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# Synthesis, Isolation, and Characterization of an Organometallic Triiodopalladium(IV) Complex. Quantitative and Regioselective Synthesis of Two C−I Reductive Elimination Products

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S *Supporting Information*

**ABSTRACT:** Iodine and the pincer complex [Pd(*O*,*N*,*C*-L)I], where L is the monoanionic ligand resulting from deprotonation of the acetyl group of the dimethylmonoketal of 2,6-diacetylpyridine, are in equilibrium at low temperatures with the palladium(IV) complex $[\mathrm{Pd}(O,N,C\text{-L})\mathrm{I}_3]$, which can be isolated at −40 °C and characterized by $^1$H NMR spectroscopy and X-ray diffraction studies, in spite of its great instability. When the same reaction is carried out at room temperature, a quantitative reductive elimination process occurs, giving L−I, which in the presence of water affords L′−I, resulting from hydrolysis of L−I.

The number of fully characterized organopalladium(IV) complexes reported is increasingly growing in recent years in parallel with the interest for their use in catalytic and stoichiometric organic reactions. The difficulty of preparing, isolating, and characterizing such complexes stands on their spontaneous tendency to undergo reductive elimination processes to give palladium(II) complexes and C−C or C−X (X = halogen, $\mathrm{RCO_2}$) coupling products, which accounts for their applications in organic synthesis.[1−3]

Since the synthesis of the first organopalladium(IV) complexes by Usón et al. in the 1970s, by reacting perfluorophenylpalladium(II) complexes with chlorine,[4] only a very recent studies devoted to obtaining palladium(IV) complexes by using dihalogens, $\mathrm{PhIX_2}$ or $\mathrm{XeF_2}$, have succeeded in giving oxidative addition products stable enough to be isolated and characterized by X-ray diffraction: $[\mathrm{PdF_2(C\hat{\ }N)(N\hat{\ }N)}]$ (X^Y is an X,Y monoanionic chelating ligand),[5] $[\mathrm{PdCl_2(C\hat{\ }N)(C\hat{\ }O)}]$,[6] $[\mathrm{PdF_2(FHF)(C_6H_4F\text{-}4)(N{\sim}N)}]$ (X∼Y is an X,Y neutral chelating ligand),[7] $[\mathrm{PdBr_2(C\hat{\ }N\hat{\ }N)(CN^tBu)}]$ (X^Y^Z is an X,Y,Z monoanionic tridentate ligand),[2] and $[\mathrm{PdX_3(C\hat{\ }N\hat{\ }O)}]$ (X = Cl, Br).[3] Neutral monohalo derivatives $[\mathrm{PdX(C\hat{\ }C)(N\hat{\ }N\hat{\ }N)}]$ (X = Cl, Br, I) are the isolated products when the halogen is reacted with some anionic complexes.[8] In the meantime, most of the reported reactions of this type in which the palladium(IV) complex has been isolated but not characterized by X-ray diffraction,[9] not isolated,[10,11] or even not detected,[12] have been used to prepare the corresponding C−X coupling products resulting from the reductive elimination process.

The above results set $\mathrm{I_2}$ quite apart from the other halogens. In fact, the only reported organometallic diiodopalladium(IV) complexes are $[\mathrm{PdI_2Me(R)L_2}]$ ($\mathrm{L_2}$ = bidentate nitrogen donor ligands; R = Me, Tol), prepared by reacting $\mathrm{I_2}$ with $[\mathrm{PdMe(R)L_2}]$, which decomposes in solution or upon attempted isolation.[13,14] The sulfur ylide complex $[\mathrm{Pd\{(CH_2)_2S(O)Me\}_2}]$ reacts with $\mathrm{I_2}$ to afford the unstable complex $[\mathrm{Pd\{(CH_2)_2S(O)Me\}_2I_2}]$,[15] which was characterized only by elemental analysis. Even palladium(IV) complexes with only one iodo ligand, usually obtained by the oxidative addition of alkyl iodides to alkylpalladium(II) complexes, are unstable when isolated or only detected in solution.[13,16] At difference with dihalopalladium(IV) complexes, which decompose to give the C−X reductive elimination products, monohalopalladium(IV) complexes usually decompose through C−C coupling processes. Only one such complex, *fac*-$[\mathrm{PdMe_3I(bpy)}]$, has been characterized by X-ray diffraction.[17] When these data on palladium(IV) complexes are compared with those of the corresponding platinum(IV) complexes, the great differences between both $\mathrm{d^6}$ ions are evident. For example, many $\mathrm{Pt^{IV}I}_n$ complexes ($n$ = 1−6), in particular stable triiodo complexes, have been isolated.[18]

