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New Palladium Complexes with S- or Se-Containing Schiff-Base Ligands as Efficient Catalysts for the Suzuki–Miyaura Cross-Coupling Reaction of Aryl Bromides with Phenylboronic Acid under Aerobic Conditions

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Four palladium chelate complexes with S- or Se-containing substituted salicylaldehyde Schiff-base derivatives have been synthesized. Spectroscopic and crystallographic data indicate that, in the complexes, the deprotonated salicylaldehyde ligand is bound to the metal in an O,N,S (or Se)-tridentate coordination mode, forming one six- and one five-membered chelate ring. The complexes are thermally and air stable and efficiently catalyze the Suzuki–Miyaura cross-coupling of aryl bromides with phenylboronic acid in air.

Introduction

Palladium-catalyzed carbon–carbon coupling reactions have now become essential tools for the organic synthetic chemist,[1] and one of the most important of these is the Suzuki–Miyaura cross-coupling of aryl halides with organoboronic acids.[1,2] This reaction now represents a key process for the synthesis of biaryls, which play an important role as intermediates in organic synthesis and as functional groups in natural products.[3] Intensive research efforts are being made into finding ways of improving and expanding the scope of this process, and one aspect that has received particular attention is the development of new ligands. As a consequence, a large number of phosphorus ligands,[4] and phosphane-free ligands,[5] have been reported that are applicable to the conventional thermal Suzuki–Miyaura reaction.

We have previously reported several nitrogen- and/or sulfur-containing phosphorus ligands and their applications to transition-metal homogeneous catalysis.[6] However, as efficient catalysis under phosphane-free conditions represents a challenge of high current importance, our interest has focused on the development of new phosphane-free ligands and recently, for the first time, we used thiosemicarbazones as effective catalyst precursors for palladium-catalyzed coupling reactions under aerobic conditions.[7] In a previous paper, we reported a synthetic route for the preparation of chalcogen (S,Se,Te)-containing substituted salicylaldehyde Schiff-base derivatives.[8] Taking into account the potential of these Schiff bases as tridentate ligands,[9] in this paper we report the synthesis of palladium complexes with S- or Se-containing Schiff-base ligands, two crystal structures of which were determined by X-ray analysis. These phosphane-free systems were applied to the Suzuki–Miyaura coupling of aryl bromides with phenylboronic acid under aerobic conditions.

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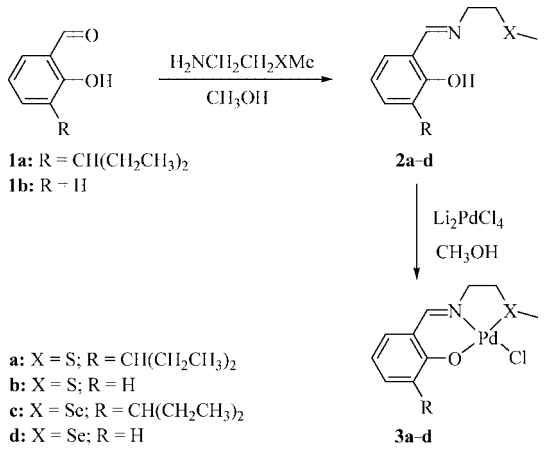
Results and Discussion

Synthesis and Characterization of the Palladium Complexes with S- or Se-Containing Schiff-Base Ligands

The synthesis of the palladium complexes **3a**–**d** is outlined in Scheme 1. Chalcogen-containing Schiff bases 2-(1-ethylpropyl)-6-({[2-(methylsulfanyl)ethyl]imino}methyl)-benzenol ("emSib", **2a**), 2-({[2-(methylsulfanyl)ethyl]imino}-methyl)benzenol ("mSib", **2b**), 2-(1-ethylpropyl)-6-({[2-(methylselanyl)ethyl]imino}methyl)benzenol ("emSEib", **2c**), and 2-({[2-(methylselanyl)ethyl]imino}methyl)benzenol ("mSEib", **2d**) were prepared by treatment of salicylaldehyde derivative **1a** or salicylaldehyde **1b** with 2-(methylsulfanyl)- or 2-(methylselanyl)ethylamine (or their hydrochlorides), according to a procedure recently published by us.[8] In the ^{1}H NMR spectra of **2a**–**d**, the signal of the phenolic proton at δ = 13.30 ppm (**2b**,**d**) or 13.50 ppm (**2a**,**c**) is consistent with hydrogen bonding between the hydroxy and the nitrogen of the imine group.[10] The syntheses of the palladium complexes **3a**–**d** were achieved by the reaction of li-

