Open-Shell Complexes

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One-Electron Oxidation of [M(P^{t}Bu$_3$)$_2$] (M = Pd, Pt): Isolation of Monomeric [Pd(P^{t}Bu$_3$)$_2$]$^+$ and Redox-Promoted C–H Bond Cyclometalation

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Abstract: *Oxidation of zero-valent phosphine complexes [M(P^{t}Bu$_3$)$_2$] (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(κ^2_{PC}-P^{t}Bu$_2$CMe$_2$CH$_2$)(P^{t}Bu$_3$)]$^+$ with concomitant formation of [Pt(P^{t}Bu$_3$)$_2$H]$^+$.*

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.[1,2] 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.[3,4] Halogen bridged palladium complexes of the type [Pd(μ-X)(P^{t}Bu$_3$)]$_2$ (X = Br, I) are notable examples and are believed to act as reservoirs for reactive {Pd^0(P^{t}Bu$_3$)} fragments in catalytic transformations.[5] In other systems, Pd^I and Pt^I species have been postulated as intermediates, but with little supporting evidence.[6] 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^{t}Bu$_3$)$_2$] (M = Pd, **1a**; Pt, **1b**).

As a starting point we determined the redox potentials of **1a** and **1b** by cyclic voltammetry (CV) in the weakly coordinating solvent 1,2-difluorobenzene (0.2 M [^{n}Bu$_4$N][PF$_6$] electrolyte, Figure 1).[7] Reversible one-electron oxidation was observed at $E_{1/2} = -0.44$ V (**1a**) and $E_{1/2} = -0.10$ V (**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 **1a** and **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 [^{n}Bu$_4$N][ClO$_4$]).[8] Consistent with the generation of a stable Pd^I species (**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).

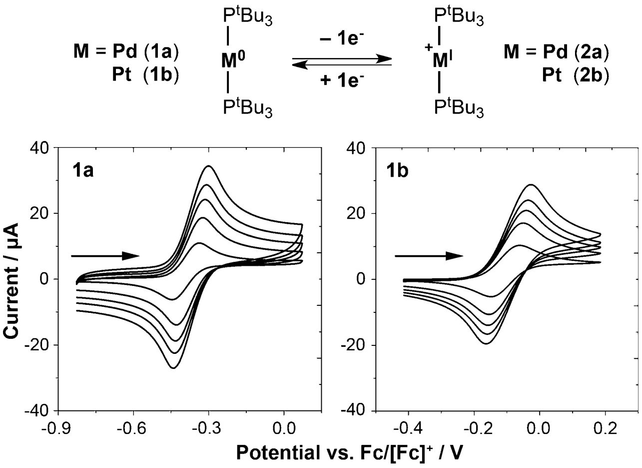

Figure 1. Cyclic voltammograms for the oxidation of **1a** and **1b** in 1,2-C$_6$H$_4$F$_2$ (2 mM **1**; 0.2 M [^{n}Bu$_4$N][PF$_6$] electrolyte; glassy carbon working electrode, Pt counter electrode and Ag wire reference electrode; scan rates = 10, 30, 50, 70, and 100 mV s^{-1}).

Encouraged by these data, **1a** was reacted with one equiv of [Fc][PF$_6$] in 1,2-difluorobenzene at 293 K and dark blue [Pd^I(P^{t}Bu$_3$)$_2$][PF$_6$] **2a** was subsequently isolated in 92% yield following addition of *n*-pentane. The electrochemical characteristics of isolated **2a** are equivalent to those measured in situ starting from **1a** ($E_{1/2} = -0.42$ V; see Supporting

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Information). This new paramagnetic species was additionally characterized in solution using UV/Vis spectroscopy (λ_{max} = 667 nm), ESI-HRMS (positive ion mode, 510.2736 m/z $[M]^+$; calculated 510.2740 m/z), and EPR spectroscopy. The EPR spectrum (1,2-$C_6H_4F_2$ 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}Pd ($I = 5/2$, 22 % abundance), corroborating formation of an $S = 1/2$ Pd^I species. The unusually large ^{105}Pd hyperfine coupling of approximately 25 mT, and lack of resolved coupling to ^{31}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 $Pa\bar{3}$ 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 (Δ(Pd−P) = + 0.062(4) Å); the P-Pd-P angles in both cases are symmetry enforced at 180°.[9] To the best of our knowledge, this is the first example of an unsupported two-coordinate Pd^I complex. A similar bond length elongation has been noted in closely related NHC complexes of Ni^0/Ni^I (Δ(Ni−C) = + 0.08(2) Å).[10] 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 ($t_{1/2} \approx 30$ 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.

