Syntheses of Palladated Aryldithioacetals. Unexpected Rearrangement Involving C−S and C−Pd Bonds†

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The reaction of $C_6HI(OMe)_3$-2,3,4-$CH(STo)_2$-6 (**1**) (To = 4-tolyl) with $[Pd(dba)_2]$ (dba = dibezylideneacetone) at room temperature gives $[Pd_2\{\kappa^2$-*C,S*-$CH(STo)(C_6H(STo$-2$)(OMe)_3$-3,4,5$)_2(\mu$-I$)_2]$ (**3**) or, in the presence of Tl(OTf) (OTf = CF_3SO_3) and bpy (2,2′-bipyridine), the cationic cyclopalladated complex $[Pd\{\kappa^2$-*C,S*-$C_6H(OMe)_3$-2,3,4-$CH(STo)_2$-6$\}$(bpy)]OTf (**2**). **3** reacts with Tl(OTf) and (i) RNC (1:2:4) to give *cis*-$[Pd\{\kappa^2$-*C,S*-$CH(STo)\{C_6H(STo$-2$)(OMe)_3$-3,4,5$\}\}(CNR)_2]$OTf [R = 2,6-dimethylphenyl (**4**), ^{t}Bu (**4′**)] or (ii) bpy to give an isomeric form of **2**, *cis*-$[Pd\{\kappa^2$-*C,S*-$CH(STo)\{C_6H(STo$-2$)(OMe)_3$-3,4,5$\}\}$(bpy)]OTf (**5**). The last reaction can be reversed by reacting **5** with NaI. The compound **2** reacts with NaI to give $[Pd(C_6H(OMe)_3$-2,3,4-$CH(STo)_2$-6$)I$(bpy)] (**6**), which can be also prepared by reaction of **1** with $[Pd(dba)_2]$ in the presence of bpy. Complex **2** isomerizes to **5** when refluxed in 1,2-dichloroethane. The crystal structures of **2** and **4** have been determined by X-ray diffraction studies.

Introduction

One of our topics of interest is the synthesis and study of arylpalladium complexes containing reactive *ortho* substituents. We have achieved their synthesis through different routes, and thus, the use of arylmercurials as transmetalating agents has permitted us to obtain arylpalladium complexes having CHO,[1−3] C(O)Me,[2] C(O)NH^{t}Bu,[4] CH_2OEt,[5] or NO_2[6] groups at the *ortho* position. We have also prepared 2-aminoarylpalladium complexes by oxidative addition to Pd(0) of the corresponding bromo- or iodoarenes.[7,8] Many of these compounds show interesting properties.[9] Thus for example, reactions with (i) alkynes gave different organic products, such as indenones, indenols,[10] spirocyclic compounds,[4,5,11] or alkenyl-[4,5] or indenylpalladium[12] complexes, those with (ii) isocyanides gave ketenimines,[4] and those with (iii) CO plus O_2 gave benzoate palladium complexes.[8] We have also shown that some *ortho*-formyl palladium complexes undergo a rare rearrangement involving a positional exchange between the formyl group and the palladium moiety with breaking and reforming of C−C and C−Pd bonds (see [a] in Scheme 1).[1,2] The mechanism of this process is not clear. We proposed a pathway through an oxallyl species,[1,2,9] although other possibilities such as the participation of a palladium benzyne species cannot be discarded.[9] A rearrangement process involving orthometalated aryl iridium complexes is also known;[13] in these cases breaking and re-forming of C−H and C−Ir bonds takes place (see [b] in Scheme 1). The authors demonstrate a mechanism involving the oxidative addition of one of the NMe C−H bonds, followed by a sequence of C−H bond-breaking and bond-reforming steps. In the present paper, we describe the first *ortho*-palladated aryldithioacetals and a new type of rearrangement involving the cleavage of alkyl−S and aryl−Pd bonds and formation of aryl−S and alkyl−Pd bonds (see [c] in Scheme 1). We propose two possible reaction pathways for this transformation.

Experimental Section

The NMR spectra, elemental analyses, conductivity measurements in acetone, and melting point determinations

† Dedicated to Professor Rafael Usón on the occasion of his 75th birthday.

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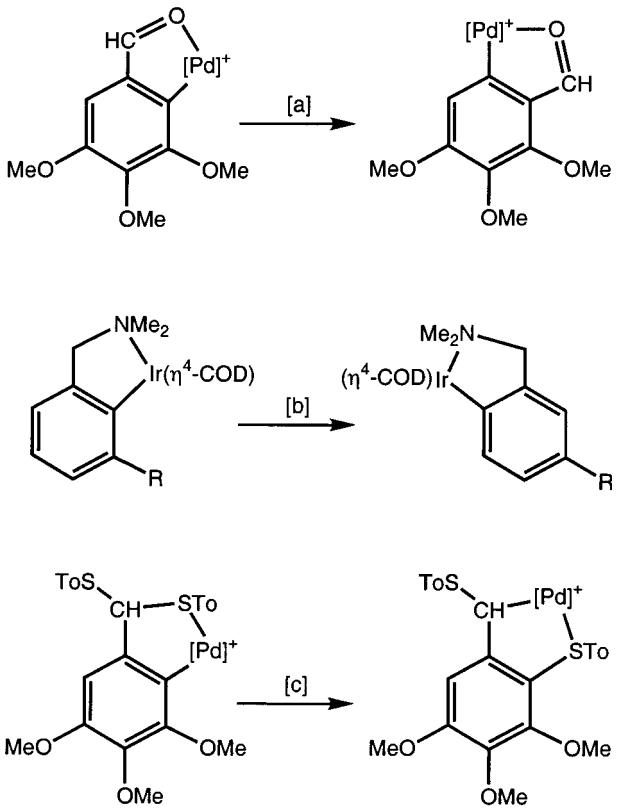
Scheme 1



