

Mono- versus Dipalladation of the Durene-Based Tetrathioether Ligand 1,2,4,5-(*t*BuSCH₂)₄C₆H₂. Structures of [PdCl((*t*BuSCH₂)₄C₆H)] and [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂

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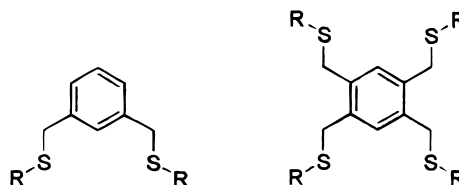
Treatment of 1,2,4,5-(*t*BuSCH₂)₄C₆H₂ with K₂PdCl₄/NaOAc in ethanol yielded only the monopalladated complex [PdCl((*t*BuSCH₂)₄C₆H)] regardless of whether 1 or 2 equiv of K₂PdCl₄ is used. Alternately, the reaction of 1,2,4,5-(*t*BuSCH₂)₄C₆H₂ with 1 or 2 equiv of [Pd(MeCN)₄][BF₄]₂ in MeCN resulted in quantitative production of the dipalladated species [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂ based on palladium starting material. The X-ray structures of the two products [PdCl((*t*BuSCH₂)₄C₆H)] and [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂ are reported. MO calculations were consistent with the idea that the ligand trans to the first Pd–C bond dictates the electrophilic aromatic substitution pattern and determines whether a second palladation will occur. Thus, Pd–Cl is deactivating while (Pd–MeCN)⁺ is activating, resulting in the formation of exclusively mono- and dipalladated products, respectively.

Introduction

Direct ortho-metalation of an aromatic ring gives rise to a M–C bond supported in a chelate ring by a M–E bond, where E is a donor atom of the ligand most commonly N or P.¹ If two such donors occupy the 1,3-positions of an aromatic ring, there exists the possibility of two supporting M–E bonds. This gives rise to a tridentate E₂C chelate, and complexes with this type of ligand have demonstrated some unique reaction chemistry.² In our research, focus has been on ligands in which E = S such as those in Chart 1, and applications have centered on utilizing organopalladium complexes as building blocks for metalloreceptors,³ metal–ligand assemblies,⁴ and coordination polymers.⁵

Two synthetic strategies have proven successful for palladation of dithioether ligands. The classical method, first employed by Shaw for the palladation of 1,3-(*t*BuSCH₂)₂C₆H₄, using M₂PdCl₄ (M = Na, K) and NaOAc in ethanol gives rise to complexes of the type [PdCl((RSCH₂)₂C₆H₃)].⁶ This type of neutral species is useful for the preparation of derivatives in which a weak

Chart 1



donor ancillary ligand replaces chloride after removal with Ag⁺ in a noncompetitive solvent. An alternate set of conditions for palladation involves using [Pd(MeCN)₄][BF₄]₂ in MeCN solution.⁷ This results in the solvated cationic species [Pd((RSCH₂)₂C₆H₃)(MeCN)]⁺ and is very useful for preparing complexes with stronger donors capable of displacing the labile MeCN ligand.

Dipalladation of the tetrathioether ligands creates bimetallic analogues of these monopalladium complexes. These are useful building blocks for metal–ligand assemblies and coordination polymers since this unit provides a linear fragment with two opposed metal binding sites on a single aromatic ring. To effect dipalladation of these tetrathioether ligands, a second palladation of the aromatic ring must occur para to the initially formed Pd–C bond. The results of our investigations into the palladation of the tetrathioether 1,2,4,5-(*t*BuSCH₂)₄C₆H₂ are presented herein.

Experimental Section

K₂PdCl₄, tetrabromodurene, and all deuterated solvents were purchased from Aldrich and used as received. [Pd-

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(MeCN)₄[BF₄]₂ was prepared by the literature method from Pd-sponge.⁸ All reactions were conducted under an atmosphere of N₂ using standard Schlenk techniques, and all solvents were degassed prior to use. ¹H and ¹³C{¹H} NMR spectra were recorded at 300.1 and 75.4 MHz, respectively, on a Bruker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analyses were performed by Canadian Microanalytical Services, Delta, British Columbia, Canada.

