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Palladium(II) Chloride Complexes of N,N'-Disubstituted Imidazole-2thiones: Syntheses, Structures, and Catalytic Performances in Suzuki-Miyaura and Sonogashira Coupling Reactions

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Supporting Information

ABSTRACT: Reactions of PdCl₂ with 2 equiv of N,N'disubstituted-imidazole-2-thiones $R^1R^2C_3N_2S$ ($\hat{R}^1 = R^2 = Me$ (1a), ⁱPr (1b), Cy (1c), C₆Me₃H₂ (1d); R¹ = Me, R² = Ph (1e)) under the different conditions afford five mononuclear complexes trans-[$(R^1R^2C_3N_2S)_2PdCl_2$] ($R^1 = R^2 = Me$ (2a), ⁱPr (2b), Cy (2c), C₆Me₃H₂ (2d); $R^1 = Me$, $R^2 = Ph$ (2e)) and five binuclear Pd(II) complexes $[(PdCl_2)\{\mu - (R^1R^2C_3N_2S)\}]_2$ $(R^{1} = R^{2} = Me(3a), Pr(3b), Cy(3c), C_{6}Me_{3}H_{2}(3d); R^{1} =$ Me, $R^2 = Ph(3e)$, respectively. Complexes 2a-2e are easily converted into the corresponding 3a-3e by adding equimolar PdCl₂ in refluxing MeOH, while the reverse reaction is



achieved at room temperature by addition of 2 equiv of 1a-1e. In 2b, 2d, and 2e, each Pd(II) holds a distorted square planar geometry completed by two trans Cl atoms and two trans S atoms. Complexes 3a-3e have a dimeric $[Pd_2S_2]$ structure in which two {PdCl₂} units are interlinked by two N,N'-disubstituted-imidazole-2-thiones. Each Pd(II) adopts a distorted square planar geometry accomplished by two cis Cl atoms and two cis bridging S atoms. Among them, complex 3d has the two largest $C_6Me_3H_2$ groups on the 2 and 5 positions of imidazole-2-thione, the longest $Pd-\mu$ -S bond, the largest S-Pd-S angle, and displays the highest catalytic activity toward Suzuki-Miyaura and copper-free Sonogashira cross-coupling reactions, which are confirmed by density functional theory calculations. The results provide an interesting insight into the introduction of various substituent groups into the periphery ligands of coordination complex-based catalysts, which could tune their geometric structures to acquire the best catalytic activity toward organic reactions.

INTRODUCTION

The palladium-catalyzed cross-coupling reactions of aryl halides with arylboronic acids (Suzuki-Miyaura reactions) or alkynes (Sonogashira reactions) have provided a powerful methodology for constructing C–C bonds.¹⁻⁶ Phosphine ligands⁷⁻⁹ are generally required to stabilize the active catalytic palladium intermediates. However, such ligands suffer from disadvantages of cost, toxicity, sensitivity to air/moisture, or difficulty of removal from the organic products, which restricts their applications in synthesis.^{10,11} Among the phosphine-free ligands, N-heterocyclic carbenes (NHCs)^{12–16} and nitrogen-donors ligands^{17–21} are arguably the most useful, but thiols²² and thioether-based SS,²³ NS,²⁴ SCS,^{25,26} NNS,²⁷ NCS,^{28,29} $\mathrm{NSN}^{30,31}$ bidentate and tridentate ligands are also emerging as viable alternatives.^{32,33} One complication with sulfur-based ligands, however, is that Pd catalysts can mediate C-S bond cleavage.³⁴⁻³⁶ Nevertheless, thiourea derivatives have been

extensively used as versatile ligands for many Pd-catalyzed organic reactions. $^{37-48}$ Imidazole-2-thiones have also attracted much attention, because their steric and electronic properties can be tuned by varying groups on the imidazolyl ring. Moreover, the C=S double bond in these ligands displays high thermal and chemical stability. A large number of Pd(II) complexes of unsubstituted imidazole-2-thiones,49,50 N-(mono)substituted imidazole-2-thiones,⁵¹⁻⁵⁴ and tripodal scorpionate tris(imidazole-2-thione) derivatives⁵⁵⁻⁶⁰ have been isolated. Currently, only a few reports deal with the synthesis of mono- and binuclear Pd(II) complexes with N,N'-disubstituted-imidazole-2-thiones⁶⁰⁻⁶² and their applications in the C-C bond formation.^{61,63} For example, one mononuclear complex [(phbtuimt)PdCl] (Hphbtuimt = 3,3'-(1,3-

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	2b	2d•MeCN	2e	3a'H ₂ O	3b	3с	3d	3e
empirical formula	$\mathrm{C}_{18}\mathrm{H}_{32}\mathrm{Cl}_{2}\mathrm{N}_{4}\mathrm{PdS}_{2}$	$\mathrm{C}_{46}\mathrm{H}_{54}\mathrm{Cl}_2\mathrm{N}_6\mathrm{PdS}_2$	$\mathrm{C_{20}H_{20}Cl_2N_4PdS_2}$	$\mathrm{C_{10}H_{18}Cl_4N_4OPd_2S_2}$	$C_{18}H_{32}Cl_4N_4Pd_2S_2$	$C_{15}H_{24}Cl_2N_2PdS$	$C_{42}H_{48}Cl_4N_4Pd_2S_2$	$C_{10}H_{10}Cl_2N_2PdS$
fw	545.90	932.37	557.82	629.00	723.20	441.72	1027.56	367.56
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	C2/c	$P\overline{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	8.3769(8)	11.4686(10)	18.4381(14)	10.1167(19)	14.8767(14)	10.8251(6)	11.081(5)	9.3885(8)
b (Å)	14.8395(9)	14.3926(12)	7.2111(6)	10.1473(19)	15.2927(14))	13.1112(7)	13.053(5)	9.2479(8)
c (Å)	9.6399(5)	13.4645(11)	16.8732(13)	11.483(2)	13.7564(13)	13.4812(8)	15.276(7)	14.5435(12)
α (deg)				72.878(4)				
β (deg)	100.063(7)	99.854(2)	107.911(2)	88.211(5)	115.886(2)	105.679(2)	103.291(14)	94.152(2)
γ (deg)				61.188(5)				
$V(\mathrm{\AA}^3)$	1179.89(15))	2189.7(3)	2134.7(3)	978.4(3)	913.66(12)	1842.19(18)	2150.4(16)	1259.41(18)
$ ho_{ m calc}~({ m g/cm}^3)$	1.537	1.414	1.736	2.135	1.706	1.593	1.587	2.050
Ζ	2	2	4	2	4	4	2	4
$\mu \ (\mathrm{mm}^{-1})$	1.201	0.681	1.331	2.603	1.819	1.406	1.217	1.939
F(000)	560	968	1120	612	1440	896	1040	720
$R_1^{\ a}$	0.029	0.0615	0.0657	0.0466	0.0332	0.0293	0.0321	0.0213
wR_2^{b}	0.05573	0.1303	0.1353	0.1372	0.0658	0.0469	0.0780	0.0458
GOF^c	1.0135	1.024	1.084	1.144	1.101	1.027	1.068	1.017
${}^{a}R_{1} = \sum F_{0} - F_{c} ,$	$\sum F_0 $, $^b wR_2 = \{\sum w(F)$	$r_0^2 - F_c^2)^2 / \sum w(F_0^2)^2 \}$	^{1/2} . ^c GOF = { $\sum w((F_0^2)$	$(n^2 - F_c^2)^2)/(n - p)\}^{1/2}, w$	where $n =$ number of re	flections, and $p = \text{tot}$	tal number of paramete	rs refined.

Table 1. Crystal Data and Structure Refinement Parameters for 2b, 2d·2MeCN, 2e, 3a·H₂O, and 3b-3e





Figure 1. View of the molecular structures of 2b (a), 3a (b), and 3d (c). All H atoms are omitted for clarity.

phenylene)bis(1-butyl-1,3-dihydro-2*H*-imidazole-2-thione) shows moderate catalytic activity for Heck, Suzuki–Miyaura, and Sonogashira coupling reactions.⁶¹ The coupling reactions of iodobenzene with phenyl boronic acid or *p*-tolyl boronic acid provide the desired coupling products in moderate yields (67% to ~74%) in 48 h. Although it is known that the bimetallic complexes can improve their catalytic activity and/or selectivity due to the existence of cooperative effects,^{64–78} there have been two dinuclear Pd(II) complexes of N,N'-disubstituted-imidazole-2-thiones, namely, *cis*-[(PdCl₂){ μ -(Et₂C₃N₂S)}]₂⁶⁰ and [PdI(ⁱPr₂C₃N₂S)(μ -I)(μ -ⁱPr₂C₃N₂S)PdI₂],⁷⁹ and their catalytic performance has not been explored yet.

