by photochemical 1,3-rearrangement of **1**, is the reactive intermediate in the formation of the rubberlike polymer. Several mechanisms are plausible for the formation of **2**, which can be obtained by oxidation of ethene-1,2-dithiolate and the photochemical reaction of **1**, and are currently under investigation.

Experimental Procedure

Oxidation of *cis*-disodium ethene-1,2-dithiolate: an aqueous solution (150 mL) of *cis*-disodium ethene-1,2-dithiolate[13] (2.78 g, 20.4 mmol) and iodine (5.18 g, 20.4 mmol) in 20% aqueous potassium iodide (150 mL)[14] were added consecutively from two dropping funnels with vigorous stirring at $-10\,^{\circ}C$ under nitrogen to a heterogeneous solution of ether (300 mL) and water (250 mL) over 7 h. After additional stirring for 1 h, the products were extracted with ether and washed with 10% sodium thiosulfate solution and water. After chromatography on a short cellulose column (chloroform), purification was achieved by gel permeation chromatography (GPC).

1: 254 mg (14%); m. p. 97.5–98.5 °C (yellow prisms); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.88$ (s); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 127.6$; IR (KBr): $\tilde{\nu} = 3010, 1515, 1170, 800, 650\ cm^{-1}$; UV (cyclohexane): $\lambda\ (\varepsilon) = 357\ (2.1 \times 10^3), 265\ (2.4 \times 10^3), 235\ (4.0 \times 10^3)$ nm; EI MS: *m/z* 180 (M^+), 147, 116, 90, 57; elemental analysis for $C_4H_4S_4$ (calcd, found): C 26.64, 26.69; H 2.24, 2.24.

2: 9.6 mg (0.5%); a *meso*-isomer could be isolated from the diastereomeric mixture by recrystallization from chloroform. Spectral data for *meso*-**2**: m. p. 127.5–128.5 °C (yellow prisms); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.77$ (d, 2H, $J = 9.5$ Hz), 6.62 (d, 2H, $J = 9.5$ Hz), 4.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 126.5, 115.4, 56.1$; IR (KBr): $\tilde{\nu} = 3030, 3020, 2905, 1540, 1125, 810\ cm^{-1}$; UV (cyclohexane): $\lambda\ (\varepsilon) \approx 325$ (sh, 1.4×10^3), 247 (6.1×10^3) nm; EI MS: *m/z* 271 ($M^+ + 1$), 207, 180, 147, 135, 116, 90, 58; elemental analysis for $C_6H_6S_6$ (calcd, found): C 26.64, 27.14; H, 2.24, 2.36.

3: 32 mg (2%); m. p. 150 °C (decomp., yellow prisms); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.48$ (s); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 131.7$; IR (KBr): $\tilde{\nu} = 3025, 1535, 1280, 1155, 910, 830, 730, 715\ cm^{-1}$; UV (cyclohexane): $\lambda\ (\varepsilon) = 243\ (2.8 \times 10^4)$ nm; EI MS: *m/z* 360 (M^+), 270, 180, 147, 116, 90, 58; elemental analysis for $C_8H_8S_8$ (calcd, found): C, 26.64, 26.76; H, 2.24, 2.29.

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[4] A *meso*-isomer of **2** could be isolated from the diastereomeric mixture by recrystallization. The structure of the *meso*-isomer was confirmed by X-ray crystallographic analysis; details will be reported later. The ratio of *meso*- and *dl*-isomers was determined by ^{1}H NMR spectroscopy in $CDCl_3$.

