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## Introduction

Platinum chemistry, particularly some of the early work by Shilov,<sup>1-4</sup> has played a central role in the development of the modern understanding of carbon–hydrogen bond activation and the current techniques for performing such transformations selectively and efficiently. Arranging for a hydrocarbon to react with a three-coordinate d<sup>8</sup> fragment is a strategy that has been used in a number of successful approaches to C–H activation and functionalization.<sup>5-8</sup> Recognized as important intermediates in C–H activation, hydrocarbon  $\sigma$ -complexes have been the subject of many studies: direct spectroscopic observations in rare accessible cases,<sup>9-12</sup> indirect investigations using the tools of kinetics,<sup>13</sup> and computational work.<sup>14</sup>

## Frustrated Lewis pair-like splitting of aromatic C–H bonds and abstraction of halogen atoms by a cationic [(<sup>F</sup>PNP)Pt]<sup>+</sup> species<sup>†</sup>

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This manuscript explores new chemistry that can be related to the unobserved 14-electron [(<sup>F</sup>PNP)Pt]<sup>+</sup> transient (<sup>F</sup>PNP =  $(4-F-2-(^{i}Pr_{2}P)C_{6}H_{3})_{2}N$ ). Its reactivity can be accessed via abstraction of triflate from (<sup>F</sup>PNP)PtOTf (1) with K[B( $C_6F_5$ )<sub>4</sub>] in various solvents serving as substrates. With benzene, toluene and fluorobenzene, net heterolytic splitting of an aromatic C-H bond across the N-Pt bond is observed, without any detectable intermediates, leading to the  $[({}^{F}PN(H)P)Pt-Ar]^{+}$  products (Ar = Ph, **3a**; Ar =  $C_6H_4Me$ , **3b** (*ortho*), **3c** (*meta*), **3d** (*para*);  $Ar = o - C_6H_4F$ , **3e**). The latter can be alternatively prepared by protonation of the neutral (<sup>F</sup>PNP)Pt–Ar compounds. Compounds **3a–3e** do not release free arene under thermolysis at 80 °C, and compounds 3b/c/d do not interconvert under ambient temperature. With chlorobenzene and bromobenzene, the kinetic product is the  $\kappa^1$ -Cl or  $\kappa^1$ -Br adduct [(<sup>F</sup>PNP)Pt-Cl-Ph]<sup>+</sup> (4) or  $[(^{F}PNP)Pt-Br-Ph]^{+}$  (10). Compound 4 rearranges into a C-H splitting product  $[(^{F}PN(H)P)Pt-C_{6}H_{4}Cl]^{+}$ (3f), while 10 slowly reacts by formal transfer of Br atom to Pt. An analogous Cl atom transfer to Pt is observed upon the reaction of **1** with  $K[B(C_6F_5)_4]$  in dichloromethane, producing  $[(^{F}PNP)PtCI][B(C_6F_5)_4]$ (9a) which features an oxidized <sup>F</sup>PNP ligand framework. X-Ray diffractometry established structures of  $[(^{F}PN(H)P)Pt-C_{6}H_{4}F-o][B(C_{6}F_{5})_{4}]$  (**3e**, disordered rotamers),  $[(^{F}PN(H)P)Pt-C_{6}H_{4}Me][B(C_{6}F_{5})_{4}]$  (disordered meta- and para-isomers **3c/d**), and [(<sup>F</sup>PNP)PtCl][HCB<sub>11</sub>Cl<sub>11</sub>] (**9b**). DFT calculations at the PBE0 and M06-L levels on the free  $[(^{F}PNP)Pt]^+$  cation predict a relatively small (10–12 kcal mol<sup>-1</sup>) separation between the singlet and the triplet states. The relatively low triplet energy is probably related to the viability of the unexpected halogen atom abstraction reactions.