Preparation of 1,2,4,5-(*t*BuSCH₂)₄C₆H₂. *tert*-Butylmercaptan (3.760 g, 41.7 mmol) was added to an anhydrous ethanol solution (150 mL) containing Na (0.958 g, 41.7 mmol). This mixture was heated to reflux and tetrabromodurene (4.689 g, 10.4 mmol) was added with stirring. The mixture was then stirred at reflux for an additional 8 h. The solvent was removed, and the gray residue was extracted with CH₂-Cl₂ (200 mL). After treatment with decolorizing charcoal, filtration, and removal of solvent, the resulting off-white solid was recrystallized from anhydrous ethanol. This compound requires storage under N₂(g) in the dark to prevent decomposition. Yield: 4.71 g (93%). Mp: 225 °C (decomp). ¹H NMR (CDCl₃): δ (ppm) 7.19 (s, 2H, Ar), 3.82 (s, 8H, Bz), 1.37 (s, 36H, Me). ¹³C{¹H} NMR (CDCl₃): δ (ppm) 135.3, 133.0 (Ar), 42.9 (Bz), 30.8, 30.1 (Me). Anal. Calcd for C₂₆H₄₆S₄: C, 64.14; H, 9.52; S, 26.34. Found: C, 63.99; H, 9.55; S, 26.45.

Preparation of [PdCl((*t*BuSCH₂)₄C₆H)]. K₂PdCl₄ (0.534 g, 1.64 mmol), anhydrous sodium acetate (0.134 g, 1.64 mmol), and 1,2,4,5-(*t*BuSCH₂)₄C₆H₂ (0.798 g, 1.64 mmol) were combined in anhydrous ethanol (50 mL), and the resulting solution was heated at reflux for 72 h. The solution gradually darkened over the reaction period. The solution was cooled to room temperature, and the solvent was removed to give a greenish residue. This material was extracted with CHCl₃ (30 mL), and the solution was treated with decolorizing charcoal. After filtration, the resulting yellow solution was concentrated to ca. 10 mL. Diffusion of *n*-hexane into this solution yielded a yellow powder, which could be recrystallized by slow evaporation of a CHCl₃ solution. Yield: 0.463 g (45%). ¹H NMR (CDCl₃): δ (ppm) 6.81 (s, 1H, Ar), 4.42 (s, 4H, Bz), 3.69 (s, 4H, Bz), 1.54 (s, 18H, Me), 1.36 (s, 18H, Me). ¹³C{¹H} NMR (CDCl₃): δ (ppm) 148.7 (Pd-C), 131.2, 127.7 (Ar), 52.6, 43.2 (Bz), 40.2, 33.2 (Me), 30.9, 30.8 (Me). Anal. Calcd for C₂₆H₄₅ClPdS₄: C, 49.73; H, 7.24; S, 20.43. Found: C, 49.56; H, 7.12; S, 19.99.

Preparation of [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂. [Pd-(MeCN)₄][BF₄]₂ (0.132 g, 0.298 mmol) and 1,2,4,5-(*t*BuSCH₂)₄-C₆H₂ (0.073 g, 0.149 mmol) were combined in MeCN (20 mL), and the resulting solution was heated at reflux for 8 h. The solution gradually turned from yellow-orange to bright yellow over the reaction period. The solution was cooled to room temperature, and the solvent was removed to give a yellow residue. Stirring with diethyl ether (40 mL) allowed isolation of a yellow powder, which could be recrystallized by diffusion of diethyl ether into a nitromethane solution of the complex. Yield: 0.064 g (45%). ¹H NMR (CD₃CN): δ (ppm) 4.15 (s, br, 8H, Bz), 1.95 (s, 6H, MeCN), 1.50 (s, 36H, Me). ¹³C{¹H} NMR (CD₃CN): δ (ppm) 154.2 (Pd-C), 146.5 (Ar), 54.1 (Bz), 41.3, 30.5 (Me). Anal. Calcd for C₃₀H₅₀B₂F₈N₂Pd₂S₄: C, 37.78; H, 5.30; S, 13.45. Found: C, 37.63; H, 5.29; S, 13.22.

