Organometallics **2002,** *21,* 121−126

Ortho-Metalated Benzenethiolate Bridging Dinuclear Palladium(II) Complexes. X-ray Structures of $[Sn_2(\mu\text{-}C_6H_4S)_2(^tBu)_4]$ and $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-dppm})_2Cl_2]$

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Received June 20, 2001

The lithium salt $C_6H_4SLi_2$ reacts with $[SnCl_2(^tBu)_2]$ and $[HgCl_2]$ to give the ortho-metalated complexes $[Sn_2(\mu\text{-}C_6H_4S)_2(^tBu)_4]$ (**1**) and $[Hg(\mu\text{-}C_6H_4S)]_n$ (**2**), respectively, which further react with $[PdCl_2(dppm)]$ (dppm = 1,1′-bis(diphenylphosphino)methane), affording the dinuclear derivative $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-dppm})_2Cl_2]$ (**3**) with a total transfer of the ortho-metalated group C_6H_4S. Reactions of **3** with different salts afford dinuclear derivatives in which the SC ortho-metalated ligand continues to bridge the two palladium centers, $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-dppm})_2X_2]$ (X = Br, I, NCS) and $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-}S_2CNR_2)_2(\mu\text{-dppm})]$ (R = Me, Et, CH_2Ph, $^1/_2$ C_4H_8). The X-ray structures of the dinuclear tin (**1**) and palladium (**3**) derivatives show the bridging C_6H_4S groups in such a way that, in each structure, the two metallic centers have different environments.

Introduction

The widespread applications of ortho-metalated palladium complexes, mainly in organic syntheses, have motivated the great deal of attention that these compounds have received in the past decades.[1−7] In addition, they are a source of complexes with interesting and unusual structures[8,9] or complexes for new areas such as organometallic liquid crystals[10,11] and catalyst precursors to promote the Heck or Suzuki coupling reactions,[7,12−20] among other catalytic processes.[21,22] Nowadays, the most studied by far are the five-membered cyclopalladated C,P and C,N materials; however, it is noteworthy that C,S-palladated complexes are less represented than the previously mentioned species, although their stability is not very different from that of the other ortho-palladated derivatives. Traditional synthetic procedures such as C−H activation[23,27] with palladium(II) acetate and oxidative addition over palladium(0)[28,29] have only restricted accessibility in the synthesis of a variety of five-membered ortho-palladated C,S complexes. In addition, insertion of alkenyl sulfides into a Pd−C bond[30,31] and transmetalation reactions, mainly with mercury complexes,

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10.1021/om010538t CCC: $22.00
Publication on Web 12/04/2001

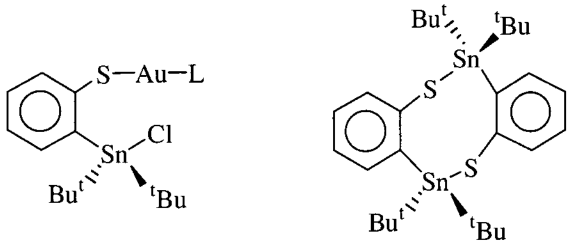

Figure 1. (a, left) Representation of $[AuSnClR_2(C_6H_4S)L]$. (b, right) Former proposed structure of $[Sn_2(C_6H_4S)_2{}^tBu_4]$.

are often a good alternative to the synthesis of such intramolecularly coordinated derivatives with Pd or different metals.[32−34]

Recently we have reported the use of $[Sn_2(\mu\text{-}C_6H_4S)_2R_4]$ as an ortho-metalated transfer reagent in gold chemistry under very mild conditions.[35] The tin centers transfer only the S−Sn bond to the gold center and not the C−Sn end. As a result, heteronuclear metalated derivatives with the skeleton Sn−C−C−S−Au (Figure 1a) were obtained. The transfer of organic groups from tin(IV) to any M−Cl bond requires some palladium catalyst (Stille reaction). In this paper we report the transfer reaction of the C_6H_4S ortho-metalated ligand from $[Sn_2(\mu\text{-}C_6H_4S)_2({}^tBu)_4]$ or $[Hg(\mu\text{-}C_6H_4S)]_n$ to a palladium (II) center, $[PdCl_2(dppm)]$ (dppm = 1,1′-bis(diphenylphosphino)methane), which occurs totally, affording $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-}dppm)_2Cl_2]$. The X-ray structures of both the starting dinuclear tin complex and the palladium derivative are reported and to the best of our knowledge represent the first two structures of bridging S,C ortho-metalated dinuclear complexes. Spectroscopic evidence will also be presented supporting the preparation of the novel derivatives $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-}dppm)_2X_2]$ (X = Br, I, NCS) and $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-}S_2CNR_2)_2(\mu\text{-}dppm)]$ (R = Me, Et, CH_2Ph, $^1/_2$ C_4H_8) through substitution reactions with the corresponding salts.