[a] Refs. 1, 2 and 9. [b] Ref. 13. [c] This work.

were carried out as described earlier.[14] The compounds "Pd(dba)$_2$"[15,16] ([Pd$_2$(dba)$_3$]·dba, dba = dibenzylideneacetone) and 2-iodo-3,4,5-trimethoxybenzaldahyde[17] were prepared as described previously.

Synthesis of C$_6$HI(OMe)$_3$-2,3,4-CH(STo)$_2$-6 (1) (To = 4-tolyl). 4-Thiocresol (2.31 g, 18.6 mmol) was added to a solution of 2-iodo-3,4,5-trimethoxybenzaldehyde (3.00 g, 9.30 mmol) and 4-toluenesulfonic acid (two small crystals) in 1,2-dichloroethane. The solution was refluxed in the presence of anhydrous $MgSO_4$ for 10 h and, then, filtered over anhydrous $MgSO_4$. The solvent was evaporated in vacuo and the residue treated with *n*-pentane (4 cm^3) at 0 °C. The white solid formed was filtered, washed with cold *n*-pentane, and air-dried. Yield: 4.49 g, 87%. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 7.26, (d, $^3J_{HH}$ = 8 Hz 4 H, C$_6H_4$Me-4), 7.05 (s, 1 H, C$_6$H), 7.04 (d, $^3J_{HH}$ = 8 Hz 4 H, C$_6H_4$Me-4), 5.92 [s, 1H, C*H*(STo)$_2$], 3.84, 3.83, 3.76 (s, 3H, 2MeO); 2.28, 1.98 (s, C$_6$H$_4$*Me*-4).

Synthesis of [Pd{κ^2-*C,S*-C$_6$H(OMe)$_3$-2,3,4-CH(STo)$_2$-6}-(bpy)]OTf (2). [Pd(dba)$_2$] (180 mg, 0.32 mmol) and bpy (2,2′-bipyridine) (52 mg, 0.34 mmol) were mixed under nitrogen in toluene (20 cm^3). The iodoarene **1** (192 mg, 0,34 mmol) and Tl(OTf) (122 mg, 0.34 mmol) were added to the resulting solution, and the mixture was stirred at room temperature under nitrogen for 20 h. The solvent was evaporated in vacuo, CH_2Cl_2 (35 cm^3) was added, and the resulting suspension was filtered over Celite. The filtrate was concentrated (ca. 2 cm^3), and Et_2O (15 cm^3) was added. A solid precipitated and was filtered off, washed with Et_2O, air-dried, and further heated in an oven at 70 °C to give **2** as a yellow solid. Yield: 210 mg, 78%; mp 184 °C (dec). Λ_M = 136 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, d_6-acetone, TMS, 20 °C): δ 8.9−6.7 (several m, 17H, bpy + C$_6H_4$Me-4 + C$_6$H), 6.17 [s, 1H, C*H*(STo)$_2$], 3.82 (s, 3H, MeO), 3.81 (s, 6H, 2MeO), 2.28, 1.98 (s, C$_6$H$_4$*Me*-4). At −60 °C the MeO signals are separated (3.77, 3.74, 3.73 ppm). Anal. Calcd for $C_{35}H_{33}F_3N_2O_6PdS_3$: C, 50.20; H, 3.98; N, 3.35; S, 11.49. Found: C, 49.90; H, 4.05; N, 3.62; S, 11.34. Single crystals were grown by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of **2**.

Synthesis of [Pd$_2${κ^2-*C,S*-CH(STo)(C$_6$H(STo-2)(OMe)$_3$-3,4,5)$_2$(μ-I)$_2$] (3). Method A. This complex was prepared as **2** from [Pd(dba)$_2$] (663 mg, 1.14 mmol) and **1** (763 mg, 1.38 mmol) to give **3** as an orange solid. Yield: 574 mg, 76%.

Method B. Complex **5** (100 mg, 0.12 mmol) was reacted with NaI (18 mg, 0.12 mmol) in acetone (10 cm^3) for 24 h. The mixture was evaporated to dryness and the residue recrystallized from CH_2Cl_2/Et_2O. Yield: 63 mg, 80%. The sample contained traces of a compound having bpy, which were easily removed by a further recrystallization. Mp: 181 °C (dec). Λ_M = 1 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 7.81, 7.50, 7.24 (d, ^3J(HH) = 7.7 Hz, 2 H; C$_6H_4$Me-4); 7.14 (b m, 3 H; C$_6H_4$Me-4 and C$_6$H); 5.57 (s, 1 H; CHPd); 3.78, 3.63, 3.27 (s, 3 H; MeO); 2.34, 2.32 (s, 3 H; C$_6$H$_4$*Me*-4). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$,): δ 155.0, 152.7, 144.1, 141.8, 140.3, 140.2 (C); 134.0 (CH); 131.2(C), 131.0, 130.2, 129.8 (CH); 129.2, 122.0 (C); 107.5 (CH); 60.8, 60.7 (MeO); 56.4 (CHPd); 55.2 (MeO); 21.3 (2xMe). Anal. Calcd for $C_{48}H_{50}I_2O_6Pd_2S_4$: C, 43.74; H, 3.83; S, 9.73. Found: C, 43.63; H, 3.77; S, 9.89.

