Dinuclear Palladium(III) Complexes with a Single Unsupported Bridging Halide Ligand: Reversible Formation from Mononuclear Palladium(II) or Palladium(IV) Precursors**

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Along with the well-known involvement of Pd⁰ and Pd^{II} oxidation states in a large number of palladium-catalyzed reactions,^[1] recent reports have proposed the intermediacy of less-common Pd^{IV} and Pd^{III} oxidation states in several chemical transformations.^[2] Among these systems, dinuclear and mononuclear Pd^{III} complexes have been shown to act as active intermediates in both two- and one-electron oxidative C-H functionalization and C-C bond formation reactions.^[3-6] For example, dinuclear organometallic Pd^{III} complexes stabilized by a Pd-Pd bond have been recently reported^[3,7] and shown to be a catalytically competent alternative to mononuclear Pd^{IV} species in carbon-heteroatom bond-formation reactions.^[3,4] In this context, we have recently shown that mononuclear Pd^{III} complexes stabilized by a tetradentate diazapyridinophane ligand can be isolated and have shown that they exhibit C-C bond-formation reactivity.^[6] Continuing our work in the study of high-valent Pd complexes, we report herein novel cationic dinuclear Pd^{III} and mononuclear Pd^{IV} complexes supported by a common tridentate nitrogendonor ligand, N,N',N''-trimethyl-1,4,7-triazacyclononane (Me₃tacn). Moreover, we provide evidence for the involvement of a Pd^{III} species in the Kharasch addition reaction and confirm the ability of Pd to catalyze one-electron radical reactions. In addition, the reported Pd^{III} systems are the first group 10 d^7 - d^7 dinuclear complexes bridged by a single unsupported halide ligand and represent a model of the delocalized Pd^{III}-X-Pd^{III} electronic structure that has been proposed to exist in some -Pd-X-Pd-X- one-dimensional (1D) chains.^[8]

While triazacyclonane $(tacn)^{[9,10]}$ and other tacn derivatives^[11] have been employed in the synthesis of Pd complexes, only one complex, $[(Me_3tacn)Pd^{II}(MeCN)_2](PF_6)_2$, has been reported for Me_3tacn.^[10] We have synthesized the Pd^{II} complexes $[(Me_3tacn)Pd^{II}X_2]$ (X = Cl **1a**, X = Br **1b**) through

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the reaction of Me₃tacn with $[(MeCN)_2Pd^{II}X_2]$.^[12] The X-ray structure analysis of **1a** reveals a square-planar arrangement of two Cl⁻ ions and two N atoms around Pd, while the third N atom of Me₃tacn is not in close proximity to the metal center (Figure 1a),^[13] in contrast to the five-coordinate geometry



Figure 1. ORTEP representation (ellipsoids set at 50% probability) of a) **1a**, b) the cation of **2a**, and c) the cation of **3a**. Selected bond distances [Å] and angles [°]: **1a**: Pd1–N1 2.0736(5), Pd1–N2 2.0878(5), Pd1–Cl1 2.30651(18), Pd1–Cl2 2.32102(17). **2a**: Pd1–N1 2.094(2), Pd1–N2 2.105(2), Pd1–N3 2.273(2), Pd1-Cl2 2.3179(7), Pd1-Cl3 2.3224(7), Pd1-Cl1 2.4801(2), Cl1–Pd1i 2.4801(2), Pd1–Pd1i 4.931; Pd1-Cl1-Pd1i 167.47(4). **3a**: Pd1–N3 2.080(8), Pd1–N1 2.0806(16), Pd1–N2 2.093(8), Pd1–Cl1 2.302, Pd1–Cl2 2.308, Pd1–Cl3 2.308.

observed for $[(Me_3tacn)Pd^{II}(MeCN)_2](PF_6)_2$.^[10] Cyclic voltammetry (CV) of both **1a** and **1b** in MeCN/Bu₄NPF₆ reveals two closely-spaced waves at 0.05–0.17 V versus Fc⁺/Fc and additional waves at higher potentials, suggestive of oxidatively induced chemical reactions.^[12,14]

Controlled potential electrolysis (CPE) at 0.3–0.4 V for both **1a** and **1b** leads to formation of a dark purple species in 60-70% yields of isolated product after passing a charge corresponding to a one-electron oxidation. X-ray-quality crystals of the electrooxidation products obtained from MeCN/Et₂O reveal the formation of dinuclear complexes [(Me₃tacn)Pd^{III}X₂(μ -X)Pd^{III}X₂(Me₃tacn)](PF₆) (X = Cl **2a**, X = Br **2b**), in which a single halide ion bridges the two Pd centers (Scheme 1 and Figure 1b; Supporting Information,



Scheme 1. Electrochemical synthesis of dinuclear Pd^{III} complexes and their interconversion to mononuclear Pd^{II} and Pd^{IV} complexes.

