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Synthesis and characterization of electronically varied XCX palladacycles with functional arene groups

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Dedicated to Professor Gerard van Koten in celebration of a scientific career of remarkable breadth.

Abstract

X-ray crystallographic studies show that varying the nature of the S-aryl ligands in SCS-Pd(II) pincer complexes and the electronic nature of the aryl substituent *para* to the Pd(II) group in PCP-Pd(II) pincer complexes do not lead to structural changes in these palladacycles that can be correlated with the changing nature of the ligands. While the original C2 symmetry for the S-aryl groups in SCS-Pd(II) pincer complexes seen in the case of the 2,5-bis(thiophenylmethyl)phenylpalladium chloride pincer complex is also seen in other SCS-Pd(II) pincer complexes, the relative stereochemistry of the S-aryl rings is not consistently maintained in 2,5-bis((4-dimethylamino-thiophenyl)methyl)-phenylpalladium chloride.
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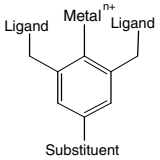
Keywords: Pincer complexes; Palladacycles; Structure; Catalysis; Synthesis

1. Introduction

Pincer-type transition metal complexes like **1** containing 2,6-disubstituted arenes rings with a σ-bonded transition metal bonded to C1 of the substituted arene are by now well-known species [1–6]. These complexes are interesting as versatile examples of stable σ-bonded organometallic derivatives and can be prepared using a variety of different metals. Such complexes have useful applications as sensors [2,7], in materials chemistry [8–10], and in catalysis as catalysts or pre-catalysts [1,3–6,11–15]. Our interests in homogeneous catalysis and the many diverse examples, where pincer complexes facilitate Kharasch couplings [16], C–H activation [4,5,17], and various cross-coupling chemistry [11,12,18,19] originally attracted our attention to these species. This interest was heightened by the many successful examples, where pincer complexes were attached to dendrimers [20,21] as this chemistry suggested that pincer complexes could similarly be attached to linear polymers. Finally, our interest in palladacycles in particular was excited by a report by Milstein describing PCP-Pd(II) species that could be used in cross-coupling chemistry in air at elevated temperature [18]. While these species exact roles as either catalysts or pre-catalysts in various reactions are not always understood [12–15], their interesting chemistry, their high stability, and the structural diversity inherent in the pincer ligand framework of these palladacycles makes them a subject of continuing interest.



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As part of a broader program aimed at developing recyclable catalysts on soluble polymers [22,23], we have

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explored the synthesis of these complexes, preparing and structurally characterizing a series of SCS- and PCP-type Pd(II) complexes like **1** that contain a *para*-substituent to immobilize a preformed metal complex onto a support. An advantage of this approach is that we can fully structurally characterize the complexes before immobilization using X-ray crystallography. Here we describe some of our work detailing the synthesis and structural details of a selection of various SCS-Pd(II) and PCP-Pd(II) complexes like **1**. The ultimate goal of these studies was to eventually bind these complexes to soluble polymer and use them in catalysis and we have previously described that approach in a number of different studies [24–30]. Below we describe another aspect of these studies where we have prepared and structurally characterized a series of SCS-Pd(II) pincer complexes to study the effects of electronically varying S-aryl ligands on structure and the Pd(II) environment. We also prepared a series of PCP-Pd(II) complexes and structurally characterized them to probe how the electronic nature of substituents *para* to the σ-bonded Pd(II) species effect the structure of PCP palladacycles.

2. Experimental

2.1. General procedures

Reagents and solvents were obtained from commercial sources and were generally used without further purification. ^{1}H NMR spectra were recorded on Varian spectrometers at 300 or 500 MHz. Chemical shifts are reported in ppm using hexamethyldisiloxane (HMDS, 0.055 ppm) as the internal standard. ^{13}C NMR spectra were recorded at 75 or 125 MHz with $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.5 ppm) as the internal reference. Infrared spectra were recorded as thin films between NaCl plates or as pressed KBr pellets using a Mattson Galaxy 4021 FT-IR spectrometer. Crystallographic data were collected on a Bruker SMART 1000 X-ray three circle diffractometer and rendered using Ortep for Windows. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and were uncorrected.

2.2. Synthesis of N-acetyl-3,5-bis((p-dimethylaminophenyl)-thiomethyl)aniline (*6b*)

A 200-mL flask and attached condenser was purged with nitrogen. Acetone (50 mL) was bubbled through with nitrogen for 15 min. Dimethylaminothiophenol (590 mg, 3.85 mmol), K_2CO_3 (604 mg, 4.38 mmol), and bis(benzyl chloride) (**5**) (407 mg, 1.75 mmol) were combined in the 200 mL flask and dissolved in 100 mL acetone. The reaction was protected from light and refluxed for 48 h. The reaction was filtered and the solvent removed. The residue was dissolved in chloroform and washed with water and brine. The solvent was evaporated and the residue purified by chromatography on silica gel (ethyl acetate: CH_2Cl_2, 1:9) to yield 574 mg (70%) of a white solid: m.p. 115–116.5 °C; ^{1}H NMR (DMSO-d^6) 1.99 (s, 3H), 2.83 (s, 12H), 3.90 (s, 4H), 6.60 (dd, 4H), 6.78 (s, 1H), 7.17 (dd, 4H), 7.39 (s, 2H), 9.84 (s, 1H); ^{13}C NMR (DMSO-d^6) 24.0, 39.9, 40.4, 112.7, 117.8, 119.8, 124.1, 133.2, 138.6, 139.2, 149.7, 168.2; IR (KBr, cm^{-1}) 3292, 1664, 1594; HRMS (*m*/*z*) [$M + H^+$] Calcd. for $C_{24}H_{21}O_5NS_2$, 466.1987; Found, 466.1984.

2.3. 4-N-Acetyl-3,5-bis((p-dimethylaminophenyl)-thiomethyl)phenylpalladium trifluoroacetate (*10b*)

In a 50-mL round-bottomed flask, dimethyl amino SCS ligand **6b** (100 mg, 0.215 mmol) was dissolved in 10 mL acetone. $Pd(TFA)_2$ (75 mg, 0.225 mmol) was dissolved in 10 mL acetone and added to the reaction via pipette. The reaction stirred at room temperature for 4 h. The reaction was filtered, the solvent removed and the resulting brownish-red solid dried under vacuum (150 mg > 99%): m.p. 185 °C (dec.); ^{1}H NMR (DMSO-d^6) 1.99 (s, 3H), 2.95 (s, 12H), 4.6 (s, 4H), 6.78 (dd, 4H), 7.20 (s, 2H), 7.66 (dd, 4H), 9.83 (s, 1H); ^{13}C NMR (DMSO-d^6) 24.6, 40.4, 52.1, 113.2, 114.2, 115.8, 134.4, 137.5, 150.5, 152.2, 168.9; HRMS (*m*/*z*) (the spectrum was obtained using a dilute acetic acid solution and compound was detected with an acetate ligand) [$M + H_2O + H^+$] Calcd. for $C_{28}H_{36}O_4N_3S_2Pd$, 648.1182; Found, 648.1085. Crystals were grown by the slow diffusion of hexane into an acetone solution of **10b**.

