

## Stable Mononuclear Organometallic Pd(III) Complexes and Their C–C Bond Formation Reactivity

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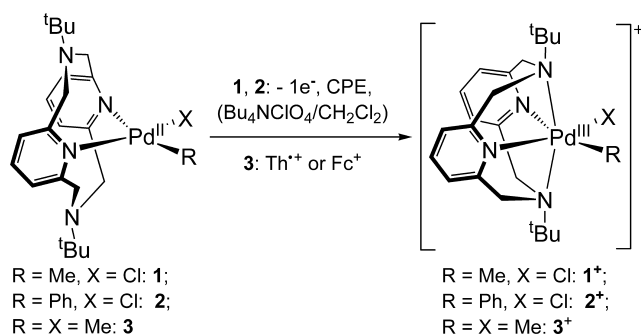
Palladium is one of the most catalytically versatile transition metals, its complexes being efficient catalysts for a wide range of C–C coupling, C–H functionalization, and hydrocarbon oxidation reactions.<sup>1</sup> While Pd(0), Pd(II),<sup>1b</sup> and Pd(IV)<sup>2</sup> complexes have been extensively characterized, much less is known about organometallic Pd(III) complexes. Ritter et al. and Sanford et al. have proposed recently that dinuclear Pd(III) complexes are the active intermediates in the oxidative functionalization of C–H bonds.<sup>3,4</sup> Moreover, mononuclear Pd(III) complexes have been proposed as transient intermediates in oxidatively induced reductive elimination of ethane from a Pd<sup>II</sup>Me<sub>2</sub> complex,<sup>5</sup> the insertion of dioxygen into a Pd–Me bond,<sup>6</sup> and Kumada coupling.<sup>7</sup>

While a few dinuclear organometallic Pd(III) complexes have been structurally characterized,<sup>3,8</sup> no mononuclear organometallic Pd(III) complexes have been isolated to date. The only two examples of mononuclear Pd(III) coordination compounds are the homoleptic 1:2 adducts with the tridentate macrocyclic ligands triazacyclononane and trithiacyclononane, respectively.<sup>9,10</sup> Considering the preferred distorted octahedral geometry for Pd(III) complexes,<sup>9</sup> we proposed that the tetradentate ligand *N,N'*-di-*tert*-butyl-2,11-diaza[3.3](2,6)pyridinophane (N4) can sufficiently stabilize a Pd(III) species, while leaving two coordination sites available for various exogenous ligands. Reported herein is the isolation and characterization of a series of stable mononuclear organometallic (N4)Pd<sup>III</sup> complexes. Interestingly, the monomethyl and monophenyl Pd(III) complexes **1**<sup>+</sup> and **2**<sup>+</sup> undergo a remarkable light-induced elimination of the homocoupled products ethane and biphenyl, respectively, the observed formation of ethane from monomethyl Pd complexes being unprecedented.

The Pd(II) precursors (N4)Pd<sup>II</sup>(R)(X) (R = Me, X = Cl: **1**; R = Ph, X = Cl: **2**; R = X = Me: **3**) were synthesized through the reaction of N4 with common Pd starting materials.<sup>11,12</sup> Cyclic voltammetry of the Pd(II) complexes in MeCN, THF, or CH<sub>2</sub>Cl<sub>2</sub> (0.1 M <sup>t</sup>Bu<sub>4</sub>NClO<sub>4</sub> or <sup>t</sup>Bu<sub>4</sub>NPF<sub>6</sub>) reveals two oxidation waves for both **1** and **2**, an oxidation peak at 150–370 mV, and a quasireversible wave at 580–710 mV vs Fc<sup>+/Fc</sup>.<sup>13</sup> Similarly, complex **3** shows two oxidation waves at more negative potentials, –326 mV and 64 mV vs Fc<sup>+/Fc</sup>.<sup>12</sup> Since the N4 ligand is not redox active within this potential range, the two oxidations are assigned to Pd(II)/Pd(III) and Pd(III)/Pd(IV) couples, respectively.<sup>14</sup>