gands **2a**–**d** with Li_2PdCl_4, prepared in situ from $PdCl_2$ and LiCl. Spectroscopic studies indicate that the ligands are bound to palladium in an O,N,S (or Se)-terdentate coordination mode. In the ^1H NMR spectra of **3a**–**d**, the signal of the phenolic proton is absent because of deprotonation and complex formation. In the ^1H and $^{13}C\{^1H\}$ NMR spectra of **3a**–**d**, the CH_2N and XCH_3 resonances are shifted to low field compared to the corresponding resonances in the free ligands, indicating Pd–N as well as Pd–X coordination (Table 1).



Scheme 1. Synthesis of the palladium complexes [PdCl(emSib)] (**3a**), [PdCl(mSib)] (**3b**), [PdCl(emSEib)] (**3c**), and [PdCl(mSEib)] (**3d**).

Yellow-orange crystals of complexes **3a** and **3c** suitable for X-ray determination were obtained by slow diffusion of diethyl ether through a diluted solution of the complexes in dichloromethane. The two complexes are isostructural and, for that reason, only the structure of **3c** is presented here. As shown in Figure 1, the monoanionic ligand is coordinated to palladium in a terdentate fashion by the phenoxy oxygen, the azomethine nitrogen and the selenium atom, forming one six- and one five-membered chelate ring. In both complexes, the coordination geometry at the metal center can be regarded as slightly distorted square-planar, and the four Pd–heteroatom distances have normal values, according to the selected data presented in Table 2.

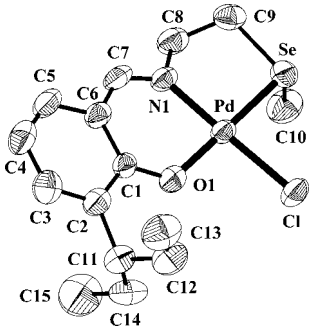


Figure 1. Labeled ORTEP diagram of **3c** with 50% thermal probability ellipsoids (hydrogen atoms have been omitted for clarity).

Table 2. Selected bond lengths [Å] and angles [°] in complexes **3a** and **3c**.

3a		**3c**	
Pd–N(1)	1.971(3)	Pd–N(1)	1.985(4)
Pd–O(1)	2.002(3)	Pd–O(1)	2.017(4)
Pd–S	2.257(2)	Pd–Se	2.365(1)
Pd–Cl	2.322(1)	Pd–Cl	2.323(2)
N(1)–Pd–O(1)	92.3(1)	N(1)–Pd–O(1)	92.3(2)
N(1)–Pd–S	87.5(1)	N(1)–Pd–Se	88.0(1)
O(1)–Pd–S	177.9(1)	O(1)–Pd–Se	177.0(1)
N(1)–Pd–Cl	177.4(1)	N(1)–Pd–Cl	177.1(1)
O(1)–Pd–Cl	89.9(1)	O(1)–Pd–Cl	90.3(1)
S–Pd–Cl	90.3(1)	Cl–Pd–Se	89.5(1)

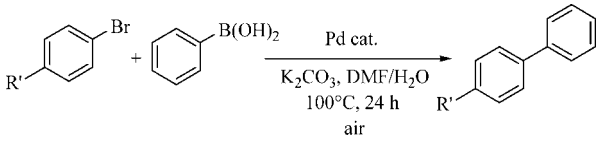
Suzuki–Miyaura Coupling Reactions Catalyzed by Palladium Complexes with S- or Se-Containing Schiff-Base Ligands under Aerobic Conditions

Complexes **3a**–**d** were applied to the Suzuki–Miyaura reaction of phenylboronic acid with some representative aryl bromides (from electron-rich to electron-poor) at 100 °C for 24 h, in DMF, using K_2CO_3 as base, without addition of free ligand or any promoting additive (Scheme 2, Table 3). All reactions were performed in air. As it is known that addition of water enhances the activity of the catalyst,[4b,7b] catalysis was performed in the presence of a small amount of water (close to 1 equiv. with respect to the substrates). Catalysts seem to be air stable at 100 °C, and palladium-black, which could indicate the degradation of the catalysts, was not observed. The reaction was performed using a 1:1000 catalyst/aryl halide molar ratio. As expected, the catalytic activity depended on the halide, while electron-withdrawing groups on the aryl ring increased the reaction rate. According to the GC and GC–MS analysis of the reaction mixtures resulting from the coupling of 4-substituted aryl halides, homocoupling of phenylboronic acid to give unsubstituted biphenyl was observed in a low yield (3–4%) only for the substrate with an electron-donating group. For the deactivated 4-bromoanisole, the reaction proceeded with conversions to the coupled product, MeO–C_6H_4–Ph,

Table 1. Comparative NMR spectroscopic data of the ligands **2a**–**d** and their corresponding palladium complexes **3a**–**d** for the groups CH_2N and XCH_3 (X = S or Se).