We have recently reported the synthesis of the pincer complexes [Pd(*O*,*N*,*C*-L)X],[3,19a] where X = Cl, Br and L is the monoanionic ligand resulting from deprotonation of the monoketal of 2,6-diacetylpyridine (dap), and its use to prepare palladium(IV) complexes $[\mathrm{Pd}(O,N,C\text{-L})\mathrm{X}_3]$ (X = Cl, Br) by reacting them with $\mathrm{Cl_2}$ or $\mathrm{Br_2}$.[3] Because this pincer ligand provides these complexes with a remarkable stability, we considered the synthetic challenge of completing the series by preparing the triiodopalladium(IV) complex $[\mathrm{Pd}(O,N,C\text{-L})\mathrm{I}_3]$ (**2**), whose stability was predicted to be very precarious considering all of the above data.

The reaction of [Pd(*O*,*N*,*C*-L)Cl] with NaI afforded quantitatively [Pd(*O*,*N*,*C*-L)I] (**1**; Scheme 1). The reaction at −40 °C, under $\mathrm{N_2}$, between a $\mathrm{CH_2Cl_2}$ solution of **1** and $\mathrm{I_2}$ (1:1.25 molar ratio) gave a very dark solution, which upon slow diffusion of $\mathrm{Et_2O}$ and standing for 5 days at −33 °C gave black single crystals of the triiodopalladium(IV) complex **2**. Although crystalline solid **2** shows no noticeable decomposition after 1 month at −33 °C, the amorphous solid decomposes immediately at 20 °C, preventing us from obtaining good elemental analyses. However, **2** has been characterized by $^1$H NMR spectroscopy and X-ray crystallography (see below). This result contrasts with that obtained in the related reaction between $[\mathrm{Pd(N\hat{\ }C\hat{\ }N)I}]$ {N^C^N = 2,6-bis[(dimethylamino)methyl]phenyl) and $\mathrm{I_2}$,

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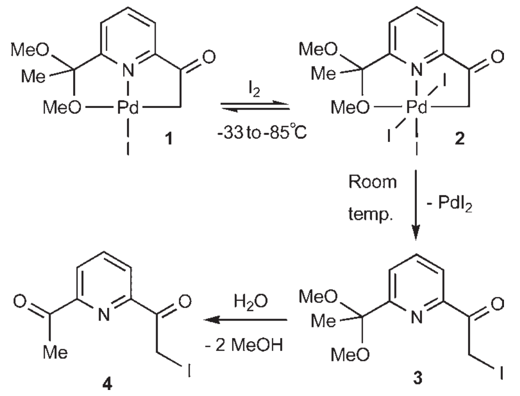
Scheme 1



which affords $[Pd(N^\wedge C^\wedge N)I\cdots(I_2)_2]$ containing two molecules of $I_2$ interacting with the iodo ligand at a distance of 3.3 Å[19b]. This complex is a possible model for the initial stage in the formation of **2**, although another with a $Pd\cdots I_2$ interaction, such as has been described for the homologous platinum(II) pincer complex,[20] cannot be discarded.

The reaction of **1** with 1 equiv of $I_2$ was followed by $^1H$ NMR in $CD_2Cl_2$ and $CDCl_3$ at various temperatures. At room temperature, the spectra of the reaction mixtures showed full and almost immediate decomposition of **2** to the C−I coupling product, L−I (**3**; Scheme 1), and precipitation of a black solid, identified as $PdI_2$. Therefore, the room temperature reaction of a $CHCl_3$ solution of **1** with 1 equiv of $I_2$ allowed the quantitative and regioselective isolation of **3**. When this reaction was carried out in the presence of water, using MeCN as the solvent, hydrolysis of **3** took place, allowing the quantitative and regioselective isolation of compound **4**. We could not isolate the chloro and bromo homologues of **3**, from the corresponding palladium(IV) complexes because they quickly hydrolyzed to give the corresponding homologues of **4**.[3] The only reported halogen derivative of dap is the symmetric dibromo-2,6-diacetylpyridine obtained by bromination.[21]

Complexes of iron(II) and cobalt(II) with bis(imino) derivatives of dap are highly active catalysts for the polymerization and oligomerization of olefins. Compound **4** and derivatives prepared by replacing iodine could be used to synthesize new catalysts with unsymmetrical dap derivatives.[22]

Although palladium(IV) intermediates have been invoked in some reactions between alkylpalladium(II) complexes and $I_2$, affording C−I coupling products, they have not even been detected in solution.[11] The same occurs with the diiodination of some arenes using $Pd(OAc)_2$ as the catalyst and IOAc as the oxidant.[23]