Controlled potential electrolysis (CPE) of **1** and **2** at potentials that are ~200 mV higher than the corresponding first anodic wave were performed to generate intensely colored dark-green complexes **1**<sup>+</sup> and **2**<sup>+</sup> that can be isolated in good yields (Scheme 1). These complexes are indefinitely stable in the solid state at –20 °C and are stable for a few weeks in solution at RT in the absence of light.<sup>12</sup>

Scheme 1. Synthesis of (N4)Pd<sup>III</sup> Complexes



While electrochemical oxidation of **3** did not give the corresponding Pd(III) product, chemical oxidation with 1 equiv of thianthrenyl hexafluoroantimonate (Th<sup>+</sup>SbF<sub>6</sub><sup>–</sup>) or ferrocenium hexafluorophosphate (Fc<sup>+</sup>PF<sub>6</sub><sup>–</sup>) yields a stable product identified as [(N4)Pd<sup>III</sup>Me<sub>2</sub>]<sup>+</sup> (**3**<sup>+</sup>, Scheme 1).<sup>12</sup> Compounds [**1**<sup>+</sup>]<sup>+</sup>PF<sub>6</sub><sup>–</sup> and [**3**<sup>+</sup>]<sup>+</sup>ClO<sub>4</sub><sup>–</sup> are to the best of our knowledge the first isolated group 10 metal(III)–methyl complexes reported to date.

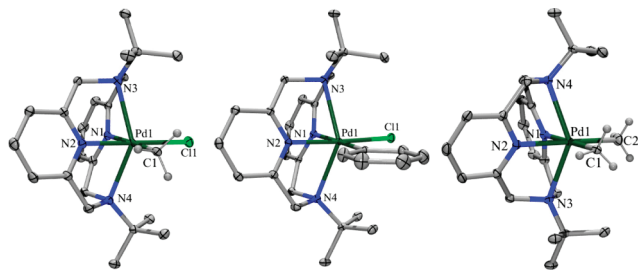


Figure 1. ORTEP representation (50% probability ellipsoids) of **1**<sup>+</sup> (left), **2**<sup>+</sup> (middle), and **3**<sup>+</sup> (right). Selected bond distances (Å), **1**<sup>+</sup>: Pd1–C1 2.0921(18), Pd1–C11 2.3403(5), Pd1–N1 2.0966(16), Pd1–N2 2.0204(16), Pd1–N3 2.4271(16), Pd1–N4 2.4265(16); **2**<sup>+</sup>: Pd1–C(Ph) 2.0713(13), Pd1–C11 2.3478(4), Pd1–N1 2.0927(11), Pd1–N2 2.0281(11), Pd1–N3 2.4241(12), Pd1–N4 2.4135(12); **3**<sup>+</sup>: Pd1–C1 2.0739(15), Pd1–C2 2.0476(16), Pd1–N1 2.0931(13), Pd1–N2 2.1099(12), Pd1–N3 2.4844(13), Pd1–N4 2.4589(13).

X-ray quality crystals for [**1**<sup>+</sup>]<sup>+</sup>PF<sub>6</sub><sup>–</sup>, [**2**<sup>+</sup>]<sup>+</sup>ClO<sub>4</sub><sup>–</sup>, and [**3**<sup>+</sup>]<sup>+</sup>ClO<sub>4</sub><sup>–</sup> were obtained from MeCN/Et<sub>2</sub>O solutions and all three structures show a tetragonally distorted octahedral geometry at the metal center, as expected for a Jahn–Teller distorted d<sup>7</sup> Pd(III) center (Figure 1).<sup>9</sup> The axial Pd–amine nitrogen bond distances (2.41–2.48 Å) are elongated compared to the equatorial Pd–pyridyl bond distances (2.02–2.11 Å) and also longer than the axial Pd–N bonds in the [Pd(tacn)<sub>2</sub>]<sup>3+</sup> complex (Pd–N<sub>ax</sub> = 2.180 Å).<sup>9a</sup>