Ligand/complex	CH_2N		XCH_3 (X = S or Se)	
	^1H NMR [ppm]	^{13}C NMR [ppm]	^1H NMR [ppm]	^{13}C NMR [ppm]
2a[8]/**3a**	3.79/4.04–3.81	58.7/63.4	2.14/2.65	15.8/21.0
2b/**3b**	3.78/4.28–3.95	58.8/63.6	2.12/2.53	15.9/19.6
2c[8]/**3c**	3.86/4.30–4.05	59.7/65.6	2.01/2.52	4.5/12.7
2d/**3d**	3.87/4.40–4.21	59.7/65.6	2.02/2.45	4.7/11.6

in the range 21–25% (entries 1–4), and for the nonactivated bromobenzene in the range 40–45% (entries 5–8). The narrow ranges for the yields for entries 1–4 and also 5–8 do not permit conclusions to be drawn concerning the influence of the bulky substituent $CHEt_2$ on the salicylaldehyde moiety or on the effect of replacing sulfur with selenium on the catalytic activity of the complexes. For the activated 4-bromobenzonitrile (entries 9–12) and 1-bromo-4-nitrobenzene (entries 13–16), the reaction proceeded with high or even quantitative yield. The results in these entries provide evidence that the presence of the $CHEt_2$ group on the aryl ring, situated away from the coordination sphere around the metal, does not significantly influence the activity of the complex. This observation is not in contrast with that broadly accepted concerning the increased reactivity of a ligand by the presence of a bulky electron-donating group, thereby making the ligand more electron-rich, because in our systems the ligand is in an anionic form. On the other hand, the presence of a selenium donor in the complex was found to promote its catalytic activity slightly compared to the sulfur analogue. For comparison purposes, coupling of 4-bromobenzonitrile with phenylboronic acid was also achieved by using Li_2PdCl_4 or $Pd(OAc)_2$ as catalysts under the same reaction conditions as those described above. The reactions proceeded with 95% (Li_2PdCl_4 as catalyst) and 92% [$Pd(OAc)_2$ as catalyst] yields of coupling product, but, in contrast to complexes **3a**–**d**, unsubstituted biphenyl was also observed (5% and 8%, respectively) because of homocoupling of phenylboronic acid. Although it is known that these simple palladium compounds may produce nanoparticles under these reaction conditions,[11] it remains to be established whether this is the case for the complexes reported here.



Scheme 2. Suzuki–Miyaura cross-coupling of aryl bromides with phenylboronic acid catalyzed by palladium complexes **3a**–**d**, in air.

Table 3. Suzuki–Miyaura cross-coupling of aryl bromides with phenylboronic acid catalyzed by palladium complexes **3a**–**d**, in air.

Entry[a]	Catalyst	R′	Conversion[b] (%)
1	**3a**	OMe	21 (3)[c]
2	**3b**	OMe	25 (4)[c]
3	**3c**	OMe	23 (4)[c]
4	**3d**	OMe	25 (4)[c]
5	**3a**	H	45
6	**3b**	H	40
7	**3c**	H	40
8	**3d**	H	42
9	**3a**	CN	79
10	**3b**	CN	80
11	**3c**	CN	96
12	**3d**	CN	96
13	**3a**	NO_2	90
14	**3b**	NO_2	94
15	**3c**	NO_2	100
16	**3d**	NO_2	100

[a] Reaction conditions: ArBr (2.0 mmol), $PhB(OH)_2$ (3.0 mmol), K_2CO_3 (4.0 mmol), H_2O (3.3 mmol), Pd complex in DMF (0.5 mM, 4 mL), 100 °C, 24 h; ArBr/Pd = 1000:1. [b] Conversion to coupled product R′-C_6H_4–Ph, based on aryl bromide (GC, decane as internal standard). [c] Conversion to unsubstituted biphenyl because of homocoupling of phenylboronic acid.