[5] Crystal structure analysis of **1** (yellow prisms from hexane): $C_4H_4S_4$, $M_r = 180.34$, crystal dimensions $0.45 \times 0.30 \times 0.15$ mm, $a = 8.092(2)$, $b = 11.254(3)$, $c = 7.674(2)$ Å, $V = 698.9(4)$ Å^3, $\rho_{calcd} = 1.71\ g cm^{-3}$, $\mu = 11.99\ cm^{-1}$, $Z = 4$, orthorhombic, space group *Pbcn* (No. 60), Mac Science MXC 18 diffractometer, $\lambda = 0.71069$ Å, $T = 296$ K, 1528 measured reflections, 1262 independent, $R = 0.042$, $Rw = 0.055$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-95. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Rd, GB-Cambridge CB21EZ, UK (fax: int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

[6] Crystal structure analysis of **3** (yellow prisms from chloroform): formula $C_8H_8S_8$, $M_r = 360.68$, crystal dimensions $0.35 \times 0.30 \times 0.20$ mm, $a = 12.075(4)$, $b = 11.566(8)$, $c = 10.592(5)$ Å, $\beta = 95.12(3)^{\circ}$, $V = 1473(1)$ Å^3, $\rho_{calcd} = 1.62\ g cm^{-3}$, $\mu = 11.38\ cm^{-1}$, $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), Mac Science MXC18 diffractometer, $\lambda = 0.71069$ Å, $T = 296$ K, 3843 measured reflections, 3368 independent, $R = 0.043$, $Rw = 0.041$.

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[11] Combustion analysis for CHS (calcd, found): C 26.64, 27.54; H 2.24, 2.23.

[12] Ratio of diastereomeric isomers = 2:1. The major isomer could be separated from diastereomeric mixture of **4** by GPC: pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.67$ (d, 1H, $J = 9.8$ Hz), 6.49 (d, 1H, $J = 9.8$ Hz), 4.57 (d, 1H, $J = 8.3$ Hz), 3.46–3.38 (m, 1H), 3.21 (d, 1H, $J = 16.6$ Hz), 3.02 (d, 1H, $J = 16.6$ Hz), 2.63–2.48 (m, 2H), 1.74 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 126.2, 125.8, 123.4, 113.9, 56.9, 43.7, 36.1, 30.9, 20.3, 19.2$; IR (neat): $\tilde{\nu} = 3020, 2990, 2910, 2870, 2810, 1535, 1440, 1420, 1380, 1170, 805\ cm^{-1}$; EI MS: *m/z* = 262 ($M^+$), 198, 127, 103, 93; elemental analysis for $C_{10}H_{14}S_4$ (calcd, found): C 45.76, 46.07; H 5.38, 5.31.

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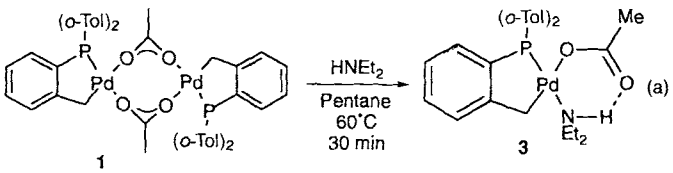
A Route to Pd^0 from Pd^{II} Metallacycles in Amination and Cross-Coupling Chemistry**

Janis Louie and John F. Hartwig*

Tri-*o*-tolylphosphane-bound palladium complexes, either isolated or generated in situ, have proven to be efficient catalysts for a wide range of coupling reactions including the Heck[1] and Suzuki[2] reactions. Amination of aryl halides has also recently been shown to be catalyzed by these palladium complexes.[3] Like the widely accepted mechanism for Heck and Suzuki reactions, the mechanism for aryl halide amination seems to involve an interconversion between Pd^0 and Pd^{II} species.[3b, d, 4] Our mechanistic and synthetic studies on such aminations led us to investigate whether the palladacycle **1** [Eq. (a)], recently reported



$[Pd\{P(o\text{-}Tol)_3\}_2]$ **2**

by Beller and Herrmann et al,[5] would operate by a mechanism different from that shown for the Pd^0 complex **2**, or whether **1** is a precursor to **2**.

[*] Prof. J. F. Hartwig, J. Louie
Department of Chemistry, Yale University
P. O. Box 208107, New Haven, CT 06520-8107 (USA)
Fax: Int. code +(203) 432-6144
e-mail: john.hartwig@yale.edu

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Our results delineate two different pathways for formation of Pd^0 complexes from **1**.[6] During the amination of aryl halides, formation and subsequent reaction of a palladium amide derived from the amine complex **3** gave the Pd^0 complex **2** by β-hydrogen elimination. During a cross-coupling reaction, **1** formed a Pd^0 complex containing the arylated P(*o*-Tol)$_3$ derivative P(*o*-Tol)$_2$(C$_6$H$_4$-*o*-CH$_2$Ph), which was formed by C–C bond-forming reductive elimination. As a result, the catalytic amination and some of the cross-coupling chemistry seen for **1** is strikingly similar to that of **2**.

