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Coordination Chemistry

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

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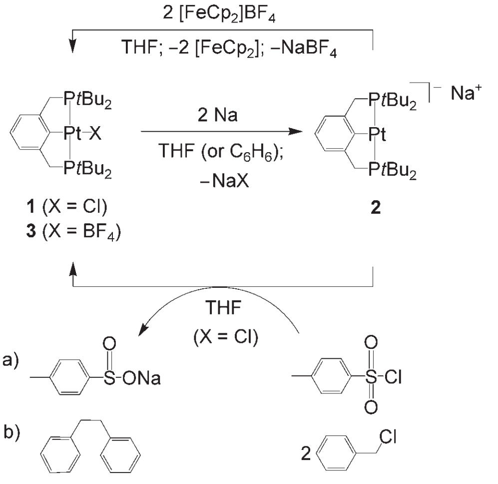
Pincer-type complexes constitute a large family of compounds that have attracted much recent interest. Among these compounds, aryl-anchored, d^8 pincer complexes of the type $[M^{II}(LCL')]$ (M = Ni, Pd, Pt; L = neutral ligand such as phosphine, amine, dialkyl sulfide) are a major group that plays important 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 $[Pd(X)C_6H_3(CH_2P\mathit{i}Pr_2)_2]$ (X = Cl, trifluoroacetate) with sodium metal results in collapse of the pincer system, leading to formation of the diamagnetic binuclear complex $[Pd\{C_6H_3(CH_2P\mathit{i}Pr_2)_2\}_2Pd]$, 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 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



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; $Cp = C_5H_5$.

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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 ($^1J_{\text{Pt,C}} = 728$ Hz). In addition, the ^{1}H 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**).

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

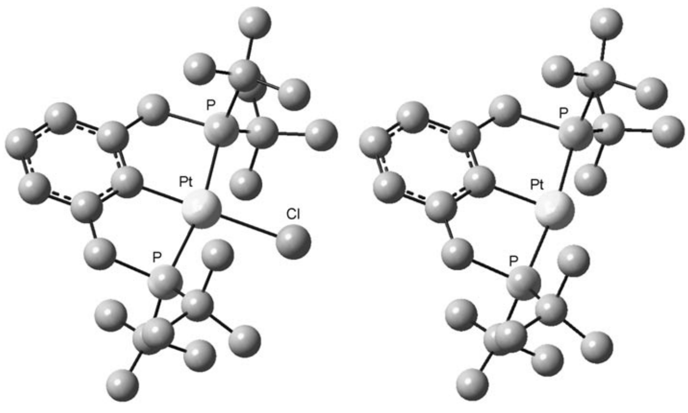
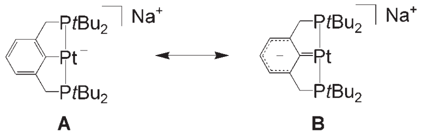
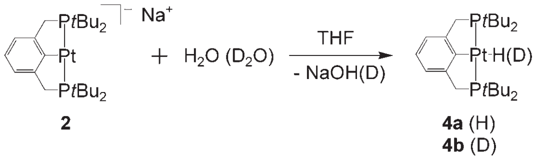


Figure 1. Optimized structures of complex **1** (left) and the anion **2** (right). Na^+ counterion and hydrogen atoms have been omitted for clarity.



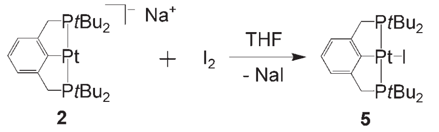
Clear evidence for the Brønsted basicity of the platinum center in the anionic complex **2** was deduced from its reaction with water. Thus, treatment of a THF solution of **2** with an excess of H_2O (D_2O) resulted in quantitative formation of the Pt^{II} hydride (deuteride) complex (**4a** and **4b**, respectively; Scheme 2) along with an immediate color change from dark red to colorless.[13] The resulting colorless THF solution was found to be basic, which is compatible with formation of sodium hydroxide.



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

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 ($^1J_{\text{H,Pt}} = 746$ Hz) and coupling to two phosphorus donor atoms ($^1J_{\text{P,Pt}} = 2918$ 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 ($^1J_{\text{D,Pt}} = 114$ Hz) and coupling to two phosphorus donor atoms ($^1J_{\text{P,Pt}} = 2918$ Hz). ^{1}H 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{^{1}H} 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 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-Pt-I-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]



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

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 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).