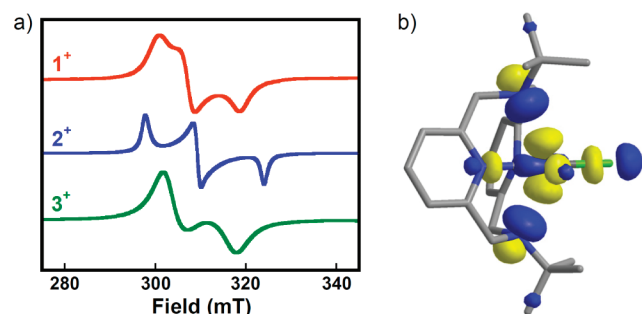
Complexes **1**<sup>+</sup>, **2**<sup>+</sup>, and **3**<sup>+</sup> are all paramagnetic and show a magnetic moment of 1.61–1.80 μ<sub>B</sub> at RT,<sup>12</sup> corresponding to one

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**Table 1.** Spectroscopic Properties of Pd<sup>III</sup> Complexes

	$E_{pc}^{III/IV}, E_{pa}^{III/IV}, E_{1/2}^{III/IV}(\Delta E_p), mV^a$	UV-vis (MeCN) $\lambda, nm (\epsilon, M^{-1} cm^{-1})$	EPR <sup>b</sup> $g_x, g_y, g_z$	$\mu_{eff}^c$ ( $\mu_B$ )
1 <sup>+</sup>	-426, 150, 585 (68)	723 (1100), 545 (sh, 490), 368 (3300), 263 (12 000)	2.183, 2.137, 2.059	1.80 <sup>d</sup>
2 <sup>+</sup>	-229, 368, 708 (65)	732 (1100), 386 (2500), 258 (20 000)	2.204, 2.123, 2.026	1.65 <sup>d</sup> , 1.72 <sup>e</sup>
3 <sup>+</sup>	-882, -326, 64 (62)	741 (360), 350 (2300), 263 (10 300)	2.175, 2.160, 2.064	1.61 <sup>e</sup>

<sup>a</sup> Measured vs Fc<sup>+</sup>/Fc by CV in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/MeCN, scan rate 100 mV/s;  $\Delta E_p$  is the peak potential separation for the Pd(III)/Pd(IV) couple (ref 12). <sup>b</sup> MeCN glass, 120 K. <sup>c</sup> Evans method, 298 K. <sup>d</sup> In CD<sub>3</sub>CN. <sup>e</sup> In DMSO-*d*<sub>6</sub>.

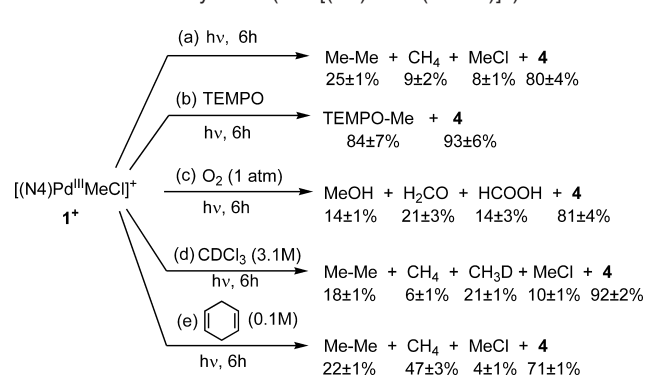
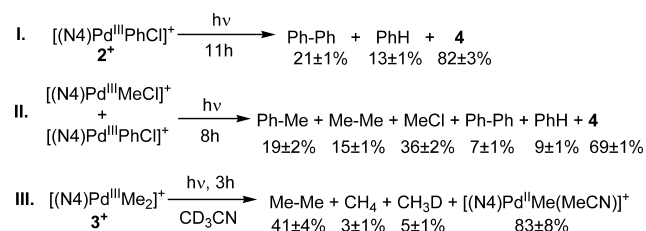
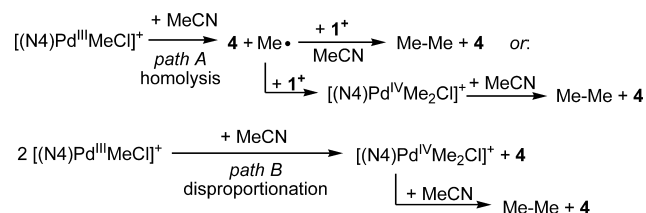


