

## Open-Shell Complexes

International Edition: DOI: 10.1002/anie.201511467  
German Edition: DOI: 10.1002/ange.201511467One-Electron Oxidation of  $[M(P^tBu_3)_2]$  ( $M = Pd, Pt$ ): Isolation of Monomeric  $[Pd(P^tBu_3)_2]^+$  and Redox-Promoted C–H Bond Cyclometalation

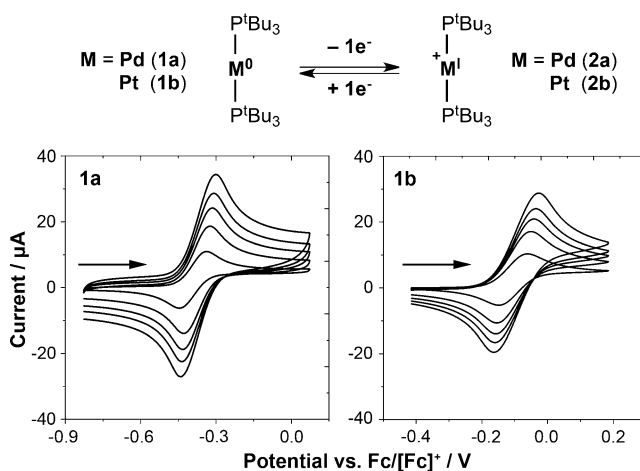
Thibault Troadec, Sze-yin Tan, Christopher J. Wedge, Jonathan P. Rourke, Patrick R. Unwin, and Adrian B. Chaplin\*

**Abstract:** Oxidation of zero-valent phosphine complexes  $[M(P^tBu_3)_2]$  ( $M = Pd, Pt$ ) has been investigated in 1,2-difluorobenzene solution using cyclic voltammetry and subsequently using the ferrocenium cation as a chemical redox agent. In the case of palladium, a mononuclear paramagnetic  $Pd^I$  derivative was readily isolated from solution and fully characterized (EPR, X-ray crystallography). While in situ electrochemical measurements are consistent with initial one-electron oxidation, the heavier congener undergoes C–H bond cyclometalation and ultimately affords the 14 valence-electron  $Pt^II$  complex  $[Pt(\kappa^2_{PC}P^tBu_2CMe_2CH_2)(P^tBu_3)]^+$  with concomitant formation of  $[Pt(P^tBu_3)_2H]^+$ .

Over the past few decades a rich variety of chemistry has emerged based on the reactions of palladium and platinum complexes in the 0 and +II formal oxidation states, epitomized by the omnipresence of palladium catalyzed cross-coupling reactions in contemporary organic chemistry.<sup>[1,2]</sup> In contrast, the organometallic chemistry of well-defined complexes of these elements bearing formal +I oxidation states is much less established and examples are largely limited to unstable or dinuclear species with distinct metal–metal bonds.<sup>[3,4]</sup> Halogen bridged palladium complexes of the type  $[Pd(\mu-X)(P^tBu_3)_2]$  ( $X = Br, I$ ) are notable examples and are believed to act as reservoirs for reactive  $\{Pd^0(P^tBu_3)\}$  fragments in catalytic transformations.<sup>[5]</sup> In other systems,  $Pd^I$  and  $Pt^I$  species have been postulated as intermediates, but with little supporting evidence.<sup>[6]</sup> With a view to isolating well-defined mononuclear complexes in the +I oxidation state relevant to catalysis, we report herein our work involving one-

electron oxidation of widely used and commercially available palladium(0) and platinum(0) complexes of tri-*tert*-butylphosphine  $[M^0(P^tBu_3)_2]$  ( $M = Pd, \mathbf{1a}$ ;  $Pt, \mathbf{1b}$ ).

