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PAPER

Palladacycles bearing tridentate CNS-type benzamidinate ligands as catalysts for cross-coupling reactions†

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Three pendant benzamidines, [Ph–C(=NC_6H_5)–{NH(E)}] [E = –$(CH_2)_2$SMe (**1**); –$(CH_2)_2S^tBu$ (**2**); –*o*-C_6H_4SMe (**3**)], are described. Reactions of **1**, **2** or **3** with one molar equivalent of $Pd(OAc)_2$ in CH_2Cl_2 give the palladacyclic complexes, [Ph–C{–NH(η^1-C_6H_4)}{=N(E)}]Pd(OAc) [E = –$(CH_2)_2$SMe (**4**); –$(CH_2)_2S^tBu$ (**5**); –*o*-C_6H_4SMe (**6**)], as mononuclear palladium complexes respectively. A minor product described as **5′**, {[Ph–C{–N(C_6H_5)}{–N$(CH_2)_2S^tBu$}]Pd(OAc)}$_2$, was isolated as benzamidinate-bridged dinuclear palladium complex upon recrystallizing from Et_2O/hexane solution. Treatment of **1**, **2** or **3** with one molar equivalent of $PdCl_2$ in the presence of NEt_3 in CH_2Cl_2 gives the palladacyclic complexes, [Ph–C{–NH(η^1-C_6H_4)}{=N(E)}]PdCl [E = –$(CH_2)_2$SMe (**7**); –$(CH_2)_2S^tBu$ (**8**); –*o*-C_6H_4SMe (**9**)], as mononuclear palladium complexes respectively. The crystal and molecular structures are reported for compounds **5**, **5′** and **6–8**. The application of these palladacyclic complexes to the Suzuki and Heck coupling reactions was examined.

Introduction

Mono-anionic amidinate ligands with the general formula $[R^1C(NR^2)(NR^3)]^{-1}$ exhibited versatile coordination properties, and displayed their potential to act as ancillary ligands in metal complexes.[1] Over the past couple of decades, many metal–amidinato compounds have been achieved and these have been reviewed by several research groups.[1,2] Due to the ease of substitution on either or both N and C atoms, the steric and electronic properties of amidinato ligands can be modified by variation of the substituents. According to reported literatures, the existence of pendant arm could play an important role in coordinated behaviour and tuned the reactivity of metal complexes in catalytic reactions.[3] Recently some palladium benzamidinato compounds bearing pendant functionalities have been reported by us.[4] We also found these complexes prefer to proceed *via* orthometallation on the phenyl group rather than deprotonation of the nitrogen atom with pendant functionalities. In this paper, we report the preparation and structural properties of pendant benzamidines with thioether functionalities and their orthometallated palladium complexes. The catalytic activities of these palladacyclic complexes towards the Suzuki and Heck coupling reactions are also investigated.

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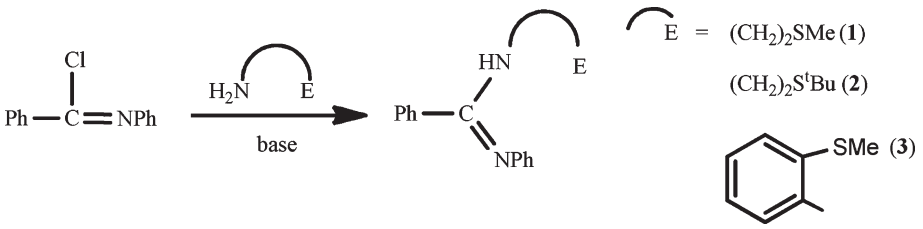
Results and discussion

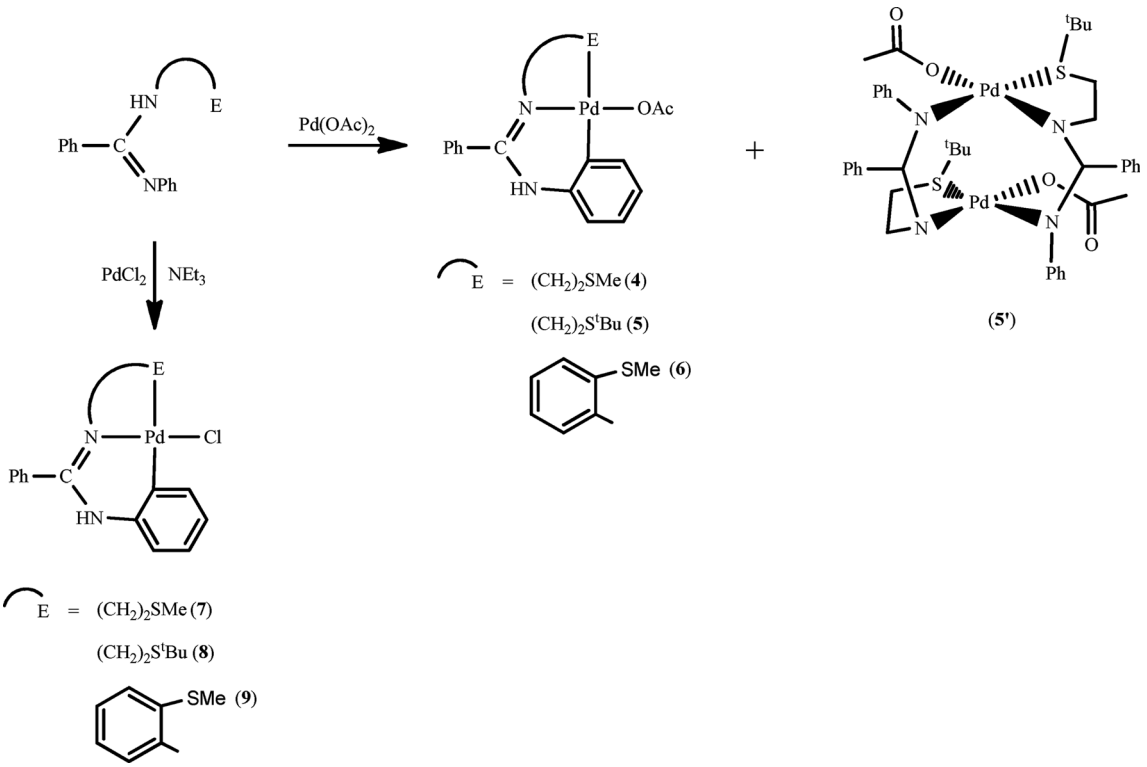
Preparation of ligand precursors and palladacycles

Ligand precursors were prepared following a classical route for the synthesis of N,N′-disubstituted amidines, as shown in Scheme 1.[4,5] Compounds are characterised by NMR spectroscopy as well as elemental analyses. Complex and broad signals were found in ^{1}H NMR spectrum for compound **3**, which are always observed for compounds with tautomeric rotation. Therefore high temperature spectroscopic data were reported for it.

