Synthesis and Reactivity of *Ortho*-Mercuriated and *Ortho*-Palladated Arylacetals and Cyclic and Acyclic Aryldithioacetals. New Examples of the Rearrangement of Acyclic Dithioacetal Aryl- to Dithioether Alkyl-Palladium Complexes[⊥]

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The arylmercurial [Hg{$C_6H_3(CHO)_2$-2,5}Cl] (**1**) reacts with $CH(OMe)_3$ or $HS(CH_2)_2SH$ to give [Hg{C_6H_3{$CH(OMe)_2$}$_2$-2,5}Cl] (**2**) or [Hg(Ar_a)Cl] [Ar_a = C_6H_3{$CH(SCH_2CH_2S)$}$_2$-2,5 (**3a**)], respectively. The mercurial **2** or **3a** reacts with $(NMe_4)_2[Pd_2Cl_6]$ and 2,2′-bipyridine (bpy) or with *trans*-[$PdCl_2(PPh_3)_2$] to give the aryl-palladium complex [Pd{C_6H_3{$CH(OMe)_2$}$_2$-2,5}Cl(bpy)] (**4**) or [Pd(κ^2-*C,S*-Ar_a)Cl(PPh_3)] (**5a***), respectively. The reaction of **1** with NaI_3 renders $IC_6H_3(CHO)_2$-2,5 (**6**), which reacts with $HS(CH_2)_2SH$ to give IAr_a (**7a**). Similarly, $IC_6H(OMe)_3$-2,3,4-(CHO)-6 (**8**) reacts with $HS(CH_2)_2SH$ or ToSH (To = C_6H_4Me-4) to give the corresponding dithioacetals IAr_b [Ar_b = $C_6H(OMe)_3$-2,3,4-{$CH(SCH_2CH_2S)$}-6 (**7b**)] or $IC_6H(OMe)_3$-2,3,4-$CH(STo)_2$-6 (**9**). The iodoarene **7a** or **7b** adds oxidatively to "Pd(dba)$_2$" (dba = dibenzylideneacetone) to give [Pd(κ^2-*C,S*-Ar)(μ-I)]$_2$ [Ar = Ar_a (**10a**), Ar_b (**10b**)], which, in turn, reacts (i) with 1 equiv of PPh_3 to give [Pd(κ^2-*C,S*-Ar)I(PPh_3)] [Ar = Ar_a (**5a**), Ar_b (**5b**)], (ii) with Tl(TfO) (TfO = CF_3SO_3) and PPh_3 (1:2:4 molar ratio) to give [Pd(κ^2-*C,S*-Ar_b)(PPh_3)$_2$]TfO (**11b**), or (iii) with 1 equiv of Tl(TfO) and bpy (1:2:2 molar ratio) to give [Pd(κ^2-*C,S*-Ar_b)(bpy)]TfO (**11b***). Complexes **10** react with 1 equiv of isonitriles to give, after a short period of reaction, the complexes [Pd(κ^2-*C,S*-Ar)I(CNR)] [Ar = Ar_a, R = Xy = 2,6-dimethylphenyl (**12a**), ^{t}Bu (**12a′**); Ar = Ar_b, R = ^{t}Bu (**12b′**)]. The iminoacyl complexes [Pd(κ^2-*C,S*-Im)(μ-I)]$_2$ [Im = Im_a (**13a**), Im_b (**13b**)] can be obtained by stirring a solution of **12a** for 5 days to give **13a** or by reacting **10b** with XyNC in 1:1 molar ratio during 22 h to give **13b**. Complexes **10** react with 2 equiv of isonitriles to give the iminoacyl complexes [Pd(κ^2-*C,S*-Im)I(CNR)] [Im = C(=NR)C_6H_3-{$CH(SCH_2CH_2S)$}$_2$-2,5, R = Xy, Im = Im_a (**14a**), R = ^{t}Bu, Im = $Im_{a'}$ (**14a′**); Im = C(=NR)-$C_6H(OMe)_3$-2,3,4-(SCH_2CH_2S)-6, R = Xy, Im = Im_b (**14b**), R = ^{t}Bu, Im = $Im_{b'}$ (**14b′**)]. Complexes **14a**,**b** react with **10a**,**b** in 2:1 molar ratio to give **13a**,**b**. Complexes **10a**,**b** react with XyNC and Tl(TfO) (1:4:1) to give the dimeric cations [Pd{(κ^2-*C,S*-Im)(CNXy)}$_2$(μ-I)]-TfO [R = Xy, Im = Im_a (**15a**), Im_b (**15b**)]. The compound [Pd{κ^2-*C,S*-Ar_c}(μ-I)]$_2$ (**16**) reacts (i) with PPh_3 and Tl(TfO) in 1:4:2 molar ratio to give [Pd^{II}(κ^2-*C,S*-Ar_c)(PPh_3)$_2$]TfO ↔ [Pd^0\{η^2-κ^3-*C,S,S*-*S*(To)=*C*HC_6H(STo)-2-$(OMe)_3$-3,4,5}(PPh_3)$_2$]TfO (**17**), (ii) with isonitriles in 1:2 or 1:4 molar ratio yielding complexes [Pd(κ^2-*C,S*-Ar_c)I(CNR)] [R = Xy (**18**), R = ^{t}Bu (**18′**)] or *trans*-[Pd(κ^1-*C*-Ar_c)I(CNR)$_2$] [R = Xy (**19**), R = ^{t}Bu (**19′**)], respectively, and (iii) with PPh_3 in 1:2 molar ratio yielding [Pd(κ^2-*C,S*-Ar_c)I(PPh_3)] (**20**). The iodoarene **9** reacts with Pd(dba)$_2$ (i) and PPh_3 (1:1:1 molar ratio) to give [Pd{κ^2-*C,S*-Ar_c}I(PPh_3)] [Ar_c = CH(STo)C_6H(STo)-2-$(OMe)_3$-3,4,5 (**20**)] and (ii) PPh_3 and Tl(TfO) (1:1:2:1 molar ratio) to give **17**. The crystal and molecular structures of **4**, **5a***, **14a**, and **14b** have been determined by X-ray diffraction studies.

Introduction

The interest in *ortho*-palladated complexes arises from their potential applications in catalytic[1−4] and stoichiometric[5−16] organic synthesis, for chiral recognition,[17] as chiral resolving agents,[18,19] as antitumorals,[20] or advanced materials.[21] *Ortho*-palladated complexes are also involved in interesting dendritic systems.[22] We have reported the synthesis of *ortho*-palladated complexes by transmetalation reactions, using arylmercurials, by oxidative additions of the corresponding haloarenes to palladium(0) species, or through *ortho*-palladation processes. The first method has allowed us to prepare aryl-palladium complexes bearing CHO,[23−25]

[⊥] Dedicated to Professor Helmut Werner on the occasion of his 70th birthday and in recognition of his leading role in organometallic chemistry.

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CH=NOH, CO_2H,[25] C(O)Me,[24] C(O)NH^{t}Bu,[15] CH_2OEt,[8] or NO_2[26] groups in *ortho*-position. By means of the oxidative addition method we have prepared complexes with the *ortho* substituents NH_2,[27−30] OH, OC(O)Me, OC(O)CH=CH_2[31] CH=CHR [R = H,[14] Ph, 2-pyridyl, Cl, CHO, C(O)Me][32] or CN.[14] We have also prepared *ortho*-palladated amines or imines by reacting them with palladium acetate.[25,33,34] Many of these complexes show interesting properties. Thus, some of them insert alkynes to give alkenyl-[8−11,13−15,32,33,35−37] or indenyl-palladium complexes,[32,36] or organic products such as indenols, indenones,[9,10,13,14] or spirocyclic compounds.[8,10−12,15] We have also studied reactions with isocyanides giving complexes resulting after mono- or tri-insertion[6,15,30,31,37−39] or organic products such as a ketenimine,[15] 2-substituted-aminoisoindolinium salts,[6] 2,3-dihydroisoindol-1-ones, benzamides, acetamides, or ac-

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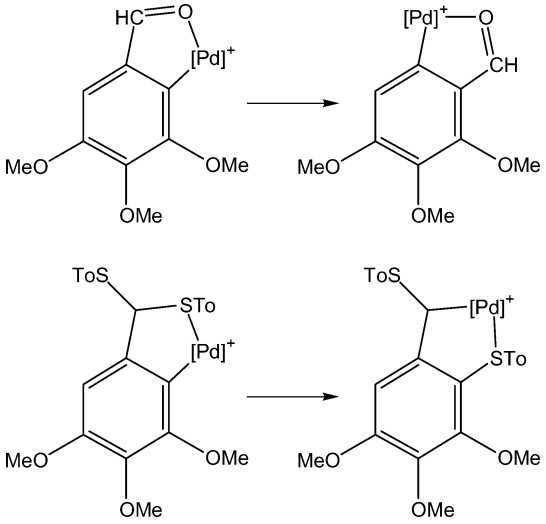
Chart 1



etamidic acids,[39] and with CO to give aroyl-palladium complexes,[28−31,37,39] 3-methylenephthalides and 3-ethoxy-3-methyl-3*H*-isobenzofuran-1-one[39] or, in the presence of O_2, palladium benzoate complexes.[28,29]

We have reported that certain 2,3,4-trimethoxy-6-formylphenylpalladium complexes undergo a rare rearrangement, involving a positional change between the formyl group and the palladium moiety with breaking and reforming of C−C and C−Pd bonds, to give the corresponding 3,4,5-trimethoxy-2-formylphenylpalladium isomers (Chart 1).[23,24,40] Similarly, when we prepared the first *ortho*-palladated acyclic dithioacetals, a new type of rearrangement involving the cleavage of alkyl−S and aryl−Pd bonds and formation of aryl−S and alkyl−Pd bonds was observed (Chart 1).[41] In the present work we describe new related results, some of which have been recently communicated.[42] In addition, we report the synthesis of the first *ortho*-palladated cyclic dithioacetal. We designed the synthesis of these complexes, prepared through transmetalation and oxidative addition reactions, to see if the same or similar rearrangents to that observed with the acyclic dithioacetals could be observed.

While many aryl S,C,S-pincer complexes have been reported,[2,4,40−43] a limited number of C−S *ortho*-palladated complexes are known.[3,7,16,41,44,45] Some of them are active catalysts for C−C coupling reactions.[3,16,45] We report here two families of C−S *ortho*-palladated complexes and also C−S iminoacyl- and alkyl-palladium complexes.

Experimental Section

The elemental analyses, conductivity measurements in acetone, and melting point determinations were carried as described previously.[46] The NMR spectra were measured at room temperature, unless otherwise stated. Chart 2 shows the notation used for the various organyl groups. The compounds "Pd(dba)$_2$"[47] ([Pd_2(dba)$_3$]·dba, dba = dibenzylideneacetone), [Hg{C_6H_3(CHO)$_2$-2,5}Cl] (**1**),[25] $IC_6H(OMe)_3$-2,3,4-CHO-6 (**8**),[48] $IC_6H(OMe)_3$-2,3,4-CH(STo)$_2$-6 (**9**),[41] and [Pd{κ^2-*C*,*S*-Ar_c}(μ-I)]$_2$ (**16**)[41] were prepared as reported previously. Unless otherwise stated, reactions were carried out without special precautions against moisture or light.

Synthesis of [Hg{C_6H_3}{CH(OMe)$_2$}$_2$-2,5}Cl] (2). The mercurial **1** (504 mg, 1.354 mmol) was reacted under nitrogen for 24 h at room temperature with $HC(OMe)_3$ (15 mL, degassed and saturated with nitrogen) and with 96% sulfuric acid (50 μL) in anhydrous methanol (20 mL). Saturated aqueous $NaHCO_3$ (50 mL) and Cl_2CH_2 (60 mL) were added, and the mixture was shaken. The organic phase was separated and washed twice with 25 mL of a saturated aqueous $NaHCO_3$. The separated organic phase was dried over $MgSO_4$ and filtered. The solvent was evaporated to dryness, the resulting pale yellow oil was dissolved in Et_2O (2 mL), and then, *n*-pentane (15 mL) and *n*-hexane (5 mL) were added. The solvent was evaporated and the residue triturated with *n*-pentane (3 mL). The solution was decanted and the residue triturated again with *n*-pentane (3 mL). This operation was repeated several times. The final residue was dried in vacuo to give a pale yellow solid. Yield: 415 mg, 66%. Mp: 61 °C. IR (cm^{-1}): ν(Hg−Cl) 345. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (m,

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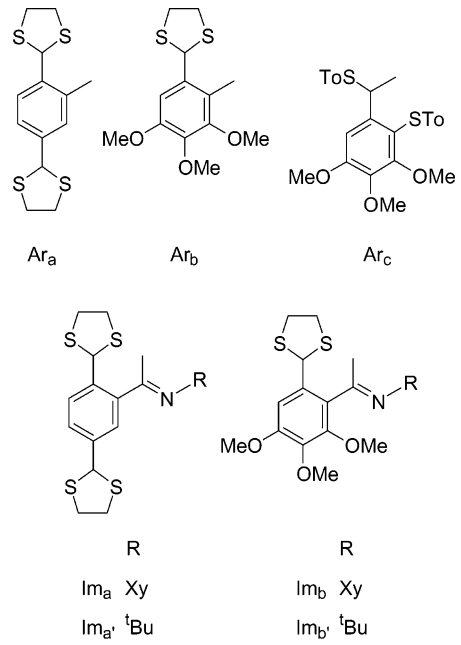
Table 1. Summary of X-ray Data for Compounds 4, 5a*, 14a, and 14b