Figure S31).^[13,15] Each metal center has a distorted octahedral geometry with two N atoms and the two terminal halides in the equatorial plane, while the third N atom of Me₃tacn and the bridging halide occupy the axial positions. The coordination geometry of Pd atoms and the overall charge of the dimer confirm the presence of Pd^{III} centers. To the best of our knowledge, complexes **2a** and **2b** are the first dinuclear Pd^{III} complexes that are not stabilized by a Pd–Pd bond.^[3,7] Furthermore, this result suggests that stabilization of the Pd^{III} oxidation state can also be achieved by a tridendate N-ligand and does not require a rigid tetradentate ligand.^[6]

The formation of dinuclear Pd^{III} complexes **2a** and **2b** from the mononuclear precursors **1a** and **1b** is intriguing. The circa 65% yield of product suggests that the bridging halide ion comes from another molecule of the Pd^{II} precursor.^[16] Indeed, addition of 0.5 equiv of external halide leads to a simpler CV that shows only two closely spaced oxidative waves (Table 1; Supporting Information Figures S1–S4), and CPE at 0.3–0.4 V leads to formation of dark purple complexes **2a** and **2b** in higher yields (ca. 80%).^[12,17] Interestingly, when Br⁻ was added to a solution of **1a**, the mixed halide complex [(Me₃tacn)Pd^{III}Cl₂(μ -Br)Pd^{III}Cl₂(Me₃tacn)](PF₆) (**2c**) formed (Scheme 1), as confirmed by X-ray crystallography (Support-

Table 1: Spectroscopic properties of dinuclear Pd^{III} complexes 2a-c.

Complex	$E_{1/2}^{1/11}, E_{1/2}^{111/1V}$ [mV] ^[a]	UV/Vis (MeCN) λ [nm] (ε [Lmol ⁻¹ cm ⁻¹])
2a	55, 163	534 (21000), 449 (sh, 4900), 360 (6100), 260 (43000)
2 b 2 c	45, 171 65, 174 ^[b]	570 (25000), 411 (8900), 273 (47000) 546 (17000), 378 (6800), 262 (41000)

[a] Potentials vs. Fc^+/Fc are measured by differential pulse voltammetry (DPV) for solutions of 1 a or 1 b in the presence of 1 equiv of Cl^- or Br^- , respectively, in 0.1 M $Bu_4NPF_6/MeCN$. Complexes 2a–c show two oxidation waves at similar potentials (see the Supporting Information). [b] Potentials are measured by DPV for a solution of 1 a in the presence of 1 equiv of Br^- . ing Information, Figure S31).^[12] This observation suggests that the use of alternate exogenous ions can lead to Pd^{III} complexes with bridging ligands and altered electronic properties.^[18] Complexes **2a–c** are structural models of the dinuclear unit found in -M-X-M-X-1D extended chains^[8] in the average-valent Mott–Hubbard (MH)^[8,19] state M^{III}–X–M^{III} (that is, a Robin–Day class III state).^[20] The bridging halide ligand in **2a–c** is located at the midpoint between the two metal centers,^[21] while the short Pd…Pd distances (**2a** 4.931 Å, **2b** 5.133 Å, **2c** 5.031 Å, Figure 1b; Supporting Information, Figure S31)^[22] suggest an intimate orbital overlap between Pd and the bridging halide that is supported by the observed strong antiferromagnetic coupling between the unpaired d_{z2} electrons of the two Pd^{III} centers,^[23] which is typical for a delocalized MH state.^[8,19b]

The UV/Vis spectra of complexes **2a–c** in MeCN reveal at least three intense absorption bands at 535-570 nm, 360-410 nm, and 260-280 nm, respectively (Table 1 and Figure 2).^[24] Density functional theory (DFT) and time-



