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A Pincer-Type Anionic Platinum(0) Complex**

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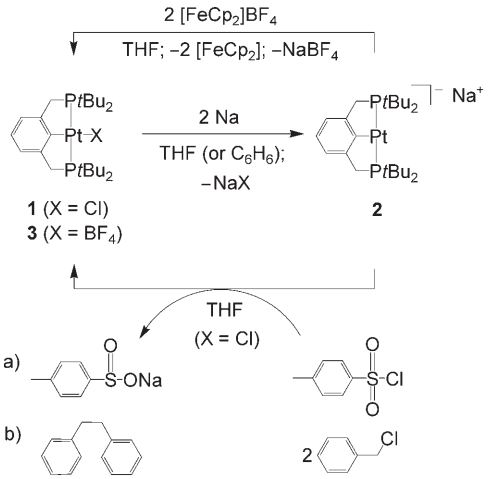
Pincer-type complexes constitute a large family of compounds that have attracted much recent interest. Among these compounds, aryl-anchored, d^8 pincer complexes of the type $[M^{II}(LCL')]$ (M = Ni, Pd, Pt; L = neutral ligand such as phosphine, amine, dialkyl sulfide) are a major group that plays important roles in organometallic reactions and mechanisms, catalysis, and in the design of new materials.[1] In contrast, and to our knowledge, no complexes of this type with the metal in the zero oxidation state have been prepared. Such d^{10} $[M^0(LCL')]$ complexes with neutral L ligands and an "anionic" aryl anchor would be anionic, and would be expected to possess distinctly different properties to neutral d^{10} (M^0) complexes. We chose to utilize bulky bis-chelating pincer-type ligands in this study as they have been shown to be effective in stabilizing reactive species and have led to unusual complexes.[1]

We have recently shown that reduction of PCP-type Pd^{II} complexes $[Pd(X)C_6H_3(CH_2PiPr_2)_2]$ (X = Cl, trifluoroacetate) with sodium metal results in collapse of the pincer system, leading to formation of the diamagnetic binuclear complex $[Pd\{C_6H_3(CH_2PiPr_2)_2\}_2Pd]$, which contains a 14-electron linear Pd^0 moiety and a completely nonplanar "butterfly"-type 16-electron Pd^{II} moiety.[2] Oxidation of the binuclear complex, or its reaction with organic halides, regenerates the original mononuclear framework.[2]

To avoid collapse of the pincer system upon reduction we decided to use a PCP-Pt^{II} complex with the hope that the more diffuse nature of the Pt orbitals (compared with Pd) might stabilize the reduced metal center.[3] In addition, increasing the steric bulk of the pincer phosphine ligand might protect the reduced metal center against intermolecular reactions and might lead to a rare monometallic Pt^0 anionic complex. We are aware of only one monometallic anionic Pt^0 complex, namely $[Pt(Me_2NCS_2)(PEt_3)]^-$, which was generated in situ at −78 °C by proton abstraction from the Pt^{II} hydride complex $[PtH(Me_2NCS_2)(PEt_3)]$.[4] This complex was not isolated but was trapped with a variety of electrophiles to give a range of Pt^{II} complexes.[4,5]

Herein we report the preparation, characterization, and computational study of the first thermally stable, monometallic anionic Pt^0 complex. The reactivity of this electron-rich, 16-electron PCP-type anionic Pt^0 complex shows that it is a Brønsted base and an effective electron-transfer reagent that is capable of C–F activation under exceedingly mild conditions.

Reduction of the bulky PCP-Pt^{II} complex **1** (Scheme 1)[6] with sodium in dry $[D_8]$THF at room temperature overnight led to a dramatic color change from colorless to dark red. A



Scheme 1. Reduction of complexes **1** and **3** to form the PCP-Pt^0 anion **2** and its oxidation to regenerate the Pt^{II} complex. See text for details; Cp = C_5H_5.

multinuclear NMR spectroscopy study of the reaction solution revealed that reduction of complex **1** had taken place to give quantitative formation of the diamagnetic 16-electron planar PCP-Pt^0 anion **2** (Scheme 1). Thus, the resonance of **1** at $\delta = 66.7$ ppm ($^1J_{Pt,P} = 2893$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum is replaced by a signal for the new complex **2** at $\delta =$ 120.5 ppm ($^1J_{Pt,P} = 3874$ Hz). The $^{31}P\{^1H\}$ NMR spectrum of the solution confirmed that this transformation is quantitative. In addition, the $^{195}Pt\{^1H\}$ NMR spectrum revealed that the diagnostic triplet of **1** at $\delta = -4105$ ppm ($^1J_{P,Pt} = 2893$ Hz) is replaced by a new triplet for **2** at $\delta = -4034$ ppm ($^1J_{P,Pt} =$ 3874 Hz), thus showing that the two phosphorus donor atoms stay bound to the metal center in **2**.[7] The increase in the Pt–P coupling constant is indicative of a decrease of the Pt–P bond length upon going from **1** to **2**. The ^1H NMR spectrum of **2** exhibits a virtual triplet for the *tert*-butyl group at $\delta =$ 1.36 ppm ($^3J_{P,H} = 6$ Hz) and a virtual triplet for the methylene group at $\delta = 3.56$ ppm ($^2J_{P,H} = 4$ Hz); this pattern is characteristic of strong phosphorus–phosphorus coupling between