> Pincer ligands<sup>15,16</sup> offer a convenient framework for studies of square-planar compounds in which only one coordination site is intended to be the "reactive" site.17 Pincer complexes are perhaps best known for their thermal stability, but equally important attributes include the prevention of undesired ligand exchange and redistribution and a high degree of control over the positioning of the ancillary donor atoms. The work we present here was inspired and influenced by two sets of findings in the literature. Peters and Harkins reported in 2002 that reacting (NNN)PtOTf with a trialkylamine base in benzene led to heterolytic C-H activation of the solvent (Scheme 1A).18 Similar findings were reported by the Liang group with (PNP<sup>Ph</sup>)PtOTf.<sup>19</sup> The mechanism that appears to be most consistent with the results of both Liang et al. and Peters et al. involves displacement of the triflate ligand with a solvent molecule (via either a dissociative or associative mechanism) to form a cationic Ptarene complex.<sup>20,21</sup> This intermediate could either be sufficiently acidic to be deprotonated by a relatively weak base or it could undergo C-H oxidative addition, giving rise to an even more acidic Pt<sup>IV</sup> aryl/hydride species.<sup>20-22</sup>

> Additionally, the seminal 2009 report by Goldberg, Brookhart *et al.* demonstrated that a neutral pyridine/bis(phosphinite) PONOP ligand can be used to allow for the observation

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Details of experimental and computational procedures and characterization, coordinate files for calculated structures. CCDC 898629 (**3c/d**), 898630 (**3e**) and 898631 (**9b**). For ESI and crystallographic data in CIF or other electronic format. See DOI: 10.1039/c2sc21385k



**Scheme 1** (A) C-H activation of benzene by pincer complexes of Pt by Peters *et al.*<sup>18</sup> and by Liang *et al.*<sup>19</sup> (B) Synthesis of a Rh-methane complex by Goldberg, Brookhart *et al.*<sup>23</sup>

of a unique square-planar d<sup>8</sup> Rh<sup>I</sup>-methane adduct (Scheme 1B).<sup>23</sup> This finding and the above mentioned results of Peters and Liang<sup>18,19</sup> suggested the possibility that an anionic pincer ligand may provide access to cationic hydrocarbon complexes of Pt<sup>II</sup>.  $\eta^2$ -C,C-arene complexes of Pt<sup>II</sup> have been observed and even isolated, but primarily in systems where the ligands are considerably less sterically encumbering than a pincer ligand with bulky flanking phosphine arms.<sup>20–22</sup> Yamashita and Nozaki very recently reported the structure of an  $\eta^2$ -C,H-arene complex involving a d<sup>8</sup> (PBP)Rh fragment (PBP is a boryl/bis(phosphine) pincer ligand)<sup>24</sup> while Peters *et al.* reported a relatively long-range interaction between a cationic Pt<sup>II</sup> center supported by a tripodal silyl/tris(phosphine) ligand in a C-H bond of toluene in the solid state.<sup>25</sup>

Our group has frequently used diarylamido/bis(phosphine) PNP pincer ligands.<sup>26-29</sup> For example, we previously reported that [(<sup>Me</sup>PNP)Ni]<sup>+</sup> acts as an efficient catalyst for the coupling of acetonitrile and aldehydes.<sup>30</sup> Additionally, we found that a masked



Scheme 2 1,2-Addition reaction of alkynyl C–H and of B–B bonds with the  $[({\rm ^{Me}PNP})Pd]^{+}$  fragment.  $^{31}$ 

form of the analogous group 10 complex [(<sup>Me</sup>PNP)Pd]<sup>+</sup> functions as a frustrated Lewis pair with the ability to heterolytically split alkynyl C–H bonds,<sup>31</sup> B–H bonds and B–B bonds (Scheme 2).<sup>32</sup>