As a starting point we determined the redox potentials of  $\mathbf{1a}$  and  $\mathbf{1b}$  by cyclic voltammetry (CV) in the weakly coordinating solvent 1,2-difluorobenzene (0.2 M  $[nBu_4N][PF_6]$  electrolyte, Figure 1).<sup>[7]</sup> Reversible one-electron oxidation was observed at  $E_{1/2} = -0.44$  V ( $\mathbf{1a}$ ) and  $E_{1/2} = -0.10$  V ( $\mathbf{1b}$ ) relative to  $Fc/[Fc]^+$  ( $Fc =$  ferrocene). The electrochemical characteristics of closely related cyclic alkyl(amino) carbene (CAAC) analogues have recently been studied by CV and the redox potentials of  $\mathbf{1a}$  and  $\mathbf{1b}$  are similar in magnitude to those found for  $[M^0(CAAC)_2]$  ( $M = Pd, -0.60$  V;  $Pt, -0.07$  V) in THF (0.1 M  $[nBu_4N][ClO_4]$ ).<sup>[8]</sup> Consistent with the generation of a stable  $Pd^I$  species ( $\mathbf{2a}$ ), the peak current ratios ( $i_p^{red}/i_p^{ox}$ ) in the palladium voltammograms are essentially unity (ca. 0.99). Conspicuously lower ratios were observed for the platinum complex (ca. 0.90).



**Figure 1.** Cyclic voltammograms for the oxidation of  $\mathbf{1a}$  and  $\mathbf{1b}$  in 1,2- $C_6H_4F_2$  (2 mM  $\mathbf{1}$ ; 0.2 M  $[nBu_4N][PF_6]$  electrolyte; glassy carbon working electrode, Pt counter electrode and Ag wire reference electrode; scan rates = 10, 30, 50, 70, and 100  $mV s^{-1}$ ).

Encouraged by these data,  $\mathbf{1a}$  was reacted with one equiv of  $[Fc][PF_6]$  in 1,2-difluorobenzene at 293 K and dark blue  $[Pd^I(P^tBu_3)_2][PF_6]$   $\mathbf{2a}$  was subsequently isolated in 92% yield following addition of *n*-pentane. The electrochemical characteristics of isolated  $\mathbf{2a}$  are equivalent to those measured in situ starting from  $\mathbf{1a}$  ( $E_{1/2} = -0.42$  V; see Supporting

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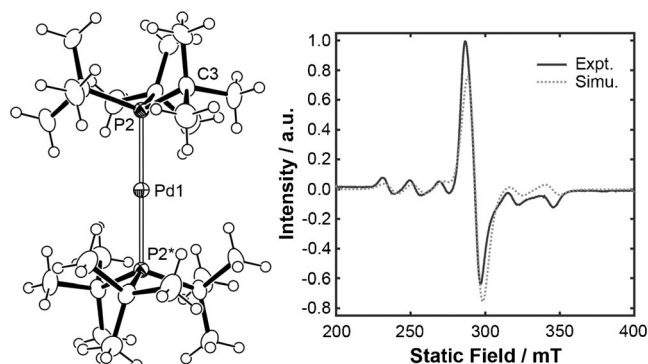
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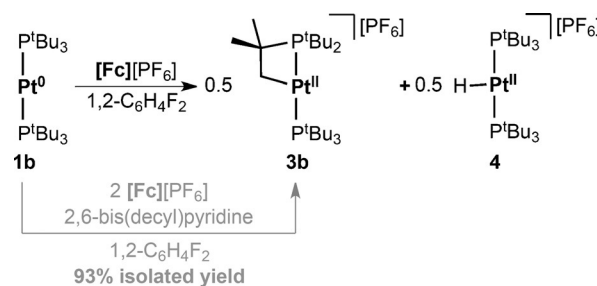
Information). This new paramagnetic species was additionally characterized in solution using UV/Vis spectroscopy ( $\lambda_{\text{max}} = 667 \text{ nm}$ ), ESI-HRMS (positive ion mode,  $510.2736 \text{ m/z } [M]^+$ ; calculated  $510.2740 \text{ m/z}$ ), and EPR spectroscopy. The EPR spectrum (1,2- $\text{C}_6\text{H}_4\text{F}_2$  glass at 200 K, Figure 2), shows a superposition of a single resonance at  $g = 2.316(5)$  with a lower intensity sextet arising from hyperfine coupling to  $^{105}\text{Pd}$