Complex **3** (150 mg, 0.11 mmol) in CH_2Cl_2 (10 cm^3) was reacted with an aqueous solution of HCl (17 cm^3, 4%) for 23 h. The organic phase was washed twice with aqueous NaOH solution (1 g/100 cm^3) and once with water (80 cm^3). The resulting organic phase was stirred with $MgSO_4$, filtered over $MgSO_4$, and evaporated to dryness. The residue was stirred with Et_2O (30 cm^3) and filtered over Celite, and the filtrate was evaporated to dryness to give an orange solid with the same IR and ^{1}H NMR data as that obtained by reacting **5** with $PhICl_2$ (see below).

Synthesis of *cis*-[Pd{κ^2-*C,S*-CH(STo){C$_6$H(STo-2)(OMe)$_3$-3,4,5}}(CNXy)$_2$]OTf (4). Complex **3** (100 mg, 0.075 mmol) was reacted with Tl(OTf) (54 mg, 0.15 mmol) in CH_2Cl_2 (20 cm^3) for 15 min, then XyNC (Xy = 2,6-dimethylphenyl, 40 mg, 0.30 mmol) was added and the mixture stirred for 2 h. The suspension was filtered over Celite, the filtrate was concentrated to ca. 1 cm^3, and Et_2O (6 cm^3) was added. The resulting suspension was filtered, and the solid was washed with Et_2O and dried, first with air, then in an oven at 70 °C for 3 h, and finally for 3 days in a vacuum desiccator over phosphorus pentoxide to give **4** as a yellow solid. Yield: 124 mg, 86%; mp 160 °C. Λ_M = 119 Ω^{-1} cm^2 mol^{-1} (dec). IR (cm^{-1}): ν(C≡N) 2184. ^{1}H NMR (300 MHz, $CDCl_3$, TMS, −60 °C): δ 7.6−7.9 (several m, 15 H, aromatic H's), 5.59 (s, 1 H, C*H*Pd), 3.97, 3.86, 3.59 (s, 3H, MeO), 2.41, 1.97 (s, 3 H; C$_6$H$_4$*Me*-4), 2.37, 2.26 (s, 6H, C$_6$H$_3$*Me*$_2$-2,6). ^{3}C{^{1}H} NMR (75 MHz, $CDCl_3$,): δ 156.5, 152.8, 144.3, 142.1, 139.7, 139.5, 135.3, 135.2 (C); 133.2 (CH); 130.8, 130.5 (C); 130.1, 130.0 (CH); 129.4 (C); 129.1, 128.2, 128.1 (CH); 116.1 (C); 108.2 (CH, C$_6$H); 65.5 (CHPd); 62.9, 60.7, 56.3 (OMe); 20.9, 20.7 (Me, STo); 18.3 (4xMe, 2xCNC$_6$H$_3$*Me*$_2$-2,6). Anal. Calcd for $C_{43}H_{43}F_3N_2O_6PdS_3$: C, 54.73; H, 4.60; N, 2.97; S, 10.19. Found: C, 54.95; H, 4.75; N, 3.10; S, 9.84. Single crystals were grown by slow diffusion of *n*-pentane into solutions of **4** in CH_2Cl_2.

Synthesis of *cis*-[Pd{κ^2-*C,S*-CH(STo){C$_6$H(STo-2)(OMe)$_3$-3,4,5}}(CN^{t}Bu)$_2$]OTf (4′). This was prepared as described for **4** from **3** (100 mg, 0.08 mmol), Tl(TfO) (54 mg, 0.15 mmol), and ^{t}BuNC (35 μL, 0.30 mmol). Yield: 118 mg, 92%; mp 80 °C. Λ_M = 133 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(C≡N) 2210. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.5−7.0 (m, 8 H,2×C$_6H_4$Me-4), 6.56 (s, 1 H, C$_6$H), 5.30 (s, 1 H, C*H*Pd), 3.78, 3.77, 3.54 (s, 3H, MeO),

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2.36, 2.35 (s, 3 H; C_6H_4*Me*-4), 1.53, 1.44 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$,): δ 156.6, 152.0, 147.1, 141.7, 140.4, 138.9, 132.4, 130.8, 129.5, 127.8, 116.1 (C); 133.9, 130.3, 130.0, 129.7 (CH, *o*- and *m*-C_6H_4); 107.5 (CH, C6); 60.8, 60.7, 56.0 (OMe); 59.4, 58.9 (C, ^{t}Bu); 55.9 (CHPd); 29.8, 29.7 (Me, ^{t}Bu); 20.9, 20.7 (Me, STo); 21.2 (2×C_6H_4*Me*-4). Anal. Calcd for $C_{35}H_{43}F_3N_2O_6PdS_3$: C, 49.61; H, 5.13; N, 3.31; S, 11.35. Found: C, 49.28; H, 5.12; N, 3.32; S, 11.65.