Results and Discussion

Reactions of lithium 2-lithiobenzenethiolate $Li_2(C_6H_4S)$, isolated as a white solid,[36] with equimolecular amounts of $[Sn({}^tBu)_2Cl_2]$ and $HgCl_2$ afford $[Sn_2(\mu\text{-}C_6H_4S)_2({}^tBu)_4]$ (**1**) and $[Hg(C_6H_4S)]_n$ (**2**), respectively, in good yields (Scheme 1, processes i and ii). While the tin derivative is soluble in most organic solvents, the mercury derivative **2** is not. Consequently, we have no evidence about the value of *n* and no spectroscopic data in solution are reported for **2**. Nevertheless, its nature was confirmed because of its behavior as a transmetalating reagent (see below). $[Sn_2(\mu\text{-}C_6H_4S)_2({}^tBu)_4]$ (**1**) was previously reported by some of us and described as a symmetrical dinuclear derivative[35] (Figure 1b). However, a new preparation led to the isolation of suitable crystals for X-ray diffraction, which showed the unsymmetrical nature of the complex (Figure 2). General conditions for this structure determination are given in Table 1, and selected bond lengths and angles are given in Table 2. The molecule consists of two $(SC_6H_4)^{2-}$ units bridging two tin(IV) centers in different environments. Thus, Sn(1) is coordinated to the bridging ligand through the sulfur atoms and Sn(2) through the C centers. The geometries around the tin atoms are quite similar and can be described as distorted tetrahedra, with angles ranging from 102.15(11) to 117.63(14)° for Sn(1) and from 99.44(14) to 121.40(13)° for Sn(2). In particular, the largest deviation from the ideal tetrahedron (109.47°) of 11.93° corresponds to C(2)−Sn(2)−C(8). The bond lengths Sn−C(^{t}Bu) of about 2.19 and 2.18 Å are in the range for other di-*tert*-butyltin complexes.[35,37−40] The Sn−C(SC_6H_4) bond lengths (2.168(10) and 2.161(3) Å) are slightly shorter than those of the ^{t}Bu groups. The Sn−S distances (2.4279(10) and 2.4221(11) Å) are similar to those found in the complexes $[Au_2Sn({}^tBu)_2(C_6F_5)_2(SC_6H_4PPh_2)_2]$[37] (2.433(3) and 2.444(3) Å) and $[Sn({}^tBu)_2(SPPh(SC_2H_4)_2]_2$39 (2.42 Å on average). On the other hand, two short intramolecular contacts are observed, $Sn(2)\cdots S(1)$ (3.536 Å) and $Sn(2)\cdots S(2)$ (3.542 Å); these are greater than the sum of the covalent radii (2.44 Å) but below the sum of the van der Waals radii (4.05 Å).[41] These distances are comparable to the intermolecular $Sn\cdots S$ contact observed in 2,2-dibutyl-1,3,2-dithiastannolane (3.69 Å),[42] which was described as reflecting weak interaction at the tin. The bridging $(SC_6H_4)^{2-}$ ligands are mutually oriented to make a dihedral angle of 78.80°. The molecule has slightly different symmetry from that proposed by us (Figure 1b); instead, complex **1** is unsymmetrically coordinated, as shown in Figure 2 and shown schematically in Scheme 1.

Although we performed the same reaction of lithium 2-lithiobenzenethiolate $Li_2(C_6H_4S)$ with different palladium complexes such as $[PdCl_2(PPh_3)_2]$, $[PdCl_2(PPh_2Me)_2]$, $[PdCl_2(dppe)]$, and $[PdCl_2(dppm)]$ (dppe = 1,2-bis(diphenylphosphino)ethane; dppm = 1,1’-bis(diphenylphosphino)methane), these were not successful and only unresolved mixtures were obtained.

With the different palladium complexes $[PdCl_2(PPh_3)_2]$, $[PdCl_2(PPh_2Me)_2]$, $[PdCl_2(dppe)]$, and $[PdCl_2(dppm)]$ as starting materials for transmetalated receptors, with either the tin (**1**) or the mercury (**2**) derivatives, only with the dppm complex was it possible to isolate a pure compound. In all the cases we obtained mixtures of products, which we could not resolve. Therefore, when $[PdCl_2(dppm)]$ was refluxed in acetone in the presence of $[Sn{}^tBu_2(SC_6H_4)]_2$ (**1**), over a period of 12 h, a light brown solid identified as $[Pd_2(\mu\text{-}SC_6H_4)(\mu\text{-}dppm)_2Cl_2]$ (**3**) was obtained in 76% yield (Scheme 1, process iii). The same complex, although in lower yield (43%), was obtained when $[Hg(SC_6H_4)]_n$ (**2**) was the starting transmetalating reagent (Scheme 1, process iv).