**Figure 2.** (a) EPR spectra of 1<sup>+</sup>, 2<sup>+</sup>, and 3<sup>+</sup> (see Table 1 for *g* values). (b) DFT (B3LYP/CEP-31G(d)) calculated SOMO of 1<sup>+</sup>.

unpaired electron (Table 1). The EPR spectra (120 K, MeCN glass) exhibit rhombic signals with different anisotropies for the three complexes and  $g_{ave} = 2.118-2.133$ , suggesting a Pd(III) center with a  $d_{z^2}$  ground state (Table 1 and Figure 2a).<sup>12,15</sup> Such an assignment is supported by the DFT-calculated singly occupied molecular orbital (SOMO) of 1<sup>+</sup>, which reveals its metal-based  $d_{z^2}$  character (Figure 2b).<sup>16</sup> Additionally, the UV-vis spectra of 1<sup>+</sup>, 2<sup>+</sup>, and 3<sup>+</sup> in MeCN show two strong absorption bands at 723–741 nm and 350–386 nm that are assigned tentatively as LMCT bands (Table 1).<sup>17</sup> Overall, the spectroscopic and magnetic properties are consistent with the formation of paramagnetic Pd(III) species for 1<sup>+</sup>, 2<sup>+</sup>, and 3<sup>+</sup>.

The isolation of these organometallic Pd(III) complexes allowed the investigation of their reactivity, in light of the recently proposed role of transient Pd(III) intermediates in reductive elimination reactions.<sup>5</sup> Complexes 1<sup>+</sup>, 2<sup>+</sup>, and 3<sup>+</sup> are stable in MeCN solutions in the absence of light,<sup>18</sup> yet when a solution of 1<sup>+</sup> in MeCN is exposed to light<sup>19</sup> elimination of ethane (25 ± 1% yield), methyl chloride (8 ± 1%), and methane (9 ± 2%) occurs along with formation of [(N4)Pd<sup>III</sup>Cl(MeCN)]<sup>+</sup> (4) in 80 ± 4% yield (Scheme 2, a).<sup>12,20</sup> While the reductive elimination of the biaryl products from Pd-aryl complexes is preceded,<sup>21</sup> formation of ethane from monomethyl Pd complexes has not been reported to date.<sup>22</sup> Such reactivity is currently of great interest due to its relevance to catalytic methane oligomerization.<sup>5,23</sup>

A similar reactivity is observed for the monophenyl complex 2<sup>+</sup> that undergoes photoinduced elimination of biphenyl and 4 (Scheme 3, I), while irradiation of an equimolar mixture of 1<sup>+</sup> and 2<sup>+</sup> gives toluene in 19 ± 2% yield along with ethane, methyl chloride, biphenyl, and 4, suggestive of crossover reactivity (Scheme 3, II).<sup>24</sup> Additionally, irradiation of the dimethyl complex 3<sup>+</sup> generates ethane and [(N4)Pd<sup>IV</sup>Me(MeCN)]<sup>+</sup> in 41 ± 4% and 83 ± 8% yield, respectively (Scheme 3, III),<sup>20a</sup> a reactivity similar to that observed recently during the oxidation of (*t*Bu<sub>2</sub>bipy)Pd<sup>II</sup>Me<sub>2</sub>.<sup>5</sup>