Conclusions

We have shown that new palladium chelate complexes with S- or Se-containing substituted salicylaldehyde Schiff-base derivatives, in which the ligand is bound to the metal in an O,N,S (or Se)-terdentate coordination mode, can serve as efficient catalysts for the Suzuki–Miyaura cross-coupling of aryl bromides with phenylboronic acid under mild reaction conditions. Se-containing ligands are slightly more active than the S-containing analogues. Although the activity is not as high as some other palladium systems, these phosphane-free catalysts are thermally and air stable, and offer the advantage of the successful coupling of aryl bromides and the synthesis of biaryls under aerobic conditions.

Experimental Section

General: 3-(1-Ethylpropyl)-2-hydroxybenzenecarbaldehyde (**1a**),[12] 2-(methylsulfanyl)ethylamine,[13] and 2-(methylselanyl)ethylamine[8] were prepared by known procedures. Syntheses of ligands emSib (**2a**) and emSEib (**2c**) have been described by us elsewhere.[8] Ligands mSib (**2b**) and mSEib (**2d**) were prepared according to the same procedure. All other chemicals were commercially available. Coupling reactions were performed on a Radleys Carousel Reactor™ with 12 tubes of about 45 mL in two stacked aluminum blocks. The lower block was placed on a heater–stirrer and maintained at a constant temperature by means of a thermostat, while water circulated in the upper block, which served to cool the tops of the tubes. NMR measurements were made using a Bruker AC 300 (300.13 MHz and 75.47 MHz for ^1H and $^{13}C\{^1H\}$, respectively). Distinction of the CH, CH_2, and CH_3 carbons in the $^{13}C\{^1H\}$ NMR spectra was performed by DEPT NMR experiments. Gas chromatography was undertaken using a Varian Star 3400 CX with a 30 m × 0.53 mm DB5 column. Electron impact gas chromatography–mass spectrometry was carried out using a Varian Saturn 2000 with a 30 m × 0.25 mm DB5-MS column. Elemental analyses for C, H, N were carried out on a Perkin–Elmer PE 2400 II instrument.

2-({[2-(Methylsulfanyl)ethyl]imino}methyl)benzenol ("mSib", 2b):[14] Reaction of salicylaldehyde **1b** (2.01 g, 16.48 mmol) with 2-(methylsulfanyl)ethylamine (1.50 g, 16.48 mmol) in MeOH (15 mL) yielded **2b** (3.09 g, 96%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 13.31 (s, 1 H, OH), 8.35 (s, 1 H, C*H*=N), 7.30 (m, 2 H, ArH), 6.95 (d, ^3J = 8.5 Hz, 1 H, ArH), 6.87 (t, ^3J = 7.3 Hz, 1 H, ArH), 3.78 (t, ^3J = 6.7 Hz, 2 H, CH_2N), 2.81 (t, ^3J = 6.7 Hz, 2 H, CH_2S), 2.12 (s, 3 H, SCH_3) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ = 165.9 (*C*H=N), 161.0 (*C*-OH), 132.3, 131.3, 118.5, and 116.9 (ArC), 58.8 (CH_2N), 34.9 (CH_2S), 15.9 (SCH_3) ppm.

2-({[2-(Methylselanyl)ethyl]imino}methyl)benzenol ("mSEib", 2d):[15] Reaction of salicylaldehyde **1b** (1.05 g, 8.61 mmol) with 2-(methylselanyl)ethylamine (1.19 g, 8.62 mmol) in MeOH (10 mL) yielded **2d** (1.98 g, 95%). ^1H NMR (300.13 MHz, $CDCl_3$): δ =

13.30 (s, 1 H, OH), 8.37 (s, 1 H, C*H*=N), 7.30 (m, 2 H, ArH), 6.96 (d, ^3J = 8.5 Hz, 1 H, ArH), 6.88 (t, ^3J = 7.3 Hz, 1 H, ArH), 3.87 (t, ^3J = 6.7 Hz, 2 H, CH_2N), 2.84 (t, ^3J = 6.7 Hz, 2 H, CH_2Se), 2.02 (s, 3 H, SeCH_3) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 165.5 (*C*H=N), 161.1 (*C*-OH), 132.3, 131.4, 118.6, and 117.0 (ArC), 59.7 (*C*H_2N), 25.9 (*C*H_2Se), 4.7 (Se*C*H_3) ppm.