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trans-bonded and magnetically equivalent phosphorus donor atoms. In the $^{13}C\{^1H\}$ NMR spectrum, the *ipso* carbon gives rise to a peak at $\delta = 221.97$ ppm with a one-bond coupling to platinum ($^1J_{Pt,C} = 728$ Hz). In addition, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** indicate conservation of the aromaticity in the ligand backbone. We can therefore conclude that the meridional PCP arrangement is maintained in **2**.[8] In accordance with the simple patterns in the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra, complex **2** appears to be a monomer in THF solution rather than a dimer of the type [PCP-Pt-Pt-PCP].[9] Coordination of dinitrogen to **2** can be excluded since the same product was obtained under both argon and nitrogen (as confirmed by $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy).

Reduction of complex **1** with sodium metal in dry C_6D_6 (rather than THF) at room temperature overnight resulted in formation of the anionic complex **2** as a dark-red precipitate along with precipitation of sodium chloride (Scheme 1). Similarly, reduction of the unsaturated cationic Pt^{II} complex **3**[10] in dry C_6D_6 under the same conditions resulted in precipitation of **2** and sodium tetrafluoroborate (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of the C_6D_6 reaction solution revealed full consumption of complexes **1** or **3** in both cases, while the $^{31}P\{^1H\}$ NMR spectrum of the dark-red precipitate dissolved in dry THF confirmed quantitative formation of **2**. Compound **2** is stable at room temperature for a few days in dry THF solution or in the solid state under an atmosphere of dry argon (or nitrogen).

The planar T-shaped geometry proposed for **2** based on the NMR spectroscopy study is supported by density functional theory (DFT) calculations (Figure 1).[11] A comparison of the computed structures of **1** and **2** (Table 1) reveals a shortening of the Pt–P bonds and a flattening of the P–Pt–P angle on going from **1** to **2**.[12] Surprisingly, the C_{ipso}–Pt bond is longer in the computed structure of **2** than in the computed structure of **1** and the reported X-ray structure of **1**[6b] (Table 1). The aryl C–C bond lengths and angles in **2** are quite similar to those of **1**, hence the computational study indicates that the negative charge is localized at the metal center of the anionic complex **2** (structure **A**) rather than being delocalized over the metal center and the σ-bound aryl backbone (structure **B**).

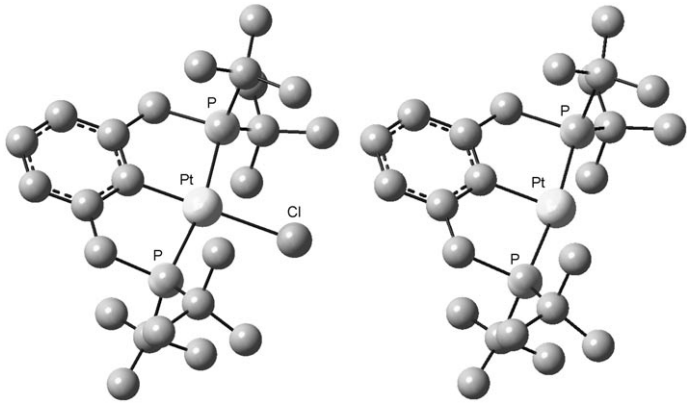
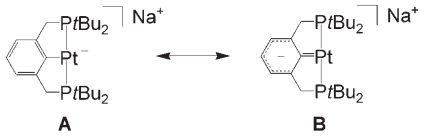


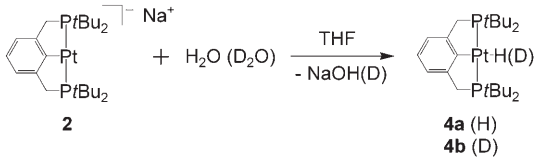
Figure 1. Optimized structures of complex **1** (left) and the anion **2** (right). Na^+ counterion and hydrogen atoms have been omitted for clarity.

Table 1: Selected bond lengths and angles for **1** and **2**.