$$\mathbf{2} + \mathrm{ArSO_2Cl} \longrightarrow [\mathrm{PCP\text{-}Pt}]^{\bullet} + \mathrm{Na^+} + \mathrm{ArSO_2}^{\bullet} + \mathrm{Cl^-}$$

$$[\mathrm{PCP\text{-}Pt}]^{\bullet} + \mathrm{ArSO_2}^{\bullet} \longrightarrow [\mathrm{PCP\text{-}Pt}]^+ + \mathrm{ArSO_2}^-$$

$$\mathrm{ArSO_2}^- + \mathrm{Na^+} \longrightarrow \mathrm{ArSO_2Na}$$

$$[\mathrm{PCP\text{-}Pt}]^+ + \mathrm{Cl^-} \longrightarrow \mathbf{1}$$

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

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]

$$\mathbf{2} + \mathrm{PhCH_2Cl} \longrightarrow [\mathrm{PCP\text{-}Pt}]^{\bullet} + \mathrm{Na^+} + \mathrm{PhCH_2Cl}^{-\bullet}$$

$$[\mathrm{PCP\text{-}Pt}]^{\bullet} + \mathrm{PhCH_2Cl} \longrightarrow [\mathrm{PCP\text{-}Pt}]^+ + \mathrm{PhCH_2Cl}^{-\bullet}$$

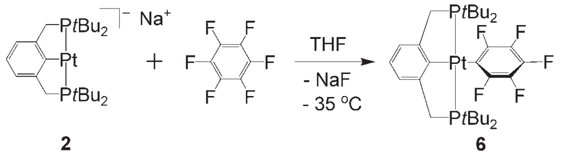
$$2\,\mathrm{PhCH_2Cl}^{-\bullet} \longrightarrow 2\,\mathrm{PhCH_2}^{\bullet} + 2\,\mathrm{Cl^-}$$

$$2\,\mathrm{PhCH_2}^{\bullet} \longrightarrow \mathrm{PhCH_2\text{-}CH_2Ph}$$

$$[\mathrm{PCP\text{-}Pt}]^+ + \mathrm{Cl^-} \longrightarrow \mathbf{1}$$

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$_6$F$_6$ in THF at −35 °C to form the Pt^{II} complex **6** and sodium fluoride within 2 h (Scheme 6). This is 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{^{1}H} NMR spectrum shows a singlet at $\delta = 67.6$ ppm flanked by platinum satellites ($^1J_{\mathrm{Pt,P}} = 2856$ Hz) and its ^{195}Pt{^{1}H} 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 ($^3J_{\mathrm{F,Pt}} = 235$ Hz) and coupling to two phosphorus donor atoms ($^1J_{\mathrm{P,Pt}} = 2856$ Hz). The *ipso* carbon of the C$_6$F$_5$ ligand gives rise to a triplet at $\delta = 150.58$ ppm ($^2J_{\mathrm{P,C}} = 8$ Hz) and the aryl backbone *ipso* carbon appears as a singlet at $\delta = 163.91$ ppm with Pt satellites ($^1J_{\mathrm{Pt,C}} = 710$ Hz) in the ^{13}C{^{1}H} NMR spectrum.



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

Two possible mechanisms for the observed C–F activation by the electron rich anionic **2** are: 1) nucleophilic displacement of fluoride ion from C$_6$F$_6$,[23] and 2) electron transfer to C$_6$F$_6$[19a,24] to generate the radical anion [C$_6$F$_6$]$^{\bullet -}$ and a Pt^I intermediate, followed by fluoride loss and coupling of the generated [C$_6$F$_5$]$^{\bullet}$ 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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[1] Reviews: a) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750; b) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759; c) B. Rybtchinski, D. Milstein, *Angew. Chem.* **1999**, *111*, 918; *Angew. Chem. Int. Ed.* **1999**, *38*, 870; d) J. T. Singleton, *Tetrahedron* **2003**, *59*, 1837; e) A. Vigalok, D. Milstein, *Acc. Chem. Res.* **2001**, *34*, 798; f) D. Milstein, *Pure Appl. Chem.* **2003**, *75*, 2003; g) C. M. Jensen, *Chem. Commun.* **1999**, 2443.

[2] C. M. Frech, L. J. W. Shimon, D. Milstein, *Angew. Chem.* **2005**, *117*, 1737; *Angew. Chem. Int. Ed.* **2005**, *44*, 1709.

[3] In analogy to nonchelating systems, where reduction of $[PtCl_2L_2]$ (L = bulky *tert*-phosphine) with Na/Hg in THF affords PtL_2 complexes while reduction of $[PdCl_2L_2]$ (L = bulky *tert*-phosphine) with Na/Hg in THF results in the formation of metallic palladium. The reduction was possible only when excess phosphine was used. See: S. Otsuka, *J. Organomet. Chem.* **1980**, *200*, 191, and references therein.

[4] a) D. L. Reger, Y. Ding, *Organometallics* **1994**, *13*, 1047; b) L. M. Rendina, T. W. Hambley in *Comprehensive Coordination Chemistry II, 2nd ed.*, *Vol. 6* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Oxford, **2004**, pp. 673–745.

[5] For non-isolated, anionic palladium(0) intermediates, and their involvement in oxidative addition reactions, see: a) C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, *33*, 314; b) C. Amatore, A. Jutand, F. Lemaitre, J. L. Ricard, S. Kozuch, S. Shaik, *J. Organomet. Chem.* **2004**, *689*, 3728.

[6] a) For the first synthesis of **1**, see: C. J. Moulton, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1976**, 1020. b) A modified preparation of **1** has also been reported: D. Vuzman, E. Poverenov, Y. Diskin-Posner, G. Leitus, L. J. W. Shimon, D. Milstein, *Dalton Trans.* **2007**, 5692.