However, we have involved in the syntheses and structures of various metal thiolate complexes and their catalytic performances in the above-mentioned cross-coupling reactions.^{80–83} For example, one tetranuclear Pd(II)/thiolate cluster $[Pd_4(IMe)_4(Tab)_6](OTf)_6(Cl)_2]$ (IMe = 1,3-dimethylimidazoline-2-ylidene; Tab = 4-(trimethylammonio)benzenethiolate; OTf = trifluoromethanesulfonate) exhibits good catalytic activity toward Suzuki–Miyaura couplings in water, though it could catalyze only a limited scope of the substrates.⁸¹ Another example is related to the catalytic systems of $Pd(OAc)_2$ and three thioether ligands with a 4-trimethylbenzeneammonium group at one side and different substituent groups (benzyl (L¹), 1-phenylethyl (L²), and naphthalen-1-yl-methyl (L³)) at the other side.⁸² The $Pd(OAc)_2/L^1$ goes most effective at catalyzing Suzuki-Miyaura couplings in water, showing effects of substituent groups on the catalytic activity. However, we have no structural information for these catalysts and do not go further into these catalytic reactions. In fact, many literature reports also mention that catalytic activity can be tuned by manipulating the substituted groups on the ancillary ligands, 84-87 but the structures of the catalysts bearing these ligands are unknown in most cases, which makes it hard to correlate the relationship between structure and catalytic activity. There always exists a strong demand to prepare a series of ligands with tunable substituted groups and their related metal coordination compounds for the systematic studies on the aforementioned coupling reactions. To this end, N,N'-disubstituted-imidazole-2-thione derivatives $(R^1R^2C_3N_2S)$ with tunable substituent groups are believed to be ideal candidates. In this article, we prepared five $R^1R^2C_3N_2S$ ($R^1 = R^2$ = Me (1a), ⁱPr (1b), Cy (1c), $C_6Me_3H_2$ (1d); R^1 = Me, R^2 = Ph (1e)) ligands and performed their reactions with 1 or 2 equiv of PdCl₂ under different reaction conditions. Five mononuclear complexes $[(R^1R^2C_3N_2S)_2PdCl_2]$ $(R^1 = R^2 =$ Me (2a), ⁱPr (2b), Cy (2c), C₆Me₃H₂ (2d); R¹ = Me, R² = Ph (2e)) and five binuclear complexes [(PdCl₂){ μ - $(R^{1}R^{2}C_{3}N_{2}S)$]₂ $(R^{1} = R^{2} = Me$ (3a), ⁱPr (3b), Cy (3c), $C_6Me_3H_2$ (3d); $R^1 = Me$, $R^2 = Ph$ (3e)) were isolated. Each mononuclear Pd(II) complex can be readily converted into its corresponding binuclear Pd(II) one. For the Suzuki-Miyaura

Table 2. Selected Bond Lengths (Å) and Angles^a (deg) for 2b, 2d·2MeCN, 2e, 3a·H₂O, and 3b-3e

	2b	2d·2MeCN	2e	$3a \cdot H_2O$	3b	3c	3d	3e
Pd(1)-Cl(1)	2.3145(7)	2.3060(11)	2.3198(17)	2.315(2)	2.3083(10)	2.3081(7)	2.3265(10)	2.3123(6)
Pd(1)-Cl(2)				2.305(2)	2.3152(9)	2.3183(7)	2.3103(12)	2.3024(6)
Pd(2)-Cl(3)				2.3066(18)	2.3056(10)			
Pd(2)-Cl(4)				2.3219(18)	2.3064(9)			
Pd(1)-S(1)	2.3352(7)	2.3318(11)	2.3194(18)	2.2876(19)	2.2867(9)	2.2784(7)	2.3196(10)	2.2898(5)
Pd(1)-S(2)				2.3049(18)	2.2918(9)			
Pd(1)-S(1A)						2.2892(7)	2.3428(11)	2.2995(5)
Pd(2)-S(1)				2.2880(18)	2.2896(10)			
Pd(2) - S(2)				2.2977(18)	2.2931(9)			
S(1)-Pd(1)-Cl(2)				90.86(7)	169.92(4)	90.98(2)	89.41(3)	90.05(2)
S(1)-Pd(1)-Cl(1A)	94.38(2)	83.23(4)	85.70(6)					
S(1) - Pd(1) - S(2)				81.63(6)	79.33(3)			
S(1) - Pd(1) - S(1A)	180.0	180.0	180.0			82.34(2)	86.17(3)	85.227(19)
Cl(2) - Pd(1) - S(2)				172.49(7)	92.03(3)			
Cl(2)-Pd(1)-S(1A)						167.57(2)	173.43(3)	171.10(2)
S(1)-Pd(1)-Cl(1)	85.62(2)	96.77(4)	94.30(6)	173.20(7)	95.19(4)	169.18(2)	177.23(3)	174.59(2)
Cl(2)-Pd(1)-Cl(1)				94.24(8)	93.22(4)	97.02(2)	90.80(4)	95.02(2)
Cl(1)-Pd(1)-Cl(1A)	180.00	180.0	180.0					
Cl(1)-Pd(1)-S(2)				93.25(7)	174.13(4)			
Cl(1)-Pd(1)-S(1A)	94.38(2)	83.23(4)	85.70(6)			91.06(2)	93.38(3)	90.00(2)
Cl(1A)-Pd(1)-S(1A)	85.62(2)	96.77(4)	94.30(6)					
S(1) - Pd(2) - S(2)				81.78(6)	79.25(3)			
S(1) - Pd(2) - Cl(3)				173.63(7)	95.19(4)			
S(2) - Pd(2) - Cl(3)				91.85(7)	174.36(4)			
S(1)-Pd(2)-Cl(4)				91.95(7)	170.50(4)			
S(2) - Pd(2) - Cl(4)				172.59(7)	91.74(3)			
Cl(3)-Pd(2)-Cl(4)				94.42(7)	93.86(4)			
Symmetry codes: (A) 1	_ ~ ? _ ~ ~ ~~	for 2b.2MoCN	1 - m - 1 - m - 1	$- \alpha$ for 2d and	2a(A) = -m	-1 -7 for 3	and 2d 2 2	$- u - \pi$ for 3

⁴Symmetry codes: (A) 1 - x, 2 - y, -z for 2b·2MeCN; 1 - x, 1 - y, 1 - z for 2d and 2e. (A) 1 - x, 1 - y, -z for 3c and 3d; -x, 2 - y, -z for 3e.

and copper-free Sonogashira cross-coupling reactions, compound **3d** exhibits the best catalytic performance, which correlates well with its presence of the largest substituted groups ($C_6Me_3H_2$) in the imidazole ring and the longest Pd- μ -S bond, the largest S-Pd-S angle, and the lowest activation barrier (11.6 kcal/mol) provided by density functional theory (DFT) calculations. Described below are the syntheses of the ligands **1a**-**1e**, complexes **2a**-**2e** and **3a**-**3e**, their structural characterization, and the catalytic properties of **2a**-**2e** and **3a**-**3e**.

EXPERIMENTAL SECTION

General Procedures. *N*-Methyl-*N*-phenylimidazolium iodide, 1,3dimethyl-1,3-dihydro-imidazole-2-thione (1a), 1,3-diisopropyl-1,3-dihydro-imidazole-2-thione (1b), 1,3-dicyclohexyl-1,3-dihydro-2*H*-imidazole-2-thione (1c), and 1,3-bis(2,4,6-trimethyl-phenyl)-1,3-dihydroimidazole-2-thione (1d) were prepared according to the literature methods.^{88–90} All commercial reagents were used without further purification. Column chromatography was performed on silica gel. The ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. The ¹H chemical shifts were referenced to Me₄Si (δ 0.0 ppm) and residual protons in CDCl₃ (δ 7.26 ppm), deuterated dimethyl sulfoxide (DMSO-*d*₆) (δ 2.50 ppm), CD₃CN (δ 1.94 ppm). The ¹³C NMR spectra were reported relative to CDCl₃ (δ 77.16 ppm) and DMSO-*d*₆ (δ 39.5 ppm).