**Scheme 2.** Reactivity of 1<sup>+</sup> (4 is [(N4)Pd<sup>III</sup>Cl(MeCN)]<sup>+</sup>)**Scheme 3.** Additional Reactivity of Pd<sup>III</sup> Complexes**Scheme 4.** Proposed Mechanisms for Ethane Formation from 1<sup>+</sup>

Formation of ethane from 1<sup>+</sup> is suppressed completely in the presence of effective alkyl radical scavengers such as TEMPO (forming Me-TEMPO quantitatively)<sup>25</sup> and O<sub>2</sub> (forming MeOH, formaldehyde, and formic acid),<sup>26</sup> which suggests a homolytic cleavage of the Pd(III)–Me bond (Scheme 2, b–c).<sup>27</sup> Deuterium abstraction from CDCl<sub>3</sub> to give CH<sub>3</sub>D in 21 ± 1% yield further supports formation of Me• (Scheme 2, d).<sup>28</sup> Ethane may thus form by a subsequent fast reaction of Me• with another molecule of 1<sup>+</sup> (Scheme 4, path A).<sup>29</sup> Similar fast bimolecular reactions ( $k \sim 10^7-10^8 M^{-1} s^{-1}$ ) of Me• with Co(III)–Me and Ni(III)–Me complexes to yield ethane were reported previously and proposed to involve a direct attack of a Me radical at the carbon atom of the methyl ligand.<sup>30</sup> An alternate mechanism may involve binding of Me• to the Pd(III) center to afford an  $[(\eta^3-N4)Pd^{IV}Me_2Cl]^+$  intermediate that can undergo reductive elimination to form ethane.<sup>31</sup> Interestingly, while photolysis of 1<sup>+</sup> in the presence of the H<sup>+</sup> donor 1,4-cyclohexadiene (CHD) generates methane in appreciable yields (Scheme 2, e),<sup>32</sup> the yield of ethane (22 ± 1%) is only slightly decreased vs the uninhibited reaction (25 ± 1%), suggesting that either another mechanism is operative or CHD is not an efficient alkyl radical trap under these conditions.<sup>33</sup>

A nonradical pathway to form  $[(N4)Pd^{IV}Me_2Cl]^+$  via a methyl group transfer between two molecules of 1<sup>+</sup> cannot be excluded unambiguously (Scheme 4, path B).<sup>34</sup> A similar nonradical disproportionation mechanism was proposed by Sanford and Mayer et al. and Tilset et al. for the reactivity of dimethyl complexes observed during 1e<sup>-</sup> chemical or electrochemical oxidation of (*t*Bu<sub>2</sub>bipy)Pd<sup>II</sup>Me<sub>2</sub> or (diimine)Pt<sup>II</sup>Me<sub>2</sub>, respectively.<sup>5,35</sup> Although the  $[(N4)Pd^{IV}Me_2Cl]^+$  intermediate was not detected during photolysis at 0 °C, 1 reacts with strong 2e<sup>-</sup> oxidants such

as  $\text{PhI}(\text{OAc})_2$  and  $\text{Bz}_2\text{O}_2$  to yield  $\text{MeCl}$  and methyl esters, suggesting that the  $\text{Pd}(\text{IV})$  oxidation state is accessible and undergoes reductive elimination.<sup>36</sup> Additionally, **3** readily reacts with  $\text{MeI}$  to yield ethane in 20% yield and  $(\text{N}4)\text{Pd}^{\text{II}}\text{MeI}$ .<sup>37</sup>