General X-ray Crystallography. Diffraction experiments were performed on a four-circle Rigaku AFC6S diffractometer with graphite-monochromated Mo K α radiation. The unit cell constants and orientation matrixes for data collection were obtained from 25 centered reflections (15° < 2 θ < 35°). Machine parameters, crystal data, and data collection parameters are summarized in Table 1. The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collections. The intensity data were collected using

Table 1. Summary of Crystal Data and Structure Refinement for [PdCl((*t*BuSCH₂)₄C₆H)] and [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂

	[PdCl- (<i>t</i> BuSCH ₂) ₄ C ₆ H)]	[Pd ₂ ((<i>t</i> BuSCH ₂) ₄ C ₆)- (MeCN) ₂][BF ₄] ₂
formula	C ₂₈ H ₄₀ ClPdS ₄	C ₃₀ H ₅₀ B ₂ F ₈ N ₂ Pd ₂ S ₄
fw	655.76	953.38
T, K	293(2)	293(2)
λ , Å	0.710 73	0.710 73
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>a</i> (No. 14)
<i>a</i> , Å	11.696(4) Å	13.227(4)
<i>b</i> , Å	13.008(6) Å	11.524(5)
<i>c</i> , Å	10.858(5) Å	14.760(5)
α , deg	106.07(3)	
β , deg	90.21(4)	103.98(3)
γ , deg	83.38(3)	
<i>V</i> , Å ³	1576(1)	2183(1)
<i>Z</i>	2	2
ρ (calc), g/cm ³	1.382	1.450
data/restraints/params	3316/0/289	2276/0/218
goodness-of-fit (<i>F</i> ²)	0.989	1.031
R1, R2 (<i>I</i> > 2 σ (<i>I</i>))	0.0509, 0.1017	0.0547, 0.1486
R1, R2 (all data)	0.1352, 0.1321	0.1454, 0.2937

the ω -2 θ scan technique, in four shells (2 θ < 30°, 40°, 45°, and 50°). Empirical absorption coefficients were calculated, and absorption corrections were applied to the data. Structure solution and refinement were performed using the SHELX-93 package of programs running on an SGI Indy computer.

Structures of [PdCl((*t*BuSCH₂)₄C₆H)] and [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂. Crystals of [PdCl((*t*BuSCH₂)₄C₆H)] were grown by slow evaporation of a CH₂Cl₂ solution of the complex. Crystals of [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂ were grown by diffusion of diethyl ether into a nitromethane solution of the complex. Statistical analysis of intensity distributions and observed extinctions were consistent with the triclinic space group *P* $\bar{1}$ for [PdCl((*t*BuSCH₂)₄C₆H)] and *P*2₁/*a* for [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂. These assignments were confirmed by successful solution refinements. A total of 3380 reflections were collected and 3316 unique reflections with *F*_o² > 3 σ (*F*_o²) were used in the refinement of [PdCl((*t*BuSCH₂)₄C₆H)], while a total of 2344 reflections were collected and 2276 unique reflections with *F*_o² > 3 σ (*F*_o²) were used in the refinement of [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂. The structures were solved by direct methods, completed by subsequent Fourier syntheses, and refined with full-matrix least-squares methods. All scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (G. Sheldrick, Siemens XRD, Madison, WI). All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. This resulted in R1 = 0.0509 and R2 = 0.1017 for [PdCl((*t*BuSCH₂)₄C₆H)] and R1 = 0.0547 and R2 = 0.1486 for [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂ at final convergence. Selected bond distances and angles are summarized in Tables 2 and 3. Full listings of atomic positional parameters (Tables S-2, S-6), bonding parameters (Tables S-3, S-7), thermal parameters (Tables S-4, S-8) and hydrogen atom parameters (Table S-5, S-9) are available as Supporting Information.