Synthesis of 1e. *N*-Methyl-*N*-phenylimidazolium iodide (2.87 g, 10 mmol) in MeOH (30 mL) was added to a 100 mL round-bottomed flask fitted with a reflux condenser. Sulfur powder (0.32 g, 10 mmol) and K_2CO_3 (1.38 g, 10 mmol) were further added, and the mixture was stirred at 40 °C for 6 h. After that the methanol was removed, and the remaining solid was extracted with 2 × 30 mL of CH₂Cl₂, which was then filtered and evaporated. The crude product was purified by flash column chromatography using petroleum ether and ethyl acetate

as the eluent to provide the pure product **1e**. Yield: 1.56 g (82%). Anal. Calcd for $C_{10}H_{10}N_2S$: C, 63.13; H, 5.30; N, 14.72%. Found: C, 63.43; H, 5.34; N, 15.11%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 14.3 Hz, 2H), 3.66 (s, 3H). ¹³C NMR (101 MHz, CDCl₃, ppm): δ 163.4, 138.5, 129.2, 128.5, 126.1, 118.6, 117.9, 35.5. IR (KBr disk, selected peak, cm⁻¹): 1144 (C = S).

Preparation of 2a. To a solution of $PdCl_2$ (0.0177 g, 0.10 mmol) in MeCN (15 mL) was added a solution of **1a** (0.0256 g, 0.20 mmol) in CH₂Cl₂ (4 mL). A large amount of brick-red precipitate was observed to form over several hours. The mixture was stirred at room temperature for 12 h, and the solid was collected by filtration, washed with Et₂O, and dried in vacuo. Yield: 0.0346 g (88%). Anal. Calcd for C₁₀H₁₆Cl₂N₄PdS₂: C, 27.69; H, 3.72; N, 12.92%. Found: C, 27.86; H, 3.86; N, 13.0%. IR (KBr disk, cm⁻¹): 3146 (w), 3118 (s), 2946 (w), 1564 (s), 1490 (s), 1469 (w), 1441 (w), 1396 (m), 1346 (w), 1238 (s), 1179 (s), 1097 (w), 744 (s), 678 (s).

Synthesis of 2b. The brick-red solid **2b** was prepared in a similar manner to that used for **2a** but using $PdCl_2$ (0.0178 g, 0.10 mmol) and **1b** (0.0371 g, 0.20 mmol) as starting materials. Yield: 0.0447 g (82%). Anal. Calcd for $C_{18}H_{32}Cl_2N_4PdS_2$: C, 39.60; H, 5.91; N, 10.26%. Found: C, 39.94; H, 6.00; N, 10.42%. IR (KBr disk, cm⁻¹): 3169 (m), 3144 (w), 2976 (m), 2933 (w), 2876 (w), 1684 (w), 1628 (w), 1577 (w), 1559 (s), 1439 (s), 1415 (m), 1400 (w), 1371 (m), 1337 (m), 1205 (s), 1175 (w), 1136 (m), 1122 (m), 1067 (w), 1052 (m), 1001 (w), 880 (w), 736 (s), 693 (s), 676 (w), 643 (w), 582 (w).

Synthesis of 2c. The brick-red solid 2c was prepared in an analogous method to that used for 2a but using $PdCl_2$ (0.0176 g, 0.10 mmol) and 1c (0.0534 g, 0.20 mmol) as starting materials. Yield: 0.0571 g (81%). Anal. Calcd for $C_{30}H_{48}Cl_2N_4PdS_2$: C, 51.03; H, 5.85; N, 7.93%. Found: C, 49.85; H, 6.22; N, 7.52%. IR (KBr disk, cm⁻¹): 3119 (m), 3082 (w), 2933 (s), 2855 (s), 1556 (s), 1495 (m), 1447 (s), 1415 (m), 1396 (m), 1365 (w), 1323 (m), 1289 (m), 1267 (w), 1246 (s), 1204 (s), 1151 (m), 1129 (w), 1058 (w), 1030 (w), 1001 (m),

Table 3. Optimizing the Reaction Conditions for Suzuki– Miyaura Cross-Coupling of 4a with 5a

\mathbb{A}		Br + 200-5a	B(OH) ₂ Cat., Base,	Temp Solvent		⋽∕─९
entry ^a	cat	cat loading (mol %)	solvent	base	temp (°C)	yield ^b
1	3d	0.25	CH ₃ CH ₂ OH	K ₂ CO ₃	60	82%
2	3d	0.25	CH ₃ CN	K ₂ CO ₃	60	62%
3	3d	0.25	dioxane	K ₂ CO ₃	60	43%
4	3d	0.25	DMF	K ₂ CO ₃	60	86%
5	3d	0.25	toluene	K ₂ CO ₃	60	63%
6	3d	0.25	H_2O	K ₂ CO ₃	60	>99%
7	2a	0.5	H_2O	K ₂ CO ₃	60	5%
8	2b	0.5	H_2O	K ₂ CO ₃	60	15%
9	2c	0.5	H ₂ O	K ₂ CO ₃	60	74%
10	2d	0.5	H ₂ O	K ₂ CO ₃	60	87%
11	2e	0.5	H ₂ O	K ₂ CO ₃	60	84%
12	3a	0.25	H ₂ O	K ₂ CO ₃	60	85%
13	3b	0.25	H_2O	K ₂ CO ₃	60	87%
14	3c	0.25	H_2O	K ₂ CO ₃	60	95%
15	3e	0.25	H_2O	K_2CO_3	60	72%
16	3d	0.25	H ₂ O	K ₃ PO₄· 3H ₂ O	60	>99%
17	3d	0.25	H_2O	NaOH	60	94%
18	3d	0.25	H ₂ O	NaAc	60	93%
19	3d	0.25	H_2O	Na_2CO_3	60	97%
20	3d	0.25	H ₂ O	КОН	60	96%
21	3d	0.25	H_2O	Et ₃ N	60	94%
22	3d	0.25	H ₂ O	$NaHCO_3$	60	60%
23	3d	0.25	H ₂ O	K ₂ CO ₃	40	97%
24	3d	0.05	H ₂ O	K ₂ CO ₃	60	>99%
25	3d	0.025	H ₂ O	K ₂ CO ₃	60	86%

^{*a*}Reaction conditions: 4a (1.0 mmol), 5a (1.5 mmol), base (2 mmol), cat, solvent (3 mL), for 5 h in N_2 . ^{*b*}Determined by gas chromatography.

986 (m), 895 (s), 820 (m), 756 (m), 735 (s), 726 (s), 687 (m), 572 (w), 531(w).

Synthesis of 2d. The red solid **2d** was prepared in a similar way to that used for **2a** but using $PdCl_2$ (0.0089 g, 0.05 mmol) and **1d** (0.0336 g, 0.10 mmol) as starting materials. Yield: 0.0425 g (75%). Anal. Calcd for $C_{42}H_{48}Cl_2N_4PdS_2$: C, 59.33; H, 5.69; N, 6.59%. Found: C, 58.75; H, 5.90; N, 8.67%. IR (KBr disk, cm⁻¹): 3160 (m), 3102 (s), 3066 (s), 2963 (w), 2918 (m), 2855 (w), 2741 (w), 1762 (w), 1608 (s), 1550 (s), 1482 (s), 1442 (m), 1415 (w), 1364 (m), 1226 (s), 1137 (m), 1081 (w), 1035 (m), 982 (w), 941 (w), 927 (m), 861 (s), 850 (s), 774 (m), 733 (w), 703 (m), 599 (w), 579 (w).

Synthesis of 2e. The brick-red solid **2e** was prepared in a similar route to that used for **2a** but using $PdCl_2$ (0.0179 g, 0.10 mmol) and **1e** (0.0380 g, 0.20 mmol) as starting materials. Yield: 0.0557 g (83%). Anal. Calcd for $C_{20}H_{20}Cl_2N_4PdS_2$: C, 43.06; H, 3.61; N, 10.04%. Found: C, 43.19; H, 3.82; N, 10.25%. IR (KBr disk, cm⁻¹): 3156 (w), 3123 (w), 3089 (w), 3048 (w), 1595 (m), 1559 (m), 1498 (s), 1464 (m), 1411 (w), 1382 (m), 1239 (s), 1154 (s), 1073 (w), 1025 (w), 961 (w), 780 (m), 747 (m), 730 (m), 696 (s), 684 (m), 564 (m).