2.4. Synthesis of N-Acetyl-3,5-bis(dicyclopentylphosphinomethyl)aniline-borane (*26*)

A solution of 4.0 g (21.76 mmol) of dicyclopentylphosphine-borane in 40 mL of freshly distilled THF under N_2 was prepared and then cooled to −78 °C. Slow addition of 20 mL of 1.6 M *n*-BuLi using a syringe formed a solution of the lithiated phosphine after stirring 2 h at −78 °C and then additional 2 h at room temperature. The reaction solution was again cooled down to −78 °C and 10 mL of a THF solution of 2.32 g (10 mmol) of *N*-acetyl-3,5-bis(chloromethyl)aniline was added using a syringe. After 2 h of stirring at −78°, the reaction mixture was allowed to warm to 25 °C and to continue stirring for 10 h. The solution was then concentrated to ca. 1/3 of its original volume. A 100 mL of CH_2Cl_2 was added and the solution was washed with 2 N NaOH (10 mL) and brine (2 × 30 mL), dried over $MaSO_4$, and the organic solvent was removed at reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc, 1/1) to yield 4.0 g of light yellow, air-stable crystals (76% yield): ^{1}H NMR (300 MHz, $CDCl_3$) 0.23–0.60 (br, m, 6H), 1.55–2.13 (m, 36H), 2.18 (s, 3H), 2.98 (d, J = 11.4 Hz, 4H), 6.91 (s, 1H), 7.26 (s, 1H), 7.38 (s, 1H); ^{31}P NMR ($CDCl_3$) 31.3; ^{13}C NMR ($CDCl_3$) 24.88, 26.10 (d, J = 8.07 Hz), 26.50 (d, J = 9.13 Hz), 28.10 (d, J = 9.05 Hz), 30.88 (d, J = 29.19 Hz), 32.78 (d, J = 33.79 Hz), 119.16, 126.73, 134.67, 137.99, 168.26.

2.5. Synthesis of 3,5-di(dicyclopentylphosphinomethyl)-aniline-borane

A solution of *N*-acetyl-3,5-di(dicyclopentylphosphinomethyl)aniline-borane complex (2.45 g) in 10 mL of 95% EtOH was allowed to react with NaOH (3.75 g) at reflux for 20 h. After neutralization with concentrated HCl, the majority of the solvent was removed under pressure. The remaining residue was taken up in 50 mL of CH_2Cl_2, washed with saturated Na_2CO_3 (3×10 mL), and dried over $MgSO_4$. The organic solvents were removed under pressure to yield after chromatography (hexane/EtOAc 1/1) 1.3 g (58% yield) of product: ^{1}H NMR (300 MHz, $CDCl_3$) 0.23–0.60 (br d, $J = 114$ Hz, 6H), 1.55–2.13 (m, 36H), 2.92 (d, $J = 10.8$ Hz, 4H), 3.48 (br, s, 2H), 6.46 (s, 2H), 6.50 (s, 1H); ^{31}P NMR ($CDCl_3$) 30.41; ^{13}C NMR ($CDCl_3$) 26.25 (d, $J = 8.3$ Hz), 26.75 (d, $J = 9.18$ Hz), 28.22 (d, $J = 12.95$ Hz), 30.80 (d, $J = 29.05$ Hz), 32.60 (d, $J = 33.58$ Hz), 115.14 (t, $J = 3.02$ Hz), 121.35, 135.16 (d, $J = 1.51$ Hz), 135.20 (d, $J = 2.26$ Hz), 146.70.

2.6. Synthesis of 4-N-acetamido-2,6-di(dicyclopentylphosphinomethyl)phenylpalladium trifluoroacetate

A solution of *N*-acetyl-3,5-bis(dicyclopentylphosphinomethyl)aniline-borane (0.3 g, 0.57 mmol) in 10 mL of freshly distilled THF and 10 mL of diethylamine was deoxygenated (freeze–pump–thaw, 5 cycles) and then heated to 60 °C for 12 h. The solvents were carefully removed under reduced pressure at room temperature. Then the free bisphosphine was dissolved in 10 mL of degassed THF and a solution of $Pd(O_2CCF_3)_2$ (189.5 mg, 0.57 mmol) in 10 mL of degassed THF was added slowly. The reaction mixture was stirred at room temperature for 12 h and then at 65 °C for 48 h. The solvents were removed under reduced pressure. Column chromatography using silica gel (hexane/EtOAc 1/1) afforded 34 mg of product (10% yield): ^{1}H NMR (300 MHz, $CDCl_3$): 1.52–2.02 (m, 32H), 2.11 (s, 3H), 2.42 (m, 4H), 3.13 (t, $J = 4.5$ Hz, 4H), 7.20 (s, 2H), 7.39 (s, 1H); ^{31}P NMR ($CDCl_3$, δ): 52.56; ^{13}C NMR ($CDCl_3$, δ): 24.59, 26.36 (t, $J = 4.53$ Hz), 26.53(t, $J = 3.55$ Hz), 28.96, 29.31 (t, $J = 3.01$ Hz), 35.48 (t, $J = 12.06$ Hz), 114.40 (t, $J = 11.09$ Hz), 135.40, 150.60 (t, $J = 11.62$ Hz), 153.89, 168.24.

The same procedure using 4-phthalimido-2,6-bis(dicyclopentylphosphinomethyl)aniline-borane 33 mg (8.5% yield) 4-phthalimido-2,6-bis(dicyclopentylphosphinomethyl)phenylpalladium trifluoroacetate (**31**): ^{1}H NMR (300 MHz, $CDCl_3$) 1.52–2.02 (m, 32H), 2.44 (m, 4H), 3.23 (t, $J = 4.2$ Hz, 4H), 7.07 (s, 2H), 7.80 (dd, $J = 3.0$ and 5.4 Hz, 2H), 7.95 (dd, $J = 3.3$ and 5.4 Hz, 2H); ^{31}P NMR ($CDCl_3$, δ) 52.88; ^{13}C NMR ($CDCl_3$) 26.28 (t, $J = 4.5$ Hz), 26.54 (t, $J = 3.5$ Hz), 29.06, 29.30 (t, $J = 2.5$ Hz), 35.32 (t, $J = 12$ Hz), 35.41 (t, $J = 12$ Hz), 120.43 (t, $J = 11$ Hz), 123.60, 128.47, 131.78, 134.29, 150.88 (t, $J = 11.5$ Hz), 159.41, 167.52.

