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One-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

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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^II 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 congeners undergoes C–H bond cyclometalation and ultimately affords the 14 valence-electron Pt^II complex [Pt(t^2-P^tBu_3CH_2CH_3)(P^tBu_3)]^+ with concomitant formation of [Pt(P^tBu_3)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^tBu_3)] (X = Br, I) are notable examples and are believed to act as reservoirs for reactive [Pd^0(P^tBu_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^tBu_3)] (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 [Bu_3N][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 Fe^2+/Fe^3+ (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 [Bu_3N][ClO_4])(6) Consistent with the generation of a stable Pd^0 species (2a), the peak current ratios (i^p/100 i^p) in the palladium voltammograms are essentially unity (ca. 0.99). Conspicuously lower ratios were observed for the platinum complex (ca. 0.90).

![Figure 1](image-url)

Figure 1. Cyclic voltammograms for the oxidation of 1a and 1b in 1,2-

Encouraged by these data, 1a was reacted with one equiv of [Fe^2+][PF_6] in 1,2-difluorobenzene at 293 K and dark blue [Pd^I(P^tBu_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 Information).

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Information). This new paramagnetic species was additionally characterized in solution using UV/Vis spectroscopy ($\lambda_{\text{max}} = 667$ nm), ESI-HRMS (positive ion mode, $m/z$ [M]$^+ =$ calculated 510.2740 [M]$^+ =$, and EPR spectroscopy. The EPR spectrum (1.2-C$_2$H$_4$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 $^{195}$Pd

$(I = 5/2, 22\%$ abundance), corroborating formation of an $S = 1/2$ Pd$^3$ species. The unusually large $^{195}$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 $Pm3$ 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) (Fig. 2). The P–Pd 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$^3$ complex. A similar bond length elongation has been noted in closely related NHC complexes of Ni$^2$/Ni$^3$ (ΔNi–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 ($t_{1/2} = 30 \text{ h}$; 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 Pt$^1$ complex 2b was attempted by reaction of 1b with one equiv of [Fe][PF$_6$], a 1:1 mixture of the new diamagnetic cyclometalated complex [Pt($\kappa^2$-P$_2$Bu$_3$CMe$_2$CH$_2$)(P$_2$Bu$_3$)][PF$_6$] 3b and known Pt$^{II}$ hydride [Pt($\kappa^3$(P$_2$Bu$_3$))H][PF$_6$] 4 (Δ($^1$H) = –36.30 ppm; $^1$J$_{Pd-H} = 8.6$, $^1$J$_{Pd-H} = 2590$ Hz; $^1$J($^31$P) = 86.3 ppm; $^1$J$_{Pd-P} = 2621$ 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$_2$H$_4$F$_2$ 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).

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)]. Selected data: Pt1–P2–C3 88.5(3), Pt1–P2–C3 90.0(3), Pt1–P–C3 166.3(2). The 3b cation is formally a 14 valence-electron (VE) complex, but is stabilized by adoption

![Scheme 1. Chemical oxidation of 1b.](image-url)

**Figure 2.** The solid-state structure[25] and EPR spectrum of 2a (1,2-C$_2$H$_4$F$_2$ 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, Pd1–P2* 180°, Pd1–P2–C3 108.81(5)°.

![Figure 3. Solid-state structures of 3b and 6.[26] 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(7) Å, Pt1–CAB+ 2.83(2) Å, Pt2–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, Pt2–Pt1–N15 166.3(2)*, C4–Pt1–N26 175.4(3)*, Pt1–P2–C3 88.5(3)*.](image-url)
of an agnostic interaction between the non-cyclometalated phosphine ligand and Pt center (Pt(1)–C4B 2.83(2)/2.84(2) Å). In solution, the structure of 3b was fully corroborated by NMR spectroscopy (CDCl3, 298 K). Formation of the metallocycle is apparent by distinctive 1H and 13C methylene resonances at δ(1H) 2.75 ppm (J_PtH = 110 Hz) and δ(13C) 10.3 ppm (J_PtC = 670 Hz) with platinum satellites, two doublet 1P resonances with a large (trans) J_PtC coupling constant and platinum satellites (δ(1P) 59.1 ppm (J_PtP = 2896 Hz, J_PtH = 317 Hz, P_Bu2), δ(1P) 25.2 ppm (J_PtP = 1916 Hz, J_PtH = 317 Hz, P_Bu2CMC2CH3)), and a platinum chemical shift of δ(1P)Pt = –3816 ppm (225 K). Although the signals associated with the non-cyclometalated phosphine ligand broadened on cooling to 185 K, the agnostic interaction could not be definitively resolved by 1H NMR spectroscopy.