	4	**5a***	**14a**·CH_2Cl_2	**14b**
formula	$C_{22}H_{25}ClN_2O_4Pd$	$C_{30}H_{28}ClPPdS_4$	$C_{31}H_{33}Cl_2IN_2PdS_4$	$C_{30}H_{33}INO_2O_3PdS_2$
cryst habit	pale yellow prism	yellow prism	yellow tablet	yellow tablet
a (Å)	9.2584(5)	9.5507(8)	12.1236(8)	18.4714(16)
b (Å)	9.9373(6)	10.4225(10)	19.9017(14)	17.5311(14)
c (Å)	13.2560(9)	15.9744(12)	14.5596(10)	18.5995(16)
α (deg)	84.966(5)	102.645(6)	90	90
β (deg)	82.327(5)	102.112(6)	100.062(3)	96.634(3)
γ (deg)	62.438(3)	102.782(8)	90	90
V (Å^3)	1071.04(11)	1456.3(2)	3458.9	5982.6
Z	2	2	4	8
T (K)	173	173	143	143
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$C2/c$
cryst size	0.62 × 0.34 × 0.32	0.58 × 0.56 × 0.42	0.46 × 0.22 × 0.14	0.19 × 0.13 × 0.08
μ (mm^{-1})	1.023	1.573	1.85	1.83
2*θ*(max)	50	50	56.6	60
no. of total/indep reflns	4944/3736	10 110/5055	65 083/8582	24 855/8711
R_{int}	0.0270	0.0114	0.061	0.065
$S(F^2)$	1.05	1.08	1.04	0.88
wR2 [all reflns]	0.0893	0.0605	0.0614	0.0524
R1 [$I>2\sigma(I)$]	0.0334	0.0228	0.0248	0.0298

Chart 2



H6, 1 H), 7.44 (d, H3 1 H, $^3J_{HH}$ = 9 Hz), 7.41 (dd, H4, $^3J_{HH}$ = 9 Hz, $^4J_{HH}$ = 2 Hz), 5.38 (s, C*H*(OMe)$_2$, 1 H), 5.34 (s, C*H*(OMe)$_2$, 1 H), 3.35 (s, 2 Me, 6 H), 3.33 (s, 2 Me, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.1 (quaternary C), 139.0 (quaternary C), 135.1 (CH), 128.3 (CH), 127.0 (CH), 103.7 (*C*H(OMe)$_2$), 102.6 (*C*H(OMe)$_2$), 53.5 (2 Me), 52.7 (2 Me). The signal corresponding to C−Hg was not observed. Anal. Calcd for $C_{12}H_{17}ClHgO_4$: C, 31.24; H, 3.71. Found: C, 31.26; H, 3.60.

Synthesis of [Hg(Ar$_a$)Cl] (3a). A solution of **2** (215 mg, 0.47 mmol) in anhydrous toluene (8 mL) was cooled to 0 °C under nitrogen. Then, HS(CH$_2$)$_2$SH (79 *μ*L, 0.94 mmol) and some crystals of *p*-toluenesulfonic acid were added. The mixture was stirred for 20 h, allowing it to reach room temperature slowly. In this way colorless **3a** precipitated. It was filtered, washed with pentane (10 mL), and air-dried. Yield: 174 mg, 72%. Mp: 195 °C (dec). IR (cm^{-1}): *ν*(Hg−Cl) 331. ^{1}H NMR (200 MHz, d_6-DMSO): *δ* 7.77 (d, H6, 1 H, $^4J_{HH}$ = 2 Hz), 7.41 (d, H3, 1 H, $^3J_{HH}$ = 8 Hz), 7.32 (dd, H4, 1 H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 5.87 (s, C*H*S$_2$, 1 H), 5.69 (s, C*H*S$_2$, 1 H), 3.7−3.3 (m, CH$_2$, 8 H). ^{13}C NMR (50 MHz, d_6-DMSO): *δ* 152.3 (quaternary C), 141.2 (quaternary C), 139.9 (quaternary C), 136.7 (CH), 129.9 (CH), 127.1 (CH), 59.0 (*C*HS$_2$), 54.7 (*C*HS$_2$), 39.8 (b, 4×CH$_2$). Anal. Calcd for $C_{12}H_{13}ClHgS_4$: C, 27.64; H, 2.51. Found: C, 27.76; H, 2.52.

Synthesis of [Pd{C$_6$H$_3${CH(OMe)$_2$}$_2$-2,5}Cl(bpy)] (4). The mercurial **2** (313 mg, 0.68 mmol), $(NMe_4)_2[Pd_2Cl_6]$ (240 mg, 0.42 mmol), and NMe_4Cl (120 mg, 1.1 mmol) were mixed under nitrogen in anhydrous acetone (30 mL), and the resulting mixture was stirred for 1 h at room temperature and for a further 4.5 h at 0 °C. The suspension was filtered over Celite into an acetone (5 mL) solution of 2,2′-bipyridine (131 mg, 0.84 mmol). From this moment it is not necessary to work under nitrogen. The resulting mixture was stirred for 45 min, the solvent evaporated to dryness, and the residue treated with Cl_2CH_2 (35 mL). The mixture was filtered over Celite and the corresponding solution concentrated (ca. 2 mL). Then Et_2O (30 mL) and *n*-hexane (50 mL) were added, causing the precipitation of a yellow solid, which was filtered, washed with *n*-hexane, and air-dried to give **4** as a yellow solid. Yield: 287 mg, 81%. Mp: 195 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 9.29 (m, 1 H, bpy), 8.1−7.1 (m, 10 H), 6.36 (s, C*H*(OMe)$_2$, 1 H), 5.37 (s, C*H*(OMe)$_2$, 1 H), 3.43 (s, MeO, 3 H), 3.34 (s, MeO, 3 H), 3.33 (s, MeO, 3 H), 3.16 (s, MeO, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 155.9 (quaternary C), 153.4 (quaternary C), 152.5 (CH), 150.5 (quaternary C), 149.6 (CH), 141.8 (quaternary C), 139.0 (CH), 138.4 (CH), 136.5 (quaternary C), 132.6 (CH), 126.4 (CH), 126.2 (CH), 125.4 (CH), 122.1 (CH), 121.7 (CH), 121.2 (CH), 106.7 (CH(OMe)$_2$), 103.6 (CH(OMe)$_2$), 54.9 (MeO), 53.4 (MeO), 52.9 (MeO), 52.8 (MeO). Anal. Calcd for $C_{22}H_{25}N_2ClO_4Pd$: C, 50.50; H, 4.82, N, 5.35. Found: C, 50.68; H, 4.66, N, 5.29. Single crystals were grown by slow diffusion of Et_2O into a solution of **4** in acetone.

Synthesis of [Pd(*κ*^{2}-*C*,*S*-Ar$_a$)Cl(PPh$_3$)] (5a*). The mercurial **3a** (210 mg, 0.40 mmol), $[PdCl_2(PPh_3)_2]$ (236 mg, 0.34 mmol), and NMe_4Cl (76 mg, 0.69 mmol) were added to a solvent system consisting of anhydrous acetone (30 mL) and 1,4-dioxane (10 mL). The resulting mixture was heated at 76 °C under nitrogen for 7 h. The mixture was cooled to room temperature and filtered over Celite. The solvent was evaporated to dryness, and the residue was treated with Cl_2CH_2 (25 mL) and filtered over Celite. The filtrate was concentrated (to ca. 3 mL), affording a yellow precipitate, which was filtered, washed with Et_2O (2 × 2 mL), and air-dried, giving impure $[PdCl_2(PPh_3)_2]$ (48 mg). A mixture of Et_2O (15 mL), *n*-pentane (5 mL), and *n*-hexane (2 mL) was added to the mother liquor, and the resulting mixture was slightly concentrated, causing the precipitation of a solid, which was filtered and chromatographed on Al_2O_3 using an acetone/CH_2Cl_2 mixture to give yellow **5a***, containing minute amounts of the mercurial **3a** shown in ^{1}H NMR spectrum. This could explain the slightly low C analysis found (relative error, −1.26%). Yield: 148 mg, 64%. Mp: 214 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, room temperature): *δ* 7.76−7.69 (m, 6 H), 7.46−7.33 (m, 9 H), 7.06

(d, H3, 1 H, $^3J_{HH}$ = 8 Hz), 6.96 (dd, H4, 1 H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 6.64 (d, H6, 1 H, $^4J_{HH}$ = 2 Hz), 5.79 (s, C*H*S_2, 1 H), 4.82 (s, C*H*S_2, 1 H), 4.5−4.35 (m, CH_2, 2 H), 3.55−3.35 (m, CH_2, 2 H), 3.03 (m, 2×CH_2, 4 H). At −55 °C: 7.78−7.71 (m, 6 H), 7.56−7.38 (m, 9 H), 7.13 (d, H3, 1 H, $^3J_{HH}$ = 8 Hz), 7.00 (apparent d, H4, 1 H, $^3J_{HH}$ = 8 Hz), 6.62 (d, H6, 1 H, $^4J_{HH}$ = 2 Hz), 5.83 (d, C*H*S_2, 1 H, $^4J_{PH}$ = 4.5 Hz), 4.81 (s, C*H*S_2, 1 H), 4.5−4.4 (m, CH_2, 2 H), 3.55−3.45 (m, CH_2, 2 H), 3.07 (m, 2×CH_2, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.9 (quaternary C), 150.0 (quaternary C), 139.5 (quaternary C), 138.9 (CH), 135.2 (d, *o*-CH PPh_3, $^2J_{PC}$ = 11.5 Hz), 130.7 (d, *p*-CH PPh_3, $^4J_{PC}$ = 2.5 Hz), 130.5 (d, *i*-C PPh_3, $^1J_{PC}$ = 48 Hz), 128.2 (d, *m*-CH PPh_3, $^3J_{PC}$ =11 Hz), 124.5 (CH), 123.7 (CH), 65.3 (*C*HS_2), 55.4 (*C*HS_2), 43.7 (2xCH_2), 40.0 (2×CH_2). ^{31}P NMR (121 MHz, $CDCl_3$, room temperature): δ 36.4 (vb s, $\omega_{1/2}$ = 55 Hz, PPh_3). At −55 °C: 37.7 (s, PPh_3). Anal. Calcd for $C_{30}H_{28}ClPPdS_4$: C, 52.25; H, 4.09. Found: C, 51.60; H, 4.19. Single crystals were grown by slow diffusion of Et_2O into a solution of **5a*** in Cl_2CH_2.

Synthesis of [Pd(κ^2-*C*,*S*-Ar$_a$)I(PPh_3)] (5a). Method A. PPh_3 (51 mg, 0.19 mmol) was added to a suspension of **10a** (100 mg, 0.10 mmol) in Cl_2CH_2 (20 mL). After stirring for 15 min the resulting mixture was filtered over Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (7 mL) was added, causing the precipitation of a solid, which was filtered, washed with Et_2O (3 × 2 mL), and air-dried to give yellow **5a**. Yield: 132 mg, 88%.

Method B. The iodoarene **7a** (150 mg, 0.36 mmol) was added to a solution of "Pd(dba)$_2$" (167 mg, 0.30 mmol) and PPh_3 (95 mg, 0.36 mmol) in toluene (20 mL) under nitrogen, and the mixture was stirred for 23 h. The solvent was removed in vacuo. From this moment it is not necessary to work under nitrogen. The residue was extracted with Cl_2CH_2 (30 mL) and this extract filtered over Celite. The solution was concentrated (ca. 1 mL), and addition of Et_2O (8 mL) caused the precipitation of a solid, which was filtered, washed with Et_2O (3 × 2 mL), and air-dried to give yellow **5a**. Yield: 145 mg, 64%. Mp: 180 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.9−7.2 (m, PPh_3, 15 H), 7.10 (d, H3, 1 H, $^3J_{HH}$ = 8 Hz), 6.96 (dd, H4, 1 H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz), 6.64 (b s, H6, 1 H), 5.87 (s, C*H*S_2, 1 H), 4.85 (s, C*H*S_2, 1 H), 4.6−4.4 (m, CH_2, 2 H), 3.6−3.4 (m, CH_2, 2 H), 3.02 (s, 2×CH_2, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.8 (quaternary C), 149.1 (quaternary C), 138.7 (CH), 138.5 (quaternary C), 135.3 (d, *o*-CH PPh_3, $^2J_{PC}$ = 11.6 Hz), 131.8 (d, *i*-C PPh_3, $^1J_{PC}$ = 49 Hz), 130.6 (2×CH), 128.1 (d, *m*-CH PPh_3, $^3J_{PC}$ = 11 Hz), 123.9 (d, *p*-CH PPh_3, $^4J_{PC}$ = 9 Hz), 67.1 (*C*HS_2), 55.4 (*C*HS_2), 44.5 (CH_2), 39.8 (3×CH_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ 15.80 (PPh_3). Anal. Calcd for $C_{30}H_{28}IPPdS_4$: C, 46.13; H, 3.62; S, 16.42. Found: C, 46.10; H, 3.24; S, 16.00.

Synthesis of [Pd(κ^2-*C*,*S*-Ar$_b$)I(PPh_3)] (5b). Method A. Yellow **5b** was prepared as for **5a** from **10b** (100 mg, 0.10 mmol) and PPh_3 (52 mg, 0.20 mmol). Yield: 135 mg, 89%.