At temperatures below −33 °C, the $^1H$ NMR spectra of the $I_2$ + **1** mixture showed only the presence of **1** and **2**. The **2**/**1** ratio increases when the temperature decreases, reaching >99% conversion of **1** into **2** at −85 °C. The temperature dependence of the equilibrium $\mathbf{1} + I_2 \leftrightarrows \mathbf{2}$ in $CDCl_3$ was investigated in the range 240−211 K. A van't Hoff analysis ($R = 0.999$) yields values of $\Delta H = -24$ kJ mol$^{-1}$ and $\Delta S = -59$ J K$^{-1}$ mol$^{-1}$. Values of $K_{eq}$ at 211 and 240 K are 757 and 142, respectively ($[\mathbf{2}] = [I_2] = 2.88 \times 10^{-2}$ mol L$^{-1}$). A similar study was reported for the reaction between $[PdMe(C_6H_4OMe\text{-}4)(bpy)]$ and $(4\text{-}ClC_6H_4)_2Se_2$ to afford $[PdMe(C_6H_4OMe\text{-}4)(SeC_6H_4Cl\text{-}4)_2(bpy)]$ ($\Delta H = -130$ kJ mol$^{-1}$, $\Delta S = -472$ J K$^{-1}$ mol$^{-1}$, and $K_{eq} = 759$ at 248 K).[24]

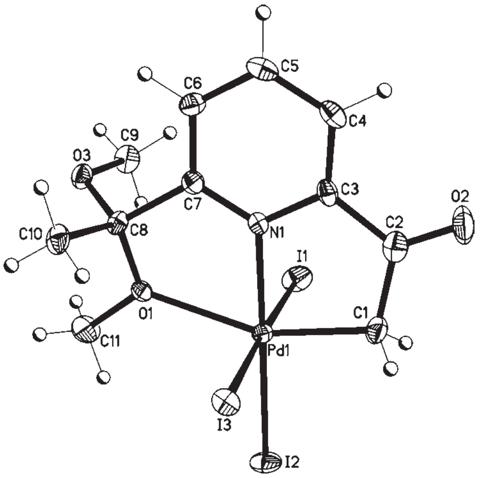


**Figure 1.** Ellipsoid representation of **2** (50% probability).

The tendency of **2** to disproportionate into the reagents used to prepare it, **1** and $I_2$, represents an essential difference with respect to its homologues trichloro and tribromo complexes[3] and other organometallic palladium(IV) complexes with the only exception shown above.[24] This can be considered normal for an organometallic complex of a highly oxidizing metal center, palladium(IV), bonded to three reducing ligands like $I^-$ and is in line with our initial skepticism on the success of the synthesis of **2**.

The $^1H$ NMR spectrum of complex **1** shows the equivalence of the MeO groups and that of the $CH_2$ protons at room temperature, while at −33 °C, the corresponding signals are broad. In the chloro and bromo derivatives, the equivalence of the MeO and $CH_2$ protons is maintained even at −60 °C, which shows that the Pd−OMe bond is stronger in the iodo complex **1** than in its halide homologues. In contrast to **1**, the MeO and $CH_2$ protons of **2** at −33 °C are observed as two singlets and an AB system, respectively, which reveals the stronger Pd−OMe bond in the palladium(IV) complex **2** with respect to the palladium(II) complex **1**. The $CH_2$ protons in complex **2** appear highly deshielded (6.29 and 6.01 ppm) with respect to that in **1** (3.49 ppm), which was also observed in the chloro and bromo derivatives.

The structure of complex **2** (Figure 1)[25] is similar to those of its chloro and bromo homologues.[3] The main difference (apart from the Pd−X bond distances) is the Pd−N bond length, which is longer in **2** [2.045(3) Å] than in the other $[PdLX_3]$ complexes {X = Br [2.0207(15) Å], Cl [2.0058(15) Å]}, according to the trans influence scale I > Br > Cl.[26]

In conclusion, we have studied (1) the reaction between an organometallic palladium(II) pincer complex and $I_2$, being able to isolate and characterize (by NMR and X-ray diffraction) the first triodo organometallic palladium(IV) complex ever reported, in spite of its instability, (2) the first equilibrium $[Pd^{II}] + X_2$ (halogen) $\leftrightarrows [Pd^{IV}X_2]$, (3) the reductive elimination process that, at room temperature, affords the unreported C−I coupling product, and (4) hydrolysis of the latter, which leads to the first monohalo derivative of dap.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Experimental details, spectroscopic data, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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