Synthesis of 3a. Ligand 1a (0.0128 g, 0.10 mmol) was loaded into a MeOH (10 mL) solution of PdCl₂ (0.0177 g, 0.10 mmol). The resulting mixture was refluxed for 12 h to yield a red precipitate, which was washed sequentially with MeOH and Et₂O and dried in vacuo. Red blocks of 3a suitable for X-ray diffraction were obtained after a few days by slow evaporation of solvents from the filtrate at room temperature. Yield: 0.0271 g (89%). Anal. Calcd for $C_{10}H_{16}Cl_4N_4Pd_2S_2$: C, 19.66; H, 2.64; N, 9.17%. Found: C, 19.19; H, 3.10; N, 9.65%. ¹H NMR (400 MHz, CD₃CN, ppm): δ 7.21 (S, 2H), 3.76 (s, 6H). IR (KBr disk, cm⁻¹): 3146 (m), 3118 (s), 2946 (w), 1625 (w), 1585 (w), 1564 (s), 1490 (s), 1470 (m), 1441 (m), 1397 (s), 1238 (s), 1179 (s), 1133 (w), 1097 (w), 745 (s), 678 (s), 665 (w), 637 (w), 617 (w), 480 (w).

Synthesis of 3b. The red solid **3b** was prepared in a similar way to that used for **3a** but using PdCl₂ (0.0179 g, 0.10 mmol) and **1b** (0.0185 g, 0.10 mmol) as starting materials. Yield: 0.0307 g (85%). Anal. Calcd for C₁₈H₃₂Cl₄N₄Pd₂S₂: C, 29.89; H, 4.46; N, 7.75%. Found: C, 29.52; H, 4.77; N, 7.76%. ¹H NMR (400 MHz, CD₃CN, ppm): δ 7.35 (s, 2H), 5.21 (m, *J* = 6.7 Hz, 2H), 1.47 (d, *J* = 6.8 Hz, 12H). IR (KBr disk, cm⁻¹): 3138 (w), 3111 (w), 3081 (m), 2977 (m), 2935 (w), 2876 (w), 1624 (m), 1556 (s), 1458 (s), 1406 (s), 1385 (s), 1375 (m), 1213 (s), 1180 (m), 1137 (m), 1083 (w), 1058 (w), 883 (w), 760 (m), 689 (m), 664 (w), 618 (w), 582 (w), 528 (w).

Synthesis of 3c. The red solid **3c** was prepared in a similar approach to that used for **3a** but using $PdCl_2$ (0.0178 g, 0.10 mmol) and **1c** (0.0264 g, 0.10 mmol) as starting materials. Yield: 0.0343 g (78%). Anal. Calcd for $C_{30}H_{48}Cl_4N_4Pd_2S_2$: C, 40.78; H, 5.48; N, 6.34%. Found: C, 39.94; H, 6.00; N, 10.42%. ¹H NMR (400 MHz, CD₃CN, ppm): δ 7.32 (s, 2H), 4.86 (m, 2H), 1.77 (d, J = 10.9 Hz, 3H), 1.58 (m, 8H), 1.28 (m, 2H). Eight hydrogen signals got lost due to peak overlap. IR (KBr disk, cm⁻¹): 3169 (m), 3144 (w), 2976 (m), 2933 (w), 2876 (w), 1684 (w), 1628 (w), 1577 (w), 1559 (s), 1439 (s), 1415 (m), 1400 (w), 1371 (m), 1337 (m), 1205 (s), 1175 (w), 1136 (m), 1122 (m), 1067 (w), 1052 (m), 1001 (w), 736 (s), 693 (s), 676 (w), 643 (w), 582 (w).

Synthesis of 3d. The red solid 3d was prepared in an analogous way to that used for 3a but using $PdCl_2$ (0.0176 g, 0.10 mmol) and 1d (0.0336 g, 0.10 mmol) as starting materials. Yield: 0.0380 g (74%). Anal. Calcd for $C_{42}H_{48}Cl_4N_4Pd_2S_2$: C, 49.09; H, 4.71; N, 5.45%. Found: C, 48.89; H, 4.88; N, 5.20%. IR (KBr disk, cm⁻¹): 3160 (m), 3102 (s), 3066 (s), 2962 (w), 2918 (m), 2858 (w), 1607 (m), 1550 (s), 1480 (s), 1443 (m), 1382 (m), 1325 (w), 1305 (w), 1225 (m), 1169 (w), 1137 (m), 1081 (w), 1100 (w), 1035 (w), 927 (w), 862 (m), 850 (m), 774 (m), 733 (w), 723 (w), 703 (m), 599 (w), 580 (w).

Synthesis of 3e. The brick-red solid **3e** was prepared in a similar method to that used for **3a** but using PdCl₂ (0.0177 g, 0.10 mmol) and **1e** (0.0190 g, 0.10 mmol) as starting materials. Yield: 0.0305 g (83%). Anal. Calcd for C₂₀H₂₀Cl₄N₄Pd₂S₂: C, 32.68; H, 2.74; N, 7.62%. Found: C, 34.44; H, 3.18; N, 7.99%. ¹H NMR (400 MHz, CD₃CN, ppm): δ 7.66 (m, 2H), 7.63 (m, 3H), 7.38 (m, 2H), 3.90 (s, 3H). IR (KBr disk, cm⁻¹): 3149 (m), 3109 (s), 3060 (w), 1619 (w), 1593 (w), 1498 (s), 1479 (w), 1457 (w), 1416 (w), 1384 (w), 1330 (w), 1239 (s), 1172 (w), 1126 (w), 1075 (w), 1023 (w), 1004 (w), 764 (s), 726 (w), 693 (s), 665 (w), 629 (w), 558 (m).

General Procedure for the Suzuki–Miyaura Reaction. A mixture of aryl bromide (1.0 mmol), arylboronic acid (1.5 mmol), 3d (0.05 mol %), K_2CO_3 (2 mmol), and deoxygenated H_2O (3 mL) was added to a 25 mL round-bottom flask. The mixture was stirred at 60 °C under N_2 and cooled to room temperature. After that it was extracted three times with diethyl ether (3 × 5 mL), and the combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4 , and concentrated to dryness under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether and ethyl acetate as the eluent to provide the corresponding pure product.

General Procedure for the Sonogashira Cross-Coupling Reaction. A mixture of aryl iodide (0.5 mmol), terminal alkyne (1.0 mmol), Et₃N (1.5 mmol), 3d (0.5 mol %), and MeCN (3 mL) was loaded into a 25 mL round-bottom flask. The mixture was stirred at 60 °C for 24 h under N₂ and cooled to ambient temperature. After that it was partitioned between water and ethyl acetate, and the organic layer was separated, while the aqueous layer was extracted with ethyl acetate (3 × 5 mL). A similar workup to that described above yielded the pure desired product.