2.7. Synthesis of 4-phthalimido-2,6-bis(dicyclopentylphosphinomethyl)aniline-borane (*30*)

A 0.6-g sample 2,6-bis(dicyclopentylphosphinomethyl)aniline-borane (**29**) (1.25 mmol) and 0.22 g (1.5 mmol) of phthalic anhydride were added to 30 mL of toluene and then refluxed for 24 h. The solvent was removed under pressure, the resulting mixture was taken up with 50 mL of dichloromethane, washed with 1 N HCl ($20 \text{ mL} \times 1$), brine ($20 \text{ mL} \times 2$), and dried over $MgSO_4$. The solvent was removed under reduced pressure. Silica gel chromatography (hexane/EtOAc 2/1) yielded 0.73 g of product (96%): ^{31}P NMR ($CDCl_3$) 31.79; ^{1}H NMR (300 MHz, $CDCl_3$) 0.40 (d, br, $J = 103$ Hz, 6H), 1.68 (m, 32H), 2.10 (m, 4H), 3.07 (d, $J = 10.8$ Hz, 4H), 7.20 (s, 3H), 7.79 (m, 2H), 7.94 (m, 2H).

2.8. Synthesis of 4-amino-2,6-bis(dicyclopentylphosphinomethyl)phenylpalladium trifluoroacetate (*33*)

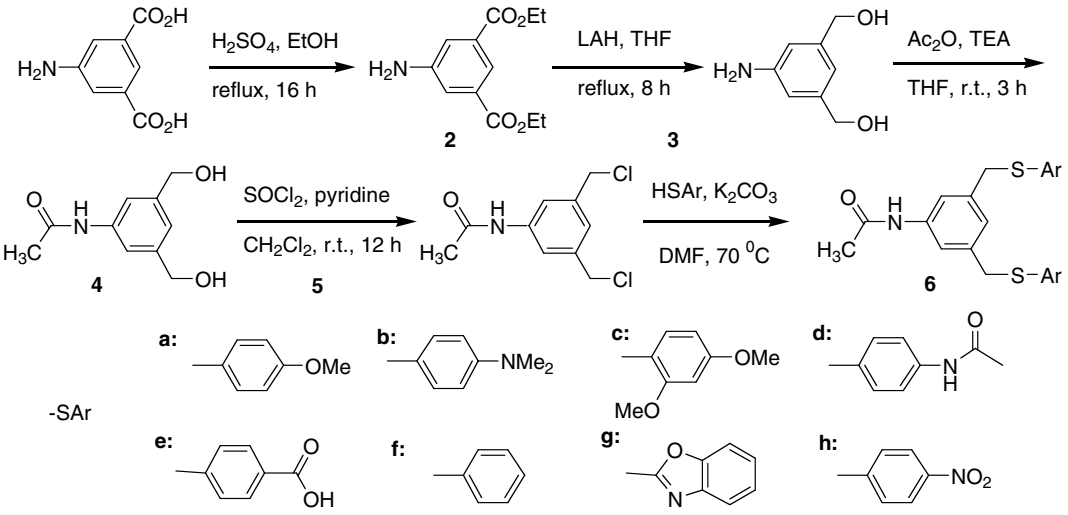
A solution of 80 mg of 4-phthalimido-2,6-bis(dicyclopentyl-phosphinomethyl)phenylpalladium trifluoroacetate and 2 mL (34.90 mmol) of hydrazine hydrate in 20 mL of ethanol was stirred at room temperature for 48 h. Afterwards the solvent was removed under reduced pressure. Silica gel chromatography (EtOAc/hexane 1/1) yielded 42 mg of product (60%): ^{31}P NMR ($CDCl_3$) 52.12; ^{1}H NMR (300 MHz, $CDCl_3$) 1.49–2.06 (m, 32H), 2.40 (m, 4H), 3.07 (t, $J = 4.5$ Hz, 4 H), 3.38 (s, br, 2H), 6.41 (s, 2H); ^{13}C NMR ($CDCl_3$) 26.29 (t, $J = 4.5$ Hz), 26.53 (t, $J = 3.54$ Hz), 28.97, 29.32 (t, $J = 3.02$ Hz), 29.67, 35.26 (t, $J = 12.60$ Hz), 35.38 (t, $J = 12.07$ Hz), 110.58 (t, $J = 11.54$ Hz), 143.26, 147.48, 150.97 (t, $J = 11.09$ Hz).

2.9. X-ray characterization of palladacycles

Crystals of the complexes **28**, **32**, and **34** were obtained from a mixture of dichloromethane and hexane. In each of these cases, the trifluoroacetate anion was replaced by a chloride anion in the crystalline solids that were isolated and in turn analyzed by X-ray crystallography. The details of the crystal data for structures **10a**, **10b**, **10c**, **25**, **28**, **32**, and **34** are provided in the supplementary material.

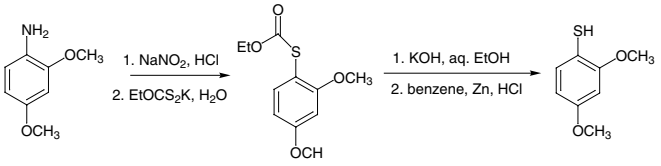
3. Results and discussion

The general route to the thioarene-containing ligands used to prepare SCS-Pd(II) complexes is shown in Scheme 1. This route typically used commercially available thioarenes. In the case of 2,4-dimethoxythiophenol and 4-dimethylaminothiophenol, we had to prepare the thioarene using established chemistry (Eqs. (1) and (2)). In all the syntheses of bisthioarene ligands, the same general route was used [13]. The starting 5-amino isophthalic acid was esterified and the resulting ester reduced using $LiAlH_4$, forming the amino diol. The NH_2 group was protected

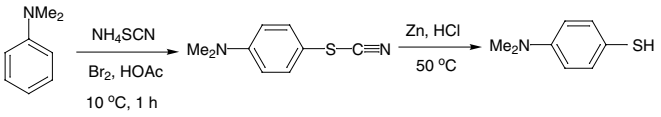


Scheme 1. Synthesis of *N*-acetyl-3,5-bis(thioarylmethyl)aniline ligands.