Method B. As described for **5a** from "Pd(dba)$_2$" (130 mg, 0.23 mmol), **5b** was prepared from PPh_3 (59 mg, 0.23 mmol) and the iodoarene **7b** (100 mg, 0.25 mmol). Yield: 92 mg, 53%. Mp: 126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2−7.0 (m, PPh_3, 15 H), 6.61 (s, C_6H, 1 H), 5.92 (s, C*H*S_2, 1 H), 4.4 (br m, CH_2, 2 H), 3.6−3.2 (m, CH_2, 2 H), 3.75 (s, MeO, 3 H), 3.40 (s, MeO, 3 H), 2.98 (s, MeO, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9 (quaternary C), 151.2 (quaternary C), 145.4 (quaternary C), 141.2 (quaternary C), 140.8 (quaternary C), 134.6 (b s, *m*-CH PPh_3), 129.9 (*p*-CH PPh_3), 127.4 (d, *o*-CH PPh_3, $^2J_{PC}$ = 10.5 Hz), 104.7 (CH5), 69.3 (CHS_2), 60.9 (MeO), 60.2 (MeO), 56.3 (MeO), 43.9 (vb s, CH_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ 29.52 (PPh_3). Anal. Calcd for $C_{30}H_{30}IO_3PPdS_2$: C, 46.98; H, 3.95; S, 8.36. Found: C, 46.67; H, 3.79; S, 8.12.

Synthesis of IC$_6$H$_3$(CHO)$_2$-2,5 (6). An excess of NaI was added to a suspension of I_2 (822 mg, 3.24 mmol) in water (225 mL) with continuous stirring until the dissolution of the I_2. The mercurial **1** (1.20 g, 3.25 mmol) was added, and the mixture was stirred for 3 days with protection against light. The resulting suspension was filtered, and the solid was washed with water and air-dried, giving a yellow solid, which was treated with Et_2O (60 mL). The resulting mixture was filtered over Celite, and the solvent was evaporated to dryness. The residue was triturated with *n*-pentane (4 mL), filtered, washed with *n*-pentane (2 mL), and air-dried to give pale yellow **6**. Yield: 585 mg, 69%. IR (cm^{-1}): ν(C=O) 1695 vs, b. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.15 (s, CHO, 1 H), 10.04 (s, CHO, 1 H), 8.44 (s, H6, 1 H), 8.02 (d, H3 or H4, 1 H, $^3J_{HH}$ = 8 Hz), 7.95 (d, H3 or H4, 1 H, $^3J_{HH}$ = 8 Hz). FAB-MS: *m*/*z*, 260 (M^+, 39%).

Synthesis of IAr$_a$ (7a). HS$(CH_2)_2$SH (81 μL, 0.96 mmol), a small crystal of *p*-toluenesulfonic acid, and anhydrous $MgSO_4$ were added to a solution of **6** (125 mg, 0.48 mmol) in 1,2-dichloroethane (15 mL). The resulting suspension was refluxed for 8.5 h and then filtered over $MgSO_4$. The resulting pale yellow solution was concentrated (ca. 1 mL), and cold *n*-pentane (3 mL) was added, causing the precipitation of a colorless solid, which was filtered, washed with cold *n*-pentane (2 mL), and air-dried to give **7a**. Yield: 140 mg, 71%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, H6, 1 H, $^4J_{HH}$ = 2 Hz), 7.75 (d, H3, 1 H, $^3J_{HH}$ = 8 Hz), 7.48 (dd, H4, 1 H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 5.87 (s, C*H*S_2, 1 H), 5.51 (s, C*H*S_2, 1 H), 3.8−3.2 (m, CH_2, 8 H). FAB-MS: *m*/*z*, 413 (M^+, 22%).

Synthesis of IAr$_b$ (7b). It was similarly prepared from **8** (400 mg, 0.12 mmol) and HS$(CH_2)_2$SH (104 μL, 0.12 mmol) during 18 h to give colorless **7b**. Yield: 271 mg, 56%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.34 (s, C_6H, 1 H), 5.99 (s, C*H*S_2, 1 H), 3.89 (s, OMe, 3 H), 3.87 (b s, 2×OMe, 6 H), 3.6−3.3 (m, CH_2, 4 H). FAB-MS: *m*/*z*, 398 (M^+, 100%), 271 (M^+ − I, 41%).

Synthesis of [Pd(κ^2-*C*,*S*-Ar$_a$)(μ-I)]$_2$ (10a). The iodoarene **7a** (557 mg, 1.35 mmol) was added to a solution of "Pd(dba)$_2$" ([Pd_2(dba)$_3$]·dba, dba = dibenzylideneacetone) (702 mg, 1.22 mmol) in toluene (22 mL) under nitrogen. The mixture was stirred under nitrogen for 1.5 h and the solvent removed in vacuo. From this moment it is not necessary to work under nitrogen. The residue was triturated with Cl_2CH_2 (5 mL), filtered, washed with Cl_2CH_2 (5 mL) and Et_2O (3 × 2 mL), air-dried, heated in an oven at 70 °C, and treated in a desiccator under P_2O_5 to give **10a** as an orange solid. Yield: 527 mg, 84%. Mp: 205 °C (dec). Anal. Calcd for $C_{24}H_{26}I_2Pd_2S_4$: C, 27.78; H, 2.53; S, 24.72. Found: C, 27.32; H, 2.32; S, 24.69. This complex is not soluble enough for NMR measurements.

Synthesis of [Pd(κ^2-*C*,*S*-Ar$_b$)(μ-I)]$_2$ (10b). Complex **10b** was prepared as for **10a** from **7b** (250 mg, 0.63 mmol) and "Pd(dba)$_2$" (327 mg, 0.57 mmol) in toluene (18 mL). Reaction time was 24 h. The residue after evaporation of the solvent was recrystallized from Cl_2CH_2/Et_2O, giving a solid, which was filtered, washed with Et_2O (3 × 2 mL), and air-dried to give orange **10b**. Yield: 201 mg, 77%. Mp: 170 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.58 (s, C_6H, 1 H), 5.8−5.5 (m, CH_2, 1 H), 5.69 (s, C*H*S_2, 1 H), 5.3−5.1 (m, CH_2, 1 H), 4.0−3.5 (m, CH_2, 2 H), 3.85 (s, MeO, 3 H), 3.68 (s, MeO, 3 H), 3.67 (s, MeO, 3 H). ^{13}C NMR: Not soluble enough. Anal. Calcd for $C_{24}H_{30}I_2O_6Pd_2S_4$: C, 28.56; H, 3.00; S, 12.70. Found: C, 28.93; H, 3.01; S, 12.67.

Synthesis of [Pd(κ^2-*C*,*S*-Ar$_b$)(PPh_3)$_2$]TfO (11b). Method A. To a suspension of complex **10b** (100 mg, 0.10 mmol) in Cl_2CH_2 (7 mL) was added Tl(TfO) (70 mg, 0.20 mmol). After 30 min stirring PPh_3 (104 mg, 0.40 mmol) was added and the mixture stirred for 6 h. The yellow suspension was filtered over Celite, giving a yellow solution, which was concentrated (ca. 1 mL). Addition of Et_2O (8 mL) caused the precipitacion of a solid, which was filtered, washed with Et_2O (2 × 3 mL), and air-dried to give yellow **11b**. Yield: 184 mg, 88%.

Method B. "Pd(dba)$_2$" (130 mg, 0.23 mmol) and PPh_3 (118 mg, 0.45 mmol) were mixed under nitrogen in toluene (20 mL) and stirred for 5 min. Then Tl(TfO) (80 mg, 0.23 mmol) and **7b** (100 mg, 0.25 mmol) were added, and the resulting suspension was stirred for 24 h. After this time it is not

necessary to work under nitrogen. The solvent was evaporated to dryness in vacuo, leaving a residue that was extracted with Cl_2CH_2 (30 mL), the extract then being filtered over Celite. The resulting solution was concentrated (ca. 1 mL), and Et_2O (10 mL) was added, precipitating a solid, which was filtered, washed with Et_2O (2 × 3 mL), air-dried, and heated in an oven at 70 °C for 10 min to give **11b**. Yield: 152 mg, 64%. Mp: 126 °C. $\Lambda_M = 120\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.8−7.0 (m, PPh_3, 30 H), 6.68 (d, C_6H, 1 H, $^5J_{PH} = 3.5$ Hz), 6.26 (s, C*H*S_2, 1 H), 4.2−2.2 (br m, CH_2, 4H). 3.75 (s, MeO, 3 H), 3.70 (s, MeO, 3 H), 3.09 (s, MeO, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.8 (d, *o*-CH PPh_3, $^2J_{PC} = 11.5$ Hz), 133.6 (d, *o*-CH PPh_3, $^2J_{PC} = 14$ Hz), 131.2 (*p*-CH PPh_3), 130.6 (*p*-CH PPh_3), 128.9 (d, *m*-CH PPh_3, $^3J_{PC} = 10$ Hz), 128.2 (d, *m*-CH PPh_3, $^3J_{PC} = 10.5$ Hz), 106.8 (CH C_6H), 69.9 (*C*HS_2), 60.9 (MeO), 60.2 (MeO), 56.2 (MeO), 42.7 (b, CH_2), 37.3 (b, CH_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ 27.84 (d, $^2J_{PP} = 38$ Hz), 10.72 (d, $^2J_{PP} = 38$ Hz), *cis*-$(PPh_3)_2$. Anal. Calcd for $C_{49}H_{45}F_3O_6P_2PdS_3$: C, 55.96; H, 4.32; S, 9.15. Found: C, 55.53; H, 4.10; S, 9.03.

Synthesis of [Pd(κ^2-*C,S*-Ar_b)(bpy)]TfO (11b*). Method A. Yellow **11b*** was prepared as for **11b** from **10b** (100 mg, 0.10 mmol), bpy (2,2′-bipyridine) (31 mg, 0.20 mmol), and Tl(TfO) (70 mg, 0.20 mmol). Yield: 110 mg, 81%.

Method B. **11b*** was prepared as described for **11b** from "$Pd(dba)_2$" (195 mg, 0.34 mmol), bpy (53 mg, 0.34 mmol), **7b** (150 mg, 0.38 mmol), and Tl(TfO) (120 mg, 0.34 mmol). Yield: 165 mg, 71%. Mp: 166 °C. $\Lambda_M = 127\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^1H NMR (300 MHz, $CDCl_3$): δ 8.71, 8.62, 8.51−8.42, 8.26−8.16, 7.86, 7.5−7.4 (m, bpy, 8 H), 6.68 (s, C_6H, 1 H), 5.97 (s, C*H*S_2, 1 H), 4.2−3.2 (br m, CH_2, 4H). 3.90 (s, MeO, 3 H), 3.87 (s, MeO, 3 H), 3.85 (s, MeO, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.8 (quaternary C), 155.7 (quaternary C), 154.4 (quaternary C), 154.1 (CH bpy), 152.4 (quaternary C), 151.7 (CH bpy), 142.2 (quaternary C), 141.0 (CH bpy), 140.7 (CH bpy), 133.2 (quaternary C), 128.4 (CH bpy), 126.0 (CH bpy), 123.8 (CH bpy), 123.6 (CH bpy), 123.0 (quaternary C), 105.5 (CH C_6H), 68.6 (b *C*HS_2), 63.0 (MeO), 61.1 (MeO), 56.2 (MeO), 41.7 (vb 2×CH_2). Anal. Calcd for $C_{23}H_{23}F_3N_2O_6PdS_3$: C, 40.44; H, 3.40; N, 4.10; S, 14.08. Found: C, 40.53; H, 3.27; N, 4.29; S, 14.08.

Synthesis of [Pd(κ^2-*C,S*-Ar_a)I(CNXy)] (12a). XyNC (23 mg, 0.18 mmol) was added to a suspension of **10a** (100 mg, 0.10 mmol) in Cl_2CH_2 (20 mL). After 10 min the mixture was filtered over Celite, the filtrate was concentrated (ca. 1 mL), and Et_2O (10 mL) was added, causing the precipitation of a solid that was filtered, washed with Et_2O (3 × 3 mL), air-dried, and heated in an oven at 70 °C for 2 h to give **12a** as a yellow solid. Yield: 78 mg, 67%. Mp: 146 °C (dec). IR (cm^{-1}): ν(C≡N) 2182. ^1H NMR (200 MHz, $CDCl_3$): δ 7.63 (d, H6, 1 H, $^4J_{HH} = 1.5$ Hz), 7.35−7.0 (m, C_6H_3 and Xy, 5 H), 5.91 (s, C*H*S_2, 1 H), 5.53 (s, C*H*S_2, 1 H), 4.26 (br m, CH_2, 2 H), 3.6−3.2 (m, 3×CH_2, 6 H), 2.61 (s, Me, 6 H). ^{13}C NMR: The compound decomposes during the experiment. Anal. Calcd for $C_{21}H_{22}INPdS_4$: C, 38.80; H, 3.42; N, 2.16; S, 19.73. Found: C, 38.40; H, 3.36; N, 2.36; S, 19.61.