Single-Crystal X-ray Crystallography. Single crystals of **2b**, **2d**-2MeCN, or **2e** were obtained by slow diffusion of a MeCN solution of PdCl₂ into a CH₂Cl₂ solution of **1b**, **1d**, or **1e**, while those of **3a**·H₂O and **3b–3e** were obtained directly from the above preparations. X-ray diffraction data collection was performed on an Xcalibur, Atlas, Gemini

Table 4. Suzuki-Miyaura Cross-Coupling Reaction of Aryl Bromides with Aryl Boronic Acids Catalyzed by 3d

	R1		$Br + \frac{3d}{K_2CO_3}$	60 °C 3, H ₂ O	\rightarrow R^1 R^2		
	ĸ	4	5		6		
Entry ^a	Ar ¹ -Br		Ar ² -B(OH) ₂		Product		Yield ^b
1	o →→Br	4 a	B(OH)2	5a	Ho	6a	99%
2	0 → → Br	4a	O- B(OH)2	5b	$\sim\sim\sim\sim$	6b	99%
3	O ₂ NBr	4b	O-B(OH)2	5b	0 ₂ N	6c	94%
4	Br	4c	0	5b	-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	6d	95%
5	,0-√_−Br	4d	O- B(OH)2	5b	$\sim \sim $	6e	92%
6	Br	4f	`о-{	5b	$\widetilde{\mathbf{A}}$	6f	92%
7	→=o →=Br	4e	о- (С)- в(он) ₂	5b		6g	56%/88% ^c
8	о ————————————————————————————————————	4 a	о ————————————————————————————————————	5c	° S S S S S S S S S S S S S S S S S S S	6h	92%
9	o →→→Br	4 a	−O →−B(OH)₂	5d	Her	6i	99%
10	o →→→Br	4 a	F ₃ CB(OH) ₂	5e		6j	98%
11	о ————————Вг	4 a	B(OH)2	5f	$\mathbf{\hat{\mathbf{A}}}$	6k	92%
12	o →→→Br	4a	S B(OH)2	5g	Hom	61	78%
13	o →→→Br	4 a	B(OH) ₂	5h	Hom	6m	92%
14	° → → Br	4 a	B(OH)2	5i	$\mathbf{\hat{\mathbf{A}}}$	6n	90%

"All reactions were performed under N2 in the presence of 1.0 mmol of aryl bromide, 1.5 mmol of arylboronic acid, 0.05 mol % of 3d, and 2 mmol of K₂CO₃ in 3 mL of H₂O, for 5 h at 60 °C. ^bIsolated yield. ^c24 h.

(2b) or a Bruker APEX-II CCD (2d·2MeCN, 2e, 3a·H₂O, 3b-3e) Xray diffractometer using graphite monochromated Mo K α (λ = 0.710 73 Å). Each single crystal was mounted on a glass fiber with grease and cooled in a liquid nitrogen stream at 223 (2b, 3d), 193 (2d-2MeCN and 2e), 173 (3a·H₂O, 3b, and 3e), or 150 (3c) K. The crystal structures of 2b, 2d·2MeCN, 2e, 3a·H₂O, and 3b-3e were solved by direct methods using the SHELXS-97 (2b, 2d-2MeCN, 2e, 3a·H₂O, 3b, 3c, 3e) or SHELXL-2014/7 (3d) and refined by full matrix least-squares on $F^{2,91}$ All of the non-H atoms were refined on F^2 anisotropically by the full-matrix least-squares method. All H atoms were introduced at the calculated positions and included in the structure-factor calculations. A summary of the pertinent crystal data and structure refinement parameters for 2b, 2d·2MeCN, 2e, 3a·H₂O, and 3b-3e is in Table 1.

Results and Discussion. Synthesis of N,N'-Disubstituted Imidazole-2-thiones and Complexes 2a-2e and 3a-3e. Reaction of 1,3-dimethyl-1H-imidazol-3-ium, 1,3-diisopropyl-1H-imidazol-3-ium, 1,3-dicyclohexyl-1H-imidazol-3-ium, 1,3-dimesityl-1Himidazol-3-ium, or 1-methyl-3-phenyl-1H-imidazol-3-ium with elemental sulfur and K2CO3 in MeOH at 40 °C afforded 1a, 1b, 1c, 1d,⁸⁸⁻⁹⁰ and 1e, respectively. In the ¹H NMR spectrum of 1e, the singlet at δ = 3.66 ppm belongs to the three protons of methyl group. The doublet at δ = 6.8 ppm is ascribed to the two protons of imidazole ring. The doublets/multiplets at δ = 7.56, 7.47, 7.38 ppm are assigned as the five protons of phenyl ring (Figure S1). The IR spectrum of 1e exhibits strong absorption band at $\lambda = 1144$ cm⁻¹ attributable to the C=S bond. Notably, the reactions of PdCl₂ with 1a-1e are stoichiometry-dependent. Treatment of PdCl₂ with 2 equiv of 1a-1e in MeCN and CH₂Cl₂ gave rise to five mononuclear Pd(II) complexes *trans*- $[(R^1R^2C_3N_2S)_2PdCl_2](R^1 = R^2 = Me(2a), {}^{i}Pr(2b),$ Cy (2c), $C_6Me_3H_2$ (2d); $R^1 = Me_1R^2 = Ph_2(2e)$ in good yields (75%) to ~88%; Scheme 1). The corresponding reactions of $PdCl_2$ with equimolar 1a-1e in refluxing MeOH produced five binuclear Pd(II) complexes $[(PdCl_2){\mu-(R^1R^2C_3N_2S)}]_2$ $(R^1 = R^2 = Me$ (3a), ⁱPr (3b),

Table 5. Comparison of the Catalytic Performances of 3d and Other Known Catalysts in the Suzuki–Miyaura Reactions of Arylboronic Acids with Arylbromides or Aryliodides

	R ¹	+ I	R ²	H) ₂ Cat., Base,	Temp. Solvent R ¹					
entry	cat	mol % Pd	R ¹ , X	R ²	solvent	base	$T(^{\circ}C)$	time	yield	ref
1	dtobimth/PdI ₂	1	OMe, Br	Н	i-PrOH/H ₂ O	K ₂ CO ₃	80	5 h	98%	37
2	1,3-bdtbbphimth/Pd(OAc) ₂	1.5	COMe, Br	OMe	i-PrOH/H ₂ O	K_2CO_3	100	24 h	99%	38
3	[(phbtuimt)PdCl ₂]	2	Ι	Н	dioxane	Cs_2CO_3	80	48 h	74%	61
4		2	Ι	Me	dioxane	Cs_2CO_3	80	48 h	67%	61
5	3,3'-Hphbdbphimth/Pd(dba) ₂	0.5	COMe, Br	Н	H ₂ O/NMP	K_2CO_3	120	10 h	33%	40
6	[(pybethim)PdCl(PPh ₃)]	0.1	OMe, Br	Me	toluene	K_2CO_3	80	5 h	93%	24
8	[(PhSCH ₂ CH ₂ SPh)PdCl ₂]	0.1	Me, Br	Н	DMF/H ₂ O	K ₂ CO ₃	100	12 h	18%	23
9		1	Me, Br	Н	DMF/H ₂ O	K_2CO_3	100	4 h	95%	23
10	[(PhSCH ₂ CH ₂ SePh)PdCl ₂]	0.1	Me, Br	Н	DMF/H ₂ O	K_2CO_3	100	12 h	33%	23
11		1	Me, Br	Н	DMF/H ₂ O	K_2CO_3	100	12 h	77%	23
12	$[Pd_2(dppe)_2(S(C_6H_4)S)]_2(OTf)_4$	0.04	Me, Br	Н	H ₂ O/1,4-dioxane	K_2CO_3	100	10 h	90%	22
13		0.04	COMe, Br	Н	$H_2O/1$,4-dioxane	K ₂ CO ₃	100	10 h	99%	22
14		0.0004	COMe, Br	Н	H ₂ O/1,4-dioxane	K_2CO_3	100	10 h	95%	22
15	$[Pd_2(dppe)_2(S(C_{12}H_8)S)]_2(OTf)_4$	0.4	Me, Br	Н	H ₂ O/1,4-dioxane	K_2CO_3	100	10 h	96%	22
16	[(phpymhcth)Pd(PPh ₃)]Cl	0.01	COMe, Br	OMe	EtOH	Na_2CO_3	75	13 h	99%	27
17	[(phphthprammph)PdCl]	0.1	Me, Br	Н	DMF/H ₂ O	K_2CO_3	100	15 h	95%	28
18	{[(PhSCH ₂ CH ₂) ₂ NH]PdCl}Cl	2	COMe, Br	Н	H ₂ O	K ₂ CO	100	12	60	31
19	{[(PhSeCH ₂ CH ₂) ₂ NH]PdCl}Cl	2	COMe, Br	Н	H ₂ O	K ₂ CO	100	12	83	31
20	3d	0.1	COMe, Br	Н	H ₂ O	K ₂ CO ₃	60	5 h	99%	this work
21	3d	0.1	Me, Br	OMe	H ₂ O	K ₂ CO ₃	60	5 h	95%	this work
22	3d	0.1	OMe, Br	OMe	H ₂ O	K ₂ CO ₃	60	5 h	92%	this work

Cy (3c), C₆Me₃H₂ (3d); R¹ = Me, R² = Ph (3e)) in reasonable yields (74% to ~89%), while the reaction of PdCl₂ with 2 equiv of Et₂C₃N₂S in EtOH/H₂O was reported to afford *cis*-[(Et₂C₃N₂S)₂PdCl₂].⁶⁰ Interestingly, these mono- and binuclear complexes could be readily converted into each other. Mononuclear complexes 2a-2e could also be formed in relatively high yields subject to the addition of 2 equiv of imidazole-2-thione into the solution of the corresponding binuclear complexes 3a-3e. Heating each of 2a-2e with equimolar PdCl₂ in MeOH at 90 °C for 12 h afforded the corresponding binuclear complexes 3a-3e.