by treatment with acetic anhydride to provide an acetamido diol. The alcohols were changed to chlorides by stirring the diol with

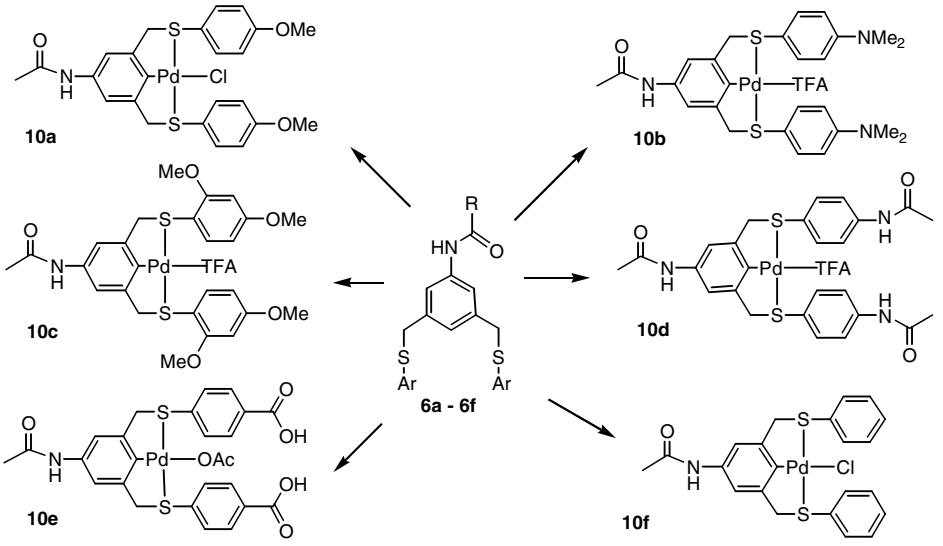


(1)



(2)

The thioarenes prepared in Scheme 1 were subsequently palladated in an electrophilic aromatic substitution reaction using a Pd(II) electrophile (e.g., $Pd(O_2CCF_3)_2$ or $Pd(NCPh)_2Cl_2$) to form an SCS palladacycle. Examples of palladacycles prepared by this palladation chemistry are shown in Scheme 2. The procedures for these palladations have been previously reported [13,19], and the catalytic chemistry seen when these and related SCS-Pd(II) palladacycles are used in cross-coupling reactions has been discussed extensively. This chemistry is not discussed here. However, in three cases we also were able to isolate X-ray quality crystals of palladated complexes. These studies allowed us to study the effect of changing the electronic nature of the S-aryl ligands on the pincer complex structure. A discussion of some these structures are presented below.



Scheme 2. SCS-Pd(II) palladacycles prepared from *N*-acetyl-3,5-bis(thioarene) ligands. $SOCl_2$. Subsequent treatment of this dichloride with thiophenol and K_2CO_3 in DMF yielded the acetamido SCS ligands **6a**–**6f**.

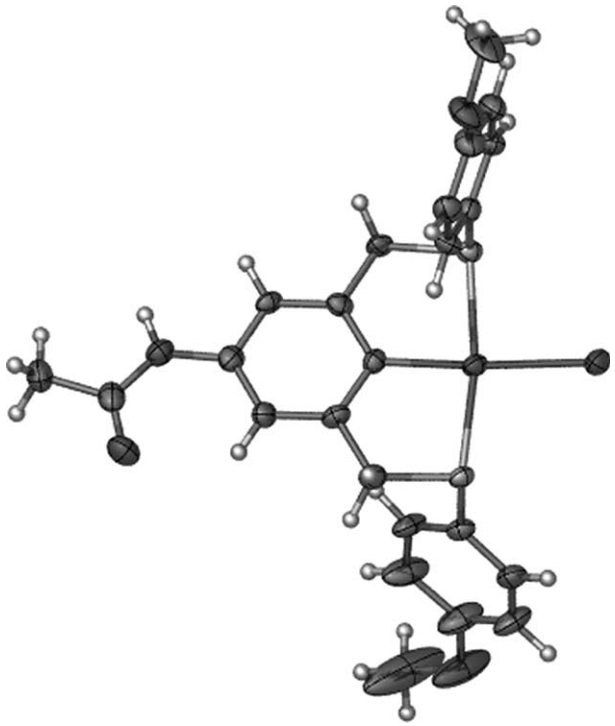


Fig. 1. Crystal structure of SCS palladacycle **10a**.

The structures of **10a–c** are shown in Figs. 1–3. The structures of complexes **10a** and **10c** are similar with pseudo C-2 symmetry for the S-arene substituents relative to the X–Pd–C_{ipso} axis. The crystal structure of palladacycle **10b** differs from these other structures in the alignment of the S-aryl rings. The thioaryl rings of **10b** are positioned on the same face of the compound, forming a cup-shaped arrangement. One thioaryl group sits at an angle of 102° and the other at 135° relative to the plane defined by the central, cyclopalladated ring. The thioaryl rings of **10a** and **10c** are positioned on opposite faces of the central ring

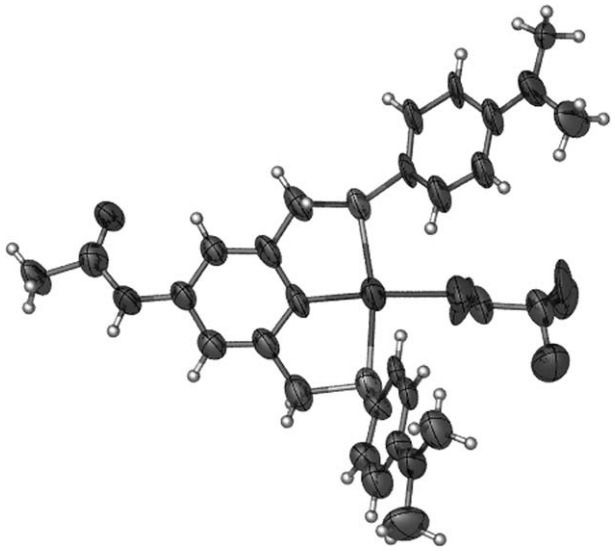


Fig. 2. Crystal structure of SCS palladacycle **10b**.