Synthesis of [Pd{κ^2-*C,S*-CH(STo){C_6H(STo-2)(OMe)$_3$-3,4,5}}(bpy)]OTf (5). Method A. A solution of **2** (100 mg, 0.12 mmol) in 1,2-dichloroethane (5 cm^3) was refluxed for 8 h. The solution was concentrated and Et_2O (10 cm^3) was added, giving **5** as a yellow solid. Yield: 85 mg, 85%.

Method B. Tl(OTf) (162 mg, 0.46 mmol) and complex **3** (100 mg, 0.23 mmol) were stirred in CH_2Cl_2 (20 cm^3) for 15 min. Then bpy (72 mg, 0.46 mmol) was added, and the mixture was stirred for 8 h and then filtered over Celite. The filtrate was concentrated (ca. 1 cm^3) and Et_2O added, causing the precipitation of yellow **4**, which was filtered, washed with Et_2O, and dried in an oven for 2 h (70 °C) and over phosphorus pentoxide for 2 days. Yield: 334 mg, 87%; mp 215 °C (dec). Λ_M = 133 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.93 (d, ^3J(HH) = 5.5 Hz, 1 H), 8.56 (t, ^3J(HH) = 7.5 Hz, 2 H), 8.20 (d, ^3J(HH) = 6.5 Hz, 2 H), 8.05 (t, ^3J(HH) = 7.5 Hz, 1 H), 7.85 (d, ^3J(HH) = 7.5 Hz, 2 H), 7.71 (t, ^3J(HH) = 6.5 Hz, 1 H), 7.51 (t, ^3J(HH) = 6.5 Hz, 1 H), 7.4−7.0 (m, 6 H), 6.27 (s, 1 H, C_6H), 4.71 (s, 1 H, CHPd), 3.79, 3.63, 3.55 (s, 3 H, MeO), 2.32 (s, 6 H, 2×C_6H_4*Me*-4). Anal. Calcd for $C_{35}H_{33}F_3N_2O_6PdS_3$: C, 50.20; H, 3.98; N, 3.35; S, 11.49. Found: C, 49.95; H, 4.12; N, 3.51; S, 11.54.

Complex **5** (125 mg, 0.15 mmol) in CH_2Cl_2 (10 cm^3) was reacted with $PhICl_2$ (41 mg. 0.15 mmol). After 1 h stirring, the suspension was filtered to give a yellow solid (mainly [$PdCl_2$(bpy)] in accord with its IR spectrum) and a solution, which was concentrated to dryness. The residue was extracted with Et_2O (8 cm^3) and filtered over Celite, the filtrate was concentrated (ca. 1 cm^3), and *n*-hexane (5 cm^3) was added to give a solid, which was filtered, washed with *n*-hexane, and dried in the air to give an orange solid that shows an IR band at 1688 (vs) cm^{-1}, assignable to ν(C═O), and ^{1}H NMR resonances (300 MHz, $CDCl_3$) at δ 10.59 (s, CHO, 1 H), 7.37 (s, C_6H, 1 H), 7.03 (s, br, C_6H_4Me-4, 4 H), 3.95 (s, 2 OMe, 6 H), 3.76 (s, OMe, 3 H), 2.27 (s, C_6H_4*Me*-4, 3 H), suggesting it to be C_6H(OMe)$_3$-4,5,6-(CHO)-2-(SC_6H_4Me-4)-1 (23 mg, 48% yield).

Synthesis of [Pd(C_6H(OMe)$_3$-2,3,4-CH(STo)$_2$-6)I(bpy)] (6). Method A. [Pd(dba)$_2$] (90 mg, 0.16 mmol) and bpy (27 mg, 0.17 mmol) were mixed under nitrogen in toluene (20 cm^3). Iodoarene **1** (96 mg, 0,17 mmol) was added to the resulting mixture, which was stirred at room temperature under nitrogen for 20 h. The solvent was evaporated in vacuo and the residue extracted with CH_2Cl_2 (20 cm^3), the extract being filtered over Celite. The resulting solution was evaporated (ca. 2 cm^3) and Et_2O (15 cm^3) added, causing the precipitation of a solid that was filtered, washed with Et_2O, and air-dried, giving yellow **6**. Yield: 97 mg, 74%.

Method B. NaI (18 mg, 0.12 mmol) was added to a solution of **5** (100 mg, 0.12 mmol) in acetone (12 cm^3). The resulting mixture was stirred for 1 h. The solvent was evaporated and the residue extracted with CH_2Cl_2 (20 cm^3). The extract was filtered over Celite, giving a yellow solution that was evaporated (ca. 1 cm^3). Addition of Et_2O (10 cm^3) caused the precipitation of **6**, which was filtered, washed with Et_2O, and air-dried. Yield: 65 mg, 67%; mp 95 °C (dec). Λ_M = 13 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS, −60 °C, see discussion): δ 9.7−6.2 (several m, 18 H, aromatic protons and C*H*(STo)$_2$); 3.96, 3.88, 3.79 (s, 3 H, MeO); 2.24, 2.00 (s, 3 H, C_6H_4*Me*-4). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$,): δ 155.2, 153.8, 153.7, 150.9, 141.4, 138.8, 131.3, 126.1, 121.9 (C); 152.0, 150.3, 138.7, 138.5, 133.2, 131.6, 129.1, 128.8, 126.3, 125.7 (CH); 106.4 (CH, C5); 66.8, 60.6, 59.9, 55.7 (OMe, CH(STo)$_2$; 20.9 (2xC_6H_4*Me*-4). Anal. Calcd for $C_{34}H_{33}N_2IO_3PdS_2$: C, 50.10; H, 4.09; N, 3.44; S, 7.87. Found: C, 49.88; H, 4.15; N, 3.60; S, 7.76.