	X-ray structure of **1**[6b]	Computed structure of **1**	Computed structure of **2**
Pt–P [Å]	2.291(2)	2.35	2.31
C_{ipso}–Pt [Å]	2.017(6)	2.01	2.06
P–Pt–P [°]	167.35(5)	169.0	173.3



Clear evidence for the Brønsted basicity of the platinum center in the anionic complex **2** was deduced from its reaction with water. Thus, treatment of a THF solution of **2** with an excess of H_2O (D_2O) resulted in quantitative formation of the Pt^{II} hydride (deuteride) complex (**4a** and **4b**, respectively; Scheme 2) along with an immediate color change from dark



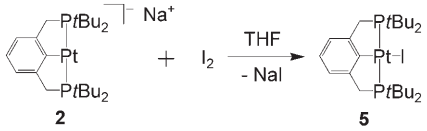
Scheme 2. Reaction of the anionic Pt^0 complex **2** with water.

red to colorless.[13] The resulting colorless THF solution was found to be basic, which is compatible with formation of sodium hydroxide.

Complex **4a**, which has been reported previously,[13] exhibits a doublet of triplets centered at $\delta = -4776$ ppm due to one-bond coupling to the hydride ligand ($^1J_{H,Pt} = 746$ Hz) and coupling to two phosphorus donor atoms ($^1J_{P,Pt} = 2918$ Hz) in its ^{195}Pt NMR spectrum (in THF). In agreement with this, the ^{195}Pt NMR spectrum of **4b** exhibits a triplet of triplets centered at the same chemical shift arising from one-bond coupling to a deuteride ligand ($^1J_{D,Pt} = 114$ Hz) and coupling to two phosphorus donor atoms ($^1J_{P,Pt} = 2918$ Hz). ^1H and ^{13}C NMR spectroscopy studies did not reveal any H/D exchange at the aryl positions upon treatment of **2** with D_2O, thus suggesting that the negative charge in **2** is localized primarily at the metal center rather than in the aromatic ring (structure **A**).

The PCP-Pt^0 anion **2** can be re-oxidized to a PCP-Pt^{II} complex. Thus, treatment of a THF solution of **2** (prepared from **3** in C_6H_6) with two equivalents of the one-electron oxidant $[FeCp_2]BF_4$ is accompanied by an

immediate color change from dark red to yellow, thereby indicating the formation of [$FeCp_2$] (Scheme 1).[14] The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution reveals regeneration of the cationic Pt^{II} complex **3** (Scheme 1),[15] which was isolated from the reaction mixture in 68% yield after extraction of [$FeCp_2$] with pentane. Oxidation of **2** to a Pt^{II} complex is also observed upon reaction with a dihalogen. Thus, treatment of a THF solution of **2** with one equivalent of I_2 leads to quantitative formation of the Pt^{II} iodo complex **5** (Scheme 3), which is accompanied by a color change from

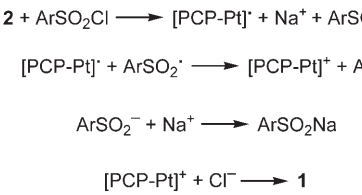


2 5

Scheme 3. Oxidation of complex **2** with iodine.

dark red to orange.[16a] A possible mechanism for this reaction involves formation of an anionic intermediate containing an end-on-bound iodine molecule, $[PCP\text{-}Pt\text{-}I\text{-}I]^-$, followed by two-electron oxidation of the metal and concomitant heterolytic cleavage of the I–I bond to quantitatively form complex **5** and NaI. The η^1-coordination of I_2 to an NCN-Pt^{II} complex has been reported previously.[16b]

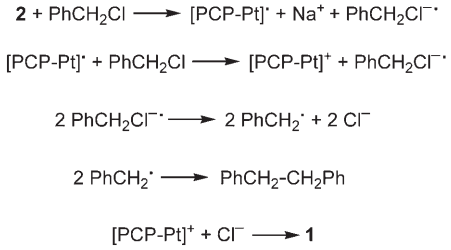
The electron-rich Pt^0 anion **2** is an effective electron-transfer reagent, as demonstrated by the transformations shown in Scheme 1. Significantly, the Pt^{II} complex **1** is regenerated quantitatively in these reactions. In the first reaction, reduction of *p*-toluenesulfonyl chloride with one equivalent of **2** in THF results in the formation of a corresponding amount of sodium *p*-toluenesulfinate and complex **1** (Scheme 1; reaction (a). We assume that electron transfer from **2** to the arenesulfonyl halides results in formation of sulfonyl radicals (Scheme 4).[17] Since sulfonyl



Scheme 4. Proposed mechanism of electron transfer from complex **2** to arenesulfonyl halides to form complex **1** and sodium arylsulfinate.