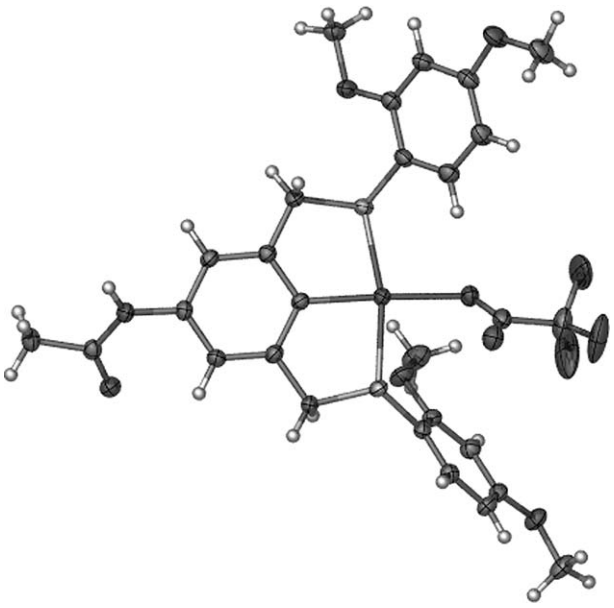


Fig. 3. Crystal structure of SCS palladacycle **10c**.

in a pseudo C-2 fashion as was seen in an earlier structure of an SCS-Pd(II) palladacycle prepared by our group [19]. While our initial impression on isolation and characterization of that earlier structure was that these S-aryl substituted palladacycles would have structures where one 'up' aromatic ring would force the other ring "down", this assumption appears not to be general based on a comparison of the structures **10a**, **10b**, and **10c**. Based on the crystal data for these three complexes and the earlier structure, the thioaryl rings may be spaced too far apart to interact significantly with one another. This stereochemical ambiguity could be significant as it might explain the relative ineffectiveness of these SCS-Pd(II) complexes in asymmetric catalysis [31]. SCS-Pd(II) palladacycles with bis(isopropylsulfoxide) ligands (cf. **11** in Fig. 4) too exist in both the *rac* and *meso* forms [32].

Other features of the SCS complexes **10a**, **10b**, and **10c** were more similar. Data comparing the four structures are assembled in Tables 1 and 2. For easy comparison, the data are normalized to the SCS substructure shown in Fig. 5. The length of the C–Pd bond ranges from 1.971 Å for **10b** to 1.98 Å for **10a**. The distances between each sulfur atom and the palladium center range from 2.297 to 2.336 Å. The S–Pd–S atom trio is nearly collinear in all the complexes. The S–Pd–S angle in **10a** is 171°, in **10b** the angle is 168°, and in **10c** the angle is 167°. The S–Pd–S axis is slightly out of alignment with the plane formed by the central aromatic ring. This twisting angle is approximately 10° for *S*-phenyl **10a**, 17° for bis(dimethoxy) **10c**, and 14° for bis(dimethylamino) **10b**.

The structural data for SCS-Pd(II) pincer complexes **10a–c** are similar to the SCS-Pd(II) chloride pincer complex we described previously [19]. The C–Pd bond lengths (ca. 1.95–2.01 Å) in a collection of other terdentate chloropalladium(II) SCS pincer complexes (Fig. 5) that have

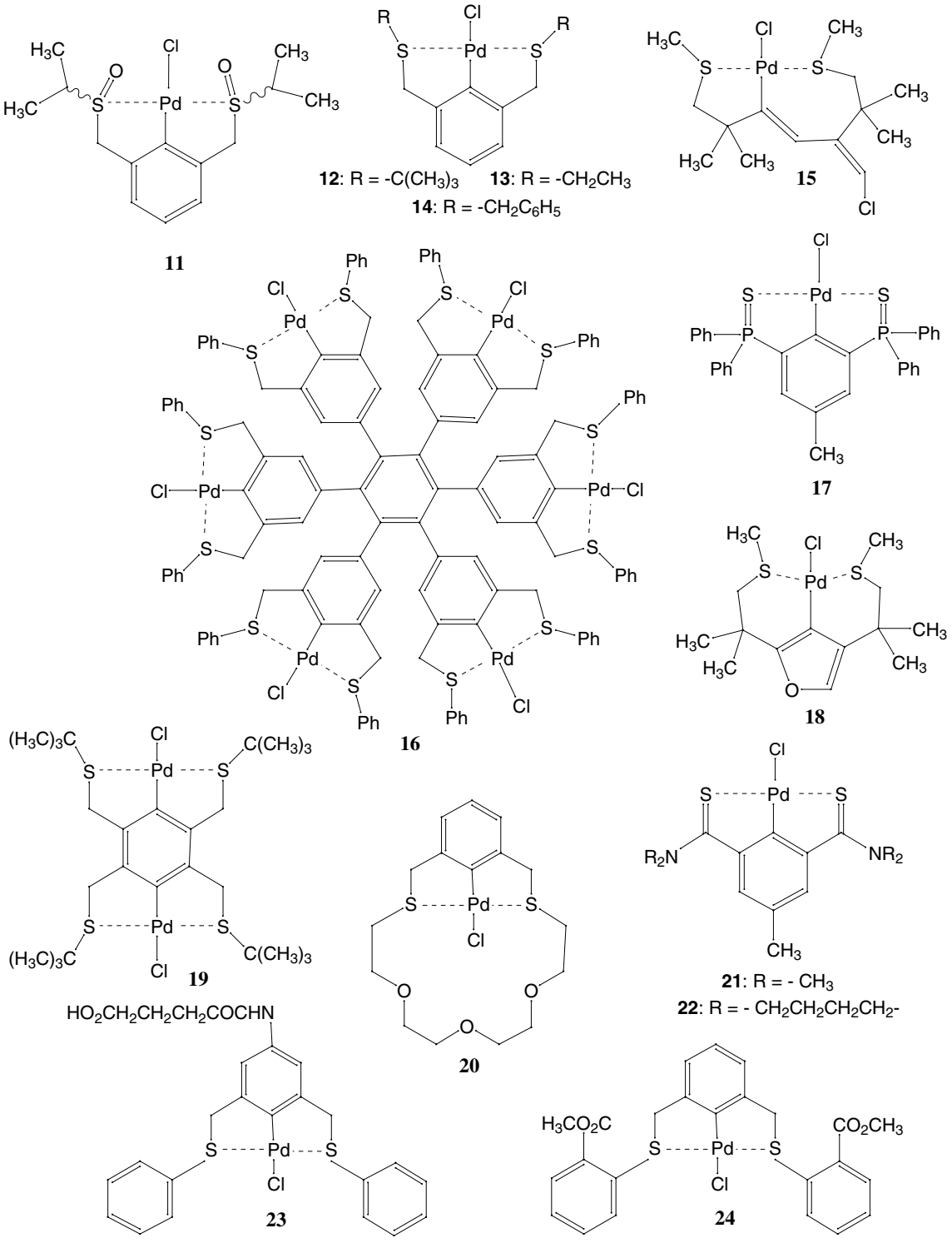


Fig. 4. Structurally characterized SCS-Pd(II) palladacycles, **11** [32], **12** [33], **13** [34], **14** [34], **15** [35], **16** [36], **17** [37], **18** [38], **19** [39], **20** [40], **21** [41], **22** [42], **23** [19], and **24** [34].

been structurally characterized by other groups are consistent with our results that show that a variation of the electronic character of ligands in SCS palladacycles have only small structural effects on the C–Pd bond [19,32–42].