Synthesis of [Pd(κ^2-*C,S*-Ar_a)I(CN^{t}Bu)] (12a′). Yellow **12a′** was prepared as for **12a** from **10a** (105 mg, 0.10 mmol) and ^{t}BuNC (21.5 μL, 0.19 mmol). Yield: 61 mg, 53%. Mp: 138 °C (dec). IR (cm^{-1}): ν(C≡N) 2214. ^1H NMR (200 MHz, $CDCl_3$): δ 7.56 (d, H6, 1 H, $^4J_{HH} = 1.8$ Hz), 7.23 (dd, H4, 1 H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.8$ Hz), 7.05 (d, H3, 1 H, $^3J_{HH} = 7.8$ Hz), 5.88 (s, C*H*S_2, 1 H), 5.57 (s, C*H*S_2, 1 H), 4.22 (br m, CH_2, 2 H), 3.6−3.2 (m, 3×CH_2, 6 H), 1.65 (s, ^{t}Bu, 9 H). ^{13}C NMR (75 MHz. $CDCl_3$): δ 153.4 (quaternary C), 151.5 (quaternary C), 138.6 (CH), 138.2 (quaternary C), 125.4 (CH), 124.7 (CH), 65.6 (*C*HS_2), 56.9 (*C*HS_2), 40.1 (4×CH_2), 43.8 (quaternary C ^{t}Bu), 30.1 (^{t}Bu). Anal. Calcd for $C_{17}H_{22}INPdS_4$: C, 33.92; H, 3.69; N, 2.33; S, 21.30. Found: C, 33.89; H, 3.70; N, 2.64; S, 21.45.

Synthesis of [Pd(κ^2-*C,S*-Ar_b)I(CN^{t}Bu)] (12b′). ^{t}BuNC (22 μL, 0.20 mmol) was added to a suspension of **10b** (103 mg, 0.10 mmol) in Cl_2CH_2 (15 mL) and the mixture stirred for 2.5 h. The mixture was filtered over Celite, the filtrate was concentrated (ca. 1 mL), and cold Et_2O (7 mL) was added, causing the precipitation of a solid, which was filtered, washed with cold Et_2O (3 × 3 mL), air-dried, and heated in an oven at 70 °C for 2 h to give **12b′** as a yellow solid. Yield: 80 mg, 69%. Mp: 114 °C (dec). IR (cm^{-1}): ν(C≡N) 2210. ^1H NMR (300 MHz, $CDCl_3$): δ 6.61 (s, C_6H, 1 H), 5.93 (s, C*H*S_2, 1 H), 4.4 (br m, CH_2, 2 H), 3.85 (MeO), 3.81 (MeO), 3.80 (MeO), 3.6−3.4 (m, CH_2, 2 H), 1.57 (s, ^{t}Bu, 9 H). ^{13}C NMR (50 MHz. $CDCl_3$): δ 156.3 (quaternary C), 151.8 (quaternary C), 145.1 (quaternary C), 141.5 (quaternary C), 140.2 (quaternary C), 107.3 (quaternary C), 104.8 (CH, C_6H), 67.4 (*C*HS_2), 61.6 (MeO), 60.8 (MeO), 56.1 (MeO), 44.2 (b, 2×CH_2), 40.4 (quaternary C ^{t}Bu), 29.8 (^{t}Bu). Anal. Calcd for $C_{17}H_{24}INO_3PdS_4$: C, 34.73; H, 4.12; N, 2.38; S, 10.91. Found: C, 34.59; H, 4.07; N, 2.30; S, 10.75.

Synthesis of [Pd(κ^2-*C,S*-Im_a)(μ-I)]$_2$ (13a). Method A. A solution of **12a** (45 mg, 0.07 mmol) in Cl_2CH_2 was stirred for 74 h. The resulting suspension was concentrated (ca. 1 mL) and Et_2O (6 mL) added. The suspension was filtered, and the solid washed with Et_2O (2 × 3 mL), air-dried, and heated in an oven at 65 °C for 20 min to give **13a** as a yellow solid. Yield: 31 mg, 71%.

Method B. Complex **10a** (50 mg, 0.05 mmol) was added to a solution of **14a** (see below) (75 mg, 0.10 mmol) in Cl_2CH_2 (10 mL). The resulting suspension was stirred for 5 days. The suspension was concentrated (ca. 1 mL) and Et_2O (6 mL) added in order to complete the precipitation. The solid was filtered, washed with Et_2O (2 × 3 mL), air-dried, and heated in an oven at 65 °C for 20 min to give **13a**. Yield: 79 mg, 63%. Mp: 165 (dec). IR (cm^{-1}): ν(C=N) 1632. Not soluble enough for NMR measurements. Anal. Calcd for $C_{21}H_{22}INPdS_4$: C, 38.80; H, 3.42; N, 2.16; S, 19.73. Found: C, 37.18; H, 3.29; N, 2.04; S, 20.38. The insolubility of **13a** prevented further purification.

Synthesis of [Pd(κ^2-*C,S*-Im_b)(μ-I)]$_2$ (13b). Method A. XyNC (23 mg, 0.18 mmol) was added to a solution of **10b** (90 mg, 0.09 mmol) in Cl_2CH_2 (20 mL). The mixture was stirred for 22 h. A yellow solid precipitated during this time. It was filtered, washed with Cl_2CH_2 (2 × 3 mL), air-dried, heated in an oven at 70 °C for 14 h, and treated in a desiccator with P_2O_5 for 2 days to give **13b** as a yellow solid. Yield: 89 mg, 79%.

Method B. Complex **10b** (75 mg, 0.07 mmol) was added to a solution of **14b** (see below) (114 mg, 0.15 mmol) in Cl_2CH_2 (15 mL). The mixture was stirred for 4 h. The resulting suspension was concentrated (ca. 1 mL) and Et_2O (6 mL) added in order to complete the precipitation. The solid was filtered, washed with Et_2O (2 × 3 mL), and air-dried to give **13b**. Yield: 152 mg, 80%. Mp: 170 (dec). IR (cm^{-1}): ν(C=N) 1666, 1644. Not soluble enough for NMR measurements. Anal. Calcd for $C_{42}H_{48}I_2N_2O_6Pd_2S_4$: C, 39.66; H, 3.81; N, 2.20; S, 10.08. Found: C, 39.49; H, 3.82; N, 2.29; S, 9.96.

Synthesis of [Pd(κ^2-*C,S*-Im_a)I(CNXy)] (14a). XyNC (50 mg, 0.38 mmol) was added to a suspension of **10a** (100 mg, 0.10 mmol) in Cl_2CH_2 (15 mL), and the resulting solution was stirred for 5 h and then filtered over Celite. The filtrate was concentrated (ca. 1 mL), Et_2O (10 mL) was added, and the resulting suspension was filtered. The solid was washed with Et_2O (2 × 3 mL), air-dried, and heated in an oven at 70 °C for 2 h to give **14a** as a yellow solid. Yield: 123 mg, 82%. Mp: 190 °C (dec). IR (cm^{-1}): ν(C≡N) 2182, ν(C=N) 1632. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (m, 1 H), 7.6−7.5 (m, 2 H), 7.21 (t, *p*-H Xy, 1 H, $^3J_{HH} = 7$ Hz), 7.1−7.0 (m, 2 H), 6.88 (b s, 3 H), 5.69 (s, C*H*S_2, 1 H), 5.21 (s, C*H*S_2, 1 H), 4.0−3.2 (several br m, CH_2, 8 H), 2.30 (b s, 2×Me, 6 H), 2.20 (s, 2×Me, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.5 (C=N), 149.7 (quaternary C), 142.3 (quaternary C), 141.1 (quaternary C), 140.4 (quaternary C), 135.2 (quaternary C), 132.5 (quaternary C), 129.7 (CH), 129.4 (CH), 128.1 (CH), 127.8 (CH), 126.9 (CH), 126.8 (quaternary C), 125.7 (CH), 123.8 (CH), 55.4 (*C*HS_2), 50.9 (*C*HS_2), 40.1 (4×CH_2), 19.2 (Me), 18.8 (Me). Anal. Calcd for $C_{30}H_{31}IN_2PdS_4$: C, 46.12; H, 4.01; N, 3.59; S, 16.42. Found: C, 46.43;

H, 4.14; N, 3.91; S, 16.48. Single crystals were grown by slow diffusion of *n*-hexane into a solution of **14a** in Cl_2CH_2.

Synthesis of [Pd(κ^2-*C,S*-Im$_{a'}$)I(CN^{t}Bu)] (14a′). This was prepared as for **14a** from **10a** (100 mg, 0.10 mmol) and ^{t}BuNC (43 μL, 0.38 mmol). The product was recrystallized from Cl_2CH_2/Et_2O and heated in an oven at 70 °C for 1 h to give **14a′** as a yellow solid. Yield: 88 mg, 67%. Mp: 156 °C (dec). IR (cm^{-1}): ν(C≡N) 2196, ν(C═N) 1666. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.80 (d, H3 or H4, 1 H, $^3J_{HH}$ = 8 Hz), 7.40 (d, H4 or H3, 1 H, $^3J_{HH}$ = 8 Hz), 7.06 (s, H6, 1 H), 5.61 (s, C*H*S$_2$, 1 H), 4.06 (s, C*H*S$_2$, 1 H), 4.2−3.9 (m, CH_2, 1 H), 3.9−3.6 (m, CH_2, 1 H), 3.6−3.2 (m, 3×CH_2, 6 H), 1.63 (s, ^{t}Bu, 9 H), 1.54 (s, ^{t}Bu, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2 (C═N), 140.9 (quaternary C), 134.1 (quaternary C), 130.5 (quaternary C), 127.8 (CH), 125.5 (CH), 122.0 (CH), 58.1 (quaternary C ^{t}Bu), 55.8 (*C*HS$_2$), 51.5 (*C*HS$_2$), 45.3 (CH_2), 40.1 (2×CH_2), 35.1 (CH_2), 31.4 (^{t}Bu), 29.9 (^{t}Bu). Anal. Calcd for $C_{22}H_{31}IN_2PdS_4$: C, 38.57; H, 4.57; N, 4.09; S, 18.72. Found: C, 38.79; H, 4.66; N, 4.17; S, 18.47.

Synthesis of [Pd(κ^2-*C,S*-Im$_b$)I(CNXy)] (14b). XyNC (78 mg, 0.59 mmol) was added to a solution of **10b** (150 mg, 0.15 mmol) in Cl_2CH_2 (15 mL). The resulting solution was stirred for 4.5 h and concentrated to ca. 1 mL, Et_2O (10 mL) was added, and the resulting suspension was cooled in an ice bath. The cold suspension was filtered and the solid washed with Et_2O (2 × 3 mL), air-dried, heated in an oven at 70 °C for 8 h, and treated in a desiccator with P_2O_5 for 3 days to give **14b** as a yellow solid. Yield: 194 mg, 85%. Mp: 182 °C (dec). IR (cm^{-1}): ν(C≡N) 2170, ν(C═N) 1660. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4−6.7 (several m, 7 H), 5.17 (s, C*H*S$_2$, 1 H), 4.3−4.1 (br m, CH_2, 1 H), 4.1−3.9 (br m, CH_2, 1 H), 4.02 (s, MeO, 3 H), 3.96 (s, MeO, 3 H), 3.95 (s, MeO, 3 H), 3.6−3.2 (m, CH_2, 2 H), 2.26 (s, 4×Me, 12 H). At −60 °C: 7.38 (s, 1 H), 7.34−7.24 (m, 2 H), 7.22−7.08 (m, 2 H), 6.98 (t, 1 H, $^3J_{HH}$ = 7.5 Hz), 6.73 (d, 1 H, $^3J_{HH}$ = 7.5 Hz), 5.18 (s, C*H*S$_2$, 1 H), 4.3−4.2 (m, CH_2, 1 H), 4.02 (s, MeO, 3 H), 3.99 (s, 2×MeO, 6 H), 3.5−3.4 (m, CH_2, 2 H), 3.3−3.2 (m, CH_2, 1 H), 2.43 (s, Me, Xy, 3 H), 2.26 (s, 2×Me, Xy, 6 H), 2.08 (s, Me Xy, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.0 (C═N), 151.7 (quaternary C), 150.1 (quaternary C), 148.5 (quaternary C), 142.1 (quaternary C), 135.4 (quaternary C), 130.1 (quaternary C), 129.6 (CH), 128.2 (quaternary C), 127.9 (CH), 126.2 (quaternary C), 123.7 (CH), 108.9 (CH, C_6H), 61.2 (MeO or *C*HS$_2$), 60.8 (MeO or *C*HS$_2$), 56.4 (MeO or *C*HS$_2$), 50.6 (MeO or *C*HS$_2$), 43.0 (CH_2), 34.2 (CH_2), 19.0 (Me), 18.6 (Me). Anal. Calcd for $C_{30}H_{33}IN_2O_3PdS_2$: C, 46.97; H, 4.35; N, 3.65; S, 8.36. Found: C, 47.04; H, 4.40; N, 3.92; S, 7.95. Single crystals were grown by slow diffusion of *n*-hexane into a solution of **14b** in Cl_2CH_2.