Three amidines with pendant thioether functionalities react readily with one molar equivalent of $Pd(OAc)_2$ in dichloromethane to afford complexes **4**, **5** and **6**, which are expected to form a mononuclear species[4,6] rather than the dimeric or oligomeric structures.[7–10] A summary of the syntheses and proposed structures of palladacycles is shown in Scheme 2. In each palladium acetate compound, one N*H* singlet around δ 10–11 ppm (10.57 ppm for **4**; 10.23 ppm for **5**; 11.27 ppm for **6**) was found on the ^{1}H NMR spectrum and one more tertiary carbon appeared in the region of the phenyl ring on the $^{13}C\{^1H\}$ NMR spectrum, which indicates the preference of carbon metallation rather than the N*H* deprotonation.[4] Suitable crystals of **5** and **6** for structural determination were obtained from a CH_2Cl_2/hexane solution. The molecular structures are depicted in Fig. 1 and 2. The structural analyses show both complexes as a mononuclear species, in which the palladium metal centre is coordinated with one thioether sulphur atom, one imine nitrogen atom, one metallated carbon atom, and one acetate oxygen atom to form one five-membered metallacycle and one six-membered metallacycle.



Scheme 1 Preparation of ligand precursors



Scheme 2 Preparation of palladium complexes

The bond angles (from 86.36(6) to 92.83(6)° for **5**; from 83.07 (9) to 96.20(10)° for **6**) around the Pd metal centres indicate that each complex has a slightly distorted square planar geometry. The bond lengths of Pd–S (2.4151(7) and 2.4256(7) Å for **5**; 2.4119(12) Å for **6**) and Pd–$C_{metallated}$ (1.983(2) and 1.976(3) Å for **5**; 1.983(4) Å for **6**) are within those (2.240(1)–2.422(1) Å for Pd–S; 1.971(4)–2.022(4) Å for Pd–$C_{metallated}$) found in metallated palladacycles.[11] The bond lengths of Pd–O_{OAc} (2.0412(17) and 2.0457(18) Å for **5**; 2.054(3) Å for **6**) are among those (2.036(2)–2.085(2) Å) found in palladacycles bearing tridentate ligands.[4,6,12] The bond lengths of Pd–$N_{C=N}$ (1.998(2) and 1.995(2) Å for **5**; 2.013(3) Å for **6**) are close to those (1.981(3)–2.030(3) Å) found in some palladacycles.[4,6,12] The difference in C–N bond lengths of the NCN moiety is around 0.019–0.045 Å respectively, indicating the localized nature of the imine C=N and amine C–N bonds.[4] A small amount of a pale-yellow crystalline solid was found and isolated by layering hexane on the diethylether extract from crude product of **5**. Further characteristic data cannot be collected due to the low yield. The molecular structure is shown in Fig. 3.

Unlike **5** produced *via* carbon metallation, the molecular structure of **5′** demonstrates the deprotonation reaction of N*H* could happen upon preparing the metallated pallacycles, which was observed upon preparing amidinato-bridged binuclear palladium complexes.[7–10] The molecular structure of **5′** exhibits a dinuclear species, in which two metal centres are bridged with two benzamidinate ligands through the NCN moiety. Each palladium metal centre is coordinated with one thioether sulphur atom, two nitrogen atoms from different benzamidinate ligands and one acetate oxygen atom to form palladium benzamidinate complexes. The bond angles (from 84.09(8) to 97.21(8)°) around Pd metal centre indicate each complex having a distorted square planar geometry. The bond length of Pd(1)–Pd(2) (2.8011(4) Å) is among those (2.576(1)–2.9435(4) Å) found in dinuclear palladium amidinate complexes.[7–10] The bond lengths of Pd–$N_{amidinate}$ (1.997(3)–2.058(3) Å) are similar to those (2.01(1)–2.112(5) Å) found in amidinato-bridged binuclear palladium complexes.[7–10] The bond lengths of Pd–O_{OAc} (2.057(2) and 2.049(2) Å) and Pd–S (2.3217(9) and 2.3119(9) Å) are similar to those discussed above.

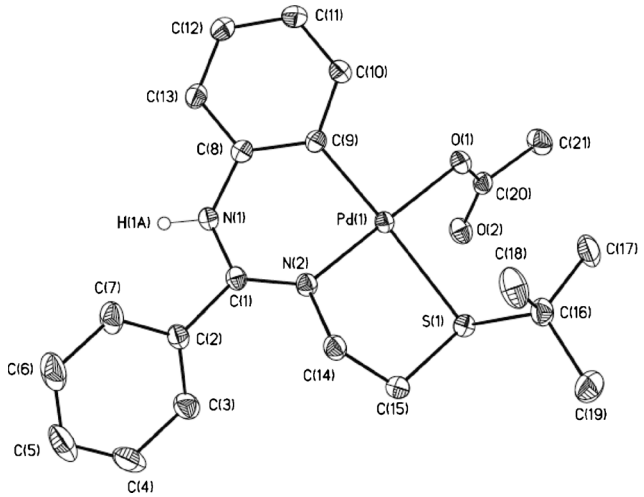


Fig. 1 Molecular structure of one of the crystallographically independent molecules of **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd(1)–C(9), 1.983(2); Pd(1)–N(2), 1.998(2); Pd(1)–O(1), 2.0412(17); Pd(1)–S(1), 2.4151(7); N(1)–C(1), 1.346(3); N(2)–C(1), 1.301(3); C(9)–Pd(1)–N(2), 90.64(9); C(9)–Pd(1)–O(1), 90.18(9); N(2)–Pd(1)–O(1), 179.14(8); C(9)–Pd(1)–S(1), 176.99(7); N(2)–Pd(1)–S(1), 86.36(6); O(1)–Pd(1)–S(1), 92.83(6).

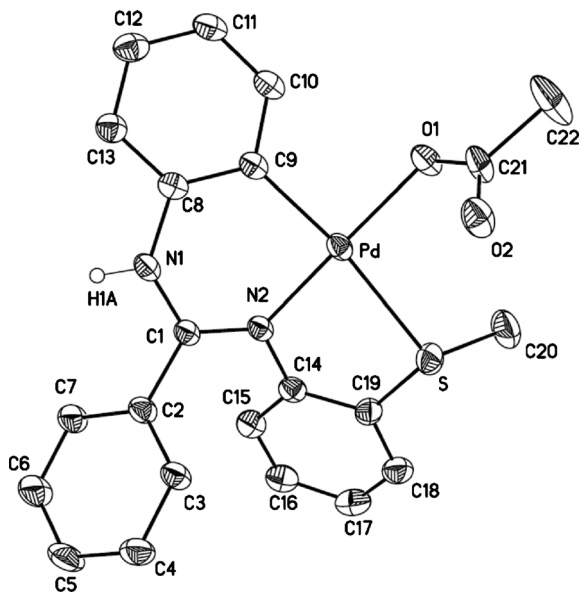


Fig. 2 Molecular structure of complex **6**. Hydrogen atoms on the carbon atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd–C(9), 1.983(4); Pd–N(2), 2.013(3); Pd–O(1), 2.054(3); Pd–S, 2.4119(12); N(1)–C(1), 1.340(5); C(1)–N(2), 1.316(5); C(9)–Pd–N(2), 89.55(13); C(9)–Pd–O(1), 91.39(13); N(2)–Pd–O(1), 175.30(12); C(9)–Pd–S, 172.10(10); N(2)–Pd–S, 83.07(9); O(1)–Pd–S, 96.20(10).