Although SCS-Pd(II) complexes serve as precatalysts in formation of very efficient Pd catalysts for cross-coupling reactions and can be modified both at the position *para* to the Pd and at positions in the arene ring of the S-aryl ligand, the reactions carried out with these complexes as a source of the catalyst are not effective for cross coupling of less active arenas-like bromobenzene. Since Milstein reported that PCP-Pd(II) species are effective with these less

Table 1
Selected bond lengths of SCS palladacycles

Bond	10f	10b	10c
C1–Pd	1.971(7)	1.98(1)	1.977(3)
C5–S1	1.808(8)	1.82(1)	1.831(3)
C7–S1	1.774(7)	1.74(1)	1.769(3)
C4–S2	1.838(7)	1.85(1)	1.847(3)
C6–S2	1.784(7)	1.82(1)	1.777(3)
Pd–S1	2.291(2)	2.336(4)	2.308(1)
Pd–S2	2.297(2)	2.336(4)	2.309(1)
C2–C4	1.497(9)	1.49(1)	1.499(4)
C3–C5	1.508(9)	1.55(1)	1.505(4)

Table 2
Selected bond angles of SCS palladacycles

Atoms	10f	10b	10c
C3–C5–S1	111.1(5)	115.1(8)	108.0(2)
C2–C4–S2	110.8(5)	107.2(9)	107.4(2)
S1–Pd–S2	170.5(1)	167.6(1)	166.8(1)
C4–S2–Pd	102.0(3)	98.5(4)	99.6(1)
C5–S1–Pd	100.2(2)	99.5(4)	97.6(1)

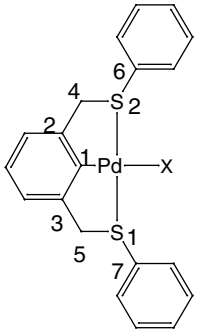


Fig. 5. Substructure of SCS palladacycles.

active substrates [18], we explored synthetic routes to *p*-amino and *p*-amido PCP-Pd(II) complexes that we could also couple to polymers. The syntheses of these complexes mirrored those used for the SCS-Pd(II) complexes described above as these syntheses too proceed through a 3,5-bis(chloromethyl)aniline derivative. Variations in the synthesis occurred with the introduction of the phosphine groups and the palladium. First we prepared an unsubstituted 2,6-bis(dicyclopentylphosphino-methyl)phenylpalladium trifluoroacetate (**25**) pincer complex. Next, we prepared a set of three PCP-Pd(II) palladacycles that had substituents with varying electronic character *para* to the Pd(II) substituent. These palladacycles included 4-acetamido-2,6-bis(dicyclopentylphosphinomethyl)phenylpalladium chloride (**28**), 4-phthalimido-2,6-bis(dicyclopentylphosphinomethyl)phenyl-palladium chloride (**32**), and 4-amino-2,6-bis(dicyclopentylphosphinomethyl)phenylpalladium chloride (**34**). While these last three palladacycles were prepared as trifluoroacetates, recrystallization yielded the palladacycle crystals as chloride salts and the

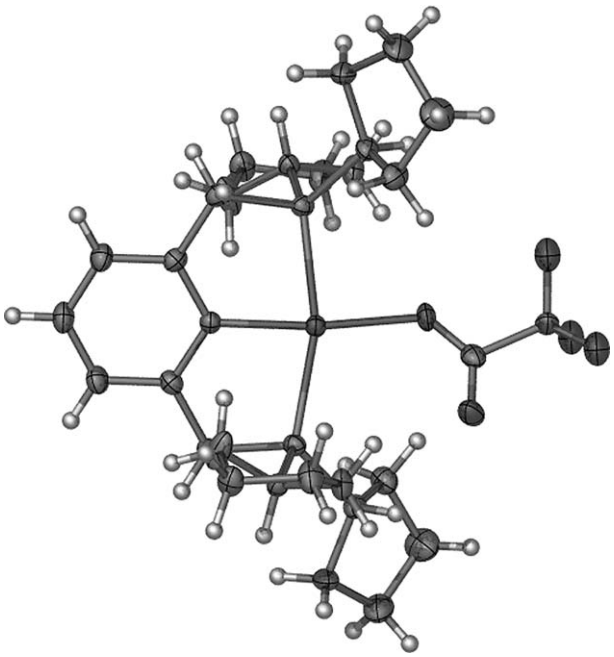
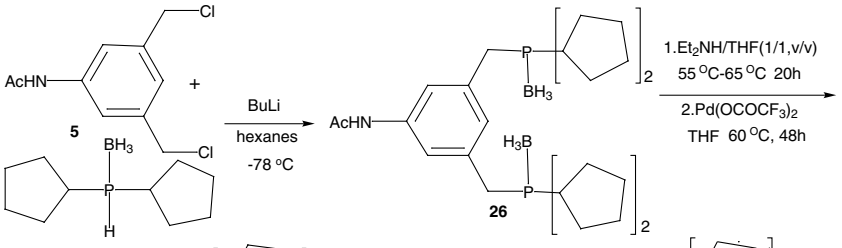


Fig. 6. X-ray crystal structure of 2,6-bis(dicyclopentylphosphinomethyl)-phenylpalladium trifluoroacetate palladacycle (**25**).

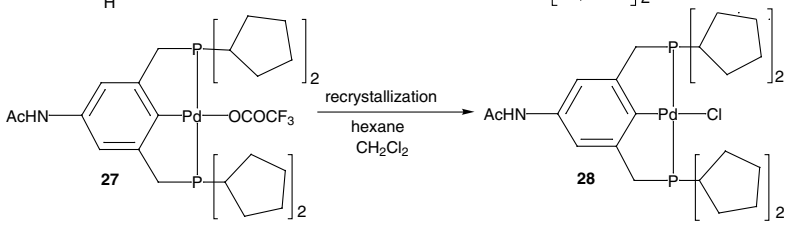
chloride salts were characterized by crystallography (see Fig. 6).

