



Review

Structure and electronic properties of Pd(III) complexes

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ABSTRACT

Despite the rich chemistry of palladium in oxidation states of 0, +2, and +4, no Pd^{III} coordination compounds have been reported until the 1980s. Moreover, while Pd complexes are among the most commonly used catalysts in organometallic chemistry, the first organometallic Pd^{III} complexes have only been reported in 2006. Since then, a significant number of Pd^{III} complexes have been isolated, characterized, and proposed as active catalytic intermediates in the functionalization of C–H bonds, oxidatively induced C–C bond formation reactions, as well as radical insertion and addition reactions. This review provides an overview of the synthesis and spectroscopic characterization of mononuclear and dinuclear Pd^{III} complexes. A detailed understanding of the steric and electronic properties of Pd^{III} complexes should provide insight for the development of novel catalysts for multi-electron redox reactions and various organometallic transformations.

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1. Introduction

Palladium is one of the most catalytically versatile transition metals, its complexes being efficient catalysts for a wide range of C–C coupling, C–H functionalization, and hydrocarbon oxidation reactions [1–3]. For example, the 2010 Nobel Prize in Chemistry was awarded for palladium-catalyzed cross-coupling reactions [4]. While Pd can exist in five oxidation states (0, +1, +2, +3, and +4) [5], the vast majority of Pd-catalyzed reactions involve Pd⁰ and Pd^{II} oxidation states and these transformations have been extensively

investigated for the past several decades [2,6–9]. In addition, Pd^{IV} complexes have been reported starting more than two decades ago [10–19], and have been shown recently to be involved in a variety of Pd-catalyzed ligand-directed C–H oxidative functionalization reactions [20–26]. By comparison, complexes of odd-electron Pd^I and Pd^{III} oxidation states are much less common. Several dinuclear Pd^I complexes stabilized by a Pd–Pd bond have been reported [27–33], however, no mononuclear Pd^I complexes have been isolated to date [34]. Herein, we provide an overview of the synthesis and spectroscopic characterization of mononuclear and dinuclear Pd^{III} complexes. Dinuclear Pd^{III} complexes have been proposed recently as active catalytic intermediates in the oxidative functionalization of C–H bonds [35–39] and aza-Claisen rearrangements [40], while mononuclear Pd^{III} complexes have been proposed as

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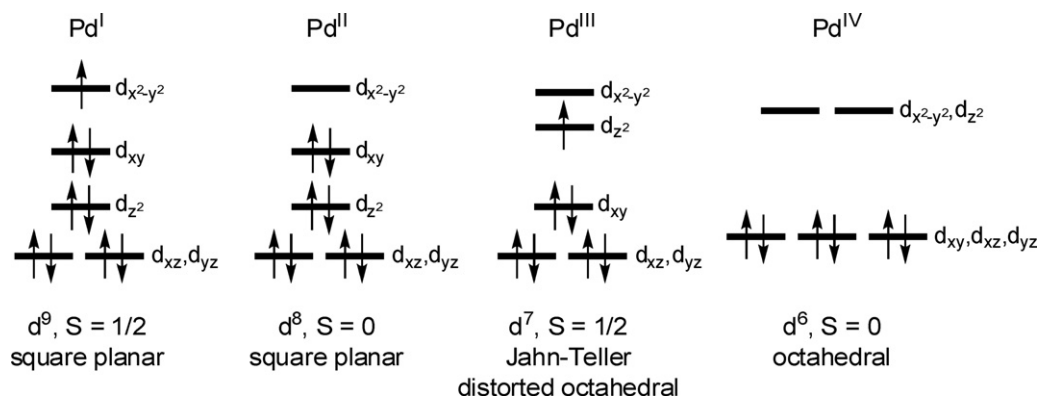


Fig. 1. Representative d electron configuration of Pd^I, Pd^{II}, Pd^{III}, and Pd^{IV} oxidation states. For square planar geometry, the energy ordering of the d_{z^2} and d_{xz}/d_{yz} orbitals can vary depending on the ligand field strength [47].

transient intermediates in oxidatively induced reductive elimination of ethane from Pd^{II}Me₂ complexes [41–43], the insertion of dioxygen into a Pd–Me bond [44], Kumada coupling [45], and the Kharasch reaction [46]. In this context, a detailed understanding of the steric and electronic properties of Pd^{III} complexes should provide insight into the development of novel catalysts for various organometallic transformations as well as other multi-electron redox reactions.