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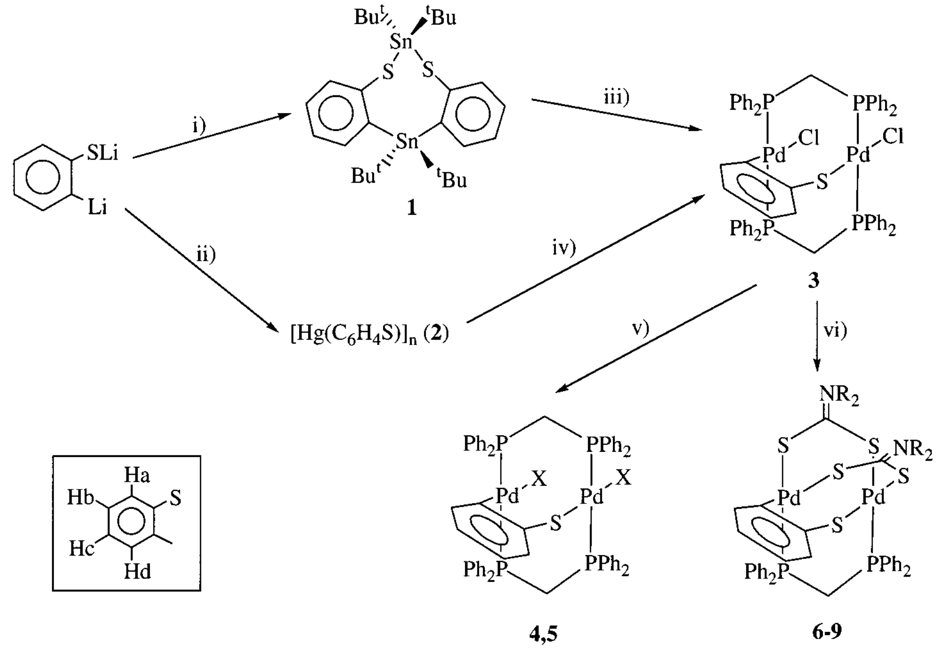
Scheme 1. Preparation of Complexes 1−7[a]



[a] Legend: (i) 2 [SnCl$_2$^{t}Bu$_2$]; (ii) 2 HgCl$_2$; (iii) 2 [PdCl$_2$(dppm)]; (iv) [PdCl$_2$(dppm)] + Me$_4$NCl; (v) 2 NaX, X = I, SCN; (vi) 2 NaS$_2$CNR$_2$, R = Me, Et, Bz, $^1/_2$ C$_4$H$_8$.

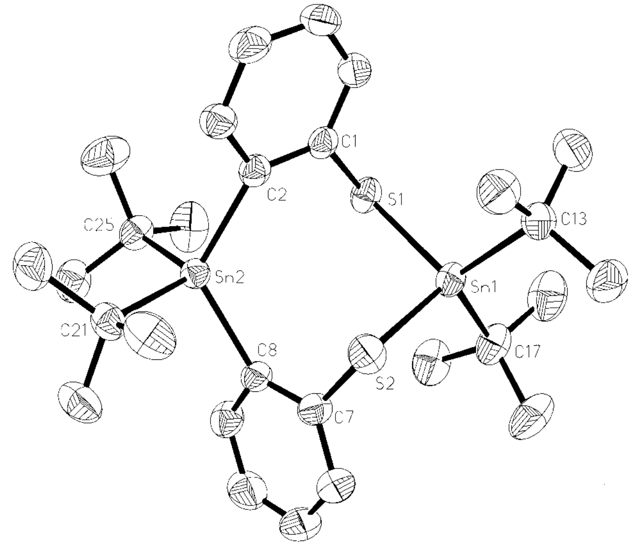


Figure 2. Compound **1** in the crystal form. Displacement parameter ellipsoids represent 50% probability. H atoms are omitted for clarity.

The ^{1}H NMR spectrum of **3** shows the C$_6$H$_4$S protons displaced to high field from the other phenyl protons, which permits us to establish the thiobenzene/diphosphine ratio in the complex and completely assign the resonances by ^{1}H,^{1}H-COSY experiments. The presence of an AA′BB′ pattern in the ^{31}P NMR and two doublets of quintuplets in the methylene region (^{1}H NMR) is indicative of a dinuclear A-frame structure for this complex.[43] The mass spectrum (positive liquid secondary ion mass spectrometry: LSIMS+) shows the parent peak to have low intensity and peaks corresponding to the loss of one and two chlorine atoms, in accordance with the proposed stoichiometry.

Table 1. Crystal Data and Data Collection and Refinement Details for the Complexes [Sn^{t}Bu$_2$(SC$_6$H$_4$)]$_2$ (1) and [Pd$_2$(SC$_6$H$_4$)Cl$_2$(dppm)$_2$] (3)

	1	3
empirical formula	$C_{28}H_{44}S_2Sn_2$	$C_{56}H_{48}Cl_2P_4Pd_2S$
mol wt	682.13	1160.58
color, habit	colorless, irregular block	orange, prismatic
space group	monoclinic, $P2_1/n$	monoclinic, $C2/c$
a (Å)	10.5408(9)	34.9734(19)
b (Å)	14.7314(12)	14.0392(8)
c (Å)	19.60227(16)	27.8062(15)
α (deg)	90	90
β (deg)	92.902(2)	127.4580(10)
γ (deg)	90	90
V (Å)^3	3040.0(4)	10837.6(10)
Z	4	8
D(calcd) (g cm^{-3})	1.490	1.423
cryst size (mm^3)	0.18 × 0.28 × 0.14	0.25 × 0.12 × 0.10
μ (mm^{-1})	1.794	0.954
temp (K)	173(2)	293(2)
θ range (deg)	$1.73 \le \theta \le 28.69$	$1.47 \le \theta \le 21.97$
no. of data collected	19 828	22 901
no. of unique data	7211 (R(int) = 0.0573)	6623 (R(int) = 0.1063)
R1^a ($F^2 > 2\sigma(F^2)$)	0.0391	0.0441
wR2^b (all data)	0.0731	0.0945
S^c (all data)	0.904	0.938

[a] $R1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$. [c] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n is the number of reflections and p the number of refined parameters.