Table 1. Crystal Data for Complexes 2 and 4

	2·$^1/_2CH_2Cl_2$	**4**
formula	$C_{35.5}H_{34}ClF_3N_2O_6PdS_3$	$C_{43}H_{43}F_3N_2O_6PdS_3$
M_r	879.68	943.37
cryst size (mm)	0.36 × 0.22 × 0.10	30 × 0.25 × 0.13
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
cell constants		
a (Å)	10.751(1)	11.426(1)
b (Å)	21.613(2)	14.429(1)
c (Å)	15.528(2)	14.591(1)
α (deg)	90	79.347(3)
β (deg)	93.187(3)	73.791(3)
γ (deg)	90	67.750(3)
V (Å^3)	3602.7(7)	2129.3(3)
Z	4	2
λ (Å)	0.71073	0.71073
D_{calc} (Mg m^{-3})	1.622	1.471
μ (mm^{-1})	0.827	0.645
transmissions	0.980−0.739	0.928−0.738
F(000)	1788	968
T (K)	143(2)	173(2)
no. of rflns		
measd	23 115	45 910
indep	7370	12 429
R_{int}	0.066	0.043
no. of params	544	532
no. of restraints	603	0
R1[a]	0.048	0.030
wR2[b]	0.126	0.079
$S(F^2)$	0.948	1.043
max. $\Delta\rho$ (e Å^{-3})	0.8	0.7

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

X-ray Structure Determinations. Compound 2·$^1/_2CH_2Cl_2$: Data were collected to $2\theta_{max}$ 52.7° on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. The structure was refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model or as rigid methyl groups. The anion, the methoxy carbon C8, and the solvent molecule are all disordered over two positions.

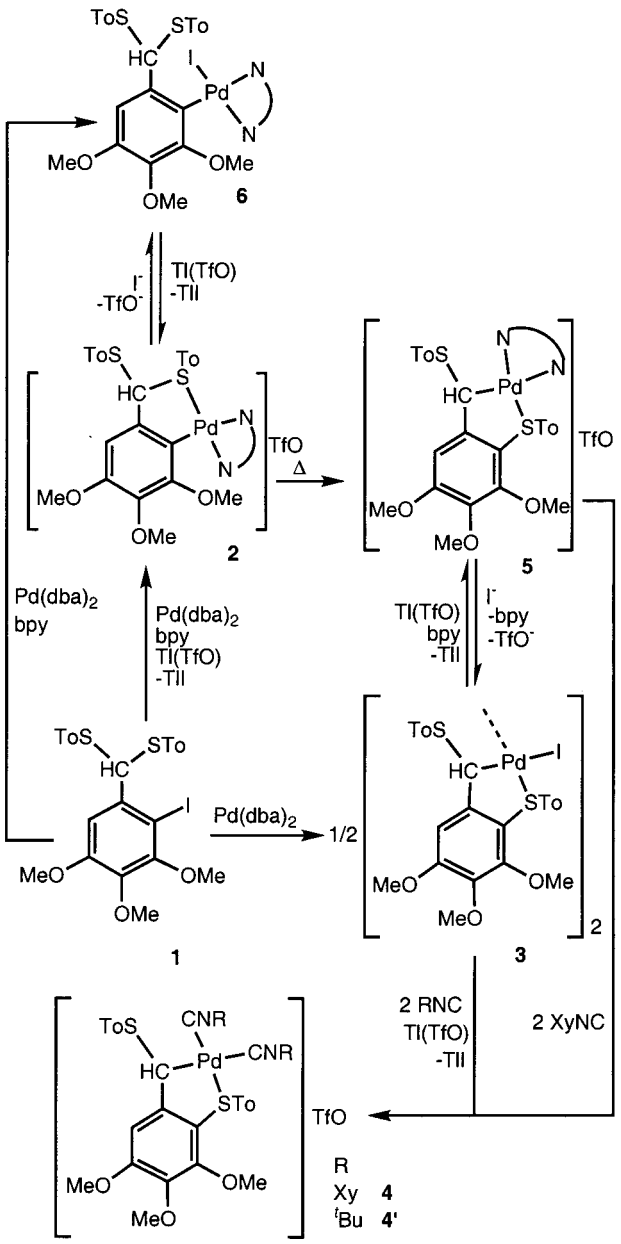
Compound 4: Data were collected to $2\theta_{max}$ 60° as above. The structure was refined as above.