Cyclometalation reactions of PtIV complexes have extensive precedent.[14,15] For instance, T-shaped complexes [PtIV(PR2C6H4CH2Me2CH2)(PR2Xyl)]+ (R = C4, Ph; Xyl = 2,6-dimethylphenyl) with similar structural and spectroscopic characteristics compared to 3b, were prepared by cyclometalation reactions involving halide abstraction from [PtIV(PR2Xyl)2(MeCl)] and subsequent elimination of methane.[16] Intramolecular C–H bond activation of P_Bu2 in [PtIV(P_Bu2)X2] (X = Cl, Br, I, OTf, NO3) has also been described and results in coordinatively saturated products [PtIV(PR2P_Bu2CMC2CH3)(P_Bu2)][17] In the case of 3b, the presence of a PtIV 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 PtIV alkyl hydride intermediate [PtIV(PR2P_Bu2CMC2CH3)(P_Bu2)]+ (5). In the latter case, subsequent concomitance (5 + 2b), disproportion (via a PtIV alkyl dihydride), or Pt–H bond homolysis (i.e. 2 × 5 → 2 × 3b + H2; 3b + H2 → 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 [Fe][PF6] in the presence of one equiv of bipy resulted in formation of a new cyclometalated complex [PtIV(PR2P_Bu2CMC2CH3)(bipy)][PF6] 6 instead, alongside protonated phosphine (δ(1H) 54.2 ppm). The identity of this new complex was verified by independent synthesis from 3b and bipy in 1,2-C2H4F2 (97% yield of isolated product). As with 3b, the cyclometalated phosphine in 6 is characterized by an acute Pt(1)–P2C3 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 13C resonance shows a reduced J_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 J_PtP coupling constant determined by 31P NMR spectroscopy (3105 versus 1916 Hz). A platinum chemical shift of δ(1P)Pt = –3788 ppm (225 K) was also measured for 6 and is very similar to that of 3b (δ(1P)Pt = –3816 ppm).

Reaction of isolated 3b with H2 (1 atm) results directly in the formation of 4, which is reconcilable with Pt–H bond homolysis or disproportion (via an unstable PtIV 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 1b20 or 2,6-bis(2,4,6-trimethylpyridine) and a second one-electron oxidation. The redox potential of the associated PtIV/PtII couple, assessed by CV experiments using both isolated 3b (E1/2 = –1.90 V, irreversible) and 6 (E1/2 = –1.68 V, i_p 1/2 ≈ 0.96) indicates that such a one-electron oxidation is at least conceptually feasible using [Fe][PF6] (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 [Fe][PF6] in the presence of excess 2,6-bis(2,4,6-trimethylpyridine) (5 equiv) resulted in the gradual appearance of a diamagnetic complex with spectroscopic characteristics consistent with cyclometalation (3a; δ(1P)Pd 7.0, –1.3 ppm; J_PtP = 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 1 formal oxidation state, as demonstrated by one-electron oxidation of [M(P_Bu2)2] (M = Pd, Pt) using [Fe][PF6]. While the PdIV derivative was readily isolated from solution and fully characterized, the heavier congener undergoes C–H bond cyclometalation to afford the 14 VE PtIV complex [PtIV(PR2P_Bu2CMC2CH3)(P_Bu2)]+ with concomitant formation of [PtIV(P_Bu2)][PF6]. 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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EPR data were obtained using 50 mW microwave power in a TM$_{5/2}$ cavity at 9.51 GHz, with 0.5 mT field modulation at 100 kHz. The simulation was performed using EasySpin: S. Stoll, A. Schweiger, J. Magn. Reson. 2006, 178, 42–55. A minimal parameter set from esfit was used; $g_{||} = 2.3165$, $A_{||} = 24.976$ mT, and phenomenological line broadening of 9.8 mT (Gaussian) and 5.25 mT (Lorentzian). No attempt was made to extract the anisotropy of the magnetic interactions.


Following these reactions in situ (293 K) by periodic analysis with EPR spectroscopy (200 K) was uninformative when using $\text{[BCl}2\text{Na]}$ as a fully soluble ferrocenium salt. For context, $\text{[BCl}2\text{Na]}$ was EPR silent at 200 K as a component in reaction mixtures or in 1,2-C$_2$H$_2$F$_2$ alone.

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