Synthesis of [Pd(κ^2-*C,S*-Im$_{b'}$)I(CN^{t}Bu)] (14b′). ^{t}BuNC (67 μL, 0.59 mmol) was added to a solution of **10b** (150 mg, 0.15 mmol) in Cl_2CH_2 (25 mL). The resulting solution was stirred for 1.5 h and the solvent evaporated to dryness. The residue was triturated with Et_2O (5 mL), the suspension filtered, and the solid washed with Et_2O (2 × 3 mL), air-dried, heated in an oven at 70°C for 2 h, and treated in a desiccator with P_2O_5 for 4 days to give **14b′** as a yellow solid. Yield: 157 mg, 79%. Mp: 142 °C (dec). IR (cm^{-1}): ν(C≡N) 2198, ν(C═N) 1664. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (s, C_6H, 1 H), 4.93 (s, C*H*S$_2$, 1 H), 4.1−3.95 (m, CH_2, 1 H), 3.91 (s, MeO, 3 H), 3.88 (s, MeO, 3 H), 3.85 (s, MeO, 3 H), 3.8−3.65 (m, CH_2, 1 H), 3.35−3.25 (m, CH_2, 2 H), 1.62 (s, ^{t}Bu, 9 H), 1.51 (s, ^{t}Bu, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0 (quaternary C), 150.9 (quaternary C), 146.9 (quaternary C), 142.6 (quaternary C), 130.0 (quaternary C), 129.1 (CH), 128.2 (quaternary C), 108.5 (CH, C_6H), 61.6 (MeO or *C*HS$_2$), 60.7 (MeO or *C*HS$_2$), 58.0 (quaternary C ^{t}Bu), 57.5 (quaternary C ^{t}Bu), 56.4 (MeO or *C*HS$_2$), 51.3 (MeO or *C*HS$_2$), 44.7 (CH_2), 35.2 (CH_2), 31.2 (^{t}Bu), 29.7 (^{t}Bu). Anal. Calcd for $C_{22}H_{33}IN_2O_3PdS_2$: C, 39.38; H, 4.97; N, 4.18; S, 9.56. Found: C, 39.50; H, 5.20; N, 4.19; S, 9.39.

Synthesis of [Pd{(κ^2-*C,S*-Im$_a$)(CNXy)}$_2$(μ-I)]TfO (15a). Tl(TfO) (35 mg, 0.10 mmol) and XyNC (50 mg, 0.38 mmol) were added to a suspension of **10a** (100 mg, 0.10 mmol) in Cl_2CH_2 (20 mL). The mixture was stirred for 4 h, the resulting suspension was filtered over Celite, and the filtrate was concentrated (ca. 1 mL). Addition of Et_2O caused the precipitation of a solid, which was filtered, washed with Et_2O (2 × 3 mL), air-dried, and heated in an oven at 70 °C for 2 h to give yellow **15a**. Yield: 110 mg, 72%. Mp: 140 °C (dec). Λ_M = 121 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C≡N) 2180, ν(C═N) 1632. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0−6.8 (several m, 9 H), 5.70 (s, C*H*S$_2$, 1 H), 5.30 (b s, C*H*S$_2$, 1 H), 4.1−3.2 (several br m, CH_2, 8 H), 2.30 (s, 2×Me, 6 H), 2.21 (s, 2×Me, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.0 (quaternary C), 142.6 (quaternary C), 139.6 (quaternary C), 135.2 (quaternary C), 132.3 (quaternary C), 130.2 (CH), 129.6 (CH), 128.2 (CH), 128.0 (CH), 127.5 (CH), 127.0 (quaternary C), 126.0 (CH), 125.1 (quaternary C), 124.2 (CH), 122.9 (quaternary C), 118.6 (quaternary C), 55.3 (*C*HS$_2$), 51.7 (b s*C*HS$_2$), 40.1 (4×CH_2), 19.3 (Me), 18.6 (Me). Anal. Calcd for $C_{61}H_{62}F_3IN_4O_3Pd_2S_9$: C, 46.23; H, 3.95; N, 3.54; S, 18.21. Found: C, 46.56; H, 4.12; N, 3.58; S, 18.69.

Synthesis of [Pd{(κ^2-*C,S*-Im$_b$)(CNXy)}$_2$(μ-I)]TfO (15b). Tl(TfO) (35 mg, 0.10 mmol) was added to a suspension of **10b** (100 mg, 0.10 mmol) in Cl_2CH_2 (20 mL), and the mixture was stirred for 15 min. XyNC (52 mg, 0.40 mmol) was added, and stirring was continued for a further 1 h. The resulting suspension was filtered, the filtrate was concentrated (ca. 1 mL), and Et_2O (10 mL) was added to complete the precipitation of a solid, which was filtered, washed with Et_2O (2 × 3 mL), air-dried, and treated in a desiccator with P_2O_5 for 3 days to give **15b** as a yellow solid. Yield: 101 mg, 66%. Mp: 156 °C (dec). IR (cm^{-1}): ν(C≡N) 2176, ν(C═N) 1682. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5−6.8 (several multiplets, C_6H + $C_6H_3Me_2$), 5.21 (s, C*H*S$_2$, 1 H), 4.01 (s, MeO, 3 H), 3.98 (s, MeO, 3 H), 3.97 (s, MeO, 3 H), 3.5−3.2 (m, CH_2, 4 H), 2.26 (s, 4×Me, 12 H). ^{13}C NMR: Decomposes during the experiment. Anal. Calcd for $C_{61}H_{66}F_3IN_4O_9Pd_2S_5$: C, 47.07; H, 4.28; N, 3.60; S, 10.30. Found: C, 46.88; H, 4.20; N, 3.60; S, 10.28.

Synthesis of [Pd^{II}(κ^2-*C,S*-Ar$_c$)(PPh$_3$)$_2$]TfO ↔ [Pd^0{η^2-*C,S*-*S*(To)═*C*HC$_6$H(STo)-2-(OMe)$_3$-3,4,5}(PPh$_3$)$_2$]TfO (17). Method A. "Pd(dba)$_2$" (140 mg, 0.24 mmol), PPh_3 (128 mg, 0.49 mmol), Tl(TfO) (86 mg, 0.24 mmol), and **9** (150 mg, 0.27 mmol) were were mixed in toluene (25 mL) under nitrogen and stirred for 26 h under nitrogen. After this time it is not necessary to work under nitrogen. The solvent was evaporated to dryness, and the residue was extracted with Cl_2CH_2 (30 mL) and filtered over Celite. The filtrate was concentrated (ca. 1 mL), Et_2O (5 mL) was added, and the suspension was filtered. The solid was washed with Et_2O (2 × 3 mL) and air-dried, affording orange **17**. Yield: 112 mg, 39%.

Method B. Complex **16** (100 mg, 0.08 mmol), Tl(OTf) (54 mg, 0.15 mmol), and PPh_3 (80 mg, 0.30 mmol) were mixed in Cl_2CH_2 (7 mL) and stirred for 6 h. The resulting mixture was filtered over Celite, the solution was concentrated (ca. 1 mL), and Et_2O (5 mL) was added. The suspension was filtered, and the solid was washed with Et_2O and air-dried to give **17** as an orange solid. Yield: 179 mg, 98%. Mp: 127 °C. Λ_M = 130 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.5−6.2 (several m, 39 H); 5.32 (apparent t, $^3J_{PH}$ = 6.3 Hz, CHPd, 1 H); 3.87 (s, MeO, 3 H), 3.76 (s, MeO, 3 H), 3.59 (s, MeO, 3 H), 2.44, (s, Me To, 3 H), 2.31 (s, Me To, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.2 (quaternary C), 155.0 (quaternary C), 142.8 (quaternary C), 140.5 (quaternary C), 133.8 (CH), 133.6 (CH), 133.1 (CH), 132.9 (CH), 132.4 (quaternary C), 132.1 (quaternary C), 131.3 (quaternary C), 131.0 (quaternary C), 130.7 (CH), 130.5 (CH), 130.2 (quaternary C), 130.0 (CH), 129.7 (CH); 128.7 (CH), 128.5 (CH), 128.3 (CH), 126.8 (CH), 109.2 (CH, C_6H), 78.4 (dd, CHPd, $^2J_{PC}$ = 56 Hz, $^2J_{PC}$ = 5 Hz), 60.8 (MeO), 60.6 (MeO), 56.3 (MeO), 21.1 (Me To), 20.8 (Me To). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 27.13 (d, $^2J_{PP}$) = 37.3 Hz); 20.38 (d, $^2J_{PP}$ = 37.3 Hz). Anal. Calcd for $C_{61}H_{55}F_3O_6P_2PdS_3$: C, 60.76; H, 4.61; S, 7.98. Found: C, 60.98; H, 4.71; S, 7.92.

Synthesis of [Pd(κ^2-*C,S*-Ar$_c$)I(CNXy)] (18). XyNC (50 mg, 0.38 mmol) was added to a solution of **16** (250 mg, 0.19 mmol) in Cl_2CH_2 (10 mL). The resulting solution was stirred for 10 min and the solvent evaporated to dryness. The residue was triturated with Et_2O (10 mL), filtered, washed with Et_2O (2 × 3 mL), and air-dried to give yellow **18**. Yield: 255 mg, 85%. Mp: 140 °C. IR (cm^{-1}): ν(C≡N) 2178. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.58 (d, 2 H, $^3J_{HH}$ = 8 Hz), 7.38 (d, 2 H, $^3J_{HH}$ = 7.6 Hz), 7.3−6.8 (m, 7 H), 6.40 (s, C_6H, 1 H), 5.49 (s, CH−Pd, 1 H), 3.79 (s, MeO, 3 H), 3.66 (s, MeO, 3 H), 3.60 (s, MeO, 3 H), 2.48 (s, 2×Me Xy, 6 H), 2.32 (s, Me To, 3 H), 2.13 (s, Me To, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.7 (quaternary C), 152.3 (quaternary C), 148.7 (quaternary C), 143.8 (quaternary C), 141.4 (quaternary C), 139.1 (quaternary C), 138.0 (quaternary C), 135.8 (quaternary C), 134.1 (CH), 132.9 (quaternary C), 130.3 (CH), 130.0 (quaternary C), 129.7 (CH), 129.6 (CH), 129.5 (CH), 128.1 (quaternary C), 127.9 (CH), 119.9 (quaternary C), 106.8 (CH, C_6H), 60.8 (MeO), 60.7 (MeO), 55.7 (MeO) (the signal corresponding to CHPd could be coincident with one of the last three signals), 21.2 (Me, To), 20.9 (Me, To), 19.0 (2×Me, Xy). Anal. Calcd for $C_{33}H_{34}INO_3PdS_2$: C, 50.16; H, 4.35; N, 1.77; S, 8.12. Found: C, 50.21; H, 4.36; N, 1.80; S, 8.49.

Synthesis of [Pd(κ^2-*C,S*-Ar$_c$)I(CN^{t}Bu)] (18′). ^{t}BuNC (26 μL, 0.29 mmol) was added to a solution of **16** (150 mg, 0.11 mmol) in Cl_2CH_2 (5 mL). The solution was stirred for 1 h and the solvent evaporated to dryness. The residue was triturated with *n*-hexane (4 mL), the suspension was filtered, and the solid was washed with *n*-hexane (2 × 3 mL), air-dried, heated in an oven at 70 °C for 2 h, and treated in a desiccator with P_2O_5 for 4 days to give **18′** as a yellow solid. Yield: 125 mg, 74%. Mp: 122 °C. IR (cm^{-1}): ν(C≡N) 2198. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, C_6H_4Me-4, 2 H, $^3J_{HH}$ = 8 Hz), 7.36 (d, C_6H_4-Me-4, 2 H, $^3J_{HH}$ = 8 Hz), 7.12 (d, C_6H_4Me-4, 2 H, $^3J_{HH}$ = 8 Hz), 7.09 (d, C_6H_4Me-4, 2 H, $^3J_{HH}$ = 8 Hz), 6.32 (s, C_6H, 1 H), 5.31 (s, CHPd, 1 H), 3.77 (s, MeO, 3 H), 3.61 (s, MeO, 3 H), 3.58 (s, MeO, 3 H), 2.32 (s, Me To, 3 H), 2.30 (s, Me To, 3 H), 1.49 (s, ^{t}Bu, 9 H). ^{13}C NMR (75 MHz, $CdCl_3$): δ 155.7 (quaternary C), 152.2 (quaternary C), 149.3 (quaternary C), 141.2 (quaternary C), 139.0 (quaternary C), 137.5 (quaternary C), 133.6 (CH), 133.3 (quaternary C), 131.3 (quaternary C), 130.3 (CH), 129.6 (CH), 129.5 (CH), 119.7 (quaternary C), 106.5 (CH, C_6H), 60.8 (MeO), 60.7 (MeO), 57.9 (quaternary C ^{t}Bu), 55.6 (MeO), 54.0 (CHPd), 29.9 (^{t}Bu), 21.1 (C_6H_4-*Me*-4), 21.0 (C_6H_4-*Me*-4). Anal. Calcd for $C_{29}H_{34}INO_3PdS_2$: C, 46.94; H, 4.63; N, 1.89; S, 8.64. Found: C, 46.83; H, 4.60; N, 2.11; S, 8.57.

Synthesis of *trans*-[Pd(κ^2-*C,S*-Ar$_c$)I(CNXy)$_2$] (19). XyNC (40 mg, 0.30 mmol) was added to a solution of **16** (100 mg, 0.08 mmol) in Cl_2CH_2 (10 mL). The resulting solution was stirred for 7 h and the solvent evaporated to dryness. The residue was triturated with Et_2O (5 mL) at 0 °C, filtered, washed with Et_2O (2 × 3 mL), air-dried, and treated in a desiccator with P_2O_5 for 16 h to give **19** as a yellow solid. Yield: 85 mg, 61%. Mp: 119 °C. IR (cm^{-1}): ν(C≡N) 2172. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4−6.7 (several m, 15 H), 5.95 (b s, CH−Pd, 1 H), 3.74 (s, MeO, 3 H), 3.67 (s, MeO, 3 H), 3.45 (s, MeO, 3 H), 2.38 (s, Me Xy, 12 H), 2.22 (s, Me To, 3 H), 2.20 (s, Me To, 3 H). ^{1}H NMR (200 MHz, $CDCl_3$, −60 °C): δ 7.44 (s, C_6H, 1 H), 7.29 (m, 2 H), 7.13 (d, 4 H, $^3J_{HH}$ = 7.8 Hz), 6.97 (m, 4 H), 6.84 (d, 2 H, $^3J_{HH}$ = 8.1 Hz), 6.75 (d, 2 H, $^3J_{HH}$ = 8.1 Hz), 6.10 (s, CH−Pd, 1 H), 3.78 (s, MeO, 3 H), 3.69 (s, MeO, 3 H), 3.35 (s, MeO, 3 H), 2.39 (s, Me Xy, 12 H), 2.27 (s, Me To, 3 H), 2.22 (s, Me To, 3 H). Anal. Calcd for $C_{42}H_{43}IN_2O_3PdS_2$: C, 54.75; H, 4.71; N, 3.04; S, 6.96. Found: C, 54.50; H, 4.93; N, 3.16; S, 6.64.