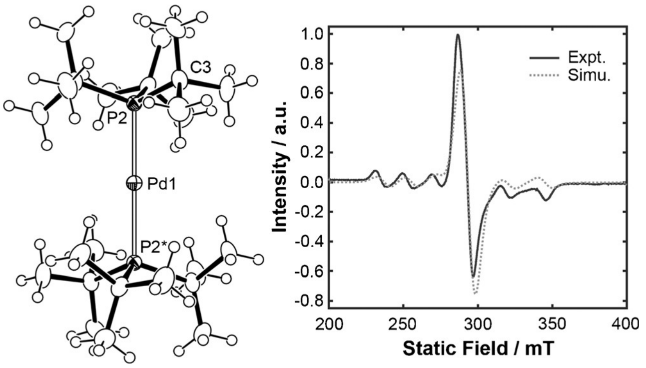
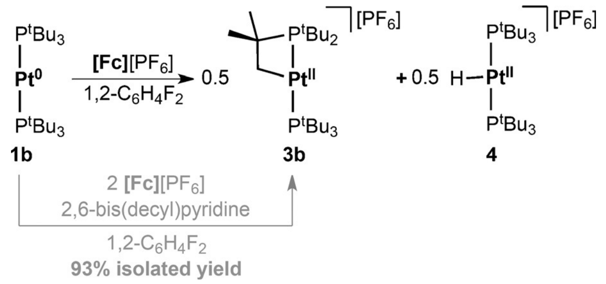


Figure 2. The solid-state structure[22] and EPR spectrum of **2a** (1,2-$C_6H_4F_2$ glass, 200 K, a.u. = arbitrary units).[11] Ellipsoids are set at 50% probability; anion omitted for clarity. The starred atom is generated by the symmetry operation 1−*x*, 1−*y*, 1−*z*. Selected data: Pd1−P2 2.3470(6) Å; P2-Pd1-P2* 180°, Pd1-P2-C3 108.81(5)°.

When preparation of the analogous Pt^I complex **2b** was attempted by reaction of **1b** with one equiv of $[Fc][PF_6]$, a 1:1 mixture of the new diamagnetic cyclometalated complex $[Pt^{II}(\kappa^2_{PC}\text{-}P^tBu_2CMe_2CH_2)(P^tBu_3)][PF_6]$ **3b** and known Pt^{II} hydride $[Pt^{II}(P^tBu_3)_2H][PF_6]$ **4** ($\delta(^1H)$ −36.30 ppm; $^2J_{PH}$ = 8.6, $^1J_{PtH}$ = 2590 Hz; $\delta(^{31}P)$ 86.3 ppm; $^1J_{PtP}$ = 2621 Hz) was formed within 15 min instead, as indicated by ^{1}H and ^{31}P NMR spectroscopy (Fc observed; Scheme 1).[12] 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.[13] Reaction of **1b** with two equiv of $[Fc][PF_6]$ 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-$C_6H_4F_2$ to remove ferrocene, excess base, and pyridinium salt.[13] For comparison, no significant reaction was detected by ^{1}H or ^{31}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).



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

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[14] 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