Treatment of **1–3** with one molar equivalent of $PdCl_2$ in the presence of NEt_3 in stirring dichloromethane at room temperature affords complexes **7–9** (Scheme 2). Complexes **7–9** were all characterized by NMR spectroscopy and elemental analyses. In each palladium chloride compound, one N*H* singlet (δ 7.16 ppm for **7**; 7.38 ppm for **8**; 9.10 ppm for **9**) was found on the ^{1}H

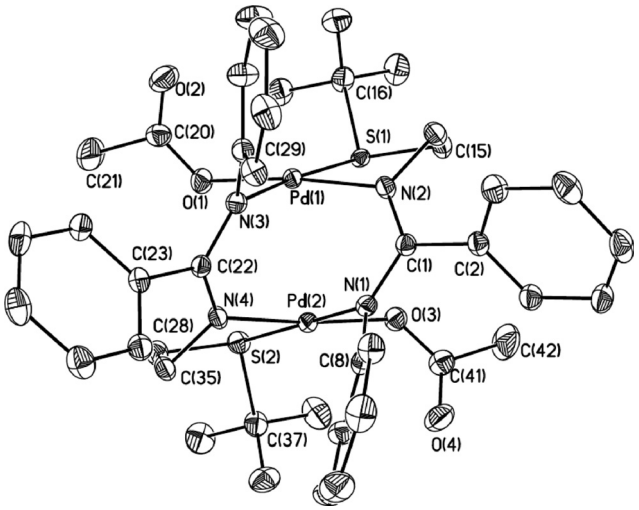


Fig. 3 Molecular structure of complex **5′**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd(1)–N(2), 2.011(3); Pd(1)–O(1), 2.057(2); Pd(1)–N(3), 2.057(3); Pd(1)–S(1), 2.3217(9); Pd(1)–Pd(2), 2.8011(4); Pd(2)–N(4), 1.997(3); Pd(2)–O(3), 2.049(2); Pd(2)–N(1), 2.058(3); Pd(2)–S(2), 2.3119(9); N(1)–C(1), 1.339(4); N(2)–C(1), 1.323(4); N(3)–C(22), 1.334(4); N(4)–C(22), 1.322(4); N(2)–Pd(1)–O(1), 173.71(12); N(2)–Pd(1)–N(3), 89.62 (11); O(1)–Pd(1)–N(3), 88.87(11); N(2)–Pd(1)–S(1), 84.09(8); O(1)–Pd(1)–S(1), 97.21(8); N(3)–Pd(1)–S(1), 173.51(8); N(4)–Pd(2)–O(3), 175.13(12); N(4)–Pd(2)–N(1), 88.95(11); O(3)–Pd(2)–N(1), 89.44(10); N(4)–Pd(2)–S(2), 85.27(9); O(3)–Pd(2)–S(2), 96.47(8); N(1)–Pd(2)–S(2), 173.92(8).

NMR spectrum and one more tertiary carbon appeared in the region of the phenyl ring in the $^{13}C\{^1H\}$ NMR spectrum, which indicates that the carbon metallation reaction could happen in the presence of a base. Suitable crystals of **7** and **8** for structural determination were obtained from concentrated CH_2Cl_2 solutions. The molecular structures are depicted in Fig. 4 and 5. Basically, compounds **7** (with substituent methyl group instead of *tert*-butyl group on sulfur atom and with coordination of chloride atom instead of acetate group to metal center for **5**) and **8** (with coordination of chloride atom instead of acetate group to metal center for **5**) are similar to compound **5**. The structural analyses show each complex as a mononuclear species, in which the palladium metal centre is coordinated with one thioether sulphur atom, one imine nitrogen atom, one metallated carbon atom, and one chloride atom to form one five-membered metallacycle and one six-membered metallacycle. Bond lengths and bond angles are similar to those discussed above. The bond lengths of Pd–Cl(2.3476(7) Å for **7**; 2.3224(8) and 2.3152(8) Å for **8**) are close to those (2.3006(17)~2.328(4) Å) found in some metallated palladacycles.[4,11*a*,*c*,*d*,12]

Catalytic studies

Since several palladium complexes containing pendant thioether functionalities can be used as catalysts for the carbon–carbon coupling reactions,[6,11*f*,13] the palladacyclic derivatives **4–9** were expected to work as catalysts toward the Suzuki-type coupling reaction. A comparison of the activity of these complexes for the

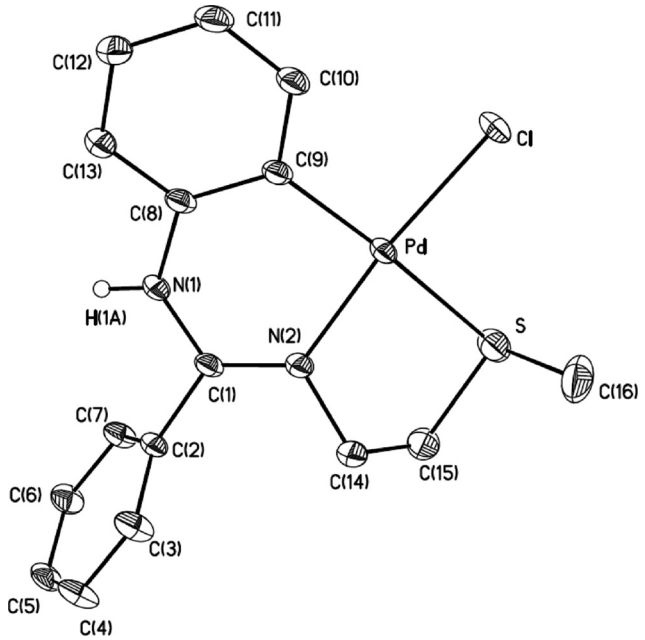


Fig. 4 Molecular structure of complex **7**. Hydrogen atoms on carbon atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd–C(9), 1.993(3); Pd–N(2), 2.018(2); Pd–Cl, 2.3476(7); Pd–S, 2.3974(8); N(1)–C(1), 1.349(3); N(2)–C(1), 1.297(3); C(9)–Pd–N(2), 90.53(9); C(9)–Pd–Cl, 95.46(7); N(2)–Pd–Cl, 173.88(7); C(9)–Pd–S, 176.01(7); N(2)–Pd–S, 85.89(7); Cl–Pd–S, 88.15(3).

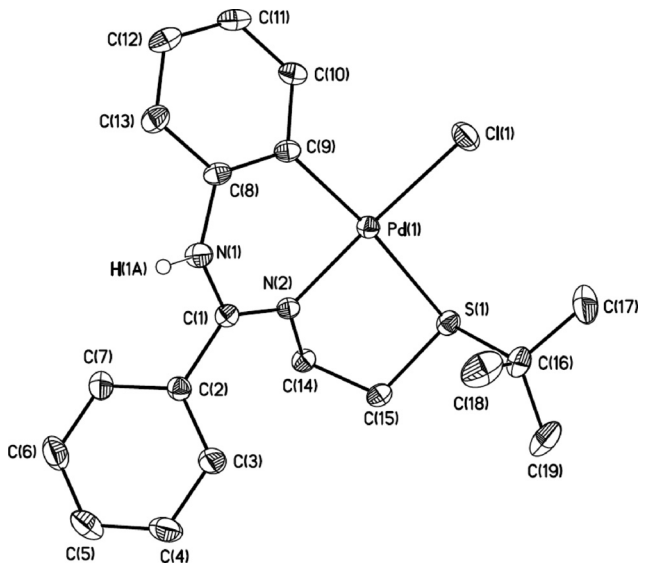


Fig. 5 Molecular structure of one of the crystallographically independent molecules of **8**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd(1)–C(9), 1.993(3); Pd(1)–N(2), 2.010(2); Pd(1)–Cl(1), 2.3224(8); Pd(1)–S(1); 2.4229(7); N(1)–C(1), 1.335(3); N(2)–C(1), 1.304(3); C(9)–Pd(1)–N(2), 89.35(10); C(9)–Pd(1)–Cl(1), 92.54(8); N(2)–Pd(1)–Cl(1), 176.87(6); C(9)–Pd(1)–S(1), 172.22(8); N(2)–Pd(1)–S(1), 84.17(6); Cl(1)–Pd(1)–S(1), 94.13(3).