Aryl halide palladium complexes with amine ligands catalyze the amination of aryl halides.[3b, d, 7] Metallacycle **1** was cleaved by secondary amines to form similar monometallic amine complexes such as the diethylamine complex **3** in Equation a. The ^{1}H NMR spectrum of **3** has broad signals at room temperature. These are resolved at $-80\,^\circ$C and show two singlets for the phosphane methyl groups along with two inequivalent sets of broad signals for amine ethyl groups. This indicates that the regions above and below the square plane are inequivalent, presumably due to a rigid and puckered metallacycle (vide infra). A broad singlet for the N–H proton is observed far downfield at $\delta = 9.24$. The amine N–H infrared vibration falls in the region of C–H vibrations. This assignment was confirmed by the synthesis of deuterated **3** and the observation of N–D stretching frequencies at 2238 cm^{-1} and 2163 cm^{-1}. The downfield ^{1}H NMR chemical shift and low infrared frequency corresponding to the amine N–H suggest the presence of a strong hydrogen bond, perhaps with the carbonyl oxygen.

An X-ray diffraction study was conducted on a single crystal of **3**, which was obtained by cooling a pentane solution from 60 °C to room temperature. All hydrogen atoms were located in successive difference maps and refined isotropically. The ORTEP drawing of **3**[8] shows that there is a hydrogen bond between the carbonyl oxygen and the amine proton (Fig. 1). The

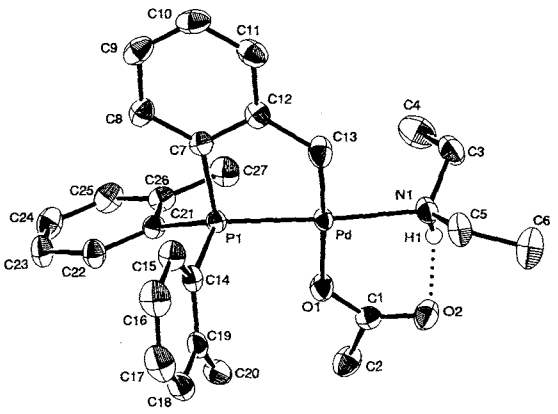
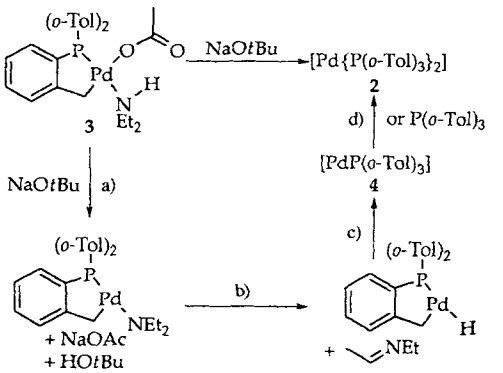


Fig. 1. Structure of **3** in the crystal. Selected bond lengths [Å] and angles [°]: O2-H1 2.10(2), Pd-P1 2.2452(5), Pd-O1 2.143(1), Pd-N1 2.150(2), Pd-C13 2.036(2), C1-O1 1.273(2), C1-O2 1.236(2), N1-H1 0.74(2); N1-H1-O2 163(2), C1-O2-H1 105.4(8), P1-Pd-O1 95.57(4), P1-Pd-C13 82.42(6), O1-Pd-N1 92.25(6), N1-Pd-C13 89.87(7), Pd-N1-H1 99(2), Pd-O1-C1 130.6(1), O1-C1-O2 126.2(2).

amine conformation, the C=O···H–N distance (2.15 Å), and the N1–H1–O2 bond angle (163°) are all characteristic of such a hydrogen bond.[8, 9] Moreover, the X-ray structure shows the ring pucker that was deduced from the ^{1}H NMR spectrum. The dihedral angle between the square plane, defined by N1-O1-P1-C13, and the metallacycle plane, defined by P1-C7-C12-C13, is 28.14°.

