (Me) ppm. IR (ATR): $\tilde{\nu}$ = 1610 (m, C=N), 1467 (m), 1376 (m), 1329 (m), 1057 (s), 730 (s) cm^{-1}. EI-MS: m/z = 653.4 [M]$^+$. $C_{32}H_{36}ClN_3OPdS{\cdot}2C_6H_6$ (652.57 + 156.23): calcd. C 65.34, H 5.98, N 5.20; found C 65.97, H 6.13, N 5.21.

[PdBr(S-Phoz)(IMes)] (5): [{PdBr(S-Phoz)}$_2$] (**2**, 0.086 g, 0.11 mmol) and IMes (0.067 g, 0.22 mmol) afforded **5** in 85 % yield (0.130 g, 0.19 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.55 (d, J = 7.9 Hz, 1 H, Ar-*H*), 7.26 (d, J = 7.8 Hz, 1 H, Ar-*H*), 6.89 (s, 1 H, Ar-*H*), 6.77 (d, J = 4.5 Hz, 4 H, Ar-*H*), 6.72 (s, 1 H, Ar-*H*), 6.21 (s, 2 H, N–C*H*=C*H*–N), 3.18 (s, 2 H, CH_2), 2.61 (s, 6 H, Me), 2.48 (s, 6 H, Me), 2.07 (s, 6 H, Me), 1.50 (s, 6 H, Me) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 163.32, 161.66, 146.62 (Ar), 138.28 (Ar), 136.56 (Ar), 135.88 (Ar), 135.45 (Ar), 130.62 (Ar), 129.72 (Ar), 129.39 (Ar), 128.91 (Ar), 123.44 (*N*–CH=CH–N), 122.17, 81.13 (CH_2), 70.43 (O–*C*Me$_2$), 27.60 (Me), 20.65 (Me), 20.52 (Me), 19.36 (Me) ppm. IR (ATR): $\tilde{\nu}$ = 1612 (s, C=N), 1466 (m), 1361 (s), 1327 (m), 1057 (s), 729 (s), 700 (d, s) cm^{-1}. EI-MS: m/z = 697.4 [M]$^+$. $C_{32}H_{36}BrN_3OPdS{\cdot}0.66C_6H_6$ (697.02 + 51.55): calcd. C 57.11, H 5.34, N 5.71; found C 57.26, H 5.65, N 5.83.

[PdI(S-Phoz)(IMes)] (6): [{PdI(S-Phoz)}$_2$] (**3**, 0.117 g, 0.13 mmol) and IMes (0.082 g, 0.27 mmol) afforded **6** in 75 % yield (0.146 g, 0.196 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.47 (dd, J = 8.0, 1.2 Hz, 1 H, Ar-*H*), 7.20 (dd, J = 7.7, 1.5 Hz, 1 H, Ar-*H*), 6.88 (td, J = 7.6, 1.6 Hz, 1 H, Ar-*H*), 6.77 (s, 4 H, Ar-*H* IMes), 6.70 (td, J = 7.5, 1.2 Hz, 1 H, Ar-*H*), 6.21 (s, 2 H, N–C*H*=C*H*–N), 3.24 (s, 2 H, CH_2), 2.59 (s, 6 H), 2.49 (s, 6 H, Me), 2.09 (s, 6 H, Me), 1.49 (s, 6 H, Me) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 163.80, 161.52, 147.34 (Ar), 138.64 (Ar), 136.49 (Ar), 136.46 (Ar), 135.94 (Ar), 130.91 (Ar), 130.44 (Ar), 130.12 (Ar), 129.93 (Ar), 129.42 (Ar), 129.05 (Ar), 124.10 (N–CH=CH–N), 122.65, 81.28 (CH_2), 70.80 (O–*C*Me$_2$), 28.79 (Me), 22.31 (Me), 21.05 (Me), 21.01 (Me), 19.98 (Me) ppm. IR (ATR): $\tilde{\nu}$ = 1614 (s, C=N), 1362 (s), 1326 (s), 1055 (s), 844 (m), 735 (s), 702 (s) cm^{-1}. EI-MS: m/z = 616.2 [M – I]$^+$. $C_{32}H_{36}IN_3OPdS{\cdot}0.66C_6H_6$ (744.03 + 51.55): calcd. C 54.31, H 5.06, N 5.28; found C 54.30, H 5.07, N 5.65.