**Figure 2.** The solid-state structure<sup>[22]</sup> and EPR spectrum of **2a** (1,2- $\text{C}_6\text{H}_4\text{F}_2$  glass, 200 K, a.u. = arbitrary units).<sup>[11]</sup> Ellipsoids are set at 50% probability; anion omitted for clarity. The starred atom is generated by the symmetry operation  $1-x, 1-y, 1-z$ . Selected data: Pd1–P2 2.3470(6) Å; P2–Pd1–P2\* 180°, Pd1–P2–C3 108.81(5)°.

( $I = 5/2$ , 22% abundance), corroborating formation of an  $S = 1/2$   $\text{Pd}^{\text{I}}$  species. The unusually large  $^{105}\text{Pd}$  hyperfine coupling of approximately 25 mT, and lack of resolved coupling to  $^{31}\text{P}$  ( $I = 1/2$ , 100% abundance) is consistent with strong localization of the unpaired electron spin on the Pd center. Complex **2a** crystallizes in the high-symmetry cubic space group  $P\bar{a}3$  with the palladium atom on a center of inversion (Figure 2). In comparison to **1a**, the Pd–P bond length is significantly elongated, from 2.285(3) to 2.3469(6) Å ( $\Delta(\text{Pd–P}) = +0.062(4)$  Å); the P–Pd–P angles in both cases are symmetry enforced at 180°.<sup>[9]</sup> To the best of our knowledge, this is the first example of an unsupported two-coordinate  $\text{Pd}^{\text{I}}$  complex. A similar bond length elongation has been noted in closely related NHC complexes of  $\text{Ni}^{\text{0}}/\text{Ni}^{\text{I}}$  ( $\Delta(\text{Ni–C}) = +0.08(2)$  Å).<sup>[10]</sup> Isolated **2a** is air-sensitive in solution, but shows good stability under an argon atmosphere. For instance, under argon the EPR spectrum intensity was essentially unchanged after 24 h at 293 K (15 mm). However, slow degradation of **2a** was observed by UV/Vis spectroscopy under high dilution conditions ( $t_{1/2} \approx 30 \text{ h}$ ; 0.15 mM), which we attribute to the presence of adventitious water as the rate of degradation increased significantly when water was added deliberately. Moreover, **2a** can be stored in the solid-state in air (72 h) with no evident change by UV/Vis spectroscopy.

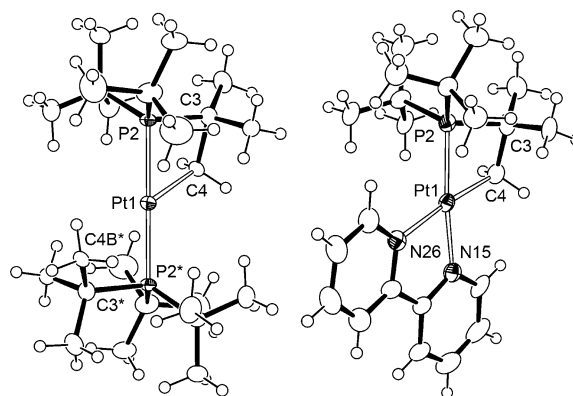
When preparation of the analogous  $\text{Pt}^{\text{I}}$  complex **2b** was attempted by reaction of **1b** with one equiv of  $[\text{Fc}][\text{PF}_6]$ , a 1:1 mixture of the new diamagnetic cyclometalated complex  $[\text{Pt}^{\text{II}}(\kappa^2_{\text{PC}}\text{-P}^{\text{t}}\text{Bu}_2\text{CMe}_2\text{CH}_2)(\text{P}^{\text{t}}\text{Bu}_3)][\text{PF}_6]$  **3b** and known  $\text{Pt}^{\text{II}}$  hydride  $[\text{Pt}^{\text{II}}(\text{P}^{\text{t}}\text{Bu}_3)_2\text{H}][\text{PF}_6]$  **4** ( $\delta(^1\text{H}) -36.30 \text{ ppm}$ ;  $^2J_{\text{PtH}} = 8.6$ ,  $^1J_{\text{PtH}} = 2590 \text{ Hz}$ ;  $\delta(^{31}\text{P}) 86.3 \text{ ppm}$ ;  $^1J_{\text{PtP}} = 2621 \text{ Hz}$ ) was formed within 15 min instead, as indicated by  $^1\text{H}$  and



