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An Unusual Palladium Complex Involved in an Unusual Rearrangement of Ortho-Palladated Aryldithioacetals

José Vicente,*,† José-Antonio Abad,*,† Francisco S. Hernández-Mata,† and Peter G. Jones‡

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia Apto. 4021, E-30071 Murcia, Spain, and Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig Postfach 3329, Braunschweig, Germany

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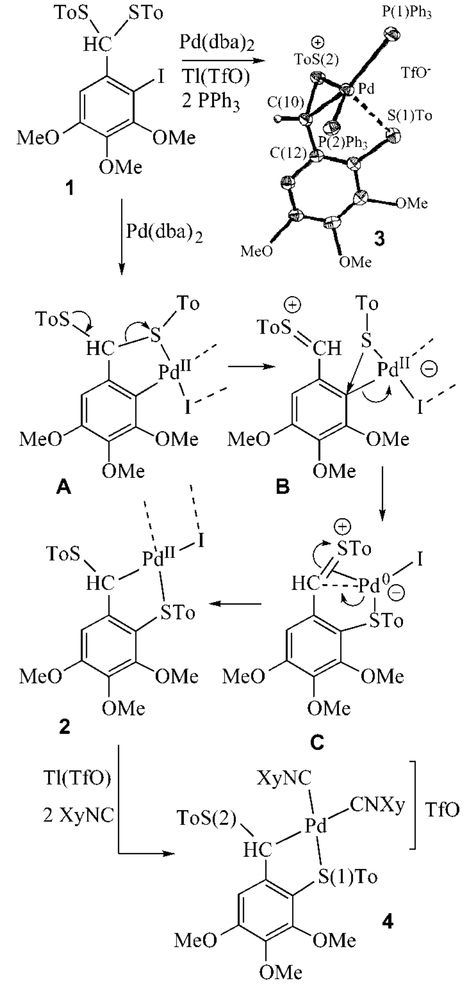
We have recently reported that $IC_6(OMe)_3$-2,3,4-$CH(STo)_2$-6 (**1**, To = 4-tolyl) adds to $Pd(dba)_2$ [dba = dibenzylideneacetone], resulting in the formation of **2** (Scheme 1) through an unexpected rearrangement involving the cleavage of aryl−I and HC−S bonds and formation of aryl−S, HC−Pd, I−Pd, and S−Pd bonds. We proposed the reaction pathway depicted in Scheme 1 to explain this rearrangement.[1] We isolated an adduct of the intermediate **A** [Pd{κ^1-*C*-CH(STo)Ar}(I)(bpy)] (Ar = $C_6H(STo)$-2-$(OMe)_3$-3,4,5; bpy = 2,2′-bipyridine), and in this communication we report the synthesis of a new complex whose structure can be related to the intermediate **C**.

The reaction of **1** with $Pd(dba)_2$, Tl(TfO) and PPh_3 in 1:1:1:2 molar ratios results in the formation of the complex [Pd{κ^2-*C*,*S*-CH(STo)Ar}$(PPh_3)_2$]TfO (**3**, 39% yield, Scheme 1) that can also be obtained by reacting **2** with PPh_3 and Tl(TfO) (1:2:1, 98% yield). The crystal and molecular structure of **3** has been determined by X-ray diffraction studies and shows great differences from the homologous complex **4** (Scheme 1).[1] Thus, in **4**, the Pd−S(1) bond length is 2.2743(10) Å, while that in **3** is much longer [2.8648(7) Å]. Distances in the range 2.877(3)−3.140(2) Å have been considered as corresponding to weak Pd−S interactions.[2] In addition, the Pd−S(2) distance in **3** [2.3843(6) Å] is much shorter than that in **4** [2.9755(5) Å]. The C(10)−S(2) distance in **3** [1.781(2) Å] is significantly shorter than that in **4** [1.8163(15) Å] and lies between the latter value, corresponding to a single bond, and that corresponding to a C═S bond [1.66−1.68 Å].[3] The C(12)−C(10)−S(2) angle in **3** [117.36(17)°] is significantly wider than that in **4** [107.14(10)°], the values being in accordance with C(sp^2) and C(sp^3), respectively. However, the angles H−C(10)−S(2) and H−C(10)−C(12) are similar in both compounds, at 113 and 112° (the H atom was fixed as for an sp^3 system, but a free refinement led to an almost identical position). These data suggest that the sulfur ligand in **3** can be viewed as intermediate between the cation η^2-[ArCH═$S^{(+)}$To], postulated in the intermediate **C**, and the anion κ^2-*C*,*S*-ArCH$^{(-)}$STo. The same intermediate role of the ligand CH_2SMe has been proposed in [Mo(η^5-Cp)(κ^2-*C*,*S*-CH_2SMe)$(CO)_2$][4] and [PdCl(κ^2-*C*,*S*-CH_2SMe)(PPh_3)].[5] Therefore, **3** can be viewed as intermediate between a tricoordinate Pd(0) complex and a square-planar Pd(II) complex. Thus, the P−Pd−P angle [105.04(2)°] is in the range 101−110° found in Pd(0) complexes [$Pd^0(PPh_3)_2$-(η^2-ligand)],[6] but [Pd^{II}(η^3-ligand)$(PPh_3)_2$][7] and the only Pd(II) complex related with **3** whose crystal structure has been reported, [Pd^{II}{κ^2-*P*,*S*-$P(S)Ph_2$}$(PPh_3)_2$]$^+$,[8] show P−Pd−P angles in the range 102−104° (*R* factors ≤5%). The angles P(1 or 2)−Pd−X (X = midpoint C−S) are 133° for P1 and 119° for P2. Alternatively, **3** can be viewed, assuming coordination of S(1) to palladium, as intermediate between a tetrahedral Pd(0) complex—the dihedral angle formed by the planes X−Pd−S(1) and P(1)−Pd−P(2) is 83.8° and that between X−Pd−P(1) and S(1)−Pd−P(2), 74.8°—and a flattened square pyramid with S(1) at the apex. Magnetic measurements indicate that **3** is diamagnetic in the solid state.