General Procedure for the Syntheses of Group 15 Donor Complexes 8 and 9: Stoichiometric amounts of [{PdCl(S-Phoz)}$_2$] (**1**) and EPPh$_3$ (E = As, Sb) were suspended in benzene, and the suspension was stirred for 24 h. The obtained solution was filtered through a pad of Celite, the solvent was evaporated in vacuo, and the residue was washed thoroughly with pentane to yield the desired complex.

[PdCl(S-Phoz)(AsPh$_3$)] (8): [{PdCl(S-Phoz)}$_2$] (**1**, 0.053 g, 0.076 mmol) and AsPh$_3$ (0.042 g, 0.14 mmol) afforded **8** in 70 % yield (0.070 g, 0.11 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.85 (s, 6 H, AsPh$_3$), 7.65 (s, 1 H, Ar-*H*), 7.40 (s, 1 H, Ar-*H*), 7.03 (s, 9 H, AsPh$_3$), 6.74 (d, J = 4.8 Hz, 2 H, Ar-*H*), 3.46 (s, 2 H, CH_2), 1.84 (s, 6 H, Me) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 163.22, 134.25 (Ar), 133.65 (Ar), 131.83 (Ar), 130.83 (Ar), 130.49 (Ar), 129.91 (Ar), 128.64 (Ar), 128.28 (Ar) 127.88 (Ar), 122.77 (Ar), 81.06 (CH_2), 71.56 (O–*C*Me$_2$), 27.80 (Me) ppm. IR (ATR): $\tilde{\nu}$ = 1610 (m, C=N), 1434 (m), 1327 (m), 1057 (s), 736 (s), 690 (s) cm^{-1}. EI-MS: m/z = 655.3 [M]$^+$. $C_{29}H_{27}AsClNOPdS{\cdot}0.5C_6H_6$ (654.37 + 39.06): calcd. C 55.42, H 4.36, N 2.02; found C 55.05, H 4.28, N 1.84.

[PdCl(S-Phoz)(SbPh$_3$)] (9): [{PdCl(S-Phoz)}$_2$] (**1**, 0.053 g, 0.076 mmol) and SbPh$_3$ (0.054 g, 0.12 mmol) afforded **9** in 65 % yield (0.070 g, 0.10 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.72 (s, 1 H, Ar-*H*), 7.66 (s, 6 H, SbPh$_3$), 7.50 (dd, J = 6.0, 3.2 Hz, 1 H, Ar-*H*), 7.04 (s, 9 H, SbPh$_3$), 6.74 (m 2 H, Ar-*H*), 3.45 (s, 2 H, CH_2), 1.81 (s, 6 H, Me) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 162.74, 136.46 (Ar), 133.44 46 (Ar), 131.35 46 (Ar), 130.08 46 (Ar), 129.32 46 (Ar), 128.96 46 (Ar), 128.21 46 (Ar), 127.86 46 (Ar), 127.53 46 (Ar), 122.97 46 (Ar), 80.81 (CH_2), 71.55 (O–*C*Me$_2$), 27.87 (Me) ppm. IR (ATR): $\tilde{\nu}$ = 1612 (m, C=N) 1366 (m), 1325 (m), 1056 (s), 997 (m), 739 (s), 690 (s) cm^{-1}. EI-MS: m/z = 700.1 [M]$^+$. $C_{29}H_{27}ClNOPdSSb{\cdot}0.66C_6H_6$ (701.20 + 51.55): calcd. C 52.62, H 4.15, N 1.86; found C 52.60, H 4.09, N 1.52.

Acknowledgments

The authors gratefully acknowledge support from NAWI Graz.

