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Quantitative Synthesis and Full Characterization of the First Isolated and Stable Pincer Palladium(IV) Complexes. Quantitative and Regioselective Synthesis of the C–X (X = Cl, Br) Reductive Elimination Products[‡]

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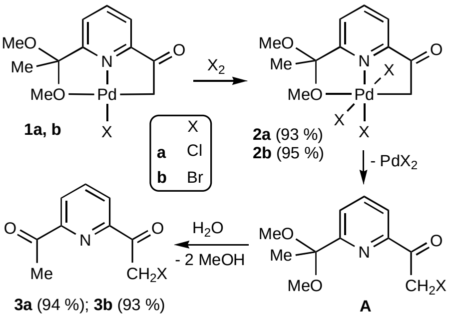
The pincer complexes [Pd(O^1,N^1,C^1-L)X], where X = Cl, Br and L is the monoanionic ligand resulting from deprotonation of the acetyl methyl group of the monoketal of 2,6-diacetylpyridine (dap), react with excess of Cl_2 or Br_2 affording, quantitatively, the Pd(IV) complexes [Pd(O^1,N^1,C^1-L)X_3], which have been characterized by X-ray difraction and studied their decomposition that quantitatively afford the reductive elimination products L-X.

Pd(IV) is usually described as a comparatively rare oxidation state. However, three very recent reviews show the extraordinary current activity in the synthesis of organometallic Pd(IV) complexes and the study of processes involving Pd(II)/Pd(IV) catalysis and C–H activation chemistry.[1] These organometallics,[2] can be classified in three categories: (1) those detected in situ or mainly characterized by NMR spectroscopy,[3-7] (2) complexes isolated but not characterized by X-ray diffraction (XRD)[6-9] and (3) those fully characterized, including XRD studies. In this group there are (3a) trimethyl,[10,11] scorpionate[12,13] or trimethyl(scorpionate)[7,10,14] complexes, (3b) alkyl[15-17] or aryl[18] complexes with a N^N chelating ligand, (3c) C^O[19] or C^N[20-22] metallacyclic complexes, or (3d) a few having Si–Pd bonds.[23] In this paper we report two Pd(IV) complexes that do not belong to any of these types.

In spite of the great number and the interest of the Pd(II) pincer complexes,[24] their Pd(IV) homologues are too unstable to be isolated and characterized[5,6,25] or even detected.[26] It has been proposed the intermediacy of Pd(IV) complexes with a P^C^P pincer ligand in Pd(II)/Pd(IV) redox cycle based Heck-type catalysis, although attempts to detect or isolate them were not carried out.[27] We report here that it is possible to isolate and characterize remarkably stable Pd(IV) complexes containing a pincer ligand instead of the bidentate chelating or scorpionate ligands that stabilize all previously reported organometallic Pd(IV) complexes.

Although some halo-complexes are among the most stable Pd(IV) complexes, the number of those being also organometallics are very limited. Thus, in the above mentioned group of fully characterized Pd(IV) organometallics, several monohalo[7,10,13,15,17,21] and only three dihalo derivatives are included: [$PdCl_2$(C^N)(C^O)],[28] [PdF_2(C^N)(N^N)],[22] and [PdF_2(FHF)(C_6H_4F-4)(N^N)][18]. We report here the first synthesis and full characterization of very stable trihalo Pd(IV) organo-complexes, of which there are examples among those not fully characterized, [$PdCl_3$(C_6F_5)(N^N)] (N^N = bpy, phen, tmeda)[9] and those very unstable and only characterized in solution by NMR spectroscopy.[4-6] As far as we are aware, not trihalo non-organometallic Pd(IV) complexes have been reported either.



Scheme 1

We have recently reported that the reaction of $PdCl_2$ with 2,6-diacetylpyridine (dap) in refluxing MeOH affords [Pd(*O*,*N*,*C*-L)Cl] (Scheme 1, **1a**);[29] its homologous bromo derivative **1b** was obtained (98% yield) by reacting **1a** with NaBr. The reaction at 0ºC during 5 min of a CH_2Cl_2 solution of **1a** with excess of Cl_2 or of **1b** with Br_2 afforded quantitatively **2a** or **2b**, respectively. The reaction of **1a** with XeF_2 did not lead to any Pd(IV) complex. Complexes **2** are the first ketonyl Pd(IV) compounds obtained from a ketonyl Pd(II) derivative. There exist only a few obtained by oxidative addition of $BrCH_2C(O)Ar$ (Ar = Ph, C_6H_4Br-2) to [$PdMe_2L_2$] (L_2 = bpy, phen).[17]

Crystaline **2a** or **2b** or amorphous solid **2a** can be stored without decomposition at 20, 4 or 4 ºC, respectively. The amorphous solid **2a** shows < 6% decomposition after 30 day at 20 ºC. The ^{1}H NMR spectra of $CDCl_3$ solutions of **2b** showed, after 24 h at room temperature, full decomposition to the coupling product **3b** (Scheme 1). During this period, formation of an intermediate, which resonances were consistent with the diketal **A** (X = Br), was observed. Attempts to isolate **A** were unfruitful because it hydrolized very easily. $CDCl_3$ solutions of complex **2a** showed only a 5% decomposition after four days, but the corresponding diketal intermediate was not observed.

The remarkable stability of complexes **2a**, greater than that of the three dihalo Pd(IV) mentioned above, can only be attributed to the pincer ligand. However, because other Pd(IV) pincer complexes could only be characterized in solution,[5,6,25] the stability of **2** must be related with the nature and/or mutual disposition of the functional groups in our pincer ligand. Further studies are being carried out in order to prepare other Pd(IV) complexes with the same or related pincer ligands.