Scheme 1



The structures of some palladium complexes with a chelating ligand κ^2-*C*,*S*-RCHSR′ show CH−S distances similar to those in **3**,[9,10] whereas those with a bridging μ_2-κ^2-*C*,*S*-RCH$^{(-)}$SR′ or a

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* To whom correspondence should be addressed. (J.V.) E-mail: jvs@um.es. WWW: http://www.scc.um.es/gi/gqo/. (J.-A.A.) E-mail: jaab@um.es. (P.G.J.) E-mail: jones@xray36.anchem.nat.tu-bs.de.

† Universidad de Murcia.

‡ Technische Universität Braunschweig.

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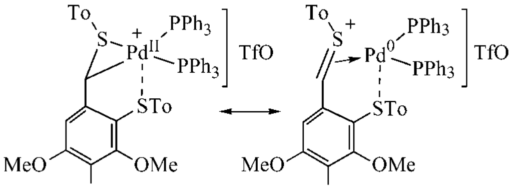
terminal κ^1-*C*-RCH$^{(-)}$SR′ ligand show CH−S distances corresponding to a C−S single bond, similar to that in **4**.[10−12]

The ^{31}P NMR spectrum of **3** shows two doublets at 27.13 and 20.38 ppm with $^2J_{PP}$ = 37 Hz. This coupling constant is within the expected range for a *cis* bis(arylphosphine)palladium(II) complex (30−58 Hz).[8,13,14] In palladium(0) complexes [Pd(PR$_3$)$_2$(olefin)], $^2J_{PP}$ is in the range 5−17 Hz.[13,15−17] Complex **3** does not react with PPh$_3$ (1:2 molar ratio) which contrasts with the behavior of [PdCl(κ^2-*C*,*S*-CH$_2$SMe)(PPh$_3$)] which reacts with PPh$_3$ to give *trans*-[PdCl(κ^1-*C*-CH$_2$SMe)(PPh$_3$)$_2$].[12] In its reactivity complex **3** bears more resemblance to the related Pd(0) complex [Pd(PR$_3$)$_2$(PhCH═CHP$^{(+)}$Ph$_3$)] so that neither reacts with PPh$_3$.[16] However, the nature of **3** in solution could be different than that in the solid state.



3

The most striking feature of our result is that changing XyNC in **4** for PPh$_3$ to give **3** induces an important change of the coordination mode of the sulfur ligand from the chelating five-membered ring to the generally less stable chelating three-membered ring and, to some extent, an intramolecular redox process involving partial reduction of Pd(II) and oxidation of the sulfur ligand. We have already shown in Pd(II) complexes that placing a phosphine ligand *trans* to some carbon donor ligands, such as aryl or aroyl, causes a destabilization leading to a C−P bond coupling[18] or facilitates an easy O$_2$ insertion into a C−Pd bond,[14,19] respectively. This destabilizing effect, which we named *transphobia*,[14,20] has been invoked by other authors.[21] A possible explanation of our present case could be that the *transphobia* of the pair of ligands Ph$_3$P/CH(STo)Ar is greater than that between the pair XyNC/CH(STo)Ar. As many stable [Pd(PR$_3$)$_2$(olefin)] complexes, similar to **3**, have been described, it can be concluded that the *transphobia* between C and P donor ligands is not operative for Pd(0). Therefore, the Ph$_3$P/CH(STo)Ar *transphobia* could induce a change of geometry allowing an intramolecular redox process leading to a more stable situation. In addition, the different steric hindrance of PPh$_3$ and XyNC could also play a significant role in this change of geometry. A reaction related with that leading to **3** is the intramolecular redox process observed when [Pd^{II}(CH$_2$C$_6$H$_4$OSiR$_3$-4)Br(L$_2$)] (L$_2$ = diphosphine) was reacted with F$^-$ to give [Pd^0(CH$_2$═C$_6$H$_4$═O-4)(L$_2$)].[17] This process could also be induced by the P/C *transphobia*.

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Supporting Information Available: Methods of synthesis, spectroscopic and analytical data, a listing of all refined and calculated atomic coordinates, all the anisotropic thermal parameters, full bond lengths and angles, and figure with atom numbering, for compound **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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