Crystallographic data (excluding structure factors) for both compounds have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC-146289 (**2**) and -146290 (**4**). Copies may be obtained without charge from: CCDC, Union Road, Cambridge CB2 1EZ, UK [fax: internat. + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

The reaction of the 2-iodoarene **1** with [Pd(dba)$_2$] (dba = dibenzylideneacetone) in the presence of Tl(OTf) (OTf = CF_3SO_3) and bpy (2,2-bipyridine) results in the formation of the cationic cyclopalladated complex **2** (Scheme 2), whose structure has been confirmed by X-ray studies (see below). To the best of our knowledge, this is the first synthesis of a palladated dithioacetal complex. We have attempted the synthesis of complexes of this type by direct palladation of thiocresol- and ethylenedithiol-dithioacetal derivatives of terephthalaldehyde with Pd(OAc)$_2$ in refluxing toluene. However, such reactions result in the formation of metallic pal-

Scheme 2



ladium; when these reactions were carried out at room temperature, palladium thiolates seem to be formed.

When **1** is reacted at room temperature with [Pd(dba)$_2$], complex **3** is obtained. We supposed that this compound was an iodine-bridging dimer having the *C*−*S* chelate ligand present in **2**. However, this compound reacts with Tl(OTf) and XyNC (Xy = 2,6-dimethylphenyl) to give **4,** whose structure has been determined by X-ray diffraction studies (see below), showing that an unexpected rearrangement has taken place. This rearrangement involves the cleavage of the HC−S(Pd) and aryl−Pd bonds and the formation of aryl−S and HC−Pd bonds (Scheme 2). The analogous complex **4′** is similarly prepared using ^{t}BuNC.

Complex **3** reacts with Tl(TfO) and bpy to give complex **5**, which is an isomer of **2**. Complex **5** reacts with XyNC (1:2) in CH_2Cl_2 to give **4** quantitatively. The compounds **2** and **5** show a different reactivity toward iodide. Thus, the former reacts with NaI, giving complex **6** in which the donor sulfur atom of the dithioacetal group is displaced by a iodo ligand (Scheme 2), while treatment of the later with NaI results in the displacement of the bpy ligand, regenerating **3**; this fact could indicate that the chelate ligand is more strongly bonded to the palladium atom in **5** than in **2**. Complex **6** can be obtained directly from **1** by reacting it with [Pd(dba)$_2$] and bpy.

Summarizing the reactivity of **1**, it is possible to observe two groups of interconnected complexes: the first one includes complexes **2** and **6**, while **3**, **4**, **4′**, and **5** are included in the second one. We only have been able to get single crystals of **2** and **4**, but it is reasonable to propose that **6** contains the same aryl ligand as **2** because both complexes can be interconverted, while **3**, **4′**, and **5** have the new isomerized alkyl ligand present in **4** because **3** and **5** can be interconverted and both give the same complex **4**. However, with these data only, the possibility that **3** had the dithioacetal ligand and that the rearrangement took place after reacting it with RNC or with bpy and Tl(OTf) to give **4** or **5**, respectively, could not be discarded. To solve this problem, we treated complex **3** with aqueous hydrochloric acid and complex **5** with $PhICl_2$ in the presence of moisture. Both gave the same organic compound, proving that both have the proposed formulation shown in Scheme 2. In accordance with its IR and ^{1}H NMR spectra this compound could be $C_6H(OMe)_3$-2,3,4-(CHO)-6-(SC_6H_4Me-4)-1.

We have also observed a connection between both families of complexes. Thus, when complex **2** is refluxed in 1,2-dichloroethane, it is converted into its isomer **5**. In fact, even freshly prepared samples of **2** show in their ^{1}H NMR spectra weak signals due to the presence of traces of complex **5**, and after a week the ratio **5**:**2** is 9. These observations indicate that the isomerized alkylpalladium complexes are thermodynamically more stable than the non-isomerized aryl complexes and that the formation of non-isomerized **2** is under kinetic control.

A possible reaction pathway for the rearrangement process leading to complex **3** is proposed in Scheme 3. The oxidative addition of **1** to Pd(0) would form the expected cyclopalladated dithioacetal **A**. The C−S bond cleavage, probably induced by the steric hindrance between the iodo ligand and the *ortho* methoxy group, would lead to an iodothiolate complex **B** containing a sulfur ylide aryl ligand. Such cleavage of one C−S bond in thioacetals has been reported, but requires the use of Ca/NH_3 or Na/NH_3,[18] lithium alkyls,[19] or $(Me_3Si)_3SiH$ under free radical conditions.[20] A C−S reductive coupling process would give a thioether, and the resulting Pd(0) could be trapped, forming an anionic three-coordinated complex **C** using the C=S π electron density of the sulfur ylide. Such a C−S coupling process is well documented[21,22] and constitutes an important step in palladium-catalyzed C−S bond formation.[23−25] Finally,