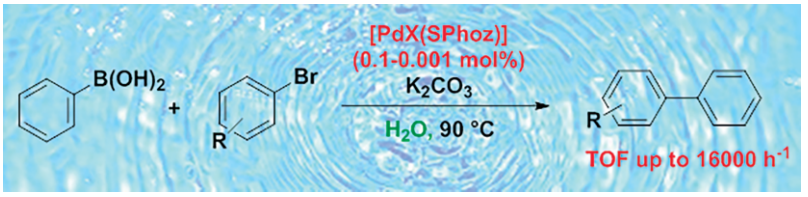
Keywords: Palladium · S ligands · C–C coupling · Ab initio calculations

[1] N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513.
[2] a) S. D. Roughley, A. M. Jordan, *J. Med. Chem.* **2011**, *54*, 3451; b) J. Almond-Thynne, D. C. Blakemore, D. C. Pryde, A. C. Spivey, *Chem. Sci.* **2017**, *8*, 40.
[3] a) G. C. Fortman, S. P. Nolan, *Chem. Soc. Rev.* **2011**, *40*, 5151; b) A. T. Normand, K. J. Cavell, *Eur. J. Inorg. Chem.* **2008**, 2781; c) N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006**, *128*, 4101; d) H. Li, C. C. C. Johansson Seechurn, T. J. Colacot, *ACS Catal.* **2012**, *2*, 1147; e) I. Maluenda, O. Navarro, *Molecules* **2015**, *20*, 7528; f) E. Levin, E. Ivry, C. E. Diesendruck, N. G. Lemcoff, *Chem. Rev.* **2015**, *115*, 4607.
[4] a) K. W. Anderson, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2005**, *44*, 6173; *Angew. Chem.* **2005**, *117*, 6329; b) R. B. Bedford, C. S. J. Cazin, *Chem. Commun.* **2001**, 1540; c) T. E. Schmid, D. C. Jones, O. Songis, O. Diebolt, M. R. L. Furst, A. M. Z. Slawin, C. S. J. Cazin, *Dalton Trans.* **2013**, *42*, 7345.
[5] L. Botella, C. Nájera, *Angew. Chem. Int. Ed.* **2002**, *41*, 187; *Angew. Chem.* **2002**, *114*, 196.
[6] a) V. Polshettiwar, A. Decottignies, C. Len, A. Fihri, *ChemSusChem* **2010**, *3*, 502; b) A. Chatterjee, T. R. Ward, *Catal. Lett.* **2016**, *146*, 820; c) N. E. Leadbeater, M. Marco, *Org. Lett.* **2002**, *4*, 2973; d) A. N. Marziale, D. Jantke, S. H. Faul, T. Reiner, E. Herdtweck, J. Eppinger, *Green Chem.* **2011**, *13*, 169; e) C. Liu, Y. Zhang, N. Liu, J. Qiu, *Green Chem.* **2012**, *14*, 2999; f) M. Mondal, U. Bora, *Green Chem.* **2012**, *14*, 1873; g) Q. Li, L.-M. Zhang, J.-J. Bao, H.-X. Li, J.-B. Xie, J.-P. Lang, *Appl. Organomet. Chem.* **2014**, *28*, 861; h) D.-X. Liu, W.-J. Gong, H.-X. Li, J. Gao, F.-L. Li, J.-P. Lang, *Tetrahedron* **2014**, *70*, 3385.
[7] a) R. Zhong, A. Pöthig, Y. Feng, K. Riener, W. A. Herrmann, F. E. Kühn, *Green Chem.* **2014**, *16*, 4955; b) C. Fleckenstein, S. Roy, S. Leuthausser, H. Plenio, *Chem. Commun.* **2007**, 2870; c) E. C. Western, J. R. Daft, E. M. Johnson II, P. M. Gannett, K. H. Shaughnessy, *J. Org. Chem.* **2003**, *68*, 6767; d) F. Godoy, C. Segarra, M. Poyatos, E. Peris, *Organometallics* **2011**, *30*, 684.
[8] G. Zhang, Y. Luan, X. Han, Y. Wang, X. Wen, C. Ding, J. Gao, *Green Chem.* **2013**, *15*, 2081.
[9] Y. Guo, J. Li, X. Shi, Y. Liu, K. Xie, Y. Liu, Y. Jiang, B. Yang, R. Yang, *Appl. Organomet. Chem.* **2017**, *31*, e3592.
[10] a) H. Hagiwara, Y. Sugawara, T. Hoshi, T. Suzuki, *Chem. Commun.* **2005**, 2942; b) N. Jiang, A. J. Ragauskas, *Tetrahedron Lett.* **2006**, *47*, 197.
[11] L. M. Peschel, C. Holzer, L. Mihajlović-Lalić, F. Belaj, N. C. Mösch-Zanetti, *Eur. J. Inorg. Chem.* **2015**, 1569.