Formation of Pd^0, along with aryl amine products, has been shown to occur from amine-ligated aryl halide complexes upon addition of base to deprotonate the amine and generate a Pd^{II} amido species.[1e, 7] Amine complex **3** also reacts with base to generate Pd^0. Treatment of **3** with a slight excess of NaO*t*Bu in THF formed Pd^0 complex **2** in 48% yield, as determined by ^{31}P NMR spectroscopy. The yield of **2** was nearly quantitative based on the number of phosphanes that could be formed from **3**; an essentially quantitative yield of **2** based on palladium was obtained when the reaction was run in the presence of 3 equiv of P(*o*-Tol)$_3$.

Scheme 1 shows a rational mechanism for the formation of **2** from **3** in the presence of base. Deprotonation of the amine

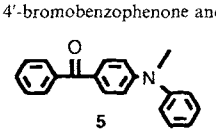


Scheme 1. Postulated mechanism for the synthesis of **2**: a) deprotonation, b) β-H elimination, c) reductive elimination, d) disproportionation.

proton would lead to the formation of a short-lived amido complex, along with NaOAc and HO*t*Bu. Rapid β-hydrogen elimination, the common reaction pathway followed by palladium amides with β-hydrogens, and subsequent reductive elimination with formation of a C–H bond would provide the palladium complex **4**, which contains a single, coordinated P(*o*-Tol)$_3$.[10] Dismutation between two of these highly unsaturated species would produce **2**, as well as an unligated Pd, in a total possible yield of 50% based on the starting palladacycle.

If the reactivity described above is relevant to amination reactions catalyzed by **1**, compound **3** must catalyze the amination of aryl halides in a fashion similar to **1** and **2**. Indeed, **3** catalyzes the reaction of aryl halides with amines in the presence of NaO*t*Bu base. The coupling of 4′-bromobenzophenone and *N*-methylaniline to form **5** with **1**, **2**, or **3** as catalyst was compared. Each catalyst gave yields between 81% and 85% (Table 1) and provided turnover numbers between 350–400 per Pd center for 0.1–0.2 mol% catalyst. Thus, metallacycles **1** and **3** clearly act as precursors to P(*o*-Tol)$_3$-ligated Pd^0 complexes in the amina-

Table 1. Reaction between 4′-bromobenzophenone and *N*-methylaniline.



5

Catalyst	Yield[a] of **5** [%] [a]	TON [b] per mole cat.	TON [b] per Pd center
1	81.3	718	359
2	85.1	314	314
3	81.5	396	396

[a] Yields of isolated products. [b] Determined by ^{1}H NMR spectroscopy.

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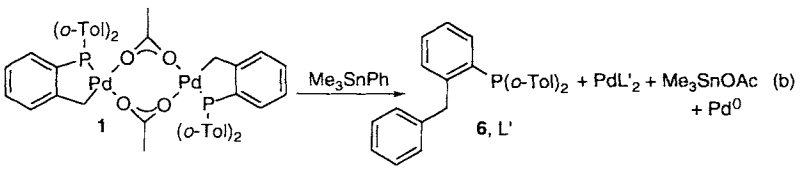
tion reactions. In order to evaluate whether the β-hydrogen elimination mechanism was necessary for activation of the catalyst, the amination of aryl bromides with diphenylamine was evaluated with **1** and **2**. Although **2** catalyzes such reactions in essentially quantitative yields, **1** was inert.

Palladacycle **1** effectively catalyzed Stille cross-coupling reactions. For example, a turnover number of 1650 was observed in the coupling of 4'-bromoacetophenone and Me_3SnPh catalyzed by 0.04 mol% catalyst **1**, as determined by ^{1}H NMR spectroscopy. An increase in catalyst concentration to 5 mol% led to complete conversion of aryl halide and a 96% yield of 4-$PhC_6H_4COCH_3$ (by ^{1}H NMR spectroscopy).