The structure of **3** was confirmed by X-ray diffraction (Figure 3 and Table 3. The benzenethiolate is bonded to each palladium atom by the sulfur and an ortho carbon atom. To our knowledge, this is the only crystallographically characterized palladium complex with an *o*-S,C-bridging thiolate unit.[44] Each palladium exhibits slightly distorted square-planar coordination and

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Table 2. Bond Lengths (Å) and Angles (deg) for $[Sn^tBu_2(SC_6H_4)]_2$ (1)

Sn(1)−C(13)	2.178(4)	Sn(2)−C(8)	2.161(3)
Sn(1)−C(17)	2.182(4)	Sn(2)−C(2)	2.168(4)
Sn(1)−S(2)	2.4221(11)	Sn(2)−C(25)	2.199(4)
Sn(1)−S(1)	2.4279(10)	Sn(2)−C(21)	2.199(3)
C(13)−Sn(1)−C(17)	117.63(14)	C(2)−Sn(2)−C(25)	104.17(14)
C(13)−Sn(1)−S(2)	102.15(11)	C(8)−Sn(2)−C(21)	99.44(14)
C(17)−Sn(1)−S(2)	114.98(13)	C(2)−Sn(2)−C(21)	109.66(13)
C(13)−Sn(1)−S(1)	114.07(11)	C(25)−Sn(2)−C(21)	110.64(14)
C(17)−Sn(1)−S(1)	102.88(11)	C(1)−S(1)−Sn(1)	99.92(11)
S(2)−Sn(1)−S(1)	104.81(3)	C(7)−S(2)−Sn(1)	99.85(13)
C(8)−Sn(2)−C(2)	121.40(13)	C(3)−C(2)−Sn(2)	119.1(3)
C(8)−Sn(2)−C(25)	111.47(14)	C(1)−C(2)−Sn(2)	123.8(3)

two trans-phosphorus atoms from dppm groups. The Pd−P distances are in the range 2.292−2.351 Å. The P−Pd−P angles of 166.47−171.3° are close to that for a rectilinear geometry.[45] The Pd−Pd distance is longer than those found in $[Pd_2Br_2(dppm)_2]$ (2.699 Å)[46] and $[Pd_2Cl(SnCl_3)(dppm)_2]$ (2.644 Å),[47] where metal−metal bonds are required to maintain a 16e configuration for each Pd center. The 3.0064 Å distance is, however, shorter than the nonbonding Pd···Pd distances found for $[Pd_2(\mu\text{-}SO)Cl_2(dppm)_2]$ (3.225 Å),[48] $[Pd_2(\mu\text{-}S)Cl_2(dppm)_2]$ (3.258 Å),[49] $[Pd_2(\mu\text{-}SO_2)Cl_2(dppm)_2]$ (3.221 and 3.383 Å),[49] and $[Pd_2(\mu\text{-}NCMe)(MeCN)_2(dppm)_2]^{2+}$ (3.215 Å)[50] and similar to the value of 3.023 Å found for the Pt···Pt separation in $[Pt_2(dppm)_3]$, which was taken to indicate some metal−metal interaction, although less than that of a single bond.[51] In complex **3** this distance, being short, should be evidence for the existence of three bridging ligands, 2 dppm and the group C_6H_4S, and does not represent any metal−metal bond. As in most A-frame complexes, the methylene groups of the dppm ligands are displaced from the M_2P_4 plane toward the apical thiolate bridging group. This conformation allows the phenyl substituents of dppm to bend away from the bridging group and minimizes steric effects. The overall conformation of the eight-membered ring is then an extended boat.[52] The terminal ligands do not lie collinear with the palladium−palladium bond (Pd(2)−Pd(1)−Cl(1) = 79.67 Å and Pd(2)−Pd(1)−Cl(2) = 127.99 Å; torsion angle (Cl(1)−Pd(1)−Pd(2)−Cl(2) = −5.13°), as has already been found even for symmetrically bridged $[M_2X_2(dppm)_2]$ metal−metal-bonded species.[53]

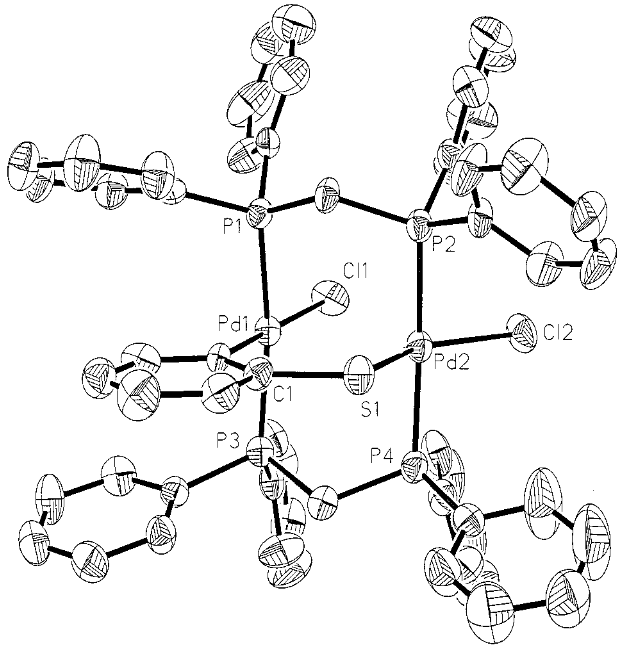

Figure 3. Compound **3** in the crystal form. Displacement parameter ellipsoids represent 50% probability. H atoms are omitted for clarity.