Complexes 2a-2e and 3a-3e are all stable toward oxygen and moisture. Complexes 2a-2e and 3d are sparingly soluble in common organic solvents, while 3a-3c and 3e are insoluble in toluene, hexane, and Et2O but slightly soluble in MeCN, CH2Cl2, DMSO, and dimethylformamide (DMF). The elemental analyses of these Pd(II) complexes are consistent with their chemical formulas. In the IR spectra of 2a-2e and 3a-3e, the peaks at 1144 (2a), 1136 (2b), 1151 (2c), 1137 (2d), 1154 (2e), 1133 (3a), 1137 (3b), 1136 (3c), 1137 (3d), and 1172 (3e) cm⁻¹ are assigned to be the ν (C=S) vibration of imidazole-2-thione ligands. The ¹H NMR spectrum of 3a shows a singlet at δ = 3.76, which is assignable to the protons of the two methyl groups (Figure S2). In the ¹H NMR spectrum of **3b**, the doublet at δ = 1.47 ppm and the multiplet at δ = 5.21 ppm belong to the protons of isopropyl groups (Figure S3). The signals at $\delta = 1.3$, 1.57, and 1.75 ppm in the ¹H NMR spectrum of 3c are ascribed to the protons of cyclohexyl group (Figure S4). One singlet at $\delta = 3.90$ ppm and multiplets at δ = 7.66 and 7.62 pmm in the ¹H NMR spectrum of 3e can be assigned as the protons of the methyl group and the protons of phenyl rings, respectively (Figure S5). The ¹H NMR spectra of 3a-3c and 3e exhibit the singlet at 7.21 ppm (3a), $\delta = 7.35$ ppm (3b), $\delta =$ 7.32 ppm (3c), or $\delta = 7.39/7.37$ ppm (3e), which belongs to the two protons of the imidazole ring. As a representative example, we examine the solution behavior of 3d in MeCN by measuring its positive-ion electrospray ionization mass (ESI-MS) spectrum. One peak at m/z = 991.0 can be assigned to be one dinuclear cation $[\{(C_6Me_3H_2)_2C_3N_2S\}_2Pd_2Cl_3]^+$, which matches well with the simulated isotopic patterns (Figure S6). Thus, we assume that 3d should keep its dinuclear structure in the solution. Finally the crystal

structures of **2b**, **2d**-2MeCN, **2e**, **3a**· H_2O , and **3b**-**3e** are determined by single-crystal X-ray crystallography.

Crystal Structures of 2b, 2d·2MeCN, 2e, 3a·H₂O, and 3b–3e. Complexes **2b, 2d**·2MeCN, and **2e** crystallize in the monoclinic space groups $P_{2_1/n}$, $P_{2_1/c}$, and $C_{2/c}$, respectively. In the structures of **2b**, **2d**, and **2e**, each Pd(II) takes a square-planar coordination geometry, coordinated by two *trans* S atoms from N,N'-disubstituted imidazole-2-thiones and two *trans* Cl atoms (Figures 1a and S7). However, each Pd(II) center in *cis*-[(Et₂C₃N₂S)₂PdCl₂] is coordinated by two *cis* Cl atoms and two *cis* S atoms from two Et₂C₃N₂S ligands.⁶⁰ The Pd–Cl bond lengths (2.060(1) to ~2.3198(17) Å; Table 2) are close to those found in [PdCl₂(L)₂] (2.318(4) to ~2.362(4) Å; L = 1,3dimesitylimidazolidine-2-thione).⁴⁴ The Pd–S bond lengths (2.3194(18) to ~2.3352(7) Å) in **2b**, **2d**·2MeCN, and **2e** are longer than those observed in [PdCl₂(L)] (2.271(3) to ~2.268(1) Å; L = 1-[1-(4-isopropyl-4,S-dihydrooxazol-2-yl)-1-methylethyl]-3-(2-isopropylphenyl)-1,3-dihydrobenzoimidazole-2-thione).⁹²

Compound 3a crystallizes in the triclinic space group $P\overline{1}$, and its asymmetric unit contains one discrete $[(PdCl_2){\mu-(Me_2C_3N_2S)}]_2$ molecule and one H₂O lattice molecule. Compounds 3b-3e crystallize in the monoclinic space groups $P2_1/c$ (3b) and $P2_1/n$ (3c-3e), and their asymmetric units contain one independent molecule $[(PdCl_2){\mu-L}]_2$ (L = ${}^{i}Pr_2C_3N_2S$ (3b), $Cy_2C_3N_2S$ (3c), $(C_6Me_3H_2)_2C_3N_2S$ (3d), or MePhC₃N₂S (3e)). These complexes contain two $[PdCl_2]$ moieties linked by two μ -S atoms from two imidazole-2-thiones to form a dimeric $[Pd(\mu-S)_2Pd]$ unit (Figures 1b,c and S8). Each Pd(II) in 3a-3e has a distorted square-planar coordination geometry completed by two *cis* bridging μ -S atoms and two *cis* terminal Cl atoms. However, the $[Pd(\mu-S)_2Pd]$ structures of 3a and 3b are somewhat different from those of 3c-3e. Two Pd atoms and two S atoms deviate from the same planarity with a dihedral angle between two "PdS2" planes of 38.1° (3a) and 41.8° (3b), forming a bent $[Pd(\mu-S)_2Pd]$ rhomb, while those in 3c-3e are located in the same plane, forming a normal $[Pd(\mu-S)_2Pd]$ rhomb. Such dihedral angles in 3a, $[(PdCl_2){\mu-(Me_2C_3N_2S)}]_2$ (40.02°)⁶⁰ and 3b increase along with the size of substituents in the order of Me < Et < ⁱPr. The two imidazole rings in 3a and 3b are situated on the same side of the bent rhomb, while those in 3c-3e are centrosymmetric with a

Table 6. Optimizing Reaction Conditions for SonogashiraCross-Coupling of 7a with 8a

/ 7a	<u>}</u>	+ 💦	Base	, Temp , Solvent	 9a	
entry ^a	cat	solvent	base	temp (°C)	time (h)	yield ^b
1	3a	MeCN	Et ₃ N	60	24	51%
2	3b	MeCN	Et ₃ N	60	24	58%
3	3c	MeCN	Et ₃ N	60	24	62%
4	3d	MeCN	Et ₃ N	60	24	>99%
5	3e	MeCN	Et_3N	60	24	30%
6	3d	H_2O	Et ₃ N	60	24	60%
7	3d	toluene	Et ₃ N	60	24	10%
8	3d	MeOH	Et_3N	60	24	60%
9	3d	THF	Et_3N	60	24	30%
10	3d	DMF	Et ₃ N	60	24	88%
11	3d	acetone	Et ₃ N	60	24	59%
12	3d	EtOH	Et ₃ N	60	24	43%
13	3d		Et ₃ N	60	24	70%
14	3d	MeCN	Na ₂ CO ₃	60	24	4%
15	3d	MeCN	K_2CO_3	60	24	47%
16	3d	MeCN	NaOAc	60	24	89%
17	3d	MeCN	NaOH	60	24	<2%
18	3d	MeCN	КОН	60	24	65%
19	3d	MeCN	NaOEt	60	24	2%
20	3d	MeCN	NMI	60	24	<2%
21	3d	MeCN	K_3PO_4	60	24	70%
22	3d	MeCN	DEA	60	24	78%
23	3d	MeCN	Et_3N	60	18	95%
24	3d	MeCN	Et ₃ N	40	24	50%
25	3d	MeCN	Et_3N	60	12	83% ^c /3% ^d