Suzuki-Miyaura coupling reaction is shown in Table 1. We performed the coupling of 4-bromoacetophenone with 1.5 equiv. phenylboronic acid catalysed by 1 mol% **4–9** in the presence of 2 equiv. K_3PO_4 at 50 °C (Table 1, entries 1–6). Catalyst **6** provided the best result (Table 1, entry 3). Although other bases and solvents were tested with this catalyst **6** for the same reaction (Table 1, entries 7–10), the combination of K_3PO_4/toluene remains the best option (compare Table 1, entry 3 with entries 7–10). Higher reactivity was observed over a period of 1 h at 80 °C (Table 1, entry 11). Similar conditions were applied in catalysing electronically deactivated compounds, resulting in percentage conversions of 90–96% within 2–2.5 h (Table 1, entries 12–14). The results exhibited better activities than those found in our previous work for electronically deactivated aryl halides.[4] In order to examine the catalytic activity in alcoholic solvents, compound **6** was tested in two alcoholic solvents and water (Table 1, entries 15–17). Excellent conversion was observed within 15 min using methanol as solvent at 50 °C. The coupling reactions were also carried out with 1 mol% **6** using electronically activated or deactivated aryl chlorides under the optimised conditions at 100 °C. As expected, the degrees of conversions became lower with longer period of time, even though in the presence of NBu_4Br (Table 1, entries 18–21).

We also examined the catalytic activities of **4–9** in the Heck reaction of 4-bromoacetophenone with 1.3 equiv. styrene in the presence of 1.5 equiv. K_3PO_4 in DMF at 135 °C with 1 mol% catalysts, resulting in percentage conversion levels from 70 to 77% within 0.5 h (Table 2, entries 1–6). Similar conditions were applied to test compounds **7–9** using electronically deactivated aryl bromide as substrate, compound **8** exhibited better catalytic activities after 3 h (Table 2, entries 7–9). The optimised conditions for the reaction were found to be K_3PO_4/DMF for **8** after a screening of various bases and solvents within 2 h at 110 °C (Table 2, entries 10–18). When the reactions were performed at 135 °C, the difference in activity is significant after 0.75 h (conversion, 91%), indicating that the active species is available in solution under elevated temperature (Table 2, entry 19). Similar conditions were applied to the reactions employing the electronically deactivated aryl bromide compounds; however, the reactions took up to 5 h and 6.5 h at 135 °C (Table 2, entries 20–21). Poor conversion levels were observed after 12 h using electronically activated 4-chloroacetophenone (Table 2, entry 22). The percentages of conversion become higher upon increasing the loading of NBu_4Br (Table 2, entries 23–24).

In conclusion, three novel benzamidines bearing pendant thioether functionalities have been prepared. Six novel palladacycles bearing CNS-type benzamidinate ligands have been prepared and have demonstrated catalytic activities for the Suzuki and Heck coupling reactions. Under optimised conditions, compound **6** exhibits catalytic efficiency in the Suzuki coupling reactions whereas compound **8** exhibits better catalytic activities in the Heck coupling reactions. A dramatic increase in activities was observed for the Suzuki coupling reaction when using methanol as reaction medium. Molecular structure of **5′** demonstrated different bonding mode for benzamidinate ligands with pendant functionalities in quite lower yield, supplying important information that versatile bonding modes could happen upon preparing the palladium complexes with multidentate benzamidinate ligands. Preliminary studies on the modification of benzamidines with different substituents and their application in the synthesis of metal complexes are currently being undertaken.

Table 1 Suzuki-type coupling reaction catalysed by new palladium complexes[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] (mol%)	*t* (h)	Conv. (%)[b]	Yield (%)[c]
1	**4**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	28	—
2	**5**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	65	—
3	**6**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	80	75
4	**7**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	75	68
5	**8**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	28	—
6	**9**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	44	—
7	**6**	4-Bromoacetophenone	Cs_2CO_3	Toluene	1	1	9	—
8	**6**	4-Bromoacetophenone	KF	Toluene	1	1	8	—
9	**6**	4-Bromoacetophenone	K_3PO_4	THF	1	1	50	—
10	**6**	4-Bromoacetophenone	K_3PO_4	DMF	1	1	35	—
11[d]	**6**	4-Bromoacetophenone	K_3PO_4	Toluene	1	1	99	93
12[d]	**6**	4-Bromotoluene	K_3PO_4	Toluene	1	2	90	82
13[d]	**6**	1-Bromo-4-*tert*-butyl-benzene	K_3PO_4	Toluene	1	2	91	85
14[d]	**6**	4-Bromoanisole	K_3PO_4	Toluene	1	2.5	96	90
15	**6**	4-Bromoacetophenone	K_3PO_4	MeOH	1	0.25	97	90
16	**6**	4-Bromoacetophenone	K_3PO_4	EtOH	1	0.25	34	—
17	**6**	4-Bromoacetophenone	K_3PO_4	H_2O	1	0.25	Trace	—
18[d]	**6**	4-Chloroacetophenone	K_3PO_4	Toluene	1	12	12	—
19[d,e]	**6**	4-Chloroacetophenone	K_3PO_4	Toluene	1	12	13	—
20[d]	**6**	4-Chloroanisole	K_3PO_4	Toluene	1	24	Trace	—
21[d,e]	**6**	4-Chloroanisole	K_3PO_4	Toluene	1	24	18	

[a] Reaction conditions: 1 mol% [Pd], 1 mmol aryl halide, 1.5 mmol phenylboronic acid, 2.0 mmol base, 2 mL solvent, 50 °C. [b] Determined by ^{1}H NMR. [c] Isolated yield (average of two experiments). [d] 100 °C. [e] 50 mol% NBu_4Br.