Typical Procedure for the Preparation of the Palladium Complexes 3a–d: $PdCl_2$ (0.10 g, 0.56 mmol) was stirred with LiCl (0.075 g, 1.76 mmol) in MeOH (10 mL). Ligand **2a** (0.15 g, 0.56 mmol) was added to the dark brown-red solution formed, yielding a yellow-orange suspension after stirring at room temperature overnight. The reaction mixture was allowed to settle and an orange solid was isolated by filtration in air, washed with small amounts of methanol and diethyl ether, and recrystallized from dichloromethane/ether yielding **3a**.

[PdCl(emSib)] (3a): Reaction of ligand **2a** with Li_2PdCl_4, prepared in situ from $PdCl_2$ and LiCl in MeOH, in the quantities indicated above, yielded **3a** (0.18 g, 79%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.37 (s, 1 H, C*H*=N), 7.16 (d, ^3J = 7.5 Hz, 1 H, ArH), 6.84 (d, ^3J = 7.5 Hz, 1 H, ArH), 6.54–6.49 (m, 1 H, ArH), 4.04–3.96 and 3.90–3.81 (m, m, 2 H, CH_2N), 3.13–3.07 and 3.03–2.95 (m, m, 2 H, CH_2S), 2.65 (s, 3 H, SCH_3), 2.58–2.50 [m, 1 H, C*H*(CH_2CH_3)$_2$], 1.73–1.54 [m, 4 H, CH(CH_2CH_3)$_2$], 0.81–0.75 [m, 6 H, CH(CH$_2$CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 163.02 (ArC), 160.50 (*C*H=N), 135.91, 133.61, 132.06, 118.38, and 115.07 (ArC), 63.35 (*C*H_2N), 41.87 [*C*H(CH$_2$CH$_3$)$_2$], 37.60 (*C*H_2S), 26.99 and 26.79 [CH(*C*H_2CH$_3$)$_2$], 20.97 (S*C*H_3), 12.24 and 12.07 [CH(CH$_2$*C*H_3)$_2$] ppm. $C_{15}H_{22}ClNOPdS$ (406.28): calcd. C 44.35, H 5.46, N 3.45; found C 44.56, H 5.53, N 3.77.

[PdCl(mSib)] (3b): Reaction of ligand **2b** (0.12 g, 0.62 mmol) with Li_2PdCl_4, prepared in situ from $PdCl_2$ (0.10 g, 0.56 mmol) and LiCl (0.075 g, 1.76 mmol) in MeOH (10 mL), yielded **3b** (0.15 g, 79%). ^{1}H NMR (300.13 MHz, [D$_6$]DMSO): δ = 8.19 (s, 1 H, C*H*=N), 7.39–7.29 (m, 2 H, ArH), 6.80 (d, ^3J = 8.5 Hz, 1 H, ArH), 6.61–6.56 (m, 1 H, ArH), 4.28–4.19 and 4.03–3.95 (m, m, 2 H, CH_2N), 2.98–2.89 and 2.74–2.66 (m, m, 2 H, CH_2S), 2.53 (s, 3 H, SCH_3) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, [D$_6$]DMSO): δ = 163.43 (ArC), 160.78 (*C*H=N), 135.32, 134.93, 119.60, 119.47, and 114.94 (ArC), 63.60 (*C*H_2N), 36.33 (*C*H_2S), 19.57 (S*C*H_3) ppm. $C_{10}H_{12}ClNOPdS$ (336.14): calcd. C 35.73, H 3.60, N 4.17; found C 36.15, H 3.96, N 4.59.

[PdCl(emSEib)] (3c): Reaction of ligand **2c** (0.18 g, 0.58 mmol) with Li_2PdCl_4, prepared in situ from $PdCl_2$ (0.10 g, 0.56 mmol) and LiCl (0.075 g, 1.76 mmol) in MeOH (10 mL), yielded **3c** (0.17 g, 68%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.34 (s, 1 H, C*H*=N), 7.16 (d, ^3J = 7.5 Hz, 1 H, ArH), 6.84 (d, ^3J = 7.5 Hz, 1 H, ArH), 6.54–6.49 (m, 1 H, ArH), 4.30–4.20 and 4.14–4.05 (m, m, 2 H, CH_2N), 3.16–3.01 (m, 2 H, CH_2Se), 2.52 (s, 3 H, SeCH_3), 2.50–2.44 [m, 1 H, C*H*(CH$_2$CH$_3$)$_2$], 1.69–1.58 [m, 4 H, CH(CH_2CH$_3$)$_2$], 0.83–0.76 [m, 6 H, CH(CH$_2$CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 163.08 (ArC), 160.82 (*C*H=N), 135.52, 133.32, 132.25, 118.51, and 114.78 (ArC), 65.61 (*C*H_2N), 41.64 [*C*H(CH$_2$CH$_3$)$_2$], 28.99 (*C*H_2Se), 26.95 and 26.70 [CH(*C*H_2CH$_3$)$_2$], 12.66 (Se*C*H_3), 12.24 and 12.07 [CH(CH$_2$*C*H_3)$_2$] ppm. $C_{15}H_{22}ClNOPdSe$ (453.18): calcd. C 39.76, H 4.89, N 3.09; found C 39.58, H 5.01, N 3.38.