"Reaction conditions: 7a (0.5 mmol), 8a (1.0 mmol), cat (0.0025 mmol), and base (1.5 mmol, 3 equiv), under N_2 . NMI = *N*-methylimidazole, DEA = diethylamine. ^bDetermined by gas chromatography. ^cWith CuI (0.01 mmol) as a cocatalyst. ^dThe yield of 1,4-diphenylbuta-1,3-diyne.

crystallographic inversion center located at the midpoint of the two Pd centers. These differences result from the different steric constraints imposed by the substituted groups on the imidazole ring. The two ligands with larger substituted groups such as Cy (3c), $C_6Me_3H_2$ (3d), and Me/Ph (3e) tend to bind Pd(II) centers in an opposite direction to minimize the steric hindrance caused by the bulky groups. Among 3a-3e, compound 3d has the two largest $C_6Me_3H_2$ groups on the 2 and 5 positions of imidazole-2-thione and thus holds the longest Pd- μ -S (2.3428(11) Å) bond length (Table 2). In addition, its S-Pd-S angle of 86.17(3)° is larger than those in 3a (81.63(6)° and 81.78(6)°), 3b (79.33(3)° and 79.25(3)°), 3c (82.34(2)°), and 3e (85.227(19)°). The average Pd- μ -S bond distance in 3d (2.3312(10) Å) is longer than those of 3a (2.2945(18) Å), 3b (2.2903(9) Å), 3c (2.2838(7) Å), and 3e (2.2947(5) Å), while the mean terminal Pd-Cl bond lengths (2.3074(6) to ~2.3184(2) Å) in 3a-3e are comparable to those in 2b, 2c, and 2d.

Suzuki–Miyaura Cross-Coupling Reactions. The catalytic performance of precatalyst 3d was first evaluated in the Suzuki–Miyaura reaction. We performed the cross-coupling reaction with 0.25 mol % of 3d, 1-(4-bromophenyl)ethanone (4a, 1.0 mmol), phenylboronic acid (5a, 1.5 mmol), and K_2CO_3 (2 mmol) in 3 mL of CH₃CH₂OH at 60 °C for 5 h. A standard workup produced the desired product 1-biphenyl-4-yl-ethanone (6a) in 82% (Table 3, entry 1). This preliminary result implied that these Pd(II) complexes of imidazole-2-thiones could initiate the cross-coupling reactions of aryl bromides with arylboronic acids with high catalytic activity. Some other common solvents (toluene, dioxane, DMF, CH₃CN, and H₂O) were also assessed. The conversion of 4a to 6a in H₂O was found to be

complete within 5 h at 60 °C (entry 6). The catalytic performances of the mononuclear precatalysts 2a-2e were also evaluated using Suzuki-Miyaura coupling reactions in water under similar reaction conditions. The desired product 6a was isolated in 5%, 15%, 74%, 87%, and 84% yields, respectively (entries 7-11). By comparison, reactions catalyzed by 3a-3e performed much better (entries 6 and 12-15) than those of the corresponding mononuclear complexes, which may be due to the cooperative effect of dinuclear unit in 3a-3e. In addition, the two *trans* thione ligands in 2a-2e depressed the ability of Pd center to oxidatively add the aryl bromide substrate. Complex 3d exhibited the highest catalytic activity of the five binuclear complexes, indicating that introducing two bulky C₆Me₃H₂ groups on the 2 and 5 positions of imidazole-2-thione did improve the catalytic performance. As discussed above, the longest Pd- μ -S bond and the enlarged S-Pd-S angle in 3d may favor the reductive elimination and thus increase the stability of coordinatively unsaturated active catalytic species.^{93,94} Such a structure-to-activity relationship is in good agreement with previous observations^{95,96} and is confirmed by our theoretical calculations described below. Complexes 3d, 4a, and 5a were thus chosen as a model system to optimize reaction conditions. The effect of base (K₃PO₄, NaOH, NaOAc, Na₂CO₃, KOH, NaHCO₃, and Et₃N) was examined (entries 16-22). It was found that either K₃PO₄ or K₂CO₃ was the most suitable base. When the reaction temperature (60 °C) was decreased to 40 °C, the yield of 6a got dropped almost imperceptibly from greater than 99% to 97% (entry 23). The catalyst loading could be decreased to 0.05 mol %, which still afforded **6a** in a quantitative yield (entry 25). Therefore, the optimized reaction conditions were determined to be 0.05 mol % of 3d, with K_2CO_3 (as a base) for 5 h at 60 °C in H_2O .

With suitable reaction conditions established, we next investigated the scope of the substrates with a series of aryl bromides and arylboronic acids (Table 4). This study revealed that the electronic nature of the substituents on the aryl bromides had some effects on the yields of the coupling products. Reaction of (4-methoxyphenyl)boronic acid (5b) with phenyl bromide bearing an electronwithdrawing substituent group (carbonyl or nitro) or electrondonating substituent group (methoxy or methyl) could afford the corresponding product in almost quantitative yields (entries 2-5). The reactions of 3- or 4-bromoacetophenone with 5b provided the corresponding products 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1one (6b, 99% yield; entry 2) and 1-(4'-methoxy-[1,1'-biphenyl]-3yl)ethan-1-one (6f, 92% yield; entry 6) in excellent yields. Reaction of 1-(2-bromophenyl)ethan-1-one with 5b, however, produced 1-(4'methoxy-biphenyl-2-yl)ethanone in only 56% yield (entry 7), presumably due to the steric hindrance by the ortho substituent. When the reaction time was extended to 24 h, the same substrates afforded 6g in a significantly higher yield (88%). Electron-rich and -neutral arylboronic acids reacted smoothly to give the corresponding products in 92%-99% yields (entries 1, 2, 8, 9, 11). The reaction also proceeded well for a para-substituted electron-deficient arylboronic acid (entry 10). Notably, the steric hindrance of an ortho substitutent on the arylboronic acids did not significantly affect the yield (entry 8). We also examined the cross-coupling reactions of heteroaryl boronic acids with 4a. Good or excellent yields were observed under the optimized conditions (entries 12-14). Table 5 lists comparison on the catalytic performances in the Suzuki-Miyaura reactions of arylboronic acids with aryl bromides or aryl iodides using 3d and other known catalysts. Complex 3d possesses higher catalytic activity than some reported catalytic systems such as 1,3-bdtbbphimth/Pd(OAc),³⁸ (1,3bdtbbphimth = 1,3-bis(4,4'-di-*tert*-butyl-[1,1'-biphenyl]-2-yl)-imidazolidine-2-thione), [(phbtuimt)PdCl₂],⁶¹ 3,3'-Hphbdbphimth/ $Pd(dba)_2^{40}$ (3,3'-Hphbdbphimth = 3,3'-(1,3-phenylene)bis(1-(2,5ditert-butylphenyl)imidazolidine-2-thione); dba = dibenzylideneacetone), $[(phpymhcth)Pd(PPh_3)]Cl^{27}$ (Hphpymhcth = 2-(phenyl-(pyridin-2-yl)methylene)hydrazine-1-carbothioamide), $[(phphthprammph)PdCl]^{28}$ (Hphphthprammph = 2-(phenyl((3-(phenylthio)propyl)amino)methyl)phenol), [(PhSCH₂CH₂SPh)-PdCl₂]²³ and [(PhSCH₂CH₂SePh)PdCl₂]²³ When the crossingcoupling reactions are performed in anisole or i-PrOH/H2O at higher temperature (80 °C), some Pd/S catalysts such as $[dtobimth/PdI_2]^3$

Table 7. Sonogashira Cross-Coupling Reactions of Aryl iodides with Alkynes Catalyzed by 3d



"Reaction conditions: 7 (0.5 mmol), 8 (1.0 mmol), 3d (0.0025 mmol), and Et_3N (1.5 mmol) in 3 mL of MeCN, 60 °C under N_2 atmosphere. ^bIsolated yield.



Figure 2. Ten possible transition states of Suzuki–Miyaura reactions of catalyzed by mono- and binuclear Pd(II) complexes (free energies in kcal/mol) at the B3LYP + SMD (H_2O)/6-31G(d) level.