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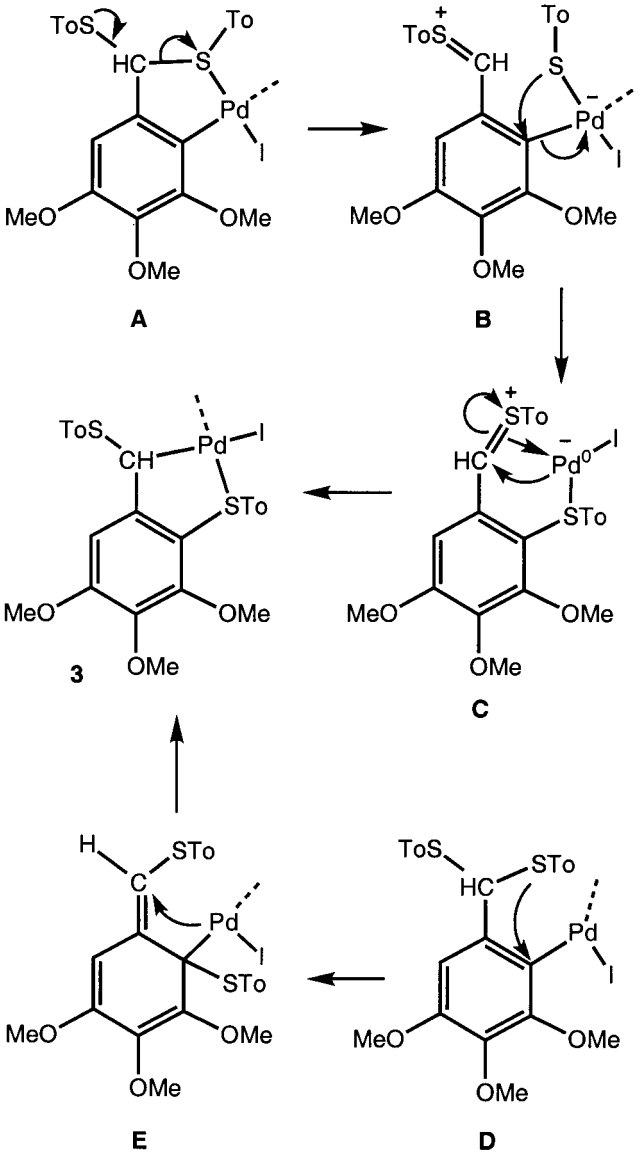
Scheme 3



the nucleophilic Pd(0) should attack the CH carbon atom to give the final Pd(II) complex **3**. An alternative pathway, suggested by one referee, could involve two [1,3] sigmatropic rearrangements. Thus, the cleavage of the S−Pd bond from **A** could give a tricoordinate complex **D**, which could undergo a [1,3] sigmatropic rearrangement to give **E**, which would evolve easily to **3** through a new [1,3] sigmatropic rearrangement involving the migration of the PdI group. The rearrangement leading to **5** from **2** could be explained similarly. When **6** was heated in solution of dichloroethane (6 or 22 h) or toluene (16 h), a mixture mainly containing **6** and **3** was obtained. Because **6** shows a slight conductivity in acetone ($\Lambda_M = 13\ \Omega^{-1}\ cm^2\ mol^{-1}$), the partial rearrangement of **6** to give **3** can be understood if **6** is in equilibrium with the iodide of the cation of **2** (in fact, **2** reacts with iodide to give **6**; see Scheme 2) and that this salt is transformed into the iodide salt of the cation of **5** that evolves to **3** by displacement of

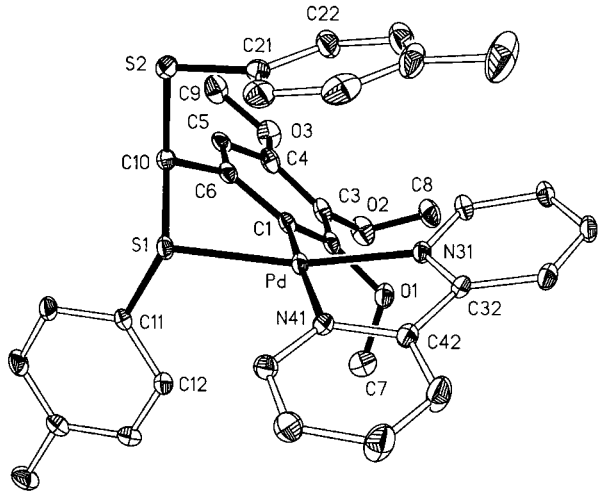


Figure 1. Thermal ellipsoid plot of the cation of **2** (20% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(1) 1.986(4), Pd−N(31) 2.063(3), Pd−N(41) 2.104(3), Pd−S(1) 2.2743(10); C(1)−Pd−N(31) 97.97(14), N(31)−Pd−N(41) 79.01(13), C(1)−Pd−S(1) 82.51(11), N(41)−Pd−S(1) 101.87(9), C(11)−S(1)−C(10) 102.60(19), C(11)−S(1)−Pd 110.45(13), C(10)−S(1)−Pd 96.48(13), C(21)−S(2)−C(10) 104.8(2).

bpy by iodide. The last reaction has been proved independently. The different result of the reaction between **1** and $Pd(dba)_2$ when performed in the presence or without bpy and Tl(OTf) can be understood if the intermediate **A** rapidly reacts with Tl(OTf) and bpy to give **2**, which rearranges to give **5** more slowly than **A** does to give **3**. A similar argument can be invoked in the case of the synthesis of complex **6** from $Pd(dba)_2$.

NMR Spectra. The ^1H resonances due to the dithioacetal carbon $CH(STo)_2$ appear at 6.17 ppm for complex **2**. In the case of **6** it cannot be assigned. The corresponding signal of the starting iodoarene **1** appears at 5.92 ppm. In the case of the isomerized species **3**−**5** the CH−Pd signals appear within the range 6.2−4.7. In consequence, the positions of these signals are not diagnostic for discerning if a given complex is an *ortho*-palladated dithioacetalarene or an isomerized alkylpalladium derivative. This happens similarly with the ^{13}C NMR spectra.