Table 2 Heck coupling reaction catalysed by new palladium complexes[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] (mol%)	*T* (°C)	*t* (h)	Conv. (%)[b]	Yield (%)[c]
1	**4**	4-Bromoacetophenone	K_3PO_4	DMF	1	135	0.5	70	
2	**5**	4-Bromoacetophenone	K_3PO_4	DMF	1	135	0.5	73	
3	**6**	4-Bromoacetophenone	K_3PO_4	DMF	1	135	0.5	73	
4	**7**	4-Bromoacetophenone	K_3PO_4	DMF	1	135	0.5	76	
5	**8**	4-Bromoacetophenone	K_3PO_4	DMF	1	135	0.5	75	
6	**9**	4-Bromoacetophenone	K_3PO_4	DMF	1	135	0.5	77	
7	**7**	4-Bromoanisole	K_3PO_4	DMF	1	135	3	51	
8	**8**	4-Bromoanisole	K_3PO_4	DMF	1	135	3	59	
9	**9**	4-Bromoanisole	K_3PO_4	DMF	1	135	3	34	
10	**8**	4-Bromoacetophenone	K_3PO_4	DMF	1	110	2	97	88
11	**8**	4-Bromoacetophenone	Cs_2CO_3	DMF	1	110	2	89	80
12	**8**	4-Bromoacetophenone	KF	DMF	1	110	2	22	
13	**8**	4-Bromoacetophenone	K_3PO_4	DMA	1	110	2	6	
14	**8**	4-Bromoacetophenone	Cs_2CO_3	DMA	1	110	2	47	
15	**8**	4-Bromoacetophenone	KF	DMA	1	110	2	4	
16	**8**	4-Bromoacetophenone	K_3PO_4	Toluene	1	110	2	24	
17	**8**	4-Bromoacetophenone	Cs_2CO_3	Toluene	1	110	2	42	
18	**8**	4-Bromoacetophenone	KF	Toluene	1	110	2	4	
19	**8**	4-Bromoacetophenone	K_3PO_4	DMF	1	135	0.75	91	77
20	**8**	4-Bromotoluene	K_3PO_4	DMF	1	135	5	92	87
21	**8**	4-Bromoanisole	K_3PO_4	DMF	1	135	6.5	93	88
22	**8**	4-Chloroacetophenone	K_3PO_4	DMF	1	135	12	30	—
23[d]	**8**	4-Chloroacetophenone	K_3PO_4	DMF	1	135	12	68	—
24[e]	**8**	4-Chloroacetophenone	K_3PO_4	DMF	1	135	12	82	75

[a] Reaction conditions: 1 mol% [Pd],1 mmol aryl halide, 1.3 mmol styrene, 1.5 mmol base, 2 mL solvent. [b] Determined by ^{1}H NMR. [c] Isolated yield (average of two experiments). [d] Added 20 mol% NBu_4Br. [e] Added 50 mol% NBu_4Br.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves.

^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by an Elementar Vario ELIV instrument.

Benzanilide (Lancaster), PCl_5 (RDH), 2-(methylthio)aniline (Alfa Aesar), DMA (TEDIA), $Pd(OAc)_2$ (Acros), $PdCl_2$ (Lancaster), KF (Acros), K_3PO_4 (Lancaster), Cs_2CO_3 (Aldrich), phenyl boronic acid (Acros), 4-bromoacetophenone (Acros), 4-chloroacetophenone (Acros) and styrene (Acros) were used as supplied. NEt_3 was dried over CaH_2 and distilled before use. *N*-(Phenyl)benzimidoyl chloride,[5] $HCl{\cdot}H_2N(CH_2)_2SMe$[14] and $HCl{\cdot}H_2N(CH_2)_2S^tBu$[14] were prepared by the modified literature methods.

Preparations

[C_6H_5–C{NH$(CH_2)_2$SMe}=NC_6H_5] (1). To a flask containing $HCl{\cdot}H_2N(CH_2)_2SMe$ (0.254 g, 2.0 mmol) in 15 mL CH_2Cl_2, 0.84 mL NEt_3 (6.0 mmol) and a solution of *N*-(phenyl)benzimidoyl chloride (0.81 g, 3.8 mmol) in 15 mL CH_2Cl_2 was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 12 h of stirring, the volatiles were removed under reduced pressure and the residue was extracted with a mixed solution of toluene (20 mL) and de-ionized water (20 mL) three times. The organic layer was separated and dried over magnesium sulphate. The filtrate was pumped to dryness. The residue was washed with 20 mL hexane to afford a white solid. Yield, 0.17 g, 62%. ^{1}H NMR (600 MHz): δ 2.14 (s, SCH_3, 3H), 2.85 (s, CH_2–CH_2, 2H), 3.72 (s, CH_2–CH_2, 2H), 5.00 (s, NH, 1H), 6.62 (d, J = 7.2 Hz, C_6H_5, 2H), 6.79 (t, J = 7.2 Hz, C_6H_5, 1H), 7.04 (t, J = 7.2 Hz, C_6H_5, 2H), 7.22–7.55 (overlap, C_6H_5, 5H). ^{13}C{^{1}H} NMR (150 MHz): δ 14.9 (s, SCH_3), 33.4 (s, CH_2), 38.5 (s, CH_2), 121.2, 122.9, 128.2, 128.3, 128.5, 129.1 (CH–C_6H_5), 135.0, 151.7, 157.1 (two C_{ipso}–C_6H_5 and one CNN). Anal. Calc. for $C_{16}H_{18}N_2S$: C, 71.07; H, 6.71; N, 10.36. Found: C, 70.69; H, 6.73; N, 10.16.

[C_6H_5–C{NH$(CH_2)_2S^tBu$}=NC_6H_5] (2). To a flask containing $HCl{\cdot}H_2N(CH_2)_2S^tBu$ (0.34 g, 2.0 mmol) in 15 mL CH_2Cl_2, 0.56 mL NEt_3 (4.0 mmol) and a solution of *N*-(phenyl)benzimidoyl chloride (0.254 g, 1.0 mmol) in 15 mL CH_2Cl_2 was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 12 h of stirring, the volatiles were removed under reduced pressure and the residue was extracted with a mixed solution of toluene (20 mL) and de-ionized water (20 mL) three times. The organic layer was separated and dried over magnesium sulphate. The filtrate was pumped to dryness. The residue was washed with 20 mL hexane to afford a white solid. Yield, 0.17 g, 78%. ^{1}H NMR (600 MHz): δ 1.36 (s, SC(CH_3)$_3$, 9H), 2.94 (s, CH_2–CH_2, 2H), 3.70 (s, CH_2–CH_2, 2H), 5.00 (s, NH, 1H), 6.62 (d, J = 6.6 Hz, C_6H_5, 2H), 6.79 (t, J = 6.6 Hz, C_6H_5, 1H), 7.04 (t, J = 7.2 Hz, C_6H_5, 2H), 7.22–7.25 (overlap, C_6H_5, 5H). ^{13}C{^{1}H} NMR (150 MHz): δ 28.0 (s, CH_2), 31.1 (s, SC(CH_3)$_3$), 41.4 (s, CH_2), 42.4 (s, SC(CH_3)$_3$), 121.2, 122.9, 128.17, 128.25, 128.5, 129.0 (CH–C_6H_5), 135.0, 150.8, 157.0 (two C_{ipso}–C_6H_5 and one CNN). Anal. Calc. for $C_{19}H_{24}N_2S$: C, 73.03; H, 7.74; N, 8.97. Found: C, 72.83; H, 7.80; N, 8.76.