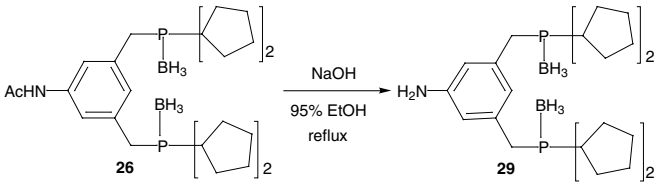
While the synthetic route used to prepare the PCP-Pd(II) complexes paralleled the route used to prepare SCS-Pd(II) complexes, the synthesis of the SCS-Pd(II) species was simplified by the fact that the intermediate thioethers unlike the phosphine intermediates were stable to ordinary handling in air. In the case of the PCP complex syntheses, oxidation of intermediate phosphine species was problematic because both phosphines must be present to form the PCP complex. In the syntheses of **28**, **32**, and **34** below, this problem was minimized by using borane complexes of the phosphine.

Originally, we thought the changing electronic nature of the *para* substituent might affect the structure of these complexes and, if the complexes were catalysts instead of precatalysts, the catalytic activity of the palladacycle. Thus, we characterized crystallographically a set of PCP complexes containing different types of substituents *para* to the Pd(II) substituent. First we prepared the palladacycle **25** with only a hydrogen *para* to the Pd(II) group of the PCP palladacycle. Then we introduced a electronically variable *para* nitrogen substituent. The first of these *para*-*N*-substituted palladacycles was prepared from **5** using the chemistry shown in Eq. (3). The *p*-acetamido group in **27** was then hydrolyzed to form an $-NH_2$ group (Eq. 4). Palladation of this compound was not successful. Therefore, we converted this $-NH_2$ group into a phthalimido group and palladated this protected phthalimido diphosphine to form **30** (Eq. 5). The palladacycle containing an $-NH_2$ group *para* to the Pd(II) center was then obtained from **31** by hydrazinolysis (Eq. 6).

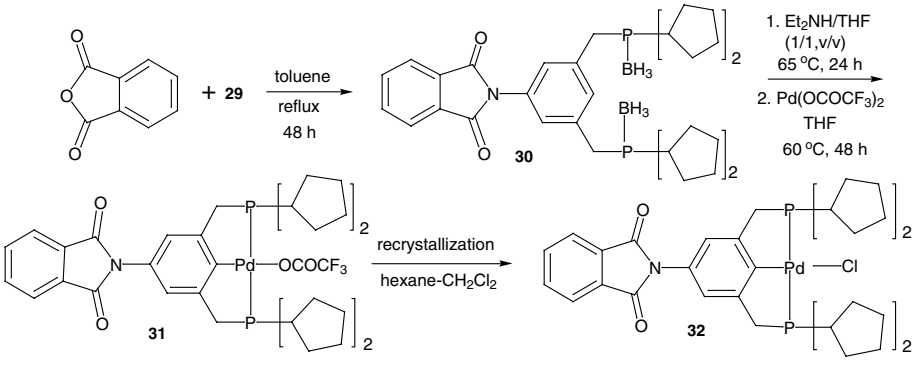


(3)

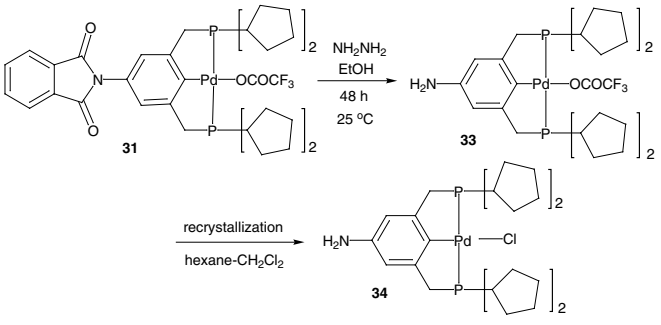




(4)



(5)



(6)

The three complexes **27**, **31**, and **33** had to be recrystallized from a hexane–CH_2Cl_2 mixture to form crystals suitable for X-ray analysis as shown in the equations above. This led to the structures **28**, **32**, and **34** shown in Figs. 7–9. While we had intended to compare these structures to each other and to the unsubstituted PCP palladacycle **25**, the conversion of the palladium's trifluoroacetate ligand into a chloride ligand presumably either by chloride abstraction from the solvent or by reaction of traces of HCl in the solvent with the initial trifluoroacetate palladacycle salts focused our attention on the structural effects of electronic variation of the *para* nitrogen substituent in the three chloropalladium palladacycles.

While we were successful in generating a set of structurally characterized PCP complexes with electronically varied *para* substituents, the results showed no consistent substituent effects. The C–Pd bond length, the Pd–P bond lengths, and the Pd–Cl bond length in these species did not vary in any consistent way with the nature of the *para* substituent (Table 3). For easy comparison, the data in Tables 3 and 4 are normalized to the PCP substructure

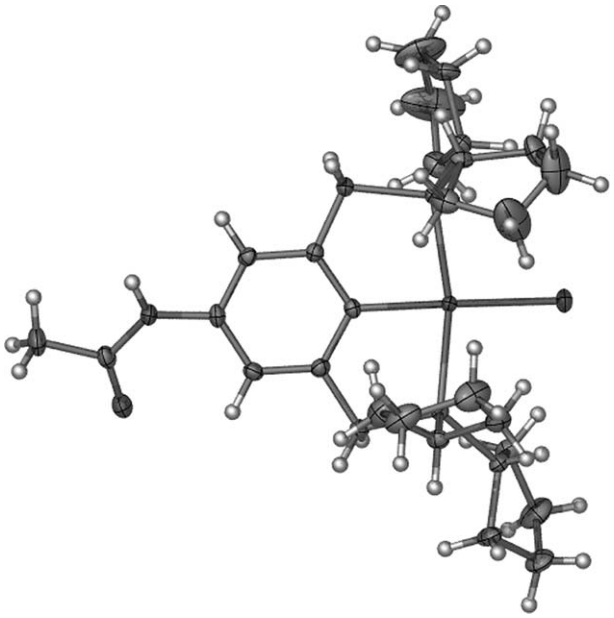


Fig. 7. X-ray crystal structure of 4-acetamido-2,6-bis(dicyclopentylphosphinomethyl)phenyl-palladium chloride palladacycle (**28**).

