Dinuclear Palladium(III) Complexes

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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 Pd^0 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 nitrogen-donor ligand, *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (Me_3tacn). 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 the reaction of Me_3tacn 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 Me_3tacn is not in close proximity to the metal center (Figure 1a),[13] in contrast to the five-coordinate geometry observed for $[(Me_3tacn)Pd^{II}(MeCN)_2](PF_6)_2$.[10] Cyclic voltammetry (CV) of both **1a** and **1b** in MeCN/Bu_4NPF_6 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]

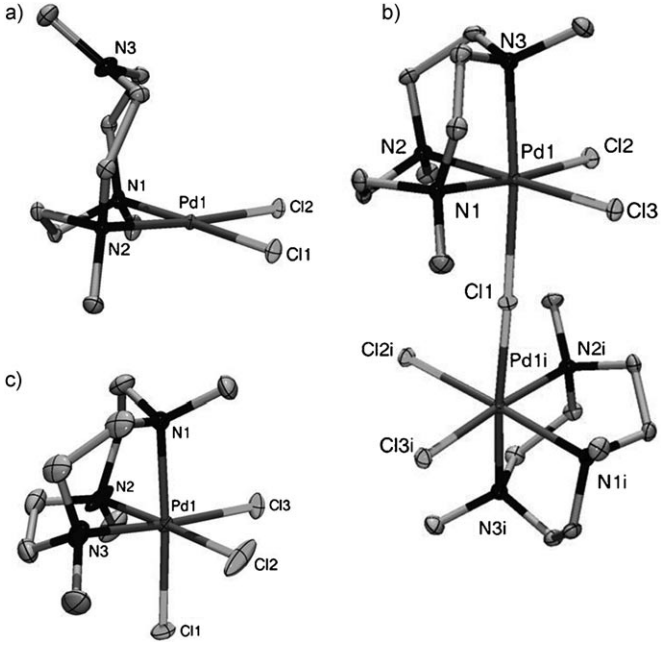

Figure 1. ORTEP representation (ellipsoids set at 50% probability) of a) **1a**, b) the cation of **2a**, and c) the cation of **3a**. Selected bond distances [Å] and angles [°]: **1a**: Pd1–N1 2.0736(5), Pd1–N2 2.0878(5), Pd1–Cl1 2.30651(18), Pd1–Cl2 2.32102(17). **2a**: Pd1–N1 2.094(2), Pd1–N2 2.105(2), 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.

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/Et_2O reveal the formation of dinuclear complexes

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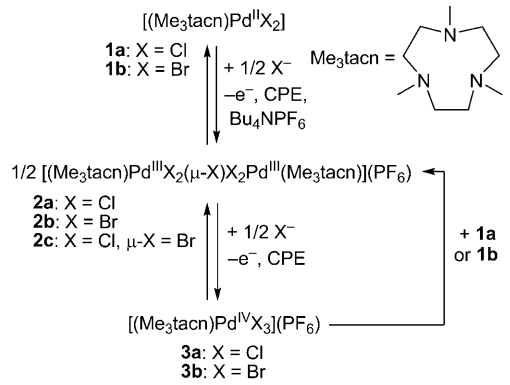
$[(Me_3tacn)Pd^{III}X_2(\mu\text{-}X)Pd^{III}X_2(Me_3tacn)](PF_6)$ (X = Cl **2a**, X = Br **2b**), in which a single halide ion bridges the two Pd centers (Scheme 1 and Figure 1b; Supporting Information, Figure S31).[13,15] Each metal center has a distorted octahedral geometry with two N atoms and the two terminal halides in the equatorial plane, while the third N atom of Me_3tacn 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]



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

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 $[(Me_3tacn)Pd^{III}Cl_2(\mu\text{-}Br)Pd^{III}Cl_2(Me_3tacn)](PF_6)$ (**2c**) formed (Scheme 1), as confirmed by X-ray crystallography (Supporting 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_{z^2} 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-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 (ε = 21000 $L\,mol^{-1}\,cm^{-1}$) and is assigned to an intermetallic Pd-to-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

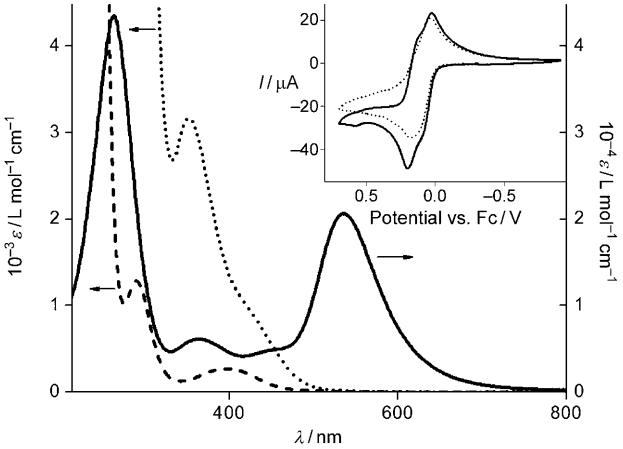


Figure 2. UV/Vis spectra of **1a** (-----), **2a** (——), and **3a** (•••••) in MeCN. Inset: CV of **1a** in the presence of 0.5 equiv Cl^- (•••••) and 1 equiv Cl^- (——) in 0.1 M Bu_4NPF_6/MeCN.