Modeling Calculations. The two structures were initially minimized by molecular mechanics utilizing crystallographic positional parameters to lock the Pd-ligand bonds. Methyl groups were used in place of *t*Bu groups. The locked bond distances were then unconstrained and the structures subjected to a ZINDO/UHF geometry optimization⁹ utilizing INDO/1 parameters and a Newton-Raphson minimization having a maximum allowed gradient of 0.001. This was performed using CAChe Scientific Inc. software (version 3.7) running on an Apple Power Macintosh 7100/66.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for [PdCl((*t*BuSCH₂)₄C₆H)]

Pd(1)–C(1)	1.994(9)	Pd(1)–S(2)	2.297(3)
Pd(1)–S(1)	2.302(3)	Pd(1)–Cl(1)	2.408(3)
S(1)–C(7)	1.807(9)	S(1)–C(11)	1.862(11)
S(2)–C(8)	1.816(9)	S(2)–C(15)	1.863(11)
S(3)–C(9)	1.798(9)	S(3)–C(19)	1.843(11)
S(4)–C(23)	1.815(11)	S(4)–C(10)	1.830(9)
C(2)–C(7)	1.502(12)	C(3)–C(9)	1.529(12)
C(5)–C(10)	1.505(13)	C(6)–C(8)	1.488(12)
C(1)–Pd(1)–S(2)	86.0(3)	C(1)–Pd(1)–S(1)	85.5(3)
S(2)–Pd(1)–S(1)	171.43(10)	C(1)–Pd(1)–Cl(1)	179.3(3)
S(2)–Pd(1)–Cl(1)	94.47(11)	S(1)–Pd(1)–Cl(1)	94.08(11)
C(7)–S(1)–C(11)	103.7(5)	C(7)–S(1)–Pd(1)	99.5(3)
C(11)–S(1)–Pd(1)	107.5(4)	C(8)–S(2)–C(15)	105.1(5)
C(8)–S(2)–Pd(1)	99.2(3)	C(15)–S(2)–Pd(1)	108.0(4)
C(9)–S(3)–C(19)	103.8(5)	C(23)–S(4)–C(10)	103.9(5)
C(2)–C(1)–C(6)	121.3(9)	C(2)–C(1)–Pd(1)	119.6(8)
C(6)–C(1)–Pd(1)	119.1(8)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂

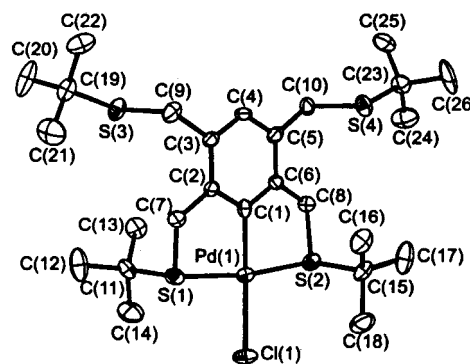
Pd(1)–C(1)	2.002(13)	Pd(1)–N(1)	2.121(13)
Pd(1)–S(1)	2.302(4)	Pd(1)–S(2)	2.304(4)
S(1)–C(4)	1.816(13)	S(1)–C(6)	1.864(13)
S(2)–C(10)	1.83(3)	S(2)–C(5)	1.835(13)
N(1)–C(14)	1.08(2)	C(2)–C(4)	1.50(2)
C(3)–C(5)	1.55(2)		
C(1)–Pd(1)–N(1)	175.8(5)	C(1)–Pd(1)–S(1)	86.3(4)
N(1)–Pd(1)–S(1)	92.7(4)	C(1)–Pd(1)–S(2)	83.4(4)
N(1)–Pd(1)–S(2)	97.2(4)	S(1)–Pd(1)–S(2)	168.68(14)
C(4)–S(1)–C(6)	104.9(6)	C(4)–S(1)–Pd(1)	100.0(4)
C(6)–S(1)–Pd(1)	107.9(5)	C(10)–S(2)–C(5)	104.1(9)
C(10)–S(2)–Pd(1)	113.5(9)	C(5)–S(2)–Pd(1)	100.2(5)
C(14)–N(1)–Pd(1)	175(2)	C(3)–C(1)–C(2)	118.4(12)
C(3)–C(1)–Pd(1)	123.0(10)	C(2)–C(1)–Pd(1)	118.5(9)

Results and Discussion

The durene-based tetrathioether 1,2,4,5-(*t*BuSCH₂)₄-C₆H₂ is easily prepared by nucleophilic displacement of bromide from tetrabromodurene employing *t*BuSNa in ethanolic solution. This off-white crystalline material possesses good solubility in most common organic solvent such as CHCl₃, CH₂Cl₂, diethyl ether, and benzene and is slightly air and moisture sensitive.