Synthesis of *trans*-[Pd(κ^2-*C,S*-Ar$_c$)I(CN^{t}Bu)$_2$] (19′). ^{t}BuNC (34.5 μL, 0.30 mmol) was added to a solution of **16** (100 mg, 0.08 mmol) in Cl_2CH_2 (10 mL). The resulting solution was stirred for 1.5 h and concentrated (ca. 1 mL). *n*-Hexane (5 mL) was added, causing the precipitation of a solid, which was filtered, washed with *n*-hexane (2 × 3 mL), air-dried, and treated in a desiccator with P_2O_5 for 3 days to give **19′** as a yellow solid. Yield: 96 mg, 77%. Mp: 120 °C (dec). IR (cm^{-1}): ν(C≡N) 2202. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.3−6.8 (br m, 9 H), 5.66 (vb s, CHPd, 1 H), 3.80 (s, MeO, 3 H), 3.75 (b s, MeO, 3 H), 3.64 (s, MeO, 3 H), 2.29 (s, Me To, 3 H), 2.20 (s, Me To, 3 H), 1.44 (s, ^{t}Bu, 9 H). At −60 °C: 7.47 (s, C_6H, 1 H), 7.2−6.8 (m, 8 H), 5.87 (s, CHPd, 1 H), 3.87 (s, MeO, 3 H), 3.84 (s, MeO, 3 H), 3.61 (s, MeO, 3 H), 2.31 (s, Me To, 3 H), 2.28 (s, Me To, 3 H), 1.47 (s, ^{t}Bu, 18 H). ^{13}C NMR (50 MHz, $CdCl_3$): δ 154.7 (quaternary C), 154.4 (quaternary C), 148.6 (quaternary C), 140.1 (quaternary C), 136.0 (quaternary C), 135.0 (quaternary C), 134.3 (quaternary C), 129.5 (CH), 129.1 (CH), 128.5 (CH), 127.1 (CH), 115.7 (quaternary C), 106.9 (CH, C_6H), 61.0 (MeO), 60.6 (MeO), 57.5 (quaternary C ^{t}Bu), 55.9 (MeO), 29.7 (^{t}Bu), 20.9 (2×C_6H_4-*Me*-4). Anal. Calcd for $C_{34}H_{43}IN_2O_3PdS_2$: C, 49.48; H, 5.26; N, 3.40; S, 7.77. Found: C, 49.55; H, 5.44; N, 3.51; S, 7.72.

Synthesis of [Pd(κ^2-*C,S*-Ar$_c$)I(PPh$_3$)] (20). Method A. "Pd(dba)$_2$" (78 mg, 0.14 mmol) was added under nitrogen to a solution of **9** (94 mg, 0.17 mmol) and PPh_3 (45 mg, 0.17 mmol) in toluene (15 mL) and stirred for 15 h under nitrogen. After this time it is not necessary to work under nitrogen. The solvent was evaporated to dryness, the residue was extracted with Cl_2CH_2 (20 mL) and filtered over Celite, and the solvent was evaporated to dryness. The residue was triturated with Et_2O (15 mL) in an ice bath for 2 h, the suspension was filtered, and the solid was washed with Et_2O (2 × 3 mL) and air-dried, affording yellow **20**. Yield: 28 mg, 22%.

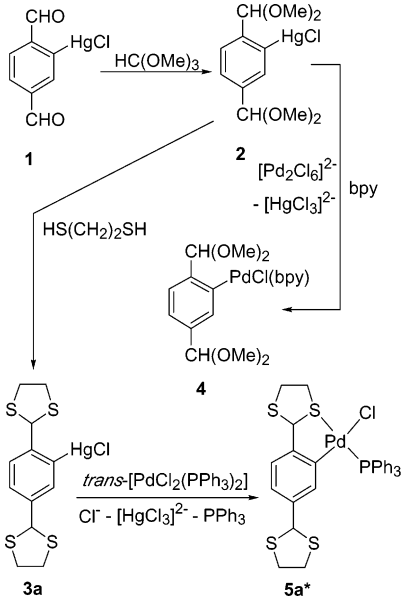
Method B. PPh_3 (40 mg, 0.15 mmol) was added to a solution of **16** (100 mg, 0.08 mmol), and the solution was stirred for 20 min. The solution was concentrated (ca. 1 mL), *n*-hexane (10 mL) was added, and the suspension was filtered. The solid was washed with *n*-hexane (2 × 3 mL) and air-dried to give yellow **20**. Yield: 97 mg, 69%. Mp: 158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0−6.8 (several m, 25 H), 3.77 (s, MeO, 3 H), 3.63 (s, MeO, 3 H), 3.51 (b s, MeO, 3 H), 2.31 (s, Me To, 3 H), 2.26 (s, Me To, 3 H). ^{31}P NMR (121 MHz, $CDCl_3$): δ 32.5 (s, PPh_3). Anal. Calcd for $C_{42}H_{40}IO_3PPdS_2$: C, 54.76; H, 4.39; S, 6.96. Found: C, 54.98; H, 4.36; S, 6.57.

X-ray Structure Determinations. Data were recorded using Mo Kα radiation (λ = 0.71073Å), a graphite monochromator, and ω and ϕ scans on a Bruker SMART 1000 CCD (**14a** and **14b**) or ω scans on a Siemens P4 diffractometer (**4** and **5a***). Absorption corrections were applied on the basis of multiple scans (program SADABS; **14b**), indexed faces (**14a**), or psi-scans (**4** and **5a***). Structures were refined anisotropically using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using rigid methyl groups or a riding model. Special features: **14a** crystallizes with one well-ordered molecule of dichloromethane.

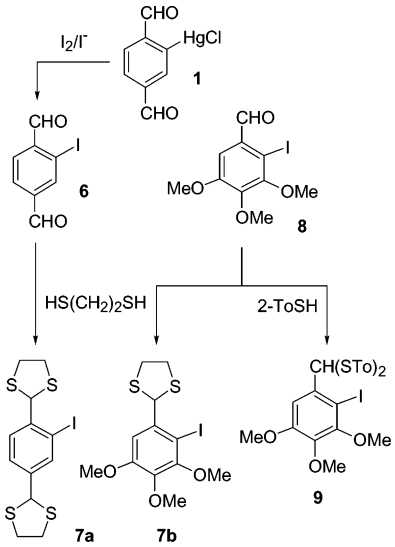
Results and Discussion

Synthesis of Acetal- and Dithioacetal-arylpalladium Complexes. All attempts to prepare complexes with the groups Ar$_a$ or Ar$_b$, or 2,5-bis(*p*-tolyldithioacetal)aryl-palladium complexes, by palladation of the corresponding dithioacetals with palladium acetate (in toluene or acetonitrile) or by reacting the corresponding 2-formylaryl-palladium complexes[23,25] with the dithiols, were unsuccessful. The resulting mixture of compounds had ToS (To = *p*-tolyl) as the only ligand. Similar mixtures were obtained by reacting [Pd(AcO)$_2$] with ToSH in acetonitrile. However, the desired complexes were obtained using the mercurial [Hg{C_6H_3(CHO)$_2$-2,5}Cl] (**1**), previously synthesized by mercuration of terephthaldehyde.[25] This compound was converted into a diacetal, which in turn was transformed into a dithioacetal and then transmetalated to palladium, or

Scheme 1



Scheme 2



transformed into $IC_6H_3(CHO)_2$-2,5 and this in turn into IAr_a (Ar_a = $C_6H_3\{CH(SCH_2CH_2S)\}_2$-2,5), which was used in oxidative addition reactions. Similarly, $IC_6H(OMe)_3$-2,3,4-(CHO)-6 was converted into IAr_b (Ar_b = $C_6H(OMe)_3$-2,3,4-{$CH(SCH_2CH_2S$}-6) and used in oxidative addition reactions.

Transmetalation Reactions. We have reported the synthesis of [Hg{$C_6H_3(CHO)_2$-2,5}Cl] (**1**) by reacting terephthaldehyde with HgO in a 1:1 volume mixture of water and triflic acid at 95 °C.[25] This mercurial reacts with $CH(OMe)_3$ and 96% sulfuric acid in anhydrous methanol to give the new arylmercury compound [Hg{$C_6H_3\{CH(OMe)_2\}_2$-2,5}Cl] (**2**), which reacts with $HS(CH_2)_2SH$ and *p*-toluenesulfonic acid to give [$Hg(Ar_a)Cl$] [Ar_a = $C_6H_3\{CH(SCH_2CH_2S)\}_2$-2,5 (**3a**)] (Scheme 1). These mercurials can be used as transmetallating agents to prepare new organopalladium complexes following a procedure that we have developed for the preparation of 2,5-diformylphenylpalladium complexes from **1**.[25] Thus, **2** reacts with $(NMe_4)_2[Pd_2Cl_6]$ in the presence of $(Me_4N)Cl$ in acetone to give the insoluble $Me_4N[HgCl_3]$. Addition of 2,2′-bipyridine (bpy) to the filtrate gave the neutral complex [Pd{$C_6H_3\{CH(OMe)_2\}_2$-2,5}Cl(bpy)] (**4**). The reaction of **3a** with *trans*-[$PdCl_2(PPh_3)_2$] in the presence of $(Me_4N)Cl$ gives $(NMe_4)[HgCl_3]$ and the aryl-palladium complex [Pd{κ-*C,S*-Ar_a}$Cl(PPh_3)_2$] (**5a***). This reaction also involves the replacement of 1 equiv of PPh_3 associated with the chelating effect of the C,S-ligand. We propose the PPh_3 to be *cis* to the aryl ligand because the aryl/phosphine *transphobia* is greater than the aryl/chloro *transphobia*. This term, which we have defined,[29,38,42,49] has been fruitfully used by other authors.[19,50]

Complexes **2** and **4** are the first mercury and palladium complexes having acetal-substituted aryl ligands. We are aware of only one such complex, [Cr{$C_6H_4CH(OCH_2CH_2O)$-2}$_3$], reported without experimental details and characterized through an X-ray diffraction study.[51] The only reported dithioacetal aryl metal complexes are those that we recently prepared by reacting the iododithioacetal $IC_6H(OMe)_3$-2,3,4-CH-$(STo)_2$-6 (see below) with $Pd(dba)_2$.[41]

Despite the above successful experiences, other attempts to prepare dithioacetal-aryl palladium complexes using mercurials were fruitless. Thus, **3a** did not react with $(Me_4N)_2[Pd_2Cl_6]$ or $[PdCl_2(NCMe)_2]$ designed to prepare complexes similar to **5a*** but with ligands easy to replace. These unsuccessful attempts prompted us to study oxidative addition reactions to prepare halo(dithioacetal)arylpalladium complexes.

Oxidative Addition Reactions. Synthesis of 2-(1,3-Dithiolan-2-yl)arylpalladium Complexes. We have used this method of synthesis starting from iododithioacetal arenes. By reacting the mercurial **1** with I_2/I^-, the iodoarene $IC_6H_3(CHO)_2$-2,5 (**6**) was obtained (Scheme 2). This is a well-known synthesis of iodoarenes.[52] By reacting **6** with $HS(CH_2)_2SH$, the desired IAr_a (**7a**) was obtained. Similarly, from $IC_6H(OMe)_3$-2,3,4-CHO-6 (**8**)[48] other iododithioacetal arenes such as $IC_6H(OMe)_3$-2,3,4-{$CH(SCH_2CH_2S)$}-6 (**7b**) or $IC_6H(OMe)_3$-2,3,4-{$CH(STo)_2$}-6 (**9**)[41] were prepared.