Table 3. Bond Lengths (Å) and Angles (deg) for $[Pd_2(SC_6H_4)Cl_2(dppm)_2]$ (3)

Pd(1)−Pd(2)	3.0064(8)	Pd(1)−Cl(1)	2.389(2)
Pd(1)−P(1)	2.346(2)	Pd(2)−Cl(2)	2.3645(18)
Pd(1)−P(3)	2.351(2)	Pd(1)−C(2)	2.003(7)
Pd(2)−P(2)	2.311(2)	Pd(2)−S(1)	2.323(2)
Pd(2)−P(4)	2.292(2)	C(1)−S(1)	1.787(7)
P(1)−Pd(1)−P(3)	166.47	P(4)−Pd(2)−Cl(2)	91.94
P(2)−Pd(2)−P(4)	171.33	Cl(2)−Pd(2)−Pd(1)	127.99
P(1)−Pd(1)−Cl(1)	94.71	Cl(1)−Pd(1)−Pd(2)	79.67
P(2)−Pd(2)−Cl(2)	94.70	S(1)−Pd(2)−Cl(2)	151.95
P(3)−Pd(1)−Cl(1)	98.81	S(1)−Pd(2)−Pd(1)	80.03

Complex **3** reacts with potassium iodide and thiocyanate replacing the chlorine atoms of the new halide or pseudohalide ligand, affording the complexes $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-}dppm)_2I_2]$ (**4**) and $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-}dppm)_2(SCN)_2]$ (**5**) (Scheme 1, process v). In both cases the NMR pattern, ^1H and $^{31}P\{^1H\}$, is similar to that reported for complex **3**, indicating the maintenance of the A-frame structure. Thus, the complexes display two multiplets for the methylene protons and an AA′BB′ patern for the four phosphorus atoms of the dppm ligands. The mass spectra show the parent peaks and the loss of one or two I^- or SCN^- groups, respectively. When complex **3** reacts with potassium bromide, independent of the ratio and the reaction time used, a mixture of the starting material and the new bromide derivative is always present in solution, which could not be resolved.

The reaction of complex **3** with different dithiocarbamate salts NaS_2CNR_2 (R = Me, Et, CH_2Ph, $^1/_2$ C_4H_8) takes place with some modifications in the structure of the starting material (Scheme 1, process vi). Thus, the elemental analyses and the ^1H NMR spectra confirm the loss of one dppm unit and the stoichiometry of $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-}S_2CNR_2)_2(\mu\text{-}dppm)]$ for the new complexes (**6**−**9**). The ^{31}P NMR spectra consist of an AB system centered at about 20 ppm, which is in accordance with a bridging coordination mode of the dppm and a slight difference in the two phosphorus atoms. Therefore, a dinuclear four-atom-bridged structure as represented in Scheme 1 is proposed for complexes **6**−**9**. In accordance with that, the two methylene protons of the dppm ligand remain inequivalent, except for complex **8**, which shows a triplet for these protons. Complexes **6**−**9** display a rather complicated pattern for the protons of the R

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groups of the S_2CNR_2 ligands, showing four different methyl resonances in complex **6**, in accordance with the inequivalence of the two ligands and the two methyl groups of each ligand. Complex **8** shows a more complicated pattern due to the inequivalence of each proton of the methylene of the CH_2Ph group, as confirmed by H,H-COSY experiments. The LSIMS+ spectra show the parent peaks for complexes **6**−**9** in addition to those corresponding to the loss of one dithiocarbamate moiety. Excess dithiocarbamate salts produce a mixture of the disubstituted derivatives and the homoleptic compounds $[Pd(S_2CNR_2)_2]$, which are easily separated by column chromatography.

In conclusion, the tin and mercury complexes $[Sn_2(\mu\text{-}C_6H_4S)_2(^tBu)_4]$ (**1**) and $[Hg(\mu\text{-}C_6H_4S)]_n$ (**2**) are good transfer reagents of the ortho-metalated $SC_6H_4^{2-}$ ligand to the palladium center in $[PdCl_2(dppm)]$, affording in both cases $[Pd_2(SC_6H_4)Cl_2(dppm)_2]$ (**3**). If we take into account the environmental problems of mercury and the lower yield of **3** obtained with this complex, the tin derivative is a more convenient reagent in these types of transfer reactions. Substitution of the chloride ligands in **3** by halide or pseudohalide ligands takes place while the structure of **3** is retained, whereas the substitution by dithiocarbamates is accompanied by displacement of one diphosphine and the thiolate group remains S,C-coordinated. The X-ray structures of $[Sn_2(\mu\text{-}C_6H_4S)_2(^tBu)_4]$ and $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-dppm})_2Cl_2]$ represent the first two structures of bridging S−C ortho-metalated homodinuclear complexes.