Initially, dipalladation of 1,2,4,5-(*t*BuSCH₂)₄C₆H₂ was attempted employing Shaw's method for the synthesis of [PdCl(*t*BuSCH₂)₂C₆H₃].⁶ However, the reaction of 2 equiv of K₂PdCl₄ with sodium acetate in anhydrous ethanol at reflux for 30 min produced no evidence of palladation, as observed by ¹H NMR spectroscopy. Continued reflux of this solution for 72 h produced *only* the monopalladated product [PdCl((*t*BuSCH₂)₄C₆H)]. The ¹H and ¹³C NMR spectra of this compound clearly show the resulting asymmetry due to metalation of only one end of the symmetrical ligand. In particular, observations of a single aromatic ¹H resonance at δ 6.81 ppm and a downfield ¹³C resonance at δ 148.7 ppm are indicative of monopalladation.⁷

An X-ray structural study of [PdCl((*t*BuSCH₂)₄C₆H)] provided solid-state evidence verifying the solution results. An ORTEP drawing of [PdCl((*t*BuSCH₂)₄C₆H)] is shown in Figure 1. The Pd atom is in a slightly distorted square-planar environment: S(1)–Pd(1)–S(2) 171.4(1)° and Cl(1)–Pd(1)–C(1) 179.3(3)°. The bonding parameters to Pd are very similar to those observed for [PdCl(*t*BuSCH₂)₂C₆H₃]:^{6a} Pd–S(1) 2.297(3) Å, Pd(1)–S(2) 2.302(3) Å, Pd(1)–Cl(1) 2.408(3) Å, Pd–C(1) 1.994(9) Å. The *t*Bu groups attached to the metal-bound

**Figure 1.** ORTEP drawing of [PdCl((*t*BuSCH₂)₄C₆H)] showing the atom numbering scheme. Thermal ellipsoids of 30% are shown.

sulfur atoms are oriented anti with respect to the square plane; a similar conformation was observed for [PdCl(*t*BuSCH₂)₂C₆H₃].^{6a} Likewise, the additional nonbonded *t*BuS groups are positioned on opposite sides of the aromatic ring.

In our work on the synthesis of supramolecular building blocks and metalloceptors, it was advantageous to prepare cationic organopalladium species of the type [Pd(L)(MeCN)]⁺, where L was a formally anionic S₂C chelate with the general formula 1,3-(RSCH₂)₂C₆H₃. In most cases, treatment of the dithioether ligand L with [Pd(MeCN)₄][BF₄]₂ in MeCN solution gave the palladated complex in near quantitative yield. Applying this method to the dipalladation of 1,2,4,5-(*t*BuSCH₂)₄C₆H₂, 2 equiv of [Pd(MeCN)₄][BF₄]₂ and 1 equiv of 1,2,4,5-(*t*BuSCH₂)₄C₆H₂ were heated at reflux in MeCN for 8 h. This resulted in the production of *only* the dipalladated complex [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂. The ¹H and ¹³C NMR spectra showed evidence of a single symmetrical product, as would be expected for dimetalation. The complete absence of aromatic proton resonances and the observation of a downfield-shifted ¹³C resonance at δ 154.2 ppm are strong solution evidence for dipalladation. Interestingly, attempts to isolate the monopalladated compound [Pd((*t*BuSCH₂)₄C₆H)(MeCN)]-[BF₄]₂ by repeating the above reaction using a 1:1 metal-to-ligand ratio resulted in exclusive production of the dipalladated compound [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂]-[BF₄]₂ and 1 equiv of unreacted ligand. No evidence for the monopalladated intermediate was observed.