Complexes **2** in MeCN solutions or when **2a** was reacted with 4,4'-di-t-butyl-2,2'-bypiridine (^{t}Bubpy) and $NaClO_4$ (also without this salt) led to the quantitative and regioselective synthesis of the monohalogenated dap **3** (Scheme 1). The bromination of dap has been reported to give the symmetric dihalogenated dap.[30] It is reasonable to assume that both MeCN and ^{t}Bubpy cleave the Pd–O bond giving adducts (not detected by ^{1}H NMR spectroscopy) that decompose through a C–X coupling process due to the steric hindrance between the entering ligand and the $CMe(OMe)_2$ group. It is well-known that palladium organometallics [Pd]–R react with halogens X_2 to give [Pd]–X and R–X.[31,32] However, only a few works report the detection of the Pd(IV) intermediates in these reactions[32] or the formation of R–X directly from an isolated Pd(IV) complex, such as **2**.[18,21,22] Complexes of Fe(II) and Co(II) with bis(imino) derivatives of dap are highly active catalysts for polymerization and oligomerization of olefins.[33] Compounds **3** and their derivatives could be used to prepare new catalysts with unsymmetrical dap ligands.[34]

The ^{1}H NMR spectra of complexes **1** show a fast exchange between the MeO groups, that even at –60 ºC causes their equivalence and that of the CH_2 protons. However, in **2** two separate (broad at room temperature and sharp at –55 ºC) resonances are observed for MeO and CH_2 protons, in keeping with the expected strenghthening of the Pd–OMe bond in **2** with respect to **1**. The high oxidation of the metal center in **2** also explains the high deshielding of the CH_2 protons (~6 ppm) with respect to those in the **1** precursors (~3.5 ppm).

Complexes **1b** (Fig. 1; CCDC 784548), **2a** (Fig. 2; CCDC 784549) and **2b** (Fig. 3; 784550) were analyzed by X-ray diffraction. The structure of **1b** is similar to that of **1a**.[29] When the bond distances in Pd(II) complexes **1** are compared with those of **2**, the main difference is that the Pd–N, Pd–C and Pd–O bond distances are longer in **2** (X = Cl: 2.0058(15), 2.0245(18), 2.2755(12) Å; Br: 2.0207(15), 2.0319(19), 2.2833(13) Å, respectively) than in **1** (X = Cl: 1.9752(19), 2.000(2), 2.2149(16) Å; Br: 1.9806(16), 1.999(2), 2.2169(14) Å, respectively) in keeping with the increase in coordination number. The same was observed when distances in homologous Pt(IV) and Pt(II) complexes are compared.[26]

In conclusion, this communication reports the quantitative synthesis of (1) the first fully characterized and highly stable Pd(IV) complexes containing a pincer ligand or having three halo ligands and (2) their C–X reductive elimination products. The great stability of these complexes is due to the specific pincer ligand used in this work. The C–X coupling products could be useful for the synthesis of catalysts for polymerization or oligomerization of olefins or as oxidative addition reagents. As a whole, the yields of Pd(IV) complexes **2** and their reductive elimination products **3** as well as the stability of complexes **2** are better than those of analogous Pd(IV).[35] These results prove that Pd(IV) complexes with pincer ligands can be stable if their arms are adequately chosen, which opens an interesting new field of research.

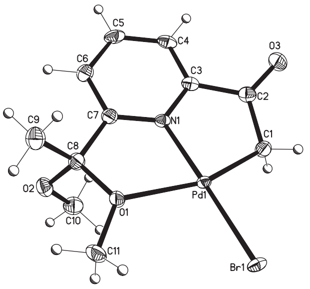


Figure 1. Ellipsoid representation of **1b** (50% probability).

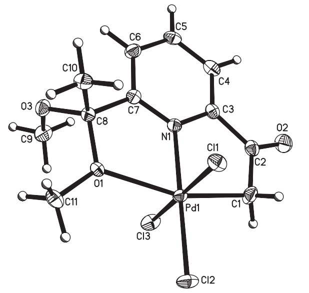


Figure 2. Ellipsoid representation of **2a** (50% probability).

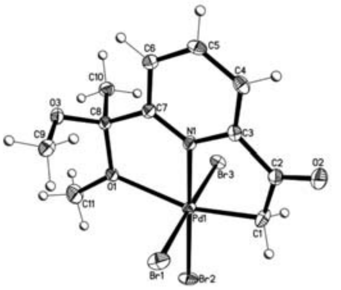


Figure 3. Ellipsoid representation of **2b** (50% probability).

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Notes and references

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‡ Dedicated to Prof. Dr. María Teresa Chicote on occasion of her 60th birthday.

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[35] $[\mathrm{PdCl_2(C{\wedge}N)(C{\wedge}O)}]$:[28] quantitatively yield, stable in MeCN solution at -35 ºC, decomposes at 33 ºC to give the Pd(II) complex $[\mathrm{PdCl(ClC{\wedge}N)(C{\wedge}O)}]$ as the major product in 75% or 46% isolated yield. $[\mathrm{PdF_2(C{\wedge}N)(N{\wedge}N)}]$:[22] 88% isolated yield, stable at 23 ºC in the solid state for at least a week and in chloroform solution at 50 ºC for at least 2h; heating it at 150 ºC in DMSO affords FC^N in 71% isolated yield. $[\mathrm{PdF_2(FHF)(C_6H_4F\text{-}4)(N{\wedge}N)}]$:[18] 38% yield; heating it at 80 ºC in nitrobenzene afforded only traces of 1,4-$C_6H_4F_2$