**Scheme 1.** Chemical oxidation of **1b**.

$^{31}\text{P}$  NMR spectroscopy (Fc observed; Scheme 1).<sup>[12]</sup> This outcome suggests only transient stability of **2b** in solution, with subsequent C–H bond homolysis accounting for the divergence from fully reversible one-electron oxidation of **1b** observed by CV.<sup>[13]</sup> Reaction of **1b** with two equiv of  $[\text{Fc}][\text{PF}_6]$  in the presence of excess hindered base 2,6-bis(decyl)pyridine (5 equiv), which is able to deprotonate **4**, resulted in selective formation of **3b** within 15 min. In this manner, **3b** was isolated in 93% yield following successive crystallizations from 1,2- $\text{C}_6\text{H}_4\text{F}_2$  to remove ferrocene, excess base, and pyridinium salt.<sup>[13]</sup> For comparison, no significant reaction was detected by  $^1\text{H}$  or  $^{31}\text{P}$  NMR spectroscopy on mixing of **1b** and 2,6-bis(decyl)pyridine in 1,2-difluorobenzene at 293 K (24 h) or heating **1b** alone in 1,2-difluorobenzene at 353 K (24 h).

Two independent but structurally similar cations are observed in the solid-state structure of **3b** (one is shown in Figure 3), both illustrating adoption of a T-shaped coordination geometry<sup>[14]</sup> and cyclometalation of one of the *tert*-butyl substituents; these are identified by distinctly acute Pt1–P2–C3 angles [90.0(3)/89.5(3)°] and Pt1–C4 bond lengths of 2.063(17)/2.065(17) Å. The **3b** cation is formally a 14 valence-electron (VE) complex, but is stabilized by adoption



**Figure 3.** Solid-state structures of **3b** and **6**.<sup>[22]</sup> Ellipsoids are set at 50% and 30% probability, respectively; minor disordered components and anions omitted for clarity; only one of the two independent molecules is shown for **3b**. Starred atoms in **3b** are generated by the symmetry operation  $1-x, 2-y, 1-z$ . Selected data **3b**: Pt1–P2 2.297(2) Å, Pt1–C4 2.063(17) Å, Pt1...C4B\* 2.83(2) Å; P2–Pt1–P2\* 180°, Pt1–P2–C3/C3\* 90.0(3)°. **6**: Pt1–P2 2.235(2) Å, Pt1–C4 2.077(10) Å, Pt1–N15 2.080(7) Å, Pt1–N26 2.156(7) Å; P2–Pt1–N15 166.3(2)°, C4–Pt1–N26 175.4(3)°, Pt1–P2–C3 88.5(3)°.