Since the reagents in these Stille reactions cannot produce ligands containing β-hydrogens, a pathway to generation of Pd^0 that is distinct from that in the amination chemistry would be required for a conventional mechanism involving Pd^0 and Pd^{II}. Palladacycle **1** and Me_3SnPh were heated to 70 °C in [D_6]benzene for 2.5 h to determine whether a Pd^0 complex formed. Monitoring of the reaction by NMR spectroscopy showed the conversion of the resonances for **1** into two new ^{31}P NMR resonances for complexed and free $P(o\text{-Tol})_2(C_6H_4\text{-}o\text{-}CH_2Ph)$ (**6**) at $\delta = -8.1$ (δ [Pd{P(*o*-Tol)$_3$}$_2$] = −6.7) and −29.9 (δ P(*o*-Tol)$_3$ = −29.1), respectively. From these reactions, the arylated *o*-tolyl phosphane **6** and P(*o*-Tol)$_3$ side product were isolated in a 5:1 ratio by column chromatography to give a total phosphane yield of 87%. As demonstrated by the two ^{31}P NMR resonances for the reaction mixture, both free and coordinated ligand **6** exist in the reaction, presumably along with unligated Pd^0 [Eq. (b)]. These results strongly suggest that Pd^0 complexes containing **5** and P(*o*-Tol)$_3$ are the active species in Stille couplings involving **1** and may be the active catalyst in Suzuki carbon–carbon bond-forming reactions.[11]



In summary, our data have shown that catalytically active Pd^0 complexes can be formed from **1** by two different routes: β-hydrogen elimination of a palladium amide or C–C bond-forming reductive elimination involving a palladium phenyl substituent. It is difficult to determine conclusively if these reactions occur in the catalytic chemistry of **1**. However, they would provide **1** with an entry into catalysis by Pd^0/Pd^{II} pathways and should be included in mechanistic considerations.

Experimental Procedure

3: Dimeric palladacycle **1** (145.0 mg, 0.155 mmol) was suspended in pentane (6 mL) under N_2. $HNEt_2$ (400 μL, 3.87 mmol) was added and the resulting mixture heated at 70 °C for 30 min. Slow cooling to room temperature produced analytically pure, air-stable, pale yellow crystals of **3** in 83.6% yield. Anal. calcd for $C_{27}H_{34}NPdO_2P$: C 59.84, H 6.32, N 2.58. Found: C 59.66, H 6.30, N 2.61; ^{31}P NMR (300 MHz, [D_8]toluene, 25 °C, H_3PO_4 standard): δ = 33.2 (s, 1P, PdP); ^{1}H NMR (300 MHz, [D_8]toluene, −80 °C, residual C_7H_8): δ = 9.24 (s, 1H, NH), 7.34–6.64 (broad m, 24H, aromatic CH), 3.16 (d, ^3J(H,H) = 14.2 Hz, 1H, $PdCH_2$), 3.06 (s, 3H, $PdC_6H_4CH_3$), 2.83 (s, 3H, $PdC_6H_4CH_3$), 2.65 (d, ^3J(H,H) = 14.9 Hz, 1H, $PdCH_2$), 2.37–2.18 (broad m, 4H, $2NCH_2$), 2.16 (s, 3H, $OCOCH_3$), 1.64 (t, ^3J(H,H) = 5.5 Hz, 3H, CH_2CH_3), 1.40 (t, ^3J(H,H) = 5.4 Hz, 3H, CH_2CH_3); ^{13}C NMR (300 MHz, [D_8]toluene, 25 °C, residual C_7H_8): δ = 179.0 (s, *CO*), 158.6 (d, ^1J(C,P) = 31.6 Hz, *PC*), 143.3 (d, ^2J(C,P) = 13.7 Hz, tolyl CCH_3), 137.4 (s, 2 overlapping tolyl CCH_3 signals), 135.2 (d, ^1J(C,P) = 53.8 Hz, 2*PC*), 132.7 (d, ^3J(C,P) = 5.5 Hz, *CH*), 132.2 (s, *CH*), 131.8 (d, ^2J(C,P) = 8.45 Hz, *CH*), 131.2 (d, ^3J(C,P) = 1.68 Hz, *CH*), 130.6 (broad s, *CH*), 128.0 (d, ^2J(C,P) = 21.0 Hz, *CH*), 125.8 (d, ^3J(C,P) = 7.3 Hz, *CH*), 125.7 (s, *CH*), 46.0 (broad s, NCH_2), 26.1 (s, $PdCH_2$), 25.6 (s, $OC(O)CH_3$), 22.6 (d, ^3J(C,P) = 10.5 Hz, $2PC_6H_4CH_3$), 14.7 (s, $2NCH_2CH_3$); IR (benzene): $\tilde{\nu}$ = 1581 cm^{-1} (C=O).