[PdCl(mSEib)] (3d): Reaction of ligand **2d** (0.15 g, 0.62 mmol) with Li_2PdCl_4, prepared in situ from $PdCl_2$ (0.10 g, 0.56 mmol) and LiCl (0.075 g, 1.76 mmol) in MeOH (10 mL), yielded **3d** (0.12 g, 56%). ^{1}H NMR (300.13 MHz, [D$_6$]DMSO): δ = 8.13 (s, 1 H, C*H*=N), 7.36–7.28 (m, 2 H, ArH), 6.79 (d, ^3J = 8.0 Hz, 1 H, ArH), 6.59–6.54 (m, 1 H, ArH), 4.40–4.21 (m, 2 H, CH_2N), 2.94–2.85 and 2.73–2.66 (m, m, 2 H, CH_2Se), 2.45 (s, 3 H, SeCH_3) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, [D$_6$]DMSO): δ = 163.76 (ArC), 161.04 (*C*H=N), 135.16, 134.93, 119.44, and 114.58 (Ar), 65.57 (*C*H_2N), 28.53 (*C*H_2Se), 11.58 (Se*C*H_3) ppm. $C_{10}H_{12}ClNOPdSe$ (383.03): calcd. C 31.36, H 3.16, N 3.66; found C 30.98, H 2.90, N 4.07.

General Procedure for the Suzuki–Miyaura Cross-Coupling Reactions: A mixture of aryl bromide (2.0 mmol), $PhB(OH)_2$ (0.366 g, 3.0 mmol), K_2CO_3 (0.553 g, 4.0 mmol), water (60 μL, 3.3 mmol), and a stock solution of palladium complex **3a–d** in DMF (0.5 mM, 4 mL, 2×10^{-3} mmol) was heated at 100 °C for 24 h, and then cooled to room temperature. After addition of water and extraction with dichloromethane, the organic phase was washed with brine, dried with Na_2SO_4, filtered, passed through Celite, and analyzed by GC and GC–MS. All the biaryls prepared were known compounds.[4b]

X-ray Crystallographic Study of 3a and 3c: Slow crystallization from CH_2Cl_2/Et_2O yielded yellow-orange crystals of **3a** ($0.20\times0.25\times0.55$ mm) and **3c** ($0.10\times0.20\times0.50$ mm), which were mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 23°$ and they appear in Table 4. Intensity data were recorded using a θ–2θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization, and absorption corrections were applied using Crystal Logic software. The structures were solved by direct methods using SHELXS-86[16] and refined by full-matrix least-squares methods on F^2 with SHELXL-97.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference maps and were refined isotropically (except those on C13 and C15 in **3a**, which were introduced at calculated positions as riding on bonded atoms). Crystal data and experimental details for the crystals of compounds **3a** and **3c** are given in Table 4.

Table 4. X-ray experimental data of compounds **3a** and **3c**.

	3a	**3c**
Empirical formula	$C_{15}H_{22}ClNOPdS$	$C_{15}H_{22}ClNOPdSe$
Formula mass	406.25	453.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	13.469(6)	13.404(7)
b [Å]	8.425(3)	8.468(5)
c [Å]	15.056(6)	15.204(9)
β [°]	94.54(2)	93.59(2)
V [Å^3]	1703(1)	1722(2)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	1.584	1.748
$F(000)$	824	896
μ [mm^{-1}]	1.364	3.341
T [K]	298	298
λ [Å]	0.71073	0.71073
Radiation	Mo-K_α	Mo-K_α
θ limits	2.77/25.00	2.68/25.00
No. of data with $I > 2\sigma(I)$	2446	2176
No. of variables	245	269
R	0.0369	0.0397
Rw	0.0950	0.1043
Gof	1.034	1.051
Largest peak in final difference [e Å^{-3}]	0.804/–0.710	1.419/–0.693

CCDC-298854 (for **3a**) and -298855 (for **3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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