2. Mononuclear Pd(III) complexes

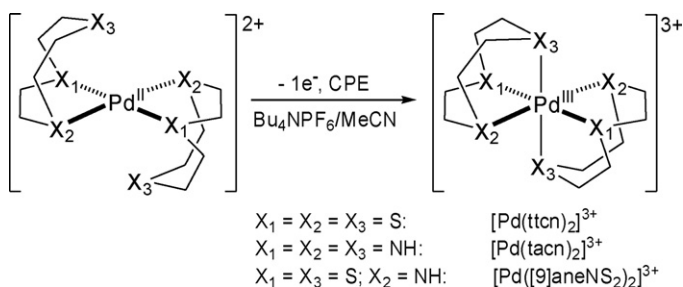
The Pd oxidation states of +1, +2, +3, and +4 correspond to d^9 , d^8 , d^7 , and d^6 electron configurations, respectively (Fig. 1). Pd^I complexes exhibit square planar d^9 metal centers, although a square pyramidal geometry can also be envisioned by analogy to Cu^{II} systems. Pd^{II} d^8 complexes almost exclusively exhibit a square planar geometry with the highest occupied molecular orbital (HOMO) being the Pd-based d_{z^2} orbital [47], although a triplet ground state can also be possible [48,49]. One-electron oxidation of these Pd^{II} systems leads to formation of paramagnetic, Pd^{III} d^7 centers that prefer a Jahn–Teller distorted octahedral geometry. By comparison, a symmetric octahedral geometry is generally observed for the Pd^{IV} d^6 centers (Fig. 1).

2.1. Pd(III) coordination compounds

Initial attempts to synthesize Pd^{III} complexes have focused on binary fluoride compounds with the PdF₃ empirical formula [50]. These compounds exhibited a magnetic moment corresponding to one unpaired electron per Pd, suggestive of Pd^{III} centers [50,51]. However, later studies have shown that these binary fluorides are better described as Pd²⁺[PdF₆]²⁻, in which the Pd²⁺ ion exhibits a high spin electron configuration with two unpaired electrons due to the weak-field fluoride anions and the Pd⁴⁺ has a low spin, diamagnetic configuration [48,49]. The first genuine Pd^{III} compound, NaPdF₄, was obtained in 1982 by solid-state synthesis from NaF and Pd₂F₆ at high pressure and temperature [52]. The Pd^{III} oxidation state has been unambiguously confirmed by the presence of an axial EPR spectrum with $g_{\parallel} = 2.0504$ and $g_{\perp} = 2.263$ that suggests the presence of an unpaired electron in the d_{z^2} orbital [53], in line with the Jahn–Teller axial elongation of the coordination geometry and the observed monoclinic unit cell. Additional elpasolite-type Pd compounds of A₂BPdF₆ formulation (A, B: alkali metals) have been reported to contain Pd^{III} centers with a doublet ground state, as confirmed by EPR spectroscopy and magnetic measurements [54–58]. In general, these compounds exhibit axial EPR spectra due to a Jahn–Teller tetragonal distortion – with g_{\parallel} and g_{\perp} values of 2.01–2.05 and 2.28–2.31, respectively, although both rhombic and

isotropic EPR spectra have also been observed (Table 1). The degree of anisotropy and presence of isotropic signals at higher temperatures have been related to changes from a static to a dynamic Jahn–Teller distortion [56].

The first structurally characterized Pd^{III} coordination compound that exists both in solution and the solid state is the homoleptic 1:2 adduct with the tridentate macrocyclic ligand 1,4,7-trithiacyclononane, ttcn, reported in 1987 by Schröder and co-workers [59]. The cyclic voltammetry of the Pd^{II} complex [Pd^{II}(ttcn)₂]²⁺ shows a reversible oxidation wave at +0.605 V vs. Fc/Fc⁺ in MeCN solution assigned to a Pd^{II/III} oxidation. Oxidation of the Pd^{II} precursor [Pd^{II}(ttcn)]²⁺ by either controlled potential electrolysis (CPE) in MeCN or chemical oxidation with 70% HClO₄ affords an orange species with a visible transition at 476 nm (Scheme 1). The presence of a paramagnetic Pd^{III} center was confirmed by the EPR spectrum that shows an anisotropic signal with $g_{\parallel} = 2.009$ and $g_{\perp} = 2.049$ with partially discernible hyperfine couplings to ¹⁰⁵Pd (22.8% abundance, $I = 5/2$) of $A_{\perp} = 20$ G and $A_{\parallel} = 5$ G. Since the ttcn ligand exhibits an oxidation potential ~400 mV higher than that of [Pd^{II}(ttcn)]²⁺, the authors concluded that a metal-based oxidation process is predominant, although it was shown recently that the redox-active S donors contribute significantly to the singly occupied molecular orbital (SOMO) [60]. The X-ray structure of the isolated red crystals reveals a [Pd(ttcn)₂]³⁺ cation with a trigonally elongated octahedral geometry, in line with a Jahn–Teller distorted Pd^{III} d^7 center (Fig. 2a), with Pd–S_{ax} = 2.545 Å and average Pd–S_{eq} = 2.362 Å. An analogous homoleptic 1:2 Pd^{III} complex using the 1,4,7-triazacyclononane ligand, tacn, was reported by the same group in 1988 (Scheme 1) [61]. The corresponding [Pd(tacn)₂]²⁺ complex exhibits a much lower oxidation potential than [Pd(ttcn)₂]²⁺ (0.07 V compared to 0.60 V vs. Fc/Fc⁺, respectively), as expected for the presence of harder N donors (Table 1). In addition, CPE of [Pd(tacn)₂]²⁺ in MeCN generates a bright yellow [Pd(tacn)₂]³⁺



Scheme 1. Synthesis of Pd^{III} complexes supported by N- and/or S-donor tridentate macrocyclic ligands [59,61,65].

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