(dtobimth = (3aR,7aR)-1,3-di-*o*-tolyloctahydro-2*H*-benzo[d]imidazole-2-thione) and [(pybethim)PdCl(PPh₃)]²⁴ (Hpybethim = *N*-(pyridin-4-yl)benzothioamide) show comparable activity to that of **3d**. In water, the catalytic activity of **3d** is much higher than those of {[(PhSCH₂CH₂)₂NH]PdCl}Cl and {[(PhSeCH₂CH₂)₂NH]PdCl}-Cl³¹ and comparable to that of [Pd₂(dppe)₂(S(C₆H₄)S)]₂(OTf)₄ (dppe = 1,2-bis(diphenylphosphino)ethane; OTf = trifluoromethanesulfonate) at 100 °C in H₂O/1,4-dioxane.²²

Sonogashira Cross-Coupling Reactions. To explore the utility of the precatalysts 3a-3e, the catalytic performances of these complexes were investigated in Sonogashira cross-coupling reactions of aryl iodines with terminal alkynes. We performed the reaction of iodobenzene (7a) with 2 equiv of phenylacetylene (8a) in CH₃CN at 60 °C with 0.5 mol % of 3a as catalyst and 3 equiv of Et₂N as base (Table 6, entry 1). The standard workup produced the desired product 1,2-diphenylethyne (9a) in 51% yield. Complexes 3b-3e were also examined (entries 2-5), and 3d again exhibited the highest catalytic activity (entry 4). 3a, 3b, 3c, and 3e provided 30-62% yields of the desired product 9a, whereas 3d gave 9a in an almost quantitative yield. Therefore, we selected 3d, 7a, and 8a as a model system to optimize the reaction conditions. Acetonitrile proved to be the best solvent (entry 4). The yield of the cross-coupling product got decreased significantly when the reaction was performed in toluene, tetrahydrofuran (THF), or CH3CH2OH. Subsequently, we examined the influence of organic bases (Et₂N, N-methylimidazole (NMI), diethylamine (DEA)) and inorganic bases including Na_2CO_3 , K_2CO_3 , NaOAc, NaOH, KOH, NaOEt, and K₃PO₄ (entries 14-22). Et₃N in CH₃CN gave the highest yield under the same conditions. At lower temperature (40 °C), the reaction gave the product in a commensurately lower yield (entry 24). When CuI was used as the cocatalyst, the reaction in 12 h produced 9a in 83% yield coupled with 1,4-diphenylbuta-1,3-diyne in 3% yield (entry 25). The results outlined in Table 6 revealed that the optimal conditions for such a Cu-free Sonogashira reaction could be fixed as MeCN as solvent, Et₃N as base at 60 °C with 0.5 mol % of catalyst (3d). The turnover frequency (TOF) of 6.9 h⁻¹ (18 h) was slightly lower than that observed in the 3d/CuI-catalyzed reaction (8.3 h⁻¹).

Again, we examined the scope of the substrates that could be employed for this catalytic system (Table 7). All of the substrates investigated gave the desired 1,2-diarylethyne products in excellent yields. Neither o- nor m-substituted group on the phenyl rings of the aryl iodide or phenylacetylene hampered the coupling reaction. The 2'-, 3'-, and 4'-methylphenylacetylenes were converted smoothly to their corresponding products (9c-9e) in 89%, 92%, and 98% yields, respectively (entries 3-5). Reactions of ethynylbenzene with 2-, 3-, and 4-iodotoluenes resulted in the formation of products in high yields (89%, 93%, and 96%, entries 6-8). Neither electron-donating nor electron-withdrawing groups on either aryl iodides or alkynes significantly affected the yields. Terminal alkynes and phenyl iodides with electron-donating substituents like -Me and -OMe reacted in excellent yields (entries 6 and 10). The presence of electronwithdrawing groups at the para position of aryl iodide or alkyne furnished the products in good yields (88% and 89%; entries 2 and 9). Notably, most reports on the Sonogashira coupling involve phosphinebased catalysts,³⁻⁵ while examples of S-based stabilizing ligands are surprisingly rare. Comparative run with (phbtuimt)PdCl₂/CuI $(76\%)^{61}$ indicated that **3d** exhibits better catalytic performance (91%) for Sonogashira cross-coupling reaction of 7a and 8a. In the presence of CuI, [(phpymhcth)Pd(PPh₃)]Cl²⁷ at higher temperature (110 °C) in EtOH and toluene (>99% yield) shows higher activity than that of 3d.

Computational Studies. The palladium-catalyzed Suzuki– Miyaura cross-coupling reactions may involve three steps: the oxidative addition of aryl halides to palladium, the transmetalation of the resulting aryl-halo-Pd(II) complexes with boronate complexes into diaryl-palladium(II) species, and the reductive elimination to yield biaryl products.^{8,14,17} To better understand their catalytic activity, the Suzuki–Miyaura cross-coupling reaction of bromobenzene with phenylboronic acid catalyzed by **2a–2e** and **3a–3e** were investigated through density functional theory (DFT) calculations. The alkylboron transmetalation was considered as the rate-determining step for Suzuki-Miyaura cross-coupling reactions.^{97,98} Thus, we only calculated the Gibbs free energy for possible diaryl-palladium(II) intermediates. Geometry and frequency calculations were performed with the B3LYP functional using the Gaussian 09 suite of program.⁹ The LANL2DZ basis set was employed for Pd, while the 6-31G(d) basis set was used for other atoms. Frequency analysis at the same level was performed to ensure the stationary point as minimum or transition state. Single-point calculations on the gas-phase optimized geometry with the SMD solvation model (solvent = H_2O for mono- and binuclear Pd(II) catalysts, respectively) were applied. The Gibbs free energy was calculated by adding the gas-phase Gibbs free energy correction with the solution-phase single-point energy. The structures of the intermediates (Int) and the transition states (TS) for 2a-2eand 3a-3e are shown in Figure S9. Cartesian coordinates of all optimized intermediates (Int) and transition states (TS) are listed in Table S1. As discussed above, 3d displays the highest activity among the mononuclear complexes (2a-2e) and binuclear complexes (3a-3e). Figure 2 shows that the activation barrier of 3d is 11.6 kcal/mol, which is the lowest among those of 2a-2e and 3a-3e. The favorability (TS_{3d}: 11.6 kcal/mol) of Suzuki-Miyaura reactions catalyzed by binuclear Pd(II) complex 3d is in excellent agreement with those obtained experimentally.

CONCLUSIONS

In this work, we demonstrated that 1:2 or 1:1 reaction of PdCl₂ with N,N'-disubstituted imidazole-2-thiones under different reaction conditions produced a series of mononuclear (2a-2e)and binuclear (3a-3e) Pd(II) complexes. Complexes 2a-2eand 3a-3e could readily be interconverted subject to changing the molar ratios of PdCl₂ and N,N'-disubstituted imidazole-2thione and controlling the reaction temperatures. According to the X-ray analysis, compound **3d** has the longest Pd- μ -S bond and the largest S-Pd-S angle among all the title complexes. Complexes 3a-3e possess much better catalytic performance than 2a-2e in Suzuki-Miyaura and Sonogashira cross-coupling reactions. We propose that the two *cis* thione ligands in 3a-3epromote oxidative addition of aryl halide to the Pd(II) center and the cooperative effect of two Pd(II) centers. The substituted groups on ligands do exert a significant influence on catalytic performance. Complex 3d displays the highest catalytic activity toward Suzuki-Miyaura cross-coupling reactions of aryl bromides with aryl boronic acids in water and Cu-free Sonogashira cross-coupling reactions of aryl iodides and alkynes in MeCN under mild conditions. DFT calculations and the experimental observations support that the bimetallic structure with the bulkier ligands are beneficial to the above two catalysis reactions. Our current work represents a good example in which the introduction of the suitable substituted groups on the auxiliary ligands could finely adjust the geometric structures of the resulting Pd(II) coordination compounds, which, in turn, greatly enhances the catalytic activity toward Suzuki-Miyaura and Sonogashira cross-coupling reactions.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01616.

Additional information regarding computational detail, the ESI-MS observed peaks and isotopic patterns of $[{(C_6Me_3H_2)_2C_3N_2S}_2Pd_2Cl_3]^+$, and the ¹H and ¹³C NMR spectra for 1-methyl-3-phenyl-1,3-dihydro-imidazole-2-thione and cross-coupling products (PDF)

Accession Codes

CCDC 1477939, 1477940, 1477941, 1494637, 1494638, 1494639, 1539252 and 1494640 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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