At room temperature, complex **4** exhibits fluxional behavior because both isonitrile ligands appear as equivalent in the ^1H and ^{13}C NMR spectra. Such equivalence disappears on cooling to −60 °C. Interestingly, on cooling, the other signals broaden slightly; this could be due to the decreasing of the sulfur inversion rate. Usually such rates are high, but fluxionality due to a sulfur inversion has been observed in cyclopalladated thioethers.[26] Surprisingly the analogous complex **4′** does not show the same behavior and both ^{t}BuNC ligands are nonequivalent at room temperature in the ^1H and ^{13}C NMR spectra.

In the ^1H NMR spectra of **6**, at room or low (−60 °C) temperatures, the signal corresponding to the hydrogen of the $CH(STo)_2$ group was not observed and the methyls of both To groups appear as two broad signals. This could be due to a restricted rotation about the C−Pd bond.[5,27]

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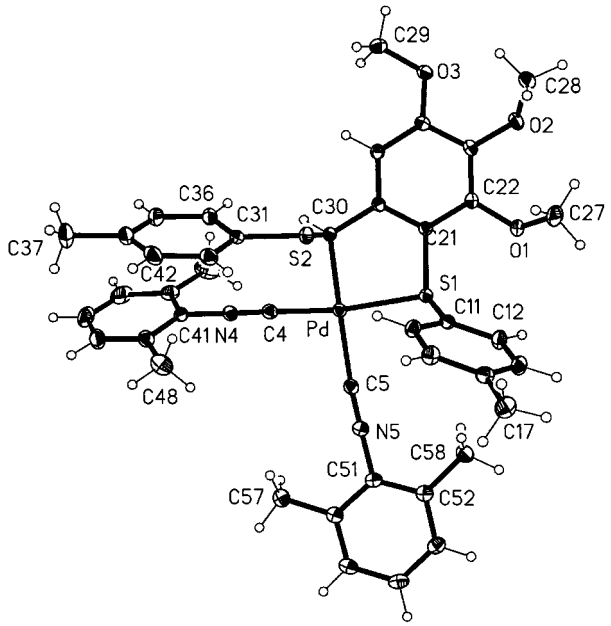

Figure 2. Thermal ellipsoid plot of the cation of **4** (30% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(4) 1.9941(16), Pd−C(5) 2.0573(16), Pd−C(30) 2.0588(15), Pd−S(1) 2.3357(4), N(4)−C(4) 1.149(2), N(5)−C(5) 1.145(2); C(4)−Pd−C(5) 95.96(6), C(4)−Pd−C(30) 88.58(6), C(5)−Pd−S(1) 91.34(4), C(30)−Pd−S(1) 85.90(4), C(21)−S(1)−C(11) 106.70(7), C(21)−S(1)−Pd 99.66(5), C(11)−S(1)−Pd 110.07(5), C(31)−S(2)−C(30) 106.51(7).

X-ray Structures. The solid state structure of **2** has been determined by X-ray diffraction methods (Figure 1, Table 1). The coordination at the palladium atom is significantly nonplanar; the atom N31 lies 0.59 Å out of the best plane through Pd, S1, C1, and N41 (mean deviation 0.03 Å). The interplanar angle of the bpy ligand is 14°. Steric crowding between the methoxy group at O1 and the bpy ligand may be responsible for these features; nonbonded distances are C36···O1 2.91 and H36···O1 2.54 Å. The ring C21−26 adopts an unusual position above the Pd atom, with nonbonded contacts Pd···C21 3.33, Pd···C22 3.67, and Pd···C26 3.48 Å. The hydrogen atom H10 at the chiral carbon C10 is *trans* to the ring C21−26 (torsion angle H10−C10−S2−C21 176°; the corresponding angle to S1−C11 is 40°). The different Pd−N distances [Pd−N41, 2.104(3); Pd−N31, 2.063(3) Å] may indicate a greater *trans* influence exerted by the aryl carbon donor ligand with respect to the sulfur donor, although the severe distortion shown by this complex may also influence these distances.

The structure of **4** (Figure 2, Table 1) shows the coordination at palladium to be nonplanar, with S1 lying 0.70 Å out of the plane through Pd, C4, C5, and C30; there is no obvious cause for this. The triflate oxygen atoms are involved in four C−H···O hydrogen bonds, of which the shortest is H25···O5 2.44 Å. The bond distances between Pd and the isocyanide carbons are significantly different [Pd−C4, 2.0573(16); Pd−C5, 1.9941(16)], suggesting again a greater *trans* influence of the carbon donor ligand (in this case an alkyl group) than of the sulfur donor (a thioether ligand).

Conclusions. The synthesis and characterization of the first palladated dithioacetal complex are reported. An unexpected and previously unreported rearrangement process is also described. This involves the transformation of a dithioacetal aryl ligand into a dithioether alkyl ligand through the cleavage of HC−S and aryl−Pd bonds and formation of aryl−S and HC−Pd bonds. We believe that such transformation takes place with the active participation of the palladium atom, which promotes a carbon−sulfur bond coupling related to that found in palladium-catalyzed arylations of thiols.

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Supporting Information Available: Atomic positional parameters, bond lengths and interbond angles, atomic displacement parameters, and hydrogen atom parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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