Catalytic aminations: In an inert atmosphere glove box, the palladium catalyst (0.036 mmol), P(*o*-Tol)$_3$ (0.12 mmol), 4'-bromobenzophenone (0.71 mmol), and NaO*t*Bu (1.1 mmol) were weighed into a screw-topped test tube equipped with a stir bar. Toluene (6 mL) was added, and the tube was sealed with a cap containing a Teflon septum. *N*-methylaniline (1.1 mmol) was syringed into the reaction mixture. The reaction was stirred at 80 °C for 5 h and cooled to room temperature. The product was isolated by adding brine, extracting the organic phases with ether, drying with $MgSO_4$, and removing the solvent. The product was purified by column chromatography (10:1 heptane/EtOAc).

Stille Couplings: In an inert atmosphere glove box, 4'-bromoacetophenone (0.34 or 0.042 mmol), Me_3SnPh (0.36 or 0.050 mmol), and 1,3,5-trimethoxybenzene (internal standard) were dissolved in C_6D_6 (0.6 mL). An initial ^{1}H NMR spectrum was taken. Palladacycle **1** (0.00013 or 0.0021 mmol, 0.04 mol% or 5.1 mol%) and P(*o*-Tol)$_3$ (0.00084 or 0.0072 mmol) were added to the mixture. The reaction with 0.04 mol% was heated at 120 °C overnight, while the reaction with 5.1 mol% was heated at 100 °C for 4 h. Afterwards, ^{1}H NMR spectra were obtained and compared to the initial spectra in order to determine the reaction yield and amount of remaining substrate.

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[8] Crystal parameters: 0.19 × 0.27 × 0.48 mm, triclinic, $P\bar{1}$ (no. 2), a = 9.379(1), b = 11.287(1), c = 13.573(2) Å, α = 70.13(1), β = 83.68(1), γ = 69.239(9)°, V = 1263.6(7) Å^3, ρ_{calc} = 1.424 g cm^{-1}. Data collection: T = −82 °C, Mo$_{K\alpha}$ radiation, (λ = 0.71069 Å, μ = 8.08 cm^{-1}), ω-2θ technique to a $2\theta_{max}$ of 52.6°. The structure was solved by direct methods. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied. The hydrogen atoms were located in successive difference maps and refined isotropically. Of the 5350 (5122 unique) reflections measured, 4889 that had $I > 3.00\sigma(I)$, along with 425 variable parameters, were used for a full-matrix least squares refinement. ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.023$, $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2} = 0.034$; min/max = −0.66 to 0.49 e$^-$ Å^{-3}). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-85. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, GB-Cambridge CB21EZ (UK) (Fax: Int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).
[9] a) N. N. Lyalina, S. V. Dargina, A. N. Sobolev, T. M. Buslaeva, I. P. Romm, *Koord. Khim.* **1993**, *19*, 57; b) G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*; Springer, New York, **1991**.
[10] We have previously shown that intermediate **4** is consistent with kinetic data for oxidative addition of aryl halides to **2**: J. F. Hartwig, F. Paul, *J. Am. Chem. Soc.* **1995**, *117*, 5373.
[11] We have observed some formation of Suzuki coupling products with pure catalyst **1**, but have not enjoyed the same high turnover numbers observed by the authors of reference [5], despite observation of Suzuki products in high yields with **2**. Thus, our studies focus on Stille chemistry that gives high yields in our hands.

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