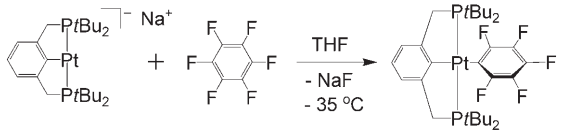
radicals have a low tendency to dimerize (in comparison with carbon-based radicals),[17] they can undergo additional reduction to yield sodium arylsulfinate (Scheme 4).

Treatment of half an equivalent of **2** in THF with benzyl chloride results in a reductive coupling reaction that yields half an equivalent of dibenzyl and complex **1** (Scheme 1; reaction (b). This reaction can be explained by electron transfer from **2** to benzyl chloride to form a benzyl chloride radical anion and a PCP-Pt^I intermediate. The latter can also transfer an electron to benzyl chloride to yield a cationic Pt^{II} intermediate. Chloride loss from the radical anions would give benzyl radicals, which can couple to yield dibenzyl. Coordination of chloride to Pt^{II} would yield complex **1** (Scheme 5).[18]



Scheme 5. Proposed mechanism of electron transfer from complex **2** to benzyl chloride to form complex **1** and dibenzyl.

Much research effort has been devoted in recent years to the activation of C–F bonds by transition-metal complexes. Indeed, C–F bond cleavage is now known in a number of intermolecular systems involving transition-metal complexes.[19–24] We found that the anionic, electron-rich Pt^0 complex **2** is very active in C–F activation. Thus, it reacts with one equivalent of C_6F_6 in THF at −35 °C to form the Pt^{II} complex **6** and sodium fluoride within 2 h (Scheme 6). This is



2 6

Scheme 6. Facile C–F activation of hexafluorobenzene by complex **2**.

one of the fastest C–F bond activation reactions reported to date.[25] Note that C–F activation by platinum complexes is relatively rare.[21] Complex **6** was identified unambiguously by multinuclear NMR spectroscopy. Thus, its $^{31}P\{^1H\}$ NMR spectrum shows a singlet at $\delta = 67.6$ ppm flanked by platinum satellites ($^1J_{Pt,P} = 2856$ Hz) and its $^{195}Pt\{^1H\}$ NMR spectrum exhibits a triplet of triplets centered at $\delta = -4393$ ppm which arises from three-bond coupling to two fluorine atoms in the *ortho* positions ($^3J_{F,Pt} = 235$ Hz) and coupling to two phosphorus donor atoms ($^1J_{P,Pt} = 2856$ Hz). The *ipso* carbon of the C_6F_5 ligand gives rise to a triplet at $\delta = 150.58$ ppm ($^2J_{P,C} = 8$ Hz) and the aryl backbone *ipso* carbon appears as a singlet at $\delta = 163.91$ ppm with Pt satellites ($^1J_{Pt,C} = 710$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum.

Two possible mechanisms for the observed C–F activation by the electron rich anionic **2** are: 1) nucleophilic displacement of fluoride ion from C_6F_6,[23] and 2) electron transfer to C_6F_6[19a,24] to generate the radical anion $[C_6F_6]^{\bullet-}$ and a Pt^I intermediate, followed by fluoride loss and coupling of the generated $[C_6F_5]^\bullet$ radical with Pt^I. As **2** is a strong electron donor and the metal center is sterically hindered by the bulky *tert*-butyl phosphine groups, both of which retard nucleophilic reactivity, we favor the electron-transfer mechanism.

In summary, the first stable monometallic anionic Pt^0 complex **2** has been prepared by reduction of a PCP-type Pt^{II} complex. This PCP-Pt^0 anion adopts a T-shaped structure and exhibits diverse reactivity. Thus, it undergoes protonation by water to give a Pt^{II} hydride complex and is an efficient electron-transfer reagent, being re-oxidized quantitatively to Pt^{II}. It is also capable of activating the strong C–F bond of hexafluorobenzene, even at −35 °C. Further studies on the reactivity of this PCP-Pt^0 anion and its catalytic potential are underway.

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Keywords: C–F activation · electron transfer · P ligands · platinum · reduction

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[11] For full details of the optimization procedure and the *xyz* coordinates of the optimized geometries of the complexes see the Supporting Information.

[12] These findings are in agreement with the observed increase in the Pt–P coupling constant (by almost 1000 Hz) in the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra upon transformation of **1** into **2**.

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[25] To compare with another anionic complex, C–F activation of hexafluorobenzene by $Na[(C_5H_5)Fe(CO)_2]$ was performed in refluxing THF for 12 h.[23] C–F activation of hexafluorobenzene at room temperature by the highly reactive 14-electron fragment $[Pt^0(dtbpm)]$ (dtbpm = bis(di-*tert*-butylphosphanyl)methane) has been reported.[21a]