[C_6H_5–C{NH(*o*-C_6H_4SMe)}=NC_6H_5] (3). A storage tube containing *N*-(phenyl)benzimidoyl chloride (0.254 g, 1.0 mmol), 2-(methylthio)aniline (0.12 mL, 1.1 mmol) and 2 mL toluene was heated at 80 °C for 3 h. The resulting mixture was cooled down to room temperature and the volatiles were removed under reduced pressure. The residue was washed with 20 mL hexane and re-dissolved with de-ionized water followed by addition of 15 mL NH_4OH (25%). The resulting mixture was extracted with a mixed solution of CH_2Cl_2 (20 mL) and de-ionized water (5 mL) three times. The organic layer was separated and dried over magnesium sulphate. The filtrate was pumped to dryness to afford a white solid. Yield, 0.238 g, 75%. ^{1}H NMR (600 MHz, C_6D_8, 373 K): δ 2.04 (s, SCH_3, 3H), 6.73 (t, J = 7.8 Hz, C_6H_5, 1H), 6.78 (t, J = 7.8 Hz, C_6H_5, 1H), 6.87 (br, 1H), 6.95 (br, 4H), 7.03 (m, 2H), 7.12 (br, 2H), 7.33 (br, 2H). Anal. Calc. for $C_{20}H_{18}N_2S$: C, 75.44; H, 5.70; N, 8.80. Found: C, 75.41; H, 5.79; N, 9.14.

[Ph–C{–NH(η^1-C_6H_4)}{=N$(CH_2)_2$SMe}]Pd(OAc) (4). To a flask containing **1** (0.14 g, 0.52 mmol) and $Pd(OAc)_2$ (0.13 g, 0.57 mmol), 20 mL of CH_2Cl_2 was added at room temperature. After 12 h of stirring, the resulting mixture was filtered and the filtrate was pumped to dryness. The residue was washed with 10 mL acetone twice to afford a pale-yellow solid. Yield, 0.125 g, 56%. ^{1}H NMR (600 MHz): δ 1.48 (s, O–C(=O)CH_3, 3H), 2.26 (br, CH_2, 2H), 2.41 (s, SCH_3, 3H), 3.28 (t, J = 4.8 Hz, CH_2, 2H), 6.81 (br, Ph–CH, 2H), 7.00 (t, J = 7.2 Hz, Ph–CH, 1H), 7.13 (t, J = 7.8 Hz, Ph–CH, 1H), 7.36 (t, J = 8.4 Hz, Ph–CH, 2H), 7.41–7.45 (overlap, Ph–CH, 3H), 10.57 (s, NH, 1H). ^{13}C{^{1}H} NMR (150 MHz): δ 17.5 (s, SCH_3), 23.4 (s, O–C(=O)CH_3), 35.0 (s, CH_2), 55.5 (s, CH_2), 117.1, 121.5, 124.5, 128.1, 128.9, 130.0, 134.4 (CH–Ph), 130.1, 131.6, 135.7, 153.5 (two C_{ipso}–Ph, one metallated *C*–Ph, and one CNN), 178.2 (s, O–C(=O)CH$_3$). Anal. Calc. for $C_{18}H_{20}N_2O_2SPd$: C, 49.72; H, 4.64; N, 6.44. Found: C, 49.69; H, 4.29; N, 6.14.

[Ph–C{–NH(η^1-C_6H_4)}{=N$(CH_2)_2S^tBu$}]Pd(OAc) (5). To a flask containing **2** (0.312 g, 1.0 mmol) and $Pd(OAc)_2$ (0.245 g, 1.1 mmol), 20 mL of CH_2Cl_2 was added at room temperature. After 12 h of stirring, the resulting mixture was filtered and the filtrate was pumped to dryness. A small portion of residue was extracted with 10 mL Et_2O. The extract was layered with 10 mL hexane and stood at room temperature for couple of days to afford brown crystals (**5′**). The residue after extraction was washed with 15 mL acetone to afford a white solid. Yield, 0.20 g, 42%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 1.47 (s, SC(CH_3)$_3$, 9H), 1.84 (s, O–C(=O)CH_3, 3H), 2.61 (t, J = 5.4 Hz, CH_2, 2H), 3.36 (t, J = 6.0 Hz, CH_2, 2H), 6.75(t, J = 7.2 Hz, Ph–CH, 1H), 6.96 (t, J = 6.6 Hz, Ph–CH, 1H), 7.03 (d, J = 7.8 Hz, Ph–CH, 1H), 7.36 (d, J = 7.8 Hz, Ph–CH, 1H), 7.51 (m, Ph–CH, 2H), 7.57–7.61 (overlap, Ph–CH, 3H), 10.23 (s, NH, 1H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 24.8 (s, O–C(=O)CH_3), 29.5 (overlap, CH_2 and SC(CH_3)$_3$), 47.4 (s, SC(CH_3)$_3$), 56.8 (s, CH_2), 115.7, 121.0, 124.5, 128.1, 129.0, 130.3, 133.9(CH–Ph), 129.2, 132.7, 134.3, 152.9 (two C_{ipso}–Ph, one metallated *C*–Ph, and one CNN), 174.2 (s, O–C(=O)CH$_3$). Anal. Calc. for $C_{21}H_{26}N_2O_2SPd$: C, 52.89; H, 5.49; N, 5.87. Found: C, 52.83; H, 5.32; N, 5.79.

[Ph–C{–NH(η^1-C_6H_4)}{=N(*o*-C_6H_4SMe)}]Pd(OAc) (6). To a flask containing **3** (0.318 g, 1.0 mmol) and $Pd(OAc)_2$ (0.246 g, 1.1 mmol), 20 mL of CH_2Cl_2 was added at room temperature.

After 12 h of stirring, the resulting mixture was filtered and the filtrate was pumped to dryness. The residue was washed with 15 mL acetone to afford a yellow solid. Yield, 0.328 g, 68.5%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 1.87 (s, O–C(=O)CH_3, 3H), 2.85 (s, SCH_3, 3H), 6.34 (d, J = 8.4 Hz, Ph–CH, 1H), 6.80 (t, J = 7.2 Hz, Ph–CH, 1H), 6.92 (t, J = 7.2 Hz, Ph–CH, 1H), 6.97 (t, J = 7.2 Hz, Ph–CH, 1H), 7.08 (t, J = 7.8 Hz, Ph–CH, 1H), 7.17 (d, J = 7.8 Hz, Ph–CH, 1H), 7.43–7.52 (overlap, Ph–CH, 6H), 7.64 (d, J = 7.2 Hz, Ph–CH, 1H), 11.27(s, NH, 1H).^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6): δ 23.9 (overlap, SCH$_3$ and O–C(=O)CH_3), 115.9, 124.0, 124.6, 124.8, 125.8, 128.5, 128.7, 130.2, 131.0, 132.6, 133.6 (Ph–CH), 128.0, 130.6, 132.1, 134.0, 153.1, 155.7 (four C_{ipso}–Ph, one metallated C–Ph and one CNN), 175.0 (s, O–C(=O)CH$_3$). Anal. Calc. for $C_{22}H_{20}N_2O_2SPd$: C, 54.72; H, 4.17; N, 5.80. Found: C, 54.20; H, 4.27; N, 5.55.