Figure 2. UV/Vis spectra of 1a (-----), 2a (——), and 3a (•••••) in MeCN. Inset: CV of 1a in the presence of 0.5 equiv Cl^- (•••••) and 1 equiv Cl^- (——) in 0.1 M Bu₄NPF₆/MeCN.

dependent DFT (TD-DFT) calculations were employed in the assignment of these transitions. For 2a, the 534 nm band exhibits an uncommonly large extinction coefficient ($\varepsilon =$ $21\,000\,\mathrm{Lmol^{-1}cm^{-1}}$) and is assigned to an intermetallic Pdto-Pd charge transfer (MMCT)^[25] transition that is strongly mixed with a µ-Cl-to-Pd CT transition (LMCT).^[26] A similar assignment has been proposed for the low-energy transitions in Pd^{III}-X-Pd^{III}-X 1D chains.^[8] TD-DFT calculations support such an assignment by revealing a large oscillator strength for the HOMO to LUMO+1 MMCT transition, where the HOMO exhibits σ-bonding Pd-µ-Cl character and the LUMO + 1 has antibonding Pd- μ -Cl character (Figure 3). Furthermore, the higher-energy bands can be assigned to a combination of bridging and terminal halide-to-Pd LMCT bands (for example, HOMO-10 and HOMO-12 to LUMO + 1, respectively; Figure 3), as suggested previously^[8] and supported by TD-DFT calculations.^[12] As expected, the replacement of Cl⁻ with Br⁻ ligands for 2a to 2c to 2b leads to

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Figure 3. DFT-calculated (UB3LYP/CEP-31G) molecular orbitals (MOs) of 2a that are proposed to be involved in the observed UV/Vis absorption bands. The calculated atomic contributions are listed for each MO (Pd1 and Pd2 represent the left and the right metal center, respectively, μ -Cl is the bridging Cl⁻ ligand, Cl refers to the terminal Cl⁻ ligands, and N to the N atoms).^[12]

lower energies of all transitions and thus supports the halide contributions to the corresponding MOs.^[19b]

CV studies show that addition of one equivalent of halide to 1a and 1b leads to an increase of the peak current corresponding to the second oxidation wave (Figure 2, inset). CPE of 1a at about 0.5 V versus Fc⁺/Fc in the presence of 1 equiv of Cl⁻ led to the appearance of an intense band at 534 nm associated with the dinuclear species **2a**, followed by its complete disappearance to give a yellow solution after a two-electron oxidation (Figure 2).^[12] While the yellow species is unstable at RT, it leads to formation of yellow crystals at -20 °C in MeCN/Et₂O. The crystal structure reveals a cationic mononuclear Pd^{IV} complex, [(Me₃tacn)Pd^{IV}Cl₃](PF₆) (3a; Scheme 1); a similar complex $[(Me_3tacn)Pd^{IV}Br_3](PF_6)$ (3b) is obtained upon CPE of **1b** in the presence of 1 equiv of Br⁻, both 3a and 3b exhibiting a pseudo-octahedral geometry around the Pd center (Figure 1c; Supporting Information, Figure S38).^[12,27] The Pd^{II}/Pd^{III}/Pd^{IV} interconversions are reversible: electrochemical reduction of the mononuclear species **3a** (or **3b**) at -0.3 V versus Fc/Fc⁺ occurs via the intermediate dinuclear complex 2a (or 2b) to eventually produce the mononuclear species 1a (or 1b). Interestingly, complexes 3a,b are unstable and slowly decay to the corresponding Pd^{III} species **2a**,**b**; moreover, a rapid reaction occurs when 1 equiv of the Pd^{II} complex **1a** (or **1b**) is added to a solution of 3a (or 3b) to generate the dinuclear Pd^{III} complex 2a (or 2b) in quantitative yield. These studies suggest that the Pd^{III} complexes **2a.b** are more stable under ambient conditions than either the corresponding Pd^{IV} species or a Pd^{II}/Pd^{IV} mixture that is equivalent to a mixed-valence Pd^{IV}-X-Pd^{II} species. This result is in contrast to the use of extreme conditions^[8] or Pd-to-Ni substitution^[19c,d] required for the generation of the Pd^{III}–X–Pd^{III} state in 1D chains. Furthermore, the interconversion between dinuclear Pd^{III} and mononuclear Pd^{IV} species parallels the proposed involvement of analogous intermediates in Pd-catalyzed C–H oxidative functionalization reactions and suggests that for a given ligand environment both types of intermediates can be present.^[3–6]