The X-ray structure of [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂]-[BF₄]₂ unambiguously confirmed the bimetallic nature of the product. An ORTEP drawing of [Pd₂((*t*BuSCH₂)₄C₆)(MeCN)₂][BF₄]₂ is shown in Figure 2. The molecule possesses a crystallographically imposed center of symmetry with the *t*Bu groups oriented in a syn fashion. The Pd atom exhibits the expected square-planar geometry, but the distortions are more pronounced than those observed for [PdCl((*t*BuSCH₂)₄-C₆H)]: S(1)–Pd(1)–S(2) 168.7(1)° and N(1)–Pd(1)–C(1) 175.8(5)°. The bonding parameters to Pd are very similar to those observed for other cationic complexes of this type:^{3,5,7} Pd–S(1) 2.302(4) Å, Pd(1)–S(2) 2.304(4) Å, Pd(1)–N(1) 2.12(1) Å, Pd–C(1) 2.00(1) Å.

These results suggest that the nature of the ancillary ligand attached to Pd (Pd–Cl versus (Pd–MeCN)⁺) has a dramatic effect on the course of the *second* palladation reaction. In the case of chloride, the addition of a second

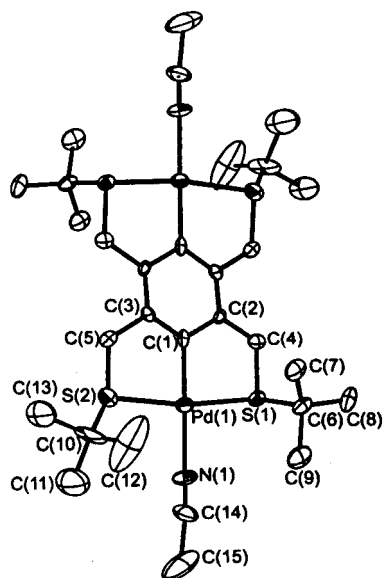


Figure 2. ORTEP drawing of the [Pd₂((*t*BuSCH₂)₄C₆H₂)(MeCN)₂]²⁺ dication showing the atom numbering scheme. Thermal ellipsoids of 30% are shown.

palladium center to the aromatic ring does not occur even in the presence of 100% excess palladium reagent. For acetonitrile, there was no evidence of a monopalladated complex and only the dipalladated material was produced, even in the presence of 100% excess ligand. Since this type of metalation is considered electrophilic aromatic substitution, addition of a highly electronegative chloride must be deactivating enough to prevent further substitution while addition of acetonitrile must activate the ring toward a second palladation. Indeed, the idea that an initial palladation would activate the

aromatic ring toward a subsequent palladation was previously suggested by Trofimenko.⁹ Molecular orbital calculations on the two monopalladated species [PdCl-(MeSCH₂)₄C₆H] and [Pd(MeCN)((MeSCH₂)₄C₆H)]⁺ were also consistent with these observations. For the Pd-Cl case, the HOMOs were primarily of metal character, while the Pd-MeCN complex showed HOMO's with ligand character that would be susceptible to electrophilic substitution at the carbon atom para to the initial metalation site.

Conclusions

The dipalladation of a single aromatic ring was first reported⁹ in 1971 by Trofimenko. In 1993, we reported^{5a} the first crystal structure of a complex containing a 1,4-dipalladated aromatic ring: [Pd₂((PhSCH₂)₄C₆H₂)(pyridine)₂][BF₄]₂. In this paper, we have shown that production of a mono- or dipalladated aromatic ring can be controlled by judicious choice of reaction conditions and that the synthesis can be quantitatively selective for either species. Additionally, we offer a simple rationale for the course of the reaction which is consistent with a MO description of electrophilic aromatic substitution controlled by activation and deactivation of the ring by a Pd(II)-containing substituent.

Acknowledgment. We thank the Natural Sciences and Engineering Council of Canada for financial support of this research.

Supporting Information Available: Full listings of atomic positional parameters, bonding parameters, thermal parameters, and hydrogen atom parameters (16 pages). Ordering information is given on any current masthead page.

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