The oxidative addition reaction of the iodoarenes **7a** and **7b** to "$Pd(dba)_2$" ([$Pd_2(dba)_3$]·dba) resulted in the formation of the *ortho*-palladated complexes [Pd(κ^2-*C,S*-

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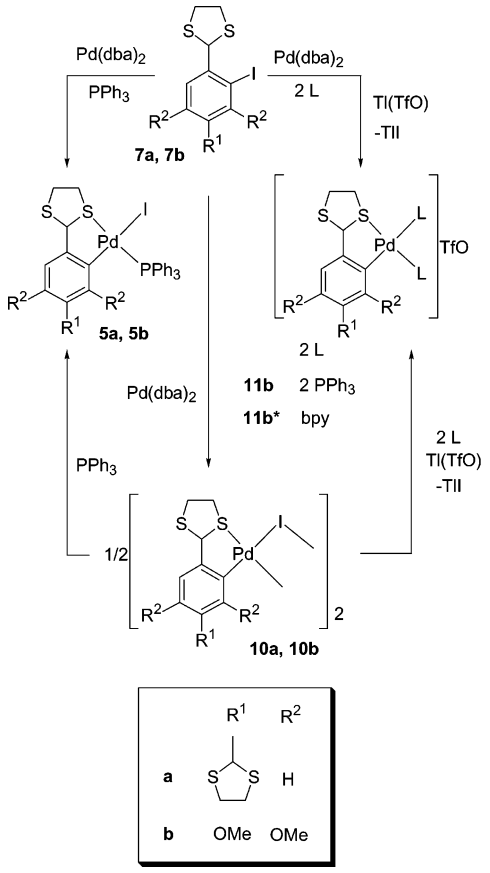
Scheme 3

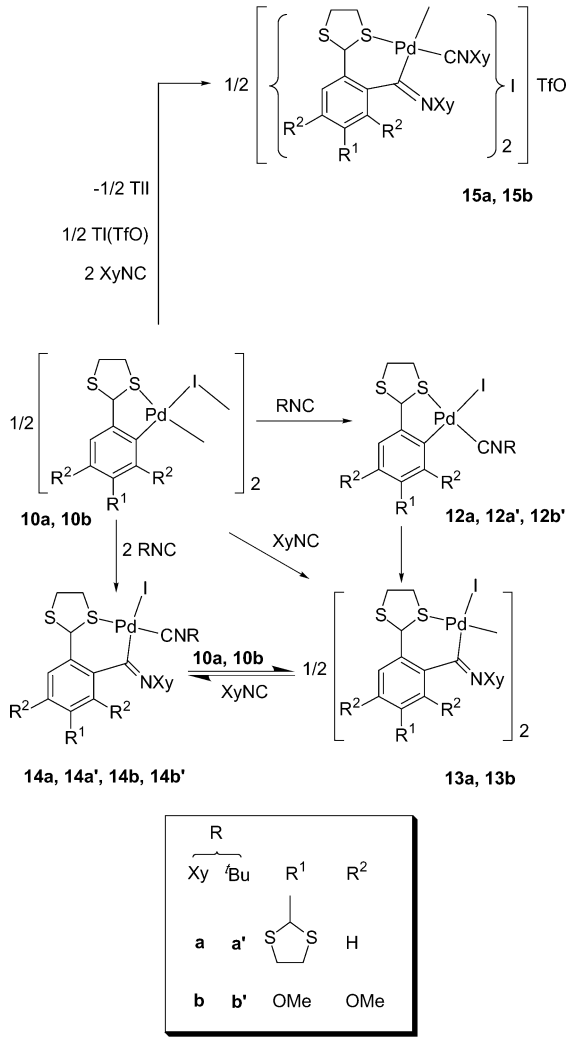


Ar)(μ-I)]$_2$ [Ar = Ar$_a$ (**10a**), Ar$_b$ (**10b**)] (Scheme 3). Although we were not able to grow single crystals in order to determine their X-ray crystal structures, we believe it reasonable to formulate them as dimers with bridging iodine atoms. These complexes react with PPh_3 to give complexes [Pd(κ^2-*C,S*-Ar)I(PPh_3)] [Ar = Ar$_a$ (**5a**), Ar$_b$ (**5b**)], which can also be prepared by reaction of **7a** or **7b** with "Pd(dba)$_2$" in the presence of PPh_3. The reaction of **10b** with 2 equiv of PPh_3 in the presence of Tl(TfO) resulted in the precipitation of TlI and the formation of the cationic complexes [Pd(κ^2-*C,S*-Ar$_b$)-(PPh_3)$_2$]TfO (**11b**). In a similar reaction, **10b** was reacted with bpy and Tl(TfO), forming [Pd(κ^2-*C,S*-Ar$_b$)-(bpy)]TfO (**11b***). Complexes **11** can also be prepared from "Pd(dba)$_2$" and the corresponding iodoarenes and ligands in the presence of Tl(TfO). As in the case of **5a***, only one isomer of **5a**,**b** was obtained because of the great aryl/PR_3 *transphobia* (see above).[29,38,49]

The iodoarenes **7a** and **7b**, which lead to **4**−**11**, behave differently from **9** because the latter reacts with "Pd(dba)$_2$" to give, in most cases, a rearrangement involving the cleavage of alkyl−S and aryl−Pd bonds and formation of aryl−S and alkyl−Pd bonds (Chart 1).[41]

We have studied the reactions of **10a** and **10b** with the isonitriles XyNC (Xy = 2,6-dimethylphenyl) and ^{t}BuNC. The 1:2 reactions starting from **10a** gave the products of bridge splitting, [Pd(κ^2-*C,S*-Ar)I(CNR)] [Ar = Ar$_a$, R = Xy = 2,6-dimethylphenyl (**12a**), ^{t}Bu (**12a′**)] (Scheme 4). Similarly, **10b** reacts with ^{t}BuNC to give **12b′** [Ar = Ar$_b$, R = ^{t}Bu], while with XyNC it gives the iminoacyl complex [Pd(κ^2-*C,S*-Im$_b$)(μ-I)]$_2$ [Im$_b$ = C(=NXy)-$C_6H(OMe)_3$-2,3,4-(SCH_2CH_2S)-6 (**13b**)]; the correspond-

Scheme 4



ing species analogous to complexes **12a** could not be isolated. Compound **12a** evolves spontaneously in solution to the corresponding insertion product **13a**, a very insoluble material that could not be characterized by NMR spectroscopy and that gave poor elemental analyses for C and S. Its proposed structure is based on the observation of the ν(C═N) band at 1632 cm^{-1} and the disappearance of ν(C≡N) at 2182 cm^{-1} and on its reaction with XyNC to give **14** (see below). This type of conversion of a coordinated into an inserted isonitrile has been reported previously, although it requires some thermal treatment.[6,53]

The reactions of complexes **10** with the isonitriles in a 1:4 molar ratio gave compounds [Pd(κ^2-*C,S*-Im)I(CNR)] [Im = C(═NR)C_6H_3{CH(SCH_2CH_2S)}$_2$-2,5, R = Xy, Im = Im$_a$ (**14a**), R = ^{t}Bu, Im = Im$_{a'}$ (**14a′**); Im = C(═NR)-$C_6H(OMe)_3$-2,3,4-(SCH_2CH_2S)-6, R = Xy, Im = Im$_b$ (**14b**), R = ^{t}Bu, Im = Im$_{b'}$ (**14b′**)]. Complex **14a** or **14b** was also accessible by reaction of **13a** or **13b** with XyNC (1:2 molar ratio), respectively. Additionally, complex **14a** or **14b** reacted with **10a** or **10b** to give **13a** or **13b**, respectively (Scheme 4). The above results suggest that the first step in the reaction of complexes **10** toward isocyanides (1:2 molar ratio) involves coordination to

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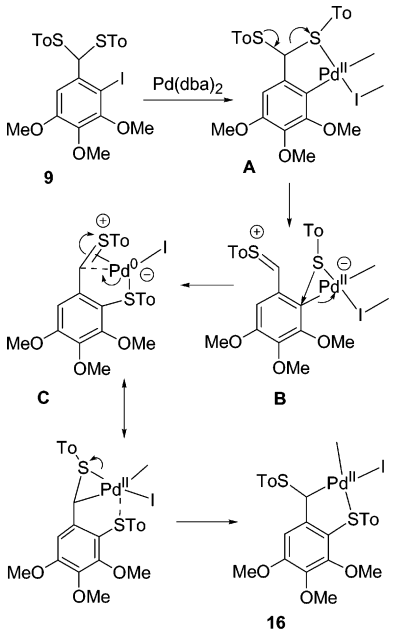
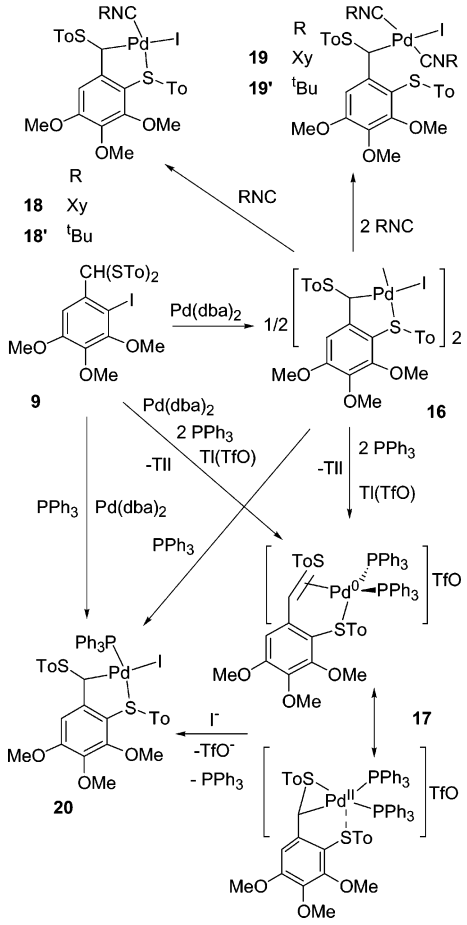
Scheme 5



Scheme 6



give, after bridge-splitting, monomers **12**; the second stage involves an insertion process to give the more thermodynamically stable dinuclear iminoacyl complexes **13**; finally, in excess of isocyanide, a bridge-splitting from **13** leads to complexes **14**. The reactions of **14a**,**b** with complexes **10a**,**b** to give **13a**,**b** suggest that complexes **14a**,**b** dissociate XyNC (to give **13a**,**b**), which would also react with **10** to give **13a**,**b**. This proposal is supported by NMR data (see below).

Complex **10a** or **10b** reacted with XyNC and Tl(TfO) (1:4:2) to give a precipitate of TlI and a solution from which the dimeric cation [Pd{(κ^2-*C*,*S*-Im)(CNXy)}$_2$(μ-I)]-TfO [Im = Im$_a$ (**15a**), Im$_b$ (**15b**)] can be isolated instead of the expected [Pd(μ-κ^3-*C*,*S*,*N*-Im)(CNXy)]$_2$(TfO)$_2$ (Scheme 4). These reactions probably occur via the corresponding complexes **14**; it is remarkable that the iodide ligand was not fully removed despite using the appropriate amount of Tl(TfO). However, it was not totally unexpected because we have found the same behavior previously.[30] Complexes **15** were also obtained when the required 1:4:1 molar ratio was used. For complexes **15a** and **15b** we propose a structure (Scheme 4) in which the bridging iodo ligand is *trans* to the iminoacyl carbons, similarly to that shown by a related complex, [Pd$_2${κ^2-*C*,*N*-C(=NXy)C$_6$H$_4$NH$_2$-2}$_2$(CNXy)$_2$(μ-I)]TfO, whose structure was determined by X-ray methods.[30]

Complexes with the Ligand CH(STo)C$_6$H(STo)-2-(OMe)$_3$-3,4,5. We have recently reported that the iodoarene **9** reacts with "Pd(dba)$_2$" to give the complex **16** by way of an unusual rearrangement involving the transformation of a 2-dithioacetalaryl ligand into an alkyl ligand bearing two thioether functions (Chart 2).[41] We proposed the mechanism depicted in Scheme 5, in which **9** adds to Pd(0) to give the expected aryldithioacetal derivative **A**, which would undergo a C−S bond cleavage giving **B**. Then, an insertion of the ToS$^-$ ligand into the C−Pd bond would give **16** via a Pd(0) intermediate **C** resulting from **B** after an intramolecular redox process. We have more recently communicated the synthesis of an unusual Pd complex **17** (Scheme 6), which could be a model of the proposed intermediate **C**.[42] We report here further aspects of the reactivity of **16** and more details on complex **17**.

The reaction of **16** with 1 equiv of an isocyanide yields complexes [Pd(κ^2-*C*,*S*-Ar$_c$)I(CNR)] [R = Xy (**18**), R = ^{t}Bu (**18′**)] resulting after bridge-splitting. This behavior is in contrast to that of the dithioacetal aryl-palladium complexes **10**, because complexes **18** do not evolve to the homologues of **13**, resulting after the insertion of the isocyanide into the Pd−C bond (Scheme 4). When **16** was reacted with 2 equiv of an isocyanide, complexes *trans*-[Pd(κ^1-*C*-Ar$_c$)I(CNR)$_2$] [R = Xy (**19**), R = ^{t}Bu (**19′**)] were obtained (Scheme 6). This result also differs from that obtained from complexes **10** (Scheme 4), not only because the isocyanide insertion does not occur but also since the κ^2-*C*,*S* chelating ligand converts into a κ^1-*C* ligand after S−Pd bond cleavage.