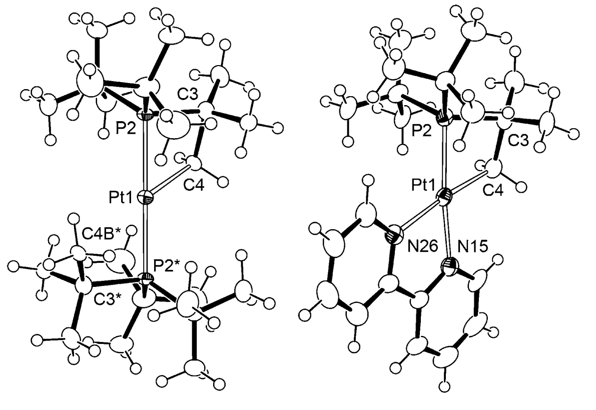


Figure 3. Solid-state structures of **3b** and **6**.[22] Ellipsoids are set at 50% and 30% probability, respectively; minor disordered components and anions omitted for clarity; only one of the two independent molecules is shown for **3b**. Starred atoms in **3b** are generated by the symmetry operation 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_2Cl_2, 298 K). Formation of the metallacycle is apparent by distinctive ^{1}H and ^{13}C methylene resonances at $\delta(^1H)$ 2.75 ppm ($^2J_{PtH} = 110$ Hz) and $\delta(^{13}C)$ 10.3 ppm ($^1J_{PtC} = 670$ Hz) with platinum satellites, two doublet ^{31}P resonances with a large (*trans*) $^2J_{PP}$ coupling constant and platinum satellites ($\delta(^{31}P)$ 59.1 ppm ($^1J_{PtP} = 2896$ Hz, $^2J_{PP} = 317$ Hz, $\underline{P}{}^tBu_3$), $\delta(^{31}P)$ 25.2 ppm ($^1J_{PtP} = 1916$ Hz, $^2J_{PP} = 317$ Hz, $\underline{P}{}^tBu_2CMe_2CH_2$)), and a platinum chemical shift of $\delta(^{195}Pt)$ −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 ^{1}H NMR spectroscopy.

Cyclometalation reactions of Pt^{II} complexes have extensive precedent.[14a,15] For instance, T-shaped complexes $[Pt^{II}(\kappa^2_{PC}\text{-}PR_2C_6H_3MeCH_2)(PR_2Xyl)]^+$ (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 $[Pt^{II}(PR_2Xyl)_2(Me)Cl]$ and subsequent elimination of methane.[16] Intramolecular C−H bond activation of P^tBu_3 in $[Pt^{II}(P^tBu_3)_2HX]$ (X = Cl, Br, I, OTf, NO_2) has also been described and results in coordinatively saturated products $[Pt^{II}(\kappa^2_{PC}\text{-}P^tBu_2CMe_2CH_2)(P^tBu_3)X]$.[17] In the case of **3b**, the presence of a Pt^{II} intermediate proceeding 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,[18] or proceeds through a common Pt^{III} alkyl hydride intermediate $[Pt^{II}(\kappa^2_{PC}\text{-}P^tBu_2CMe_2CH_2)(P^tBu_3)H]^+$ (**5**). In the latter case, subsequent comproportionation (**5** + **2b**), disproportion (via a Pt^{IV} alkyl dihydride), or Pt−H bond homolysis (i.e. 2 × **5** → 2 × **3b** + H_2; **3b** + H_2 → **4**) would afford the observed 1:1 mixture of **3b** and **4**.[19]

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 $[Fc][PF_6]$ in the presence of one equiv of bipy resulted in formation of a new cyclometalated complex $[Pt^{II}(\kappa^2_{PC}\text{-}P^tBu_2CMe_2CH_2)(bipy)][PF_6]$ **6** instead, alongside protonated phosphine ($\delta(^{31}P)$ 54.2 ppm). The identity of this new complex was verified by independent synthesis from **3b** and bipy in 1,2-$C_6H_4F_2$ (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 ^{13}C resonance shows a reduced $^1J_{PtC}$ 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 $^1J_{PtP}$ coupling constant determined by ^{31}P NMR spectroscopy (3105 versus 1916 Hz). A platinum chemical shift of $\delta(^{195}Pt)$ −3788 ppm (225 K) was also measured for **6** and is very similar to that of **3b** ($\delta(^{195}Pt)$ −3816 ppm).

Reaction of isolated **3b** with H_2 (1 atm) results directly in the formation of **4**, which is reconcilable with Pt−H bond homolysis or disproportion (via an unstable Pt^{IV} 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**[20] or 2,6-bis(decyl)pyridine) and a second one-electron oxidation. The redox potential of the associated Pt^I/Pt^{II} couple, assessed by CV experiments using both isolated **3b** ($E_{1/2} = -1.90$ V, irreversible) and **6** ($E_{1/2} = -1.68$ V, $i_p^{ox}/i_p^{red} \approx 0.96$), indicates that such a one-electron oxidation is at least conceptually feasible using $[Fc][PF_6]$ (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 $[Fc][PF_6]$ 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**; $\delta(^{31}P)$ 57.0, −1.3 ppm; $^2J_{PP} = 316$ Hz).[21] 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 $[M^0(P^tBu_3)_2]$ (M = Pd, Pt) using $[Fc][PF_6]$. While the Pd^I derivative was readily isolated from solution and fully characterized, the heavier congener undergoes C−H bond cyclometalation to afford the 14 VE Pt^{II} complex $[Pt^{II}(\kappa^2_{PC}\text{-}P^tBu_2CMe_2CH_2)(P^tBu_3)]^+$ with concomitant formation of $[Pt^{II}(P^tBu_3)_2H]^+$. 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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Keywords: C−H activation · oxidation · palladium · phosphane ligands · platinum

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[22] CCDC 1440602 (**2a**), 1440603 (**3b**), 1440604 (**6**, *C*2/*c*), and 1440605 (**6**, $P2_1/c$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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