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

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

[a] Potentials vs. Fc^+/Fc are measured by differential pulse voltammetry (DPV) for solutions of **1a** or **1b** 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 **1a** in the presence of 1 equiv of Br^-.

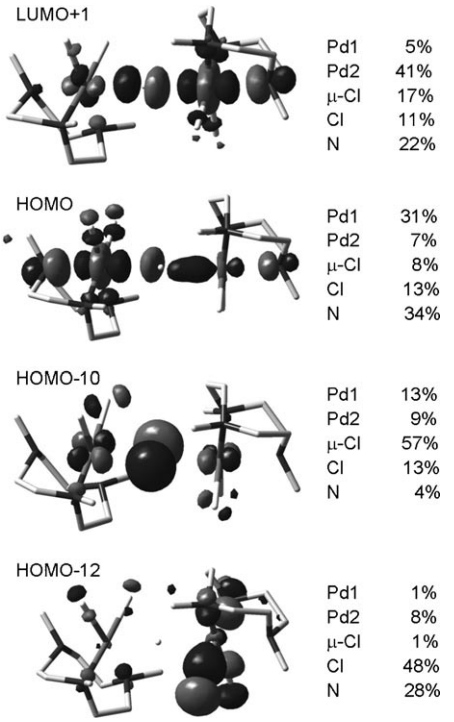
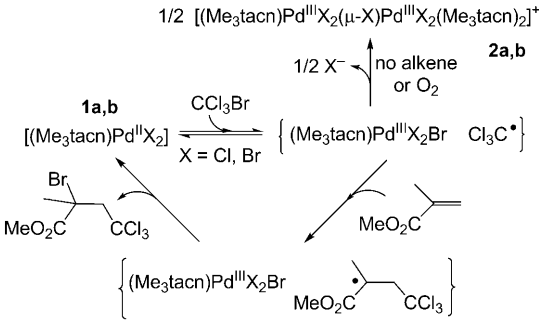


Figure 3. DFT-calculated (UB3LYP/CEP-31G) molecular orbitals (MOs) of **2a** that are proposed to be involved in the observed UV/Vis absorption bands. The calculated atomic contributions are listed for each MO (Pd1 and Pd2 represent the left and the right metal center, respectively, μ-Cl is the bridging 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/Et_2O. The crystal structure reveals a cationic mononuclear Pd^{IV} complex, $[(Me_3tacn)Pd^{IV}Cl_3](PF_6)$ (**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 one-electron redox reactions, such as the Kharasch addition of polyhaloalkanes to alkenes.[28] Both **1a** and **1b** exhibit catalytic activity in the addition of CCl_3Br 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 N_2 (Supporting Information, Chart S1, Table S1).[12] Kinetic studies of the CCl_3Br 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 CCl_3Br concentration, thus suggesting a mechanism that involves a reversible electron transfer/halogen transfer from CCl_3Br to Pd^{II} to form a Pd^{III} species and a $Cl_3C^\bullet$ radical that subsequently reacts with the alkene and leads to the addition-product formation (Scheme 2).[28] While no Pd^{III} 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 CCl_3Br in presence of O_2, a known radical trap that can react with the $Cl_3C^\bullet$ 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 polyhaloal-



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

kane 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 Me_3tacn 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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[12] See the Supporting Information.
[13] CCDC 809190 (**1a**), 809186 (**2a**, $T = 100$ K), 809187 (**2a**, $T = 293$ K), 809183 (**2b**), 809185 (**2c**), 809188 (**3a**), 809189 (**3b**), and 809184 ($[(Me_3tacn)Pd^{II}Cl(MeCN)]ClO_4$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[14] Coulometry measurements confirm that both oxidations correspond to one electron processes (see the Supporting Information).
[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 one-electron 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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[22] For example, the Pd···Pd distance of the only known Pd^{III}–Br–Pd^{III} 1D chain is 5.21 Å at 110 K (Ref. [8a]).
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[31] Chemical oxidation of **1b** with 0.5 equiv Br_2 generates **2b** in 40% yield (see the Supporting Information). No Pd^{IV} complexes were detected during chemical oxidation with excess Br_2 or CCl_3Br.