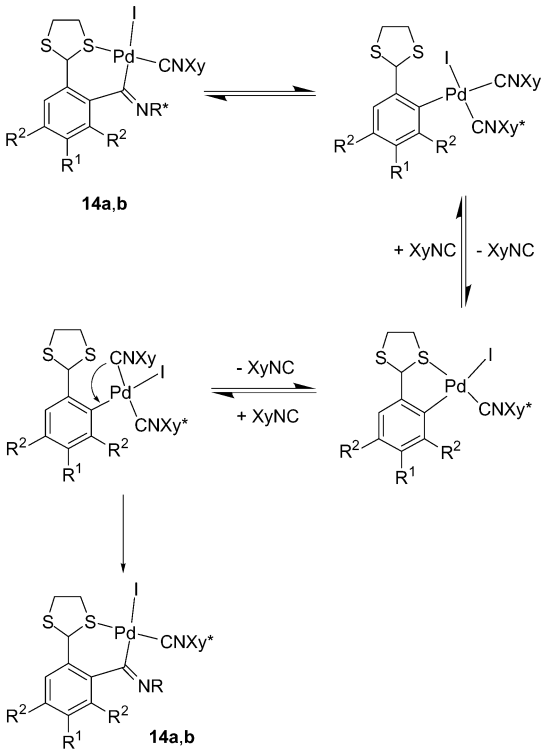
The reaction of **16** with PPh$_3$ (1:4) in the presence of Tl(TfO) results in the formation of the cationic complex **17**, whose structure has been resolved by X-ray diffraction studies.[42] The main features of this structure reveal that **17** could be considered as intermediate between a tricoordinate Pd(0) complex with the ligand η^2-*C*,*S*-[To*S*$^{(+)}$=*C*HC$_6$H(STo)-2-(OMe)$_3$-3,4,5] and a square-planar Pd(II) complex with the ligand κ^2-*C*,*S*-[To*S*C*H*$^{(-)}$C$_6$H(STo)-2-(OMe)$_3$-3,4,5]. Alternatively, if the coordination of the STo-2 group is considered, it could be described as intermediate between a tetracoordinate Pd(0) complex with the ligand (η^2-*C*,*S*),*S*-[To*S*$^{(+)}$=*C*HC$_6$H-(*S*To)-2-(OMe)$_3$-3,4,5] and a flattened square-pyramid Pd(II) complex with the ligand κ^3-*C*,*S*,*S*-[To*S*C*H*$^{(-)}$C$_6$H-

(*S*To)-2-(OMe)$_3$-3,4,5] (Scheme 6). The partial reduction of the metal center was postulated as a consequence of the strong alkyl/PPh_3 *transphobia* if the complex was a pure Pd(II) complex and of the inoperativity of the C-donor/P-donor *transphobia* in Pd(0) complexes. A similar behavior has been reported when [$Pd^{II}(CH_2C_6H_4$-$OSiR_3$-4)Br(diphosphine)] was reacted with F^- to give [$Pd^0(CH_2{=}C_6H_4{=}O$-4)Br(diphosphine)].[54] An additional support for this proposal was the reaction of **17** with NaI to give [Pd(κ^2-*C,S*-Ar_c)I(PPh_3)] (**20**). The facile substitution of PPh_3 by I^- could be another consequence of the strong alkyl/PPh_3 *transphobia* associated with the residual Pd(II) character of complex **17**. This complex could also be one-pot prepared by an oxidative addition reaction of **9** to "Pd(dba)$_2$" in the presence of the appropriate amounts of PPh_3 and Tl(TfO). The reaction of equimolar amounts of **9**, "Pd(dba)$_2$", and PPh_3 or of **16** and PPh_3 (1:2) also yields the neutral complex *cis*-[Pd(κ^2-*C,S*-Ar_c)I(PPh_3)] (**20**) (Scheme 6). We have not been able to grow single crystals of complex **20**, but we assume it has a structure similar to that of *cis*-[Pd(κ^2-*C,S*-Ar_c)(CNXy)$_2$]TfO,[41] with the P- and C-donor ligands arranged *cis* in accordance with their mutual *transphobia*. The NMR data indicate that **20** is constituted of only one isomer.

Spectroscopic Properties of Complexes. Most spectroscopic data of the new compounds are in accordance with the proposed structures. However, in complexes **14b** and **15b** (Scheme 4) only one singlet integrating for four methyls is observed at room temperature. At −60 °C three singlets appear corresponding to 3/6/3 protons. This suggests that, at low temperature, one of the xylyl groups has restricted rotation around the N−$C_6H_3Me_2$ bond, making both methyl groups inequivalent, while the other one has free rotation. The above data suggest that an interchange between coordinated and inserted XyNC ligands occurs at room temperature. We propose the series of equilibria depicted in Scheme 7 to account for this behavior. The proposed dissociation of XyNC is in accordance with the reactions of **14a**,**b** with complexes **10a**,**b** to give **13a**,**b** (see above). The ^{1}H NMR spectra of complexes **19** show a broadening affecting the signals of the CHPd, the To groups, and one of the methoxy groups; such signals sharpen on cooling to −60 °C.

It would be expected that the ^{13}C NMR spectra of complexes having the κ^2-*C,S*-Ar_a ligand show the presence of three resonances assignable to the methylene carbons. However, this is only true for **14a′** (see Experimental Section). Only two signals are observed for complexes **5a** and **5a***. Similarly, among the compounds containing the ligand Ar_b, only **14b** and **14b′** show the expected two methylene signals, while in **11b** these two signals are broad and in **5b**, **11b*** and **12b′** only one signal is observed. The spectra of **5a**, **5a***, **5b**, **11b***, **11b**, and **12b′** could be explained assuming that the *ortho* 1,3-dithiolan-2-yl group underwent an exchange between the coordinated and the other sulfur through an S−Pd bond breaking and re-forming process within the response time of the apparatus. Such an exchange could be responsible for making similar both *ortho* and *meta* 1,3-dithiolan-2-yl groups in Ar_a complexes, which could explain why **12a′**, **14a**, and **15a** show only one signal for the four methylene carbons.

Scheme 7



The ν(C≡N) band of coordinated isonitriles appears in the IR spectra at 2170−2222 cm^{-1}, and the ν(C=N) band of the inserted isonitriles is observed in the range 1632−1668 cm^{-1}.

X-ray Difraction Studies. The crystal and molecular structures of complexes **4**, **5a***, **14a**, and **14b** have been determined (Figures 1-4). Compound **4** shows a square-planar coordination around the palladium atom, somewhat distorted because of the small bite angle of the bpy ligand (N(1)−Pd−N(2) 79.15(10)°). The greater *trans* influence of the aryl with respect to the chloro ligand causes the Pd−N(2) distance (2.122(3) Å) to be longer than the Pd−N(1) bond length (2.050(3) Å). The molecule shows a weak intramolecular C(bpy)−H···Cl hydrogen bond [C30···Cl 3.348(4) Å, H30···Cl 2.75 Å, C30−H30···Cl 121.4°]. Weak intermolecular C−H···Cl

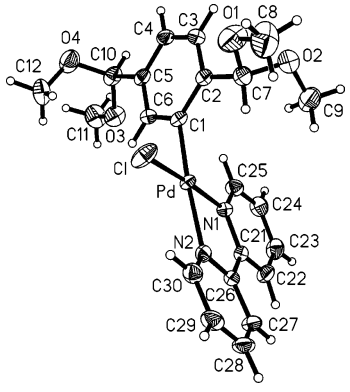


Figure 1. Ellipsoid representation of **4** (50% probability). Selected bond lengths (Å) and angles (deg): Pd−C(1) 1.994(3), Pd−N(1) 2.050(3), Pd−N(2) 2.122(3), Pd−Cl 2.2985(9), C(1)−Pd−N(1) 95.49(11), N(1)−Pd−N(2) 79.15(10), C(1)−Pd−Cl 90.05(9), N(2)−Pd−Cl 95.29(8).

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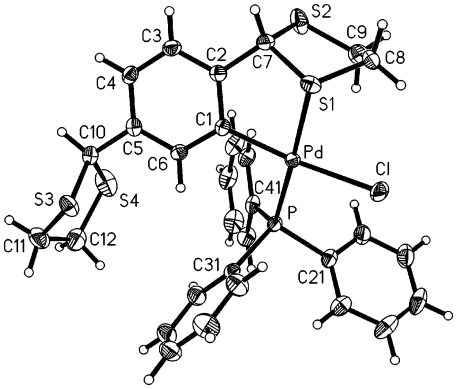

Figure 2. Ellipsoid representation of **5a*** (50% probability). Selected bond lengths (Å) and angles (deg): Pd−C(1) 2.0207(19), Pd−P 2.2828(5), Pd−S(1) 2.3286(5), Pd−Cl 2.3868(6), S(1)−C(8) 1.805(2), S(1)−C(7) 1.820(2), S(2)−C(9) 1.805(2), S(2)−C(7) 1.837(2), S(3)−C(10) 1.805(2), S(3)−C(11) 1.805(2), S(4)−C(12) 1.815(3), S(4)−C(10) 1.837(2), C(1)−Pd−P 93.76(6), C(1)−Pd−S(1) 83.62(6), P−Pd−Cl 93.596(19), S(1)−Pd−Cl 89.10(2), C(7)−S(1)−Pd 96.65(7), C(2)−C(1)−Pd 117.24(14), C(1)−C(2)−C(7) 119.50(17), C(2)−C(7)−S(1) 108.23(14).

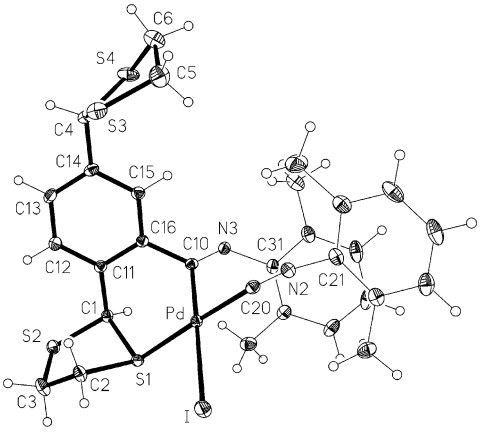

Figure 3. Ellipsoid representation of **14a** (solvent omitted) with 30% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(20) 1.965(2), Pd−C(10) 2.0250(19), Pd−S(1) 2.3067(5), Pd−I 2.6995(3), S(1)−C(2) 1.812(2), S(1)−C(1) 1.8318(19), S(2)−C(1) 1.823(2), S(2)−C(3) 1.833(2), S(3)−C(5) 1.803(3), S(3)−C(4) 1.834(2), S(4)−C(6) 1.799(3), S(4)−C(4) 1.827(2), C(10)−N(3) 1.262(2), C(20)−N(2) 1.149(3), C(21)−N(2) 1.403(2), C(31)−N(3) 1.435(2); C(20)−Pd−C(10) 91.81(8), C(10)−Pd−S(1) 87.34(5), C(20)−Pd−I 91.27(6), S(1)−Pd−I 89.408(13), N(3)−C(10)−C(16) 121.78(17), N(3)−C(10)−Pd 127.51(14), C(16)−C(10)−Pd 110.63(13), N(2)−C(20)−Pd 174.30(18), C(20)−N(2)−C(21) 171.1(2), C(10)−N(3)−C(31) 120.32(16).

and C−H···O hydrogen bonds have been found in the crystal (see Supporting Information).

The structure of **5a*** shows a square-planar palladium center, slightly distorted due to the small bite angle of the chelated ligand (C(1)−Pd−S(1) 83.62(10)°). The phosphine ligand is *trans* to the coordinated sulfur atom, and the chlorine atom is *trans* to the aryl group, in

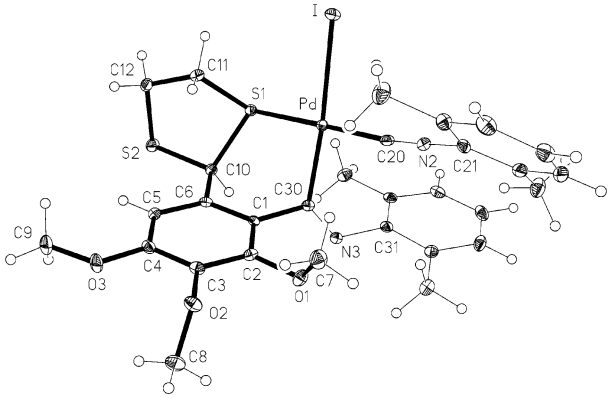

Figure 4. Ellipsoid representation of **14b** with 30% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(20) 1.965(3), Pd−C(30) 2.033(2), Pd−S(1) 2.3200(6), Pd−I 2.7219(3), S(1)−C(11) 1.810(3), S(1)−C(10) 1.835(2), S(2)−C(10) 1.802(2), S(2)−C(12) 1.833(2), N(2)−C(20) 1.154(3), N(2)−C(21) 1.406(3), N(3)−C(30) 1.251(3), N(3)−C(31) 1.424(3); C(20)−Pd−C(30) 92.12(9), C(30)−Pd−S(1) 86.87(7), C(20)−Pd−I 90.98(7), S(1)−Pd−I 90.059(16), C(20)−N(2)−C(21) 170.3(2), N(2)−C(20)−Pd 169.9(2), C(30)−N(3)−C(31) 124.9(2), N(3)−C(30)−C(1) 122.2(2), N(3)−C(30)−Pd 129.09(18), C(1)−C(30)−Pd 108.74(15).

agreement with the great aryl/phosphine *transphobia* (see above). The five-membered metallocycle adopts an envelope conformation with the sulfur atom out of the ring main plane. Both thioacetal rings adopt a twist boat conformation. The most relevant interactions found in the crystal include an intramolecular C−H···Cl and intermolecular C−H···S and C−H···Cl weak hydrogen bonds (see Supporting Information).

The structures of **14a** (Figure 3) and **14b** (Figure 4) are similar. In both cases the iodo ligand is located *trans* to the iminoacyl carbon, while the isonitrile is *trans* to the sulfur atom, avoiding the unfavorable situation (greater *transphobia*) that would occur with both carbon donor ligands in *trans* position. The short intermolecular contacts C(1)−H(1)···N(3) in **14a** [H(1)···N(3) 2.49 Å, C(1)−H(1)···N(3) 154°] and C(11)−H(11a)···O(3) [H(11a)···O(3) 2.42 Å, C(11)−H(11a)···O(3) 161°] and C(12)−H(12b)···O(2) [H(12b)···O(2) 2.47 Å, C(12)−H(12b)···O(2) 148°] in **14b** could be regarded as weak hydrogen bonds.

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Supporting Information Available: CIF files for **4**, **5a***, **14a**, and **14b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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