Overall, our radical scavenging studies suggest that homolysis of a  $\text{Pd}(\text{III})\text{—C}$  bond is involved in the observed photoreactivity of the  $\text{Pd}(\text{III})$  complexes. Formation of ethane may proceed via the initial homolytic cleavage of the  $\text{Pd}(\text{III})\text{—Me}$  bond, although nonradical pathways cannot be excluded.<sup>38</sup> While the observed reactivity for the  $\text{Pd}(\text{III})$  complexes requires the presence of light, suggestive of a radical mechanism, the photoactivation of octahedral  $\text{Pd}(\text{III})$  complexes may lead to dissociation of an amine donor and creation of an empty coordination site required for a subsequent  $\text{Me}$  or  $\text{Ph}$  group transfer.<sup>39</sup>

In summary, we have been able to isolate and characterize a series of mononuclear organometallic  $\text{Pd}(\text{III})$  complexes that exhibit interesting reactivity profiles. The stability of these  $\text{Pd}(\text{III})$  complexes vs  $\text{Pd}(\text{II})$  or  $\text{Pd}(\text{IV})$  species is presumably due to the steric properties of the  $\text{N}4$  ligand. While the axial nitrogens of this tetradentate ligand can coordinate and stabilize the Jahn–Teller distorted  $\text{Pd}(\text{III})$  center vs a square planar  $\text{Pd}(\text{II})$  center,<sup>9</sup> the rigidity of the macrocycle cannot accommodate a more symmetric octahedral geometry preferred by a  $d^6$   $\text{Pd}(\text{IV})$  center.<sup>40</sup> Moreover, the systems described herein can allow for a direct investigation of  $\text{Pd}(\text{III})$  chemistry by taking advantage of their light-triggered reactivity. *Particularly remarkable is the observation for the first time of ethane formation from monomethyl Pd complexes.* This transformation has direct implications in the development of catalysts for oxidative oligomerization of methane in particular<sup>5,23</sup> and oxidatively induced  $\text{Pd}$ -catalyzed  $\text{C—C}$  bond formation reactions in general.<sup>2</sup> Our current research efforts are aimed at understanding in more detail the properties and reactivity of these  $\text{Pd}(\text{III})$  complexes.

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**Supporting Information Available:** Experimental details, synthesis of  $\text{Pd}$  complexes, spectroscopic characterization, reactivity studies, computational details, and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) The  $\text{Pd}(\text{III})/\text{Pd}(\text{II})$  reduction wave is observed at potentials  $\sim 500$  mV lower than the corresponding  $\text{Pd}(\text{II})/\text{Pd}(\text{III})$  oxidation wave. The large separation between the anodic and cathodic waves of the  $\text{Pd}(\text{III})/\text{Pd}(\text{II})$  couple in **1**, **2**, and **3** is attributed to a significant ligand conformational change from the *syn* chair–chair conformation ( $\eta^2$ ) in  $\text{Pd}(\text{II})$  complexes (ref 11) to a *syn* boat–boat conformation ( $\eta^2$ ) needed to stabilize the distorted octahedral geometry of  $\text{Pd}(\text{III})$ .
- (15) Spin integration of the EPR spectra vs a Cu standard confirms the formation of the  $\text{Pd}(\text{III})$  species in more than 95% yield.
- (16) Similar SOMOs were calculated for  $2^+$  and  $3^+$ , using the B3LYP/CEP-31G(d) functional/basis set combination (see Supporting Information).
- (17) Detailed DFT and TD-DFT computational studies are ongoing.
- (18) Less than 1% of  $\text{MeCl}$  and no ethane were observed when  $\mathbf{1}^+$  was heated in the dark at 51 °C for 65 h.
- (19) Samples were irradiated with either two 100 W halogen lamps or a 450 W medium pressure mercury lamp.
- (20) (a) The theoretical yield of ethane is 50% (ref 12). (b) Complex **4** was independently synthesized and characterized by NMR, ESI-MS, and elemental analysis (ref 12). (c) A small amount of the protonated ligand  $[\text{N}4^*\text{H}]^+$  ( $5 \pm 1\%$ ) was also formed.
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