Experimental Section

General Data. The C, H, N, and S analyses were measured on a Perkin-Elmer 2400 microanalyzer. The infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000−200 cm^{-1}, using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on Varian Unity 300 and Bruker ARX 300 spectrometers, in $CDCl_3$ or CD_2Cl_2 at room temperature if not otherwise mentioned (300 MHz for ^1H and 121.4 MHz for ^{31}P). Chemical shifts are cited relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (external, ^{31}P). Mass spectra were recorded on a VG Autospec, by liquid secondary ion mass spectrometry (LSIMS+) using nitrobenzyl alcohol as matrix and a cesium gun.

Materials. The starting materials $[PdCl_2(dppm)]$[54] and $Li_2(SC_6H_4)$[36] were prepared by published procedures. All other reagents were commercially available and were used as supplied.

Preparation of Compounds. $[Sn_2(\mu\text{-}C_6H_4S)_2(^tBu)_4]$ (1). This compound was prepared as described elsewhere.[35] Yield: 70%. Anal. Calcd for $C_{28}H_{44}S_2Sn_2$: C, 49.3; H, 6.5; S, 9.4. Found: C, 49.4; H, 6.8; S, 9.7. ^1H NMR: δ 7.69−7.51 (m, 4H, C_6H_4S); 7.12 (m, 4H, C_6H_4S); 1.23 (s, $J_{^{119}Sn-H} = 64.2$ Hz, $J_{^{117}Sn-H} = 61.8$ Hz, 18H, ^tBu); 0.96 (s, $J_{^{119}Sn-H} = 93$ Hz, $J_{^{117}Sn-H} = 88.8$ Hz, 18H, ^tBu).

$[Hg(C_6H_4S)]_n$ (2). Lithium 2-lithiobenzenethiolate was prepared as described previously from thiophenol (1.09 g, 10 mmol), TMDA (3.4 mL, 22.2 mmol), and *n*-buthyllithium (8.8 mL, 22.2 mmol, 2.5 M). The white solid obtained corresponding to $Li_2(C_6H_4S)$ was isolated under argon, washed with *n*-hexane (3 × 20 mL), dissolved in THF (20 mL), and precooled to −78 °C. $HgCl_2$ (1.9 g, 7 mmol) was then added to the THF solution. The mixture was warmed to room temperature overnight. A gray solid precipitated, which was filtered off and washed with diethyl ether. Yield: 60%. Anal. Calcd for $(C_6H_4SHg)_n$: C, 23.34; H, 1.30; S, 10.38. Found: C, 22.9; H, 1.1; S, 9.9.

$[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-dppm})_2Cl_2]$ (3). (a) To an acetone suspension (25 mL) of $[PdCl_2(dppm)]$ (0.225 g; 0.4 mmol) was added an acetone solution (10 mL) of **1** (0.068 g; 0.1 mmol) at room temperature. The yellow solution became orange, and it was refluxed overnight and then concentrated to ca. 5 mL. Addition of *n*-hexane (10 mL) gave a brown solid, **1**, which was recrystallized from dichloromethane/hexane. Yield: 76%.

(b) To an acetone suspension (25 mL) of $[PdCl_2(dppm)]$ (0.112 g; 0.2 mmol) was added **2** (0.061 g; 0.1 mmol) and Me_4NCl (0.022 g, 0.2 mmol) at room temperature. A dark orange solid precipitated immediately, which was refluxed overnight. After this time, a brown solid was obtained, which was filtered off and washed with diethyl ether (2 × 10 mL). Yield: 43%. Anal. Calcd for $C_{56}H_{48}Cl_2P_4SPd_2$: C, 57.9; H, 4.2; S, 2.8. Found: C, 57.5; H, 4.5; S, 2.6. IR (Nujol): ν(Pd−Cl) 297 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.01−6.87 (m, 40H, PPh_2); 6.42 (d, $J_{H-H} = 6.6$ Hz, 1H, C_6H_4S, H_a); 6.14 (t, $J_{H-H} = 7.5$ Hz, 1H, C_6H_4S, H_b); 5.65 (t, $J_{H-H} = 6.6$ Hz, 1H, C_6H_4S, H_c); 5.56 (d, $J_{H-H} = 6$ Hz, 1H, C_6H_4S, H_d); 3.73 (dq, $J_{H-H} = 13.3$ Hz, $J_{P-H} = 5.8$ Hz, 2H, $P-CH_2-P$); 3.27 (dq, $J_{P-H} = 4.2$ Hz, 2H, $P-CH_2-P$). ^{31}P NMR (AA′XX′ system): δ_A 14.41; δ_B 8.61; $J_{AA'} = 294$ Hz; $J_{AX} = J_{A'X'} = 0$ Hz; $J_{AX'} = 54.3$ Hz; $J_{A'X} = 50.7$ Hz; $J_{XX'} = 299.5$ Hz. MS (LSIMS+; *m/z* (%)): 1158 (2) $[M]^+$; 1125 (7) $[M - Cl]^+$; 1089 (10) $[M - 2Cl]^+$.