of an agostic interaction between the non-cyclometalated phosphine ligand and Pt center (Pt1...C4B 2.83(2)/2.84(2) Å). In solution, the structure of **3b** was fully corroborated by NMR spectroscopy (CD<sub>2</sub>Cl<sub>2</sub>, 298 K). Formation of the metallacycle is apparent by distinctive <sup>1</sup>H and <sup>13</sup>C methylene resonances at δ(<sup>1</sup>H) 2.75 ppm (<sup>2</sup>J<sub>PtH</sub> = 110 Hz) and δ(<sup>13</sup>C) 10.3 ppm (<sup>1</sup>J<sub>PtC</sub> = 670 Hz) with platinum satellites, two doublet <sup>31</sup>P resonances with a large (*trans*) <sup>2</sup>J<sub>PP</sub> coupling constant and platinum satellites (δ(<sup>31</sup>P) 59.1 ppm (<sup>1</sup>J<sub>PtP</sub> = 2896 Hz, <sup>2</sup>J<sub>PP</sub> = 317 Hz, P<sup>1</sup>Bu<sub>3</sub>), δ(<sup>31</sup>P) 25.2 ppm (<sup>1</sup>J<sub>PtP</sub> = 1916 Hz, <sup>2</sup>J<sub>PP</sub> = 317 Hz, P<sup>1</sup>Bu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)), and a platinum chemical shift of δ(<sup>195</sup>Pt) –3816 ppm (225 K). Although the signals associated with the non-cyclometalated phosphine ligand broadened on cooling to 185 K, the agostic interaction could not be definitively resolved by <sup>1</sup>H NMR spectroscopy.

Cyclometalation reactions of Pt<sup>II</sup> complexes have extensive precedent.<sup>[14a,15]</sup> For instance, T-shaped complexes [Pt<sup>II</sup>(κ<sup>2</sup><sub>PC</sub>-PR<sub>2</sub>C<sub>6</sub>H<sub>3</sub>MeCH<sub>2</sub>)(PR<sub>2</sub>Xyl)]<sup>+</sup> (R = Cy, Ph; Xyl = 2,6-dimethylphenyl) with similar structural and spectroscopic metrics compared to **3b**, were prepared by cyclometalation reactions involving halide abstraction from [Pt<sup>II</sup>(PR<sub>2</sub>Xyl)<sub>2</sub>(Me)Cl] and subsequent elimination of methane.<sup>[16]</sup> Intramolecular C–H bond activation of P<sup>1</sup>Bu<sub>3</sub> in [Pt<sup>II</sup>(P<sup>1</sup>Bu<sub>3</sub>)<sub>2</sub>HX] (X = Cl, Br, I, OTf, NO<sub>2</sub>) has also been described and results in coordinatively saturated products [Pt<sup>II</sup>(κ<sup>2</sup><sub>PC</sub>-P<sup>1</sup>Bu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(P<sup>1</sup>Bu<sub>3</sub>)X].<sup>[17]</sup> In the case of **3b**, the presence of a Pt<sup>II</sup> intermediate preceding cyclometalation can be discounted on the basis of the electrochemical characteristics of **1b**. Instead the formation of **3b** and **4** presumably occurs via concerted bimetallic (radical) oxidative addition,<sup>[18]</sup> or proceeds through a common Pt<sup>III</sup> alkyl hydride intermediate [Pt<sup>III</sup>(κ<sup>2</sup><sub>PC</sub>-P<sup>1</sup>Bu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(P<sup>1</sup>Bu<sub>3</sub>)H]<sup>+</sup> (**5**). In the latter case, subsequent comproportionation (**5** + **2b**), disproportionation (via a Pt<sup>IV</sup> alkyl dihydride), or Pt–H bond homolysis (i.e. 2 × **5** → 2 × **3b** + H<sub>2</sub>; **3b** + H<sub>2</sub> → **4**) would afford the observed 1:1 mixture of **3b** and **4**.<sup>[19]</sup>