[Ph–C{–NH(η^1-C$_6$H$_4$)}{N(CH$_2$)$_2$SMe}]PdCl (7). To a flask containing **1** (0.13 g, 0.48 mmol) and $PdCl_2$ (0.087 g, 0.53 mmol), 20 mL of CH_2Cl_2 and 0.3 mL NEt_3 (2 mmol) were added at room temperature. After 12 h of stirring, the resulting mixture was washed with 20 mL de-ionized water three times. The organic layer was separated and dried over magnesium sulphate. The filtrate was pumped to dryness and the residue was extracted with 20 mL toluene to afford yellow-brown solid. Yield, 0.16 g, 81%. ^{1}H NMR (600 MHz): δ 2.51 (br, CH_2, 2H), 2.55 (s, SCH_3, 3H), 3.65 (br, CH_2, 2H), 6.72 (dd, J = 7.8, 1.8 Hz, Ph–CH, 1H), 6.94 (m, Ph–CH, 1H), 7.05 (m, Ph–CH, 1H), 7.16 (s, NH, 1H), 7.38–7.40 (m, Ph–CH, 2H), 7.54–7.61 (overlap, Ph–CH, 3H), 8.30 (dd, J = 7.8, 1.2 Hz, Ph–CH, 1H). ^{13}C{^{1}H} NMR (150 MHz): δ 18.3(s, SCH$_3$), 35.6 (s, CH$_2$), 57.1 (s, CH$_2$), 115.7, 123.0, 125.4, 127.5, 129.6, 131.1, 138.8 (CH–Ph), 129.3, 132.5, 133.5, 153.0 (two C_{ipso}–Ph, one metallated C–Ph, and one CNN). Anal. Calc. for $C_{16}H_{17}ClN_2SPd$: C, 46.73; H, 4.17; N, 6.81. Found: C, 45.92; H, 4.46; N, 6.49.

[Ph–C{–NH(η^1-C$_6$H$_4$)}{=N(CH$_2$)$_2$S^{t}Bu}]PdCl (8). To a flask containing **2** (0.165 g, 0.52 mmol) and $PdCl_2$ (0.103 g, 0.58 mmol), 20 mL of CH_2Cl_2 and 0.15 mL NEt_3 (1 mmol) were added at room temperature. After 48 h of stirring, the resulting mixture was filtered and the filtrate was washed with 20 mL de-ionized water three times. The organic layer was separated and dried over magnesium sulphate. The filtrate was pumped to dryness and the residue was extracted with 20 mL toluene to afford a pale-yellow solid. Yield, 0.146 g, 62%. ^{1}H NMR (600 MHz): δ 1.62 (s, SC(CH_3)$_3$, 9H), 2.49 (br, CH_2, 2H), 3.52 (br, CH_2, 2H), 6.79 (d, J = 6.6 Hz, Ph–CH, 1H), 6.92 (t, J = 6.0 Hz, Ph–CH, 1H), 7.02 (t, J = 6.6 Hz, Ph–CH, 1H), 7.34 (d, J = 6.6 Hz, Ph–CH, 2H), 7.38 (s, NH, 1H), 7.55–7.58 (overlap, Ph-CH, 3H), 8.19 (d, J = 6.6 Hz, Ph–CH, 1H). ^{13}C{^{1}H} NMR (150 MHz): δ 30.56 (s, SC(CH$_3$)$_3$), 30.61 (s, CH$_2$), 49.0 (s, SC(CH$_3$)$_3$), 57.1 (s, CH$_2$), 115.8, 123.0, 125.1, 127.6, 129.5, 131.1, 138.8 (CH–Ph), 129.1, 132.3, 133.6, 153.3 (two C_{ipso}–Ph, one metallated C–Ph, and one CNN). Anal. Calc. for $C_{19}H_{23}ClN_2SPd$: C, 50.34; H, 5.11; N, 6.18. Found: C, 49.90; H, 5.42; N, 6.00.

[Ph–C{–NH(η^1-C$_6$H$_4$)}{=N(*o*-C$_6$H$_4$SMe)}]PdCl (9). To a flask containing **3** (0.318 g, 1.0 mmol) and $PdCl_2$ (0.177 g, 1.0 mmol), 20 mL of CH_2Cl_2 and 0.30 mL NEt_3 (2 mmol) were added at room temperature. After 36 h of stirring, the resulting mixture was filtered and the filtrate was washed with 20 mL de-ionized water three times. The organic layer was separated and dried over magnesium sulphate. The filtrate was pumped to dryness and the residue was extracted with 20 mL toluene to afford a yellow solid. Yield, 0.170 g, 37.2%. ^{1}H NMR (600 MHz): δ 2.88 (s, SCH_3, 3H), 6.15 (d, J = 8.4 Hz, Ph–CH, 1H), 6.69 (m, Ph–CH, 1H), 6.80 (m, Ph–CH, 1H), 6.88 (m, Ph–CH, 1H), 7.12 (m, Ph–CH, 1H), 7.23 (br, Ph–CH, 1H), 7.32–7.37 (overlap, Ph–CH, 3H), 7.42 (m, Ph–CH, 3H), 7.46 (t, J = 7.8 Hz, Ph–CH, 1H), 9.10 (s, NH, 1H).^{13}C{^{1}H} NMR (150 MHz): δ 23.0 (s, SCH$_3$), 117.1, 124.6, 124.8, 126.0, 126.2,

Table 3 Summary of crystal data for compounds **5**, **5′**, **6**, **7**, and **8**

	5	**5′**	**6**	**7**	**8**
Formula	$C_{21}H_{26}N_2O_2PdS$	$C_{42}H_{52}N_4O_4Pd_2S_2$	$C_{22}H_{20}N_2O_2PdS$	$C_{16}H_{17}ClN_2PdS$	$C_{77}H_{94}Cl_6N_8Pd_4S_4$
Fw	476.90	953.80	482.86	411.23	1898.18
T/K	297(2)	297(2)	298(2)	297(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$	$P\bar{1}$
a/Å	12.4397(11)	12.7571(10)	21.165(5)	7.6575(6)	9.7871(7)
b/Å	13.6472(12)	16.4673(13)	20.675(4)	13.7665(12)	11.3669(8)
c/Å	14.2697(12)	25.1706(19)	11.302(2)	15.5516(13)	19.8986(14)
α/°	83.055(2)	90	90	90	102.632(10)
β/°	66.2150(10)	98.628(2)	117.472(4)	103.395(2)	96.538(10)
γ/°	75.150(2)	90	90	90	106.833(10)
V/Å^3	2142.3(3)	5227.9(7)	4388.0(16)	1594.8(2)	2030.0(2)
Z	4	4	8	4	1
ρ_c/Mg m^{-3}	1.479	1.212	1.462	1.713	1.553
μ(Mo-Kα)/mm^{-1}	0.981	0.804	0.959	1.456	1.219
Reflections collected	12004	10255	12136	8708	11427
No. of parameters	487	493	253	190	466
R_1[a]	0.0287	0.0398	0.0422	0.0296	0.0281
wR_2[a]	0.0810	0.1015	0.1326	0.0799	0.0855
GoF[b]	1.016	1.038	1.004	1.098	1.085

[a] $R_1 = [\Sigma (|F_0| - |F_c|]/\Sigma |F_0|]$; $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$, w = 0.10. [b] GoF = $[\Sigma w(F_0^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

128.0, 128.7, 130.3, 131.3, 131.5, 137.5 (Ph–*C*H), 128.7, 131.1, 131.2, 132.8, 153.1, 155.5 (four C_{ipso}–Ph, one metallated *C*–Ph and one *C*NN). Anal. Calc. for $C_{20}H_{17}ClN_2SPd$: C, 52.30; H, 3.73; N, 6.10. Found: C, 53.02; H, 4.42; N, 6.29.