$[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-dppm})_2X_2]$ (X = I (4), NCS (5)). To a dichloromethane solution (10 mL) of **3** (0.081 g; 0.070 mmol) was added the potassium salt KX (0.210 mmol) dissolved in acetone (10 mL). The red-brown solution was stirred overnight and concentrated to dryness under reduced pressure. Dichloromethane was added (5 mL), and the KCl was removed by filtration. Addition of *n*-hexane (10 mL) afforded a red-brown solid. Yield: 65% (**4**), 45% (**5**). Data for **4** are as follows. Anal. Calcd for $C_{54}H_{48}I_2P_4SPd_2$: C, 50.1; H, 3.6; S, 2.4. Found: C, 50.5; H, 3.5; S, 2.8. IR (Nujol): ν(Pd−I) 356 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.02−6.90 (m, 40H, PPh_2); 6.22 (d, $J_{H-H} = 7.5$ Hz, 1H, C_6H_4S, H_a); 6.10 (t, $J_{H-H} = 8.4$ Hz, 1H, C_6H_4S, H_b); 5.71 (t, $J_{H-H} = 8$ Hz, 1H, C_6H_4S, H_c); 5.68 (d, $J_{H-H} = 8.7$ Hz, 1H, C_6H_4S, H_d); 3.90 (dq, $J_{H-H} = 12.9$ Hz, $J_{P-H} = 5.2$ Hz, 2H, $P-CH_2-P$); 3.48 (dq, $J_{P-H} = 3.7$ Hz, 2H, $P-CH_2-P$). ^{31}P NMR (AA′XX′system): δ_A 11.62; δ_B 9.82; $J_{AA'} = 345$ Hz; $J_{AX} = 9$ Hz; $J_{A'X'} = 6.8$ Hz; $J_{AX'} = 22.3$ Hz; $J_{A'X} = 60.1$ Hz; $J_{XX'} = 223.3$ Hz. MS (LSIMS+; *m/z* (%)): 1342 (12) $[M]^+$; 1217 (100) $[M - I]^+$; 1089 (18) $[M - 2I]^+$. Data for **5** are as follows. Anal. Calcd for $C_{58}H_{48}N_2P_4S_3Pd_2$: C, 57.8; H, 4.0; N, 2.3; S, 8.0. Found: C, 57.5; H, 3.9; N, 2.5; S, 8.4. ^1H NMR: δ 8.02−6.84 (m, 40H, PPh_2); 6.57 (d, $J_{H-H} = 6.9$ Hz, 1H, C_6H_4S, H_a); 6.26 (t, $J_{H-H} = 7$ Hz, 1H, C_6H_4S, H_b); 5.34 (t, $J_{H-H} = 7.5$ Hz, 1H, C_6H_4S, H_c); 5.15 (d, $J_{H-H} = 6.6$ Hz, 1H, C_6H_4S, H_d); 4.15 (dq, $J_{H-H} = 13.1$ Hz, $J_{P-H} = 6.3$ Hz, 2H, $P-CH_2-P$); 3.05 (dq, $J_{P-H} = 3.7$ Hz, 2H, $P-CH_2-P$). ^{31}P NMR (AA′XX′ system): δ_A 18.05; δ_B 6.68; $J_{AA'} = 201$ Hz; $J_{AX} = 9$ Hz; $J_{A'X'} = 5.3$ Hz; $J_{AX'} = 14.3$ Hz; $J_{A'X} = 52.5$ Hz; $J_{XX'} = 220.5$ Hz. MS (LSIMS+; *m/z* (%)): 1148 (33) $[M]^+$; 1089 (8) $[M - 2SCN]^+$.

$[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-}S_2CNR_2)_2(\mu\text{-dppm})]$ (R = Me (6), Et (7), CH_2Ph (8), ½ C_4H_8 (9)). To a dichloromethane solution (10 mL) of **3** (0.081 g; 0.070 mmol) was added an acetone solution of NaS_2CNR_2 (0.140 mmol) at room temperature. The reddish solution turned orange-red and was stirred overnight and then concentrated to ca. 5 mL. Addition of diethyl ether (10 mL) afforded a red solid, which was purified by column chromatography (silica gel, dichloromethane/hexane (1:1)). A second yellow band was eluted with acetone and identified as the homolepticc $[Pd(S_2CNR_2)_2]$. Yield: 82% (**6**), 73% (**7**), 74% (**8**), 75% (**9**). Data for **6** are as follows. Anal. Calcd for $C_{33}H_{28}N_2P_2S_5Pd_2$: C, 41.9; H, 3.0; N, 3.0; S, 16.9. Found: C, 41.7; H, 3.2; N, 2.9; S, 16.5. ^1H NMR (CD_2Cl_2): δ 8.05−6.99 (m, 20H, PPh_2); 6.71 (m, 1H, C_6H_4S, H_a); 6.56 (d, $J_{H-H} = 12$ Hz, 1H, C_6H_4S, H_d); 6.40 (t, $J_{H-H} = 6$ Hz, 1H, C_6H_4S, H_c); 6.30 (t, $J_{H-H} = 6$ Hz, 1H, C_6H_4S, H_b); 3.32 (s, 3H, $-CH_3$); 3.28 (s, 3H, $-CH_3$);