[12] L. M. Peschel, J. A. Schachner, C. H. Sala, F. Belaj, N. C. Mösch-Zanetti, *Z. Anorg. Allg. Chem.* **2013**, *639*, 1559.
[13] a) A. Kumar, G. K. Rao, S. Kumar, A. K. Singh, *Dalton Trans.* **2013**, *42*, 5200; b) J. A. Balam-Villarreal, C. I. Sandoval-Chávez, F. Ortega-Jiménez, R. A. Toscano, M. P. Carreón-Castro, J. G. López-Cortés, M. C. Ortega-Alfaro, *J. Organomet. Chem.* **2016**, *818*, 7; c) A. K. Sharma, H. Joshi, R. Bhaskar, S. Kumar, A. K. Singh, *Dalton Trans.* **2017**, *46*, 2485–2496; d) M. Basauri-Molina, S. Hernández-Ortega, R. A. Toscano, J. Valdés-Martínez, D. Morales-Morales, *Inorg. Chim. Acta* **2010**, *363*, 1222.
[14] A. Dervisi, D. Koursarou, L.-L. Ooi, P. N. Horton, M. B. Hursthouse, *Dalton Trans.* **2006**, 5717.
[15] H. Wang, R. Zhong, X.-Q. Guo, X.-Y. Feng, X.-F. Hou, *Eur. J. Inorg. Chem.* **2010**, 174.
[16] a) C. A. Kruithof, A. Berger, H. P. Dijkstra, F. Soulimani, T. Visser, M. Lutz, A. L. Spek, R. J. M. K. Gebbink, G. van Koten, *Dalton Trans.* **2009**, 3306; b) H. Nakai, S. Ogo, Y. Watanabe, *Organometallics* **2002**, *21*, 1674; c) S. Ogo, Y. Takebe, K. Uehara, T. Yamazaki, H. Nakai, Y. Watanabe, S. Fukuzumi, *Organometallics* **2006**, *25*, 331; d) D. Yuan, H. V. Huynh, *Molecules* **2012**, *17*, 2491; e) Y.-T. Wang, B.-B. Gao, F. Wang, S.-Y. Liu, H. Yu, W.-H. Zhang, J.-P. Lang, *Dalton Trans.* **2017**, *46*, 1832–1839.
[17] D. Yuan, H. V. Huynh, *Organometallics* **2010**, *29*, 6020.
[18] D. Yuan, Q. Teng, H. V. Huynh, *Organometallics* **2014**, *33*, 1794.
[19] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955.
[20] a) M. S. Viciu, O. Navarro, R. F. Germaneau, R. A. Kelly, W. Sommer, N. Marion, E. D. Stevens, L. Cavallo, S. P. Nolan, *Organometallics* **2004**, *23*, 1629; b) H. M. Lee, J. Y. Zeng, C.-H. Hu, M.-T. Lee, *Inorg. Chem.* **2004**, *43*, 6822; c) A. Chartoire, X. Frogneux, A. Boreux, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2012**, *31*, 6947; d) M. S. Viciu, R. A. Kelly III, E. D. Stevens, F. Naud, M. Studer, S. P. Nolan, *Org. Lett.* **2003**, *5*, 1479; e) E. A. B. Kantchev, G.-R. Peh, C. Zhang, J. Y. Ying, *Org. Lett.* **2008**, *10*, 3949; f) J. Nasielski, N. Hadei, G. Achonduh, E. A. B. Kantchev, C. J. O'Brien, A. Lough, M. G. Organ, *Chem. Eur. J.* **2010**, *16*, 10844; g) J. Yang, L. Wang, *Dalton Trans.* **2012**, *41*, 12031.
[21] a) D. V. Aleksanyan, V. A. Kozlov, N. E. Shevchenko, V. G. Nenajdenko, A. A. Vasil'ev, Y. V. Nelyubina, I. V. Ananyev, P. V. Petrovskii, I. L. Odinets, *J. Organomet. Chem.* **2012**, *711*, 52; b) V. A. Kozlov, D. V. Aleksanyan, Y. V. Nelyubina, K. A. Lyssenko, A. A. Vasil'ev, P. V. Petrovskii, I. L. Odinets, *Organometallics* **2010**, *29*, 2054; c) V. A. Kozlov, D. V. Aleksanyan, Y. V. Nelyubina, K. A. Lyssenko, P. V. Petrovskii, A. A. Vasil'ev, I. L. Odinets, *Organometallics* **2011**, *30*, 2920; d) J. A. Casares, S. Coco, P. Espinet, Y.-S. Lin, *Organometallics* **1995**, *14*, 3058; e) L. Canovese, F. Visentin, C. Santo, C. Levi, A. Dolmella, *Organometallics* **2007**, *26*, 5590; f) A. Singh, A. Ramanan, D. Bandyopadhyay, *Cryst. Growth Des.* **2011**, *11*, 2743.