The relatively low oxidation potentials of complexes 1a,b have prompted us to investigate their reactivity in oneelectron redox reactions, such as the Kharasch addition of polyhaloalkanes to alkenes.^[28] Both 1a and 1b exhibit catalytic activity in the addition of CCl₃Br to a number of alkenes (methyl methacrylate, methyl acrylate, styrene, norbornene, cyclopentene) to give selectively the 1:1 addition product in good to high yields at 65 °C under N₂ (Supporting Information, Chart S1, Table S1).^[12] Kinetic studies of the CCl₃Br addition to methyl methacrylate (MMA) catalyzed by 1a reveal a first-order dependence on 1a and MMA concentration and a saturation behavior with respect to CCl₃Br concentration, thus suggesting a mechanism that involves a reversible electron transfer/halogen transfer from CCl₃Br to Pd^{II} to form a Pd^{III} species and a Cl₃C radical that subsequently reacts with the alkene and leads to the addition-product formation (Scheme 2).^[28] While no Pd^{III}



Scheme 2. Proposed mechanism for the Kharasch reaction catalyzed by 1a,b and the formation of the dinuclear Pd^{III} complexes 2a,b.

intermediate was observed under optimal catalytic conditions, the dinuclear complex **2a** was detected by UV/Vis at RT, both in absence and in presence of MMA (Supporting Information, Figure S24).^[29] Moreover, a higher yield of **2a** (or **2b**) was obtained when **1a** (or **1b**) was reacted with CCl₃Br in presence of O₂, a known radical trap that can react with the Cl₃C radical^[30] and thus drive the formation of the dinuclear Pd^{III} species. As the catalytic reaction rate shows a first-order dependence in catalyst concentration, and the complex **2a** was not observed under optimal catalytic conditions, the formation of the dinuclear Pd^{III} complex is most likely a means of stabilizing the transient mononuclear Pd^{III} intermediate (Scheme 2).^[12] Moreover, the observed chemical oxidation of **1a,b** to form **2a,b** suggests that the polyhaloalkane acts as both the oxidant and the halogen-atom donor and thus parallels the electrosynthesis of complexes **2a**,**b** through electrochemical oxidation in presence of an external halide (Scheme 1).^[31]

In conclusion, we have presented herein the synthesis and characterization of stable dinuclear Pd^{III} complexes formed by oxidation of mononuclear Pd^{II} precursors. Effective stabilization of the Pd^{III} oxidation state was accomplished using the common tridentate ligand Me₃tacn and halide ions and does not require the formation of a Pd^{III}-Pd^{III} bond. Moreover, these dinuclear Pd^{III} complexes seem to be more stable than the corresponding mononuclear Pd^{IV} (and Pd^{III}) complexes under an analogous ligand environment. These results support our hypothesis that Pd^{III} complexes are more common than previously anticipated and can play important roles in various Pd-catalyzed reactions. Furthermore, we suggest that under a given ligand environment, the involvement of either Pd^{III} or Pd^{IV} species as reactive intermediates cannot be unambiguously ruled out or confirmed, given their facile interconversion. Moreover, the reported dinuclear Pd^{III} complexes are models of the delocalized Pd^{III}-X-Pd^{III} electronic structure found in Group 10 M-X-M-X 1D extended chains. Current research efforts are aimed at characterizing the reactivity and electronic properties of these unique dinuclear systems.

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- [15] The presence of dimers 2a and 2b in solution was confirmed by ESI-MS and the lack of an EPR signal for the corresponding solutions at 77 K or RT.
- [16] The presence of $[(Me_3tacn)PdCl(MeCN)]^+$ in solution after oneelectron oxidation of **1a** was detected by CV and confirmed by independent synthesis (see the Supporting Information). If $(Me_3tacn)PdCl(MeCN)^+$ is the only halide abstraction product, then the theoretical yield of **2a** is 67%.
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