Seeking to gain more insight into this mechanism, trapping of the postulated intermediate **5** was attempted by coordination of 2,2'-bipyridine (bipy). However, oxidation of **1b** with either one or two equiv of [Fc][PF<sub>6</sub>] in the presence of one equiv of bipy resulted in formation of a new cyclometalated complex [Pt<sup>II</sup>(κ<sup>2</sup><sub>PC</sub>-P<sup>1</sup>Bu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(bipy)][PF<sub>6</sub>] **6** instead, alongside protonated phosphine (δ(<sup>31</sup>P) 54.2 ppm). The identity of this new complex was verified by independent synthesis from **3b** and bipy in 1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (97% yield of isolated product). As with **3b**, the cyclometalated phosphine in **6** is characterized by an acute Pt1–P2–C3 angle (88.5(3)°) and bears a similar Pt1–C4 bond length of 2.077(10) Å (Figure 3). Moreover, both solution and solid-state data are fully consistent with a coordinatively saturated metal complex. Notably, the substantially higher *trans*-influence of the methylene ligand is reflected in different Pt–N bond lengths (Pt1–N15, 2.156(7) versus Pt1–N26, 2.080(7) Å); the associated <sup>13</sup>C resonance shows a reduced <sup>1</sup>J<sub>PtC</sub> coupling in comparison to **3b** (580 versus 670 Hz). Stronger Pt–P bonding is apparent in **6** relative to **3b**, on the basis of a shorter Pt–P bond (2.235(2) versus 2.297(2)/2.299(3) Å), and a larger <sup>1</sup>J<sub>PtP</sub> coupling constant determined by <sup>31</sup>P NMR spectroscopy (3105 versus 1916 Hz). A platinum chemical shift of δ(<sup>195</sup>Pt)

–3788 ppm (225 K) was also measured for **6** and is very similar to that of **3b** (δ(<sup>195</sup>Pt) –3816 ppm).

Reaction of isolated **3b** with H<sub>2</sub> (1 atm) results directly in the formation of **4**, which is reconcilable with Pt–H bond homolysis or disproportionation (via an unstable Pt<sup>IV</sup> alkyl dihydride intermediate) during the formation of **3b/4**. However, the underlying mechanism is still not completely clear at this time. For instance, we cannot discount the formation of **3b** through a pathway involving deprotonation of **5** (mediated by **1b**<sup>[20]</sup> or 2,6-bis(decyl)pyridine) and a second one-electron oxidation. The redox potential of the associated Pt<sup>I</sup>/Pt<sup>II</sup> couple, assessed by CV experiments using both isolated **3b** (*E*<sub>1/2</sub> = –1.90 V, irreversible) and **6** (*E*<sub>1/2</sub> = –1.68 V, *i*<sub>p</sub><sup>ox</sup>/*i*<sub>p</sub><sup>red</sup> ≈ 0.96), indicates that such a one-electron oxidation is at least conceptually feasible using [Fc][PF<sub>6</sub>] (see Supporting Information for CVs).

Motivated by the cyclometalation observed on oxidation of **1b**, we have also preliminarily investigated whether similar reactivity can be induced in the palladium analogue. Our studies are on-going, but we do note that reaction of **1a** with two equiv of [Fc][PF<sub>6</sub>] in the presence of excess 2,6-bis(decyl)pyridine (5 equiv) resulted in the gradual appearance of a diamagnetic complex with spectroscopic characteristics consistent with cyclometalation (**3a**; δ(<sup>31</sup>P) 57.0, –1.3 ppm; <sup>2</sup>J<sub>PP</sub> = 316 Hz).<sup>[21]</sup> However, this species was only formed in situ in about 30% yield after 72 h at 293 K, as measured by NMR spectroscopy (using an internal standard), and the resulting reaction mixture has proved intractable so far to further characterization.

In summary, we have described a simple method for accessing the reaction chemistry of mononuclear palladium and platinum complexes bearing a +I formal oxidation state, as demonstrated by one-electron oxidation of [M<sup>0</sup>(P<sup>1</sup>Bu<sub>3</sub>)<sub>2</sub>] (M = Pd, Pt) using [Fc][PF<sub>6</sub>]. While the Pd<sup>I</sup> derivative was readily isolated from solution and fully characterized, the heavier congener undergoes C–H bond cyclometalation to afford the 14 VE Pt<sup>II</sup> complex [Pt<sup>II</sup>(κ<sup>2</sup><sub>PC</sub>-P<sup>1</sup>Bu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(P<sup>1</sup>Bu<sub>3</sub>)]<sup>+</sup> with concomitant formation of [Pt<sup>II</sup>(P<sup>1</sup>Bu<sub>3</sub>)<sub>2</sub>H]<sup>+</sup>. Future work is focused on charting the reactivity and catalytic activity of these novel Group 10 species, and will be published in due course.

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