[22] a) See ref.[13d] b) D. Yuan, H. V. Huynh, *Inorg. Chem.* **2013**, *52*, 6627.
[23] B. Inés, R. SanMartin, M. J. Moure, E. Domínguez, *Adv. Synth. Catal.* **2009**, *351*, 2124.
[24] L. R. Martin, F. W. B. Einstein, R. K. Pomeroy, *Inorg. Chem.* **1985**, *24*, 2777.
[25] S. Diez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612.
[26] a) J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* **1996**, *54*, 16533; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396; c) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
[27] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
[28] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.
[29] a) F. Aryasetiawan, O. Gunnarsson, *Rep. Prog. Phys.* **1998**, *61*, 237; b) S. Lebègue, B. Arnaud, M. Alouani, P. E. Bloechl, *Phys. Rev. B* **2003**, *67*, B864; c) A. Marini, G. Onida, R. Del Sole, *Phys. Rev. Lett.* **2002**, *88*, 16403; d) F. Aryasetiawan, O. Gunnarsson, *Phys. Rev. Lett.* **1995**, *16*, 3221; e) H. Shi, H. Pan, Y.-W. Zhang, B. I. Yakobson, *Phys. Rev. B* **2013**, 87; f) A. Miglio, D. Waroquiers, G. Antonius, M. Giantomassi, M. Stankovski, M. Côté, X. Gonze, G.-M. Rignanese, *Eur. Phys. J. B* **2012**, *85*, 322.
[30] X. Blase, C. Attaccalite, V. Olevano, *Phys. Rev. B* **2011**, *83*, 19158.
[31] M. J. van Setten, F. Weigend, F. Evers, *J. Chem. Theory Comput.* **2013**, *9*, 232.
[32] a) M. J. van Setten, F. Caruso, S. Sharifzadeh, X. Ren, M. Scheffler, F. Liu, J. Lischner, L. Lin, J. R. Deslippe, S. G. Louie, C. Yang, F. Weigend, J. B. Neaton, F. Evers, P. Rinke, *J. Chem. Theory Comput.* **2015**, *11*, 5665; b) J. Wilhelm, M. Del Ben, J. Hutter, *J. Chem. Theory Comput.* **2016**, *12*, 3623.
[33] a) D. Jacquemin, I. Duchemin, X. Blase, *J. Chem. Theory Comput.* **2015**, *11*, 3290; b) C. Rostgaard, K. W. Jacobsen, K. S. Thygesen, *Phys. Rev. B* **2010**, 81; c) F. Bruneval, M. A. L. Marques, *J. Chem. Theory Comput.* **2013**, *9*, 324.
[34] G. A. Zhurko, D. A. Zhurko, http://www.chemcraftprog.com **2009**.
[35] a) M. Rimoldi, F. Ragaini, E. Gallo, F. Ferretti, P. Macchi, N. Casati, *Dalton Trans.* **2012**, *41*, 3648; b) A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530.
[36] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123.
[37] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
[38] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.* **2014**, *4*, 91.

Received: July 17, 2017

Palladium–Sulfur Catalysts



Palladium(II) complexes bearing a mercaptoaryl-oxazoline ligand are synthesized and characterized. These complexes show high activities as catalysts for C–C coupling reactions in water with turnover frequencies (TOFs) of up to 16000 h^{-1}. DFT and G_0W_0 calculations help to rationalize the catalytic behaviors of these complexes.

DOI: 10.1002/ejic.201700823