General procedure for the Suzuki-type coupling reaction. Appropriate amounts of catalyst, aryl halide (1.0 equiv.), phenylboronic acid (1.5 equiv.), base (2.0 equiv.), and a magnetic stir bar were placed in a Schlenk tube under nitrogen. Solvent (2 mL) was added by syringe, and the reaction mixture was heated in an oil bath to the appropriate temperature for the appropriate time.

General procedure for the Heck coupling reaction. Appropriate amounts of catalyst, base (2 equiv.) and aryl halide (1 equiv.) were placed in a Schlenk tube under nitrogen. Solvent (2 mL) and styrene (1.5 equiv.) were added by syringe, and the reaction mixture was heated in an oil bath to the appropriate temperature for the appropriate time.

Crystal structure data

Crystals were grown from CH_2Cl_2/hexane solution (**5** and **6**), ether/hexane solution (**5′**), or concentrated dichloromethane solution (**7** and **8**), and isolated by filtration. Suitable crystals of **5**, **5′**, **6**, **7** or **8** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 3.

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References

1 (*a*) J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219; (*b*) F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; (*c*) M. P. Coles, *Dalton Trans.*, 2006, 985; (*d*) P. C. Junk and M. L. Cole, *Chem. Commun.*, 2007, 1579.

2 (*a*) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428; (*b*) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.

3 (*a*) M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Eur. J. Inorg. Chem.*, 1998, 1867; (*b*) K. Kincaid, C. P. Gerlach, G. R. Giesbrecht, J. R. Hagadorn, G. D. Whitener, A. Shafir and J. Arnold, *Organometallics*, 1999, **18**, 5360; (*c*) D. Doyle, Y. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 2000, 4093; (*d*) C. L. Boyd, A. E. Guiducci, S. R. Dubberley, B. R. Tyrrell and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 2002, 4175; (*e*) A. C. R. Croft, C. L. Boyd, A. R. Cowley and P. Mountford, *J. Organomet. Chem.*, 2003, **683**, 120; (*f*) C. L. Boyd, E. Clot, A. E. Guiducci and P. Mountford, *Organometallics*, 2005, **24**, 2347.

4 K.-M. Wu, C.-A. Huang, K.-F. Peng and C.-T. Chen, *Tetrahedron*, 2005, **61**, 9679.

5 R. T. Boeré, V. Klassen and G. Wolmershäuser, *J. Chem. Soc., Dalton Trans.*, 1998, 4147.

6 M.-T. Chen, C.-A. Huang and C.-T. Chen, *Eur. J. Inorg. Chem.*, 2006, 4642.

7 C.-L. Yao, L.-P. He, J. D. Korp and J. L. Bear, *Inorg. Chem.*, 1988, **27**, 4389.

8 F. A. Cotton, M. Matusz, R. Poli and X. Feng, *J. Am. Chem. Soc.*, 1988, **110**, 1144.

9 A. Singhal, V. K. Jain, M. Nethaji, A. G. Samuelson, D. Jayaprakash and R. J. Butcher, *Polyhedron*, 1998, **17**, 3531.

10 J. F. Berry, F. A. Cotton, S. A. Ibragimov, C. A. Murillo and X. Wang, *Inorg. Chem.*, 2005, **44**, 6129.

11 (*a*) X. Riera, A. Caubet, C. López, V. Moreno, E. Freisinger, M. Willermann and B. Lippert, *J. Organomet. Chem.*, 2001, **629**, 97; (*b*) G. Ebeling, M. R. Meneghetti, F. Rominger and J. Dupont, *Organometallics*, 2002, **21**, 3221; (*c*) A. Fernández, D. Vázquez-García, J. J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J. M. Ortigueirab and J. M. Vila, *New J. Chem.*, 2002, **26**, 105; (*d*) C. López, S. Pérez, X. Solans and M. Font-Bardia, *J. Organomet. Chem.*, 2002, **650**, 258; (*e*) S. Pérez, C. López, A. Caubet, R. Bosque, X. Solans, M. F. Bardía, A. Roig and E. Molins, *Organometallics*, 2004, **23**, 224; (*f*) C. S. Consorti, G. Ebeling, F. R. Flores, F. Rominger and J. Dupont, *Adv. Synth. Catal.*, 2004, **346**, 617; (*g*) I. D. Kostas, B. R. Steele, A. Terzis, S. V. Amosova, A. V. Martynov and N. A. Makhaeva, *Eur. J. Inorg. Chem.*, 2006, 2642.

12 (*a*) C.-T. Chen, Y.-S. Chan, Y.-R. Tzeng and M.-T. Chen, *Dalton Trans.*, 2004, 2691; (*b*) K.-F. Peng, M.-T. Chen, C.-A. Huang and C.-T. Chen, *Eur. J. Inorg. Chem.*, 2008, 2463; (*c*) M.-T. Chen, C.-A. Huang and C.-T. Chen, *Eur. J. Inorg. Chem.*, 2008, 3142.

13 (*a*) D. E. Bergbreiter, P. L. Osburn and Y.-S. Liu, *J. Am. Chem. Soc.*, 1999, **121**, 9531; (*b*) A. S. Gruber, D. Zim, G. Ebeling, A. L. Monteiro and J. Dupont, *Org. Lett.*, 2000, **2**, 1287; (*c*) D. Zim, A. S. Gruber, G. Ebeling, J. Dupont and A. L. Monteiro, *Org. Lett.*, 2000, **2**, 2881; (*d*) J. Dupont, A. S. Gruber, G. S. Fonseca, A. L. Monteiro and G. Ebeling, *Organometallics*, 2001, **20**, 171; (*e*) P. B. Silveira, V. R. Lando, J. Dupont and A. L. Monteiro, *Tetrahedron Lett.*, 2002, **43**, 2327; (*f*) V. V. Thakur, N. S. C. R. Kumar and A. Sudalai, *Tetrahedron Lett.*, 2004, **45**, 2915; (*g*) Z. Xiong, N. Wang, M. Dai, A. Li, J. Chen and Z. Yang, *Org. Lett.*, 2004, **6**, 3337; (*h*) R. B. Bedford, C. S. J. Cazin, M. B. Hursthouse, M. E. Light and V. J. M. Scordia, *Dalton Trans.*, 2004, 3864; (*i*) K. Yu, W. Sommer, J. M. Richardson, M. Weck and C. W. Jones, *Adv. Synth. Catal.*, 2005, **347**, 161; (*j*) J. Spencer, D. P. Sharratt, J. Dupont, A. L. Monteiro, V. I. Reis, M. P. Stracke, F. Rominger and I. M. McDonald, *Organometallics*, 2005, **24**, 5665; (*k*) H. V. Huynh, C. H. Yeo and Y. X. Chew, *Organometallics*, 2010, **29**, 1479; (*l*) C. Fliedel, A. Sabbatini and P. Braunstein, *Dalton Trans.*, 2010, **39**, 8820.

14 M. Fujita, M. Otsuka and Y. Sugiura, *J. Med. Chem.*, 1996, **39**, 503.