[7] The ^{195}Pt NMR spectroscopic data of two Pt^0 phosphine complexes (measured at 310 K) is presented here for comparison: a) $[Pt(PtBu_3)_2]$: $^{195}Pt\{^1H\}$ NMR ($[D_8]$THF): $\delta = -6471$ ppm (t, $J_{P,Pt} = 4420$ Hz); b) $Pt(PEt_3)_3$: $^{195}Pt\{^1H\}$ NMR ($[D_8]$toluene): $\delta = -4517$ ppm (q, $J_{P,Pt} = 4216$ Hz). Taken from: R. Benn, H. M. Buch, R. D. Reinhardt, *Magn. Reson. Chem.* **1985**, *23*, 559.

[8] The meridional planar ML_3 arrangement of anionic **2** can be compared to the trigonal-planar ML_3 arrangement of neutral 16-electron Pt^0 phosphine complexes. F. R. Hartley in *Comprehensive Organometallic Chemistry*, *Vol. 6* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**, pp. 471–762 and reference [4b].

[9] The $^{31}P\{^1H\}$ NMR spectrum of the Pt–Pt dimer $[\{Pt(tBu)_2P(CH_2)_3P(tBu)_2\}_2]$ in THF shows a complex resonance pattern arising from three possible combinations of two platinum atoms with different nuclear spins. T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers, S. Otsuka, *J. Am. Chem. Soc.* **1978**, *100*, 2063.

[10] a) The unsaturated cationic Pt^{II} complex **3** was prepared from **1** by chloride ligand abstraction with $AgBF_4$. For preparation and characterization of **3** see reference [6b]; b) Reduction of **3** to **2** with sodium metal directly in THF is accompanied by formation of unidentified by-products and thus is not applicable on a preparative scale.

[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**.

[13] Complex **4a** has been prepared previously from **1** by chloride ligand nucleophilic substitution with hydride (see reference [6a]). For a modified procedure, see: B. F. M. Kimmich, R. M. Bullock, *Organometallics* **2002**, *21*, 1504.

[14] For review of chemical redox agents for organometallic chemistry see: N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877.

[15] Similar oxidation of a THF solution of **2** prepared directly by reduction of **1** in THF (in other words a THF solution containing partially dissolved chloride anions) resulted in formation of a mixture of several compounds, which included the cationic complex **3** (30 %) and the original complex **1** (40 %) according to NMR spectroscopy.

[16] a) Complex **5** has been prepared previously by a cyclometalation reaction between $[PtI_2(cod)]$ (cod = cyclooctadiene) and the ligand C_6H_4-2,6-$(CH_2PtBu_2)_2$, see: M. A. Bennett, H. Jin, A. C. Willis, *J. Organomet. Chem.* **1993**, *451*, 249; b) R. A. Gossage, A. D. Ryabov, A. L. Spek, D. J. Stufkens, J. A. M. van Beek, R. van Eldik, G. van Koten, *J. Am. Chem. Soc.* **1999**, *121*, 2488.

[17] V. Percec, B. Barboiu, H.-J. Kim, *J. Am. Chem. Soc.* **1998**, *120*, 305, and references cited therein.

[18] A mechanism involving oxidative addition of organic halide to generate dibenzyl is also possible. See, for example: H. B. Kraatz, M. E. van der Boom, Y. Ben-David, D. Milstein, *Isr. J. Chem.* **2001**, *41*, 16.

[19] For examples of catalytic C–F activation see: a) M. Aizenberg, D. Milstein, *Science* **1994**, *265*, 359; b) M. Aizenberg, D. Milstein, *J. Am. Chem. Soc.* **1995**, *117*, 8674; d) T. Braun, R. N. Perutz, M. I. Sladek, *Chem. Commun.* **2001**, 2254; c) T. Schaub, M. Backes, U. Radius, *J. Am. Chem. Soc.* **2006**, *128*, 15964.

[20] Reviews: a) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373; b) H. Torrens, *Coord. Chem. Rev.* **2005**, *249*, 1957.

[21] a) P. Hofmann, G. Unfried, *Chem. Ber.* **1992**, *125*, 659; b) S. Hinterman, P. S. Pregosin, H. Ruger, H. C. Clark, *J. Organomet. Chem.* **1992**, *435*, 225; c) N. Jasim, R. N. Perutz, *J. Am. Chem. Soc.* **2000**, *122*, 8685; d) N. A. Jasim, R. N. Perutz, A. C. Whitwood, T. Braun, J. Izundu, B. Neumann, S. Rothfeld, H. G. Stammler, *Organometallics* **2004**, *23*, 6140.

[22] M. Reinhold, J. E. McGrady, R. N. Perutz, *J. Am. Chem. Soc.* **2004**, *126*, 5268.

[23] R. B. King, M. B. Bisnette, *J. Organomet. Chem.* **1964**, *2*, 38.

[24] O. Blum, F. Frolow, D. Milstein, *J. Chem. Soc. Chem. Commun.* **1991**, 258.

[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]