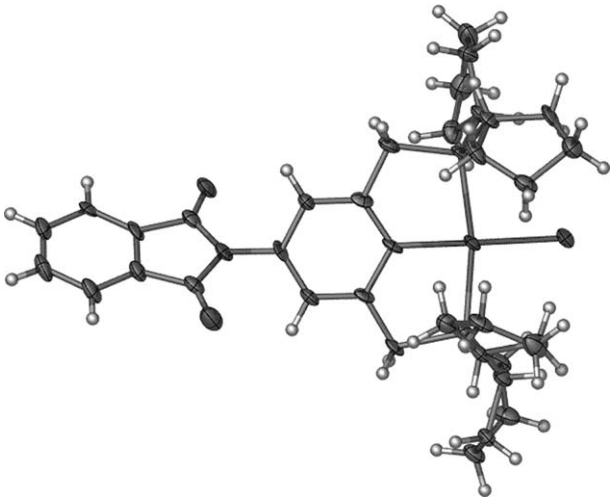


Fig. 8. X-ray crystal structure of 4-phthalimido-2,6-bis(dicyclopentylphosphinomethyl)phenyl-palladium chloride palladacycle (**32**).

shown in Fig. 10. The most electron-donating substituent – the *para*-NH_2 group – had a C–Pd bond length that was intermediate in length. Similarly, there were no clear correlations between the Pd–P or the Pd–Cl bond lengths and the electron-donating ability of the nitrogen group *para* to the Pd(II) group. van Koten in earlier work has pointed out that various *para* substituents on similar palladacycles generally have minimal effects on catalysis, an effect that has been seen both in experimental studies and in theoretical calculations [43].

Bond angles were similarly not affected by the N-substituent in any predictable way (Table 4). The bond length and angle differences were well with experimental error.

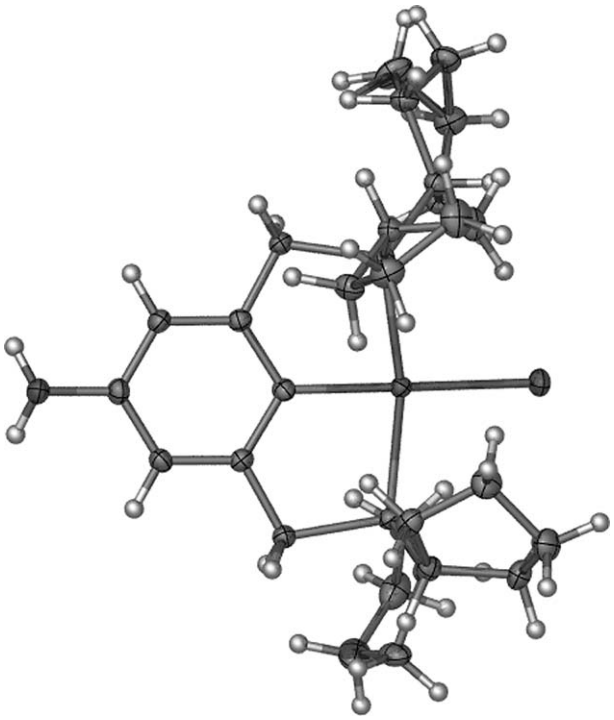


Fig. 9. X-ray crystal structure of 4-amino-2,6-bis(dicyclopentylphosphinomethyl)phenyl-palladium chloride palladacycle (**34**).

Table 3
Selected bond lengths of PCP palladacycles

Bond	**25**	**28**	**32**	**34**
C1–Pd	2.003(4)	2.010(2)	2.055(7)	2.022(2)
C5–P1	1.838(3)	1.826(3)	1.883(7)	1.839(2)
C7–P1	1.831(3)	1.826(3)	1.848(7)	1.827(2)
C6–P1	1.829(3)	1.821(2)	1.839(8)	1.830(2)
C4–P2		1.841(3)	1.849(7)	1.826(2)
C8–P2		1.827(3)	1.890(7)	1.822(2)
C9–P2		1.821(3)	1.852(7)	1.831(2)
Pd–P1	2.304(1)	2.272(1)	2.318(2)	2.279(1)
Pd–P2		2.281(1)	2.316(2)	2.285(1)
C2–C4	1.514(5)	1.508(3)	1.563(9)	1.509(2)
C3–C5		1.513(3)	1.538(9)	1.513(2)
Pd–Cl		2.396(1)	2.430(2)	2.409(1)

Table 4
Selected bond angles of PCP palladacycles

Atoms	**25**	**28**	**32**	**34**
C3–C5–P1	114.1(2)	106.8(2)	107.8(4)	109.4(1)
C2–C4–P2		109.1(2)	109.6(5)	108.2(1)
P1–Pd–P2	163.8(1)	162.9(1)	165.4(1)	163.92(2)
C4–P2–Pd		104.1(1)	104.1(2)	102.94(6)
C5–P1–Pd	100.4(1)	103.0(1)	104.2(2)	104.79(6)

A survey of the Cambridge Crystallographic Database (Feb 2005) for C–Pd(P)(P)–Cl structures matched 149 compounds and resulted in 182 observed C–Pd bond distances. The C–Pd mean bond length of 2.03(5) Å for these observations is similar to the mean deviation of the C–Pd

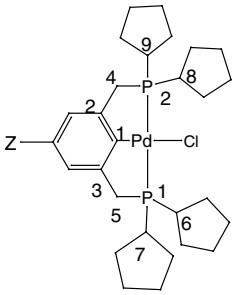


Fig. 10. Substructure of PCP palladacycles.

distance of 2.02(2) Å for the palladacycles structurally characterized in this report.

4. Conclusions

Crystal structures for a set of three SCS-Pd(II) pincer compounds with S-aryl groups of varying electronic character were prepared. X-ray crystallography studies showed that the S-aryl rings orientation relative to one another varied – the C2 symmetry seen with the simplest example was not consistently seen in all structures. Other bond distances and bond angles were not found to be affected in a consistent way by the electronic character of the palladium's S-aryl ligands. Four PCP-Pd(II) pincer compounds were also prepared and characterized structurally. Electronically different $–NH_2$, $–NHCOCH_3$, and phthalimido substituents para to the Pd(II) substituent on the phenyl ring showed no consistent effect on C–Pd, Pd–P or Pd–Cl bond lengths or on the solid-state structure of these palladacycles. The four PCP palladacycles characterized had C–Pd bond lengths consistent with other PCP palladacycles described in the literature.

Acknowledgements

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Appendix A. Supplementary data

Experimental details for synthesis of thioarenes and some of the intermediates used in the syntheses of the palladacycles described above are provided in supplementary material. Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre (281740-281746). Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005. 09.030.

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