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3.27 (s, 3H, $-CH_3$); 3.20 (s, 3H, $-CH_3$); 3.18 (m, 1H, $P-CH_2-P$); 3.05 (m, 1H, $P-CH_2-P$). ^{31}P NMR (CD_2Cl_2; AB: system): δ_A 22.95; δ_B 22.45; $J_{AB} = 65.8$ Hz. MS (LSIMS+; *m*/*z* (%)): 946 (12) $[M]^+$; 826 (7) $[M - S_2CNMe_2]^+$. Data for **7** are as follows. Anal. Calcd for $C_{37}H_{36}N_2P_2S_5Pd_2$: C, 44.4; H, 3.6; N, 2.8; S, 16.0. Found: C, 44.3; H, 3.9; N, 3.0; S, 15.6. ^{1}H NMR ($CDCl_3$): δ 7.99−6.87 (m, 21H, $PPh_2 + H_a$, C_6H_4S); 6.72 (m, 1H, C_6H_4S, H_d); 6.35 (t, 2H, C_6H_4S, $H_b + H_c$); 3.65 (m, 8H, $-CH_2CH_3$); 3.51 (m, 1H, $P-CH_2-P$); 3.02 (m, 1H, $P-CH_2-P$); 1.2 (m, 12H, CH_2-CH_3). ^{31}P NMR (AB system): δ_A 23.18; δ_B 22.3; $J_{AB} = 72$ Hz. MS (LSIMS+; *m*/*z* (%)): 1000 (10) $[M]^+$; 852 (5) $[M - S_2CNEt_2]^+$. Data for **8** are as follows. Anal. Calcd for $C_{58}H_{50}N_2P_2S_5Pd_2$: C, 58.60; H, 4.35; N, 2.24; S, 12.82. Found: C, 58.5; H, 3.8; N, 2.29; S, 11.9. ^{1}H NMR ($CDCl_3$): δ 8.08−7.02 (m, 20H, *Ph*); 6.9 (m, $J_{H-H} = 6.3$ Hz, 1H, C_6H_4S, H_a); 6.74 (t, $J_{H-H} = 7.8$ Hz, 1H, C_6H_4S, H_b); 6.55 (t, $J_{H-H} = 8.1$ Hz, 1H, C_6H_4S, H_d); 6.37 (t, $J_{H-H} = 6.6$ Hz, 1H, C_6H_4S, H_c); 5.02 (d, $J_{H-H} = 9.9$ Hz, 1H, CH_2-Ph); 4.97 (d, $J_{H-H} = 9.9$ Hz, 1H, CH_2-Ph); 4.89 (d, $J_{H-H} = 6$ Hz, 1H, CH_2-Ph); 4.84 (d, $J_{H-H} = 6$ Hz, 1H, CH_2-Ph); 4.44 (d, $J_{H-H} = 15$ Hz, 2H, CH_2-Ph); 4.32 (d, $J_{H-H} = 15.3$ Hz, 1H, CH_2-Ph); 4.25 (d, $J_{H-H} = 15.3$ Hz, 1H, CH_2-Ph); 3.06 (t, $J_{P-H} = 11.4$ Hz, 2H, $P-CH_2-P$). ^{31}P NMR (AB system): δ_A 22.53; δ_B 20.3; $J_{AB} = 69.8$ Hz. MS (LSIMS+; *m*/*z* (%)): 1250 (5) $[M]^+$; 978 (6) $[M - S_2CNBz_2]^+$; 1141 (4) $[M - C_6H_4S]^+$; Data for **9** are as follows. Anal. Calcd for $C_{41}H_{42}N_2P_2S_5Pd_2$: C, 49.35; H, 4.24; N, 2.81; S, 16.06. Found: C, 49.5; H, 4.1; N, 2.5; S, 15.6. ^{1}H NMR (CD_2Cl_2): δ 8.03−6.95 (m, 20H, *Ph*); 6.68 (m, 1H, C_6H_4S, H_a); 6.6 (m, 1H, C_6H_4S, H_d); 6.41 (t, $J_{H-H} = 7$ Hz, 1H, C_6H_4S, H_c); 6.28 (t, $J_{H-H} = 7$ Hz, 1H, C_6H_4S, H_b); 3.64 (m, 8H, C_4H_8); 3.86 (m, 1H, $P-CH_2-P$); 3.16 (m, 1H, $P-CH_2-P$); 1.91 (m, 8H, C_4H_8). ^{31}P NMR (AB system): δ_A 23.13; δ_B 21.60; $J_{AB} = 62.8$ Hz; MS (LSIMS+; *m*/*z* (%)): 995 (7) $[M]^+$.

X-ray Structure Determination of $[Sn_2(\mu\text{-}C_6H_4S)_2(^tBu)_4]$ (1) and $[Pd_2(\mu\text{-}C_6H_4S)(\mu\text{-dppm})_2Cl_2]$ (3). A summary of the fundamental crystal and refinement data of the compounds **1** and **3** is given in Table 1. Crystals of **1** and **3** were mounted on a glass fiber on a Bruker-Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) with a nominal crystal to detector distance of 4.0 cm. A hemisphere of data was collected on the basis of three ω-scan runs (starting ω 28°) at values $\phi = 0$, 90, 180° with the detector at $2\theta = 28°$. At each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 35 s per frame. Space group assignments are based on systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using SHELX97[55] and the SHELXTL 5.1 software package. Hydrogen atoms were assigned to ideal positions and refined using a riding model. The diffraction frames were integrated using the SAINT[56] package and corrected for absorption with SADABS.[57]

Acknowledgment. We thank the Dirección General de Enseñanza Superior for financial support (Grant No. PB98-542), the University Simon Bolivar for a sabbatical leave (H.T.), and the Centro de Excelencia BRUKER-ICMA for supporting the X-ray facilities.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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