We envisioned that the three-coordinate d<sup>8</sup> fragment [(<sup>F</sup>PNP)Pt]<sup>+</sup> (FPNP ligand drawn in Scheme 3) would be a promising design for observing hydrocarbon complexes of cationic Pt<sup>II</sup> and set out to explore whether [(<sup>F</sup>PNP)Pt]<sup>+</sup> could be generated with a weakly coordinating counter-anion. Aromatic hydrocarbons and halogenated hydrocarbons seemed suitable as somewhat polar and weakly coordinating solvents that could either give rise to C-H complexes themselves, or permit an added hydrocarbon substrate to bind. While we were easily able to remove an anionic ligand from a four-coordinate Pt precursor, the results we obtained were rather unexpected. Instead of hydrocarbon complexes, we observed heterolytic splitting of aromatic C-H bonds across the Pt–N bond of the [(<sup>F</sup>PNP)Pt]<sup>+</sup> fragment. On the other hand, certain halogenated hydrocarbons reacted with  $[(^{F}PNP)Pt]^{+}$  via the net transfer of a halogen atom – a very unusual reaction for a Pt<sup>II</sup> cation. Both of these pathways derive from the non-innocence of the central amido ligand of <sup>F</sup>PNP: as a Brønsted base in the first case, and as an oxidizable ligand in the other. Nitrogenous ligands have been ubiquitous in the studies of Pd and Pt-mediated C-H activation, but a clear demonstration of the potential for these new reactivity pathways has not been previously reported.

## **Results and discussion**

### C-H activation of arenes

Desiring to test whether the (FPNP)Pt system performs similarly to the NNN- and PNP<sup>Ph</sup>-supported systems,<sup>18,19</sup> we prepared complex (FPNP)PtOTf analogously to the reported (MePNP) PtOTf.<sup>30</sup> We specifically chose the <sup>F</sup>PNP ligand because of its fluorine substituents, which do not have much influence<sup>33</sup> on the reactivity at the metal but provide a very convenient and informative NMR spectroscopic probe.34 As expected, thermolysis of 1 at 115 °C with Et<sub>3</sub>N in C<sub>6</sub>D<sub>6</sub> or *protio*-toluene produced results (Scheme 3) analogous to the findings of Peters et al.18 and Liang et al.<sup>19</sup> The consumption of 1 was slow; 7 days were required for completion of the reaction with toluene and in the reaction with C<sub>6</sub>D<sub>6</sub>, only 83% conversion was seen after 2 weeks. The corresponding Pt-aryl complexes 2a-d were observed by NMR spectroscopy, along with <10% of (FPNP)PtH.35 In the case of toluene, a mixture of Pt-tolyl isomers was produced. An o: m: p ratio of *ca.* 1:68:31 was determined by comparison with independently synthesized authentic samples (vide infra).



Scheme 3 C-H activation of arenes with (FPNP)PtOTf and base.

In order to access the  $[({}^{F}PNP)Pt]^{+}$  cation, we used  $K[B(C_6F_5)_4]$ (K-BARF) to abstract the triflate from **1**. Stirring a mixture of ( ${}^{F}PNP$ )PtOTf and K-BARF in  $C_6H_6$  for 4 days at ambient temperature resulted in complete consumption of **1** and full conversion to **3a**. The rate of the reaction was probably depressed by the limited solubility and the low rate of dissolution of K-BARF in benzene. Heating accelerated the reaction, and at 80 °C, the analogous products **3a-D**, **3b-d** or **3e** could be synthesized from ( ${}^{F}PNP$ )PtOTf and K-BARF in  $C_6D_6$ , toluene or fluorobenzene after just 2–16 h.

Compounds 3a-f are the products resulting from formal additions of aromatic C-H bonds across the Pt-N bond in [(<sup>F</sup>PNP)Pt]<sup>+</sup>. In our previous work,<sup>31</sup> we pointed out that the analogous [(MePNP)Pd]<sup>+</sup> fragment can be viewed as a frustrated Lewis pair.<sup>36</sup> The lone pair on N and the empty orbital on the metal are orthogonal to each other, while the steric bulk prevents the N<sub>amido</sub> from bridging, resulting in a "frustrated" arrangement. We did not observe aromatic C-H splitting with [(<sup>Me</sup>PNP)Pd]<sup>+</sup>. A single product 3a/3a-D was observed in each of the reactions with  $C_6H_6$  or  $C_6D_6$ . The assigned structures of 3a and 3a-D are consistent with the NMR spectra, including the NH proton resonance at 7.26 ppm in the <sup>1</sup>H NMR spectrum of 3a and the overall time-averaged  $C_s$  symmetry in the <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F NMR spectra. We have previously commented on the sensitivity of the <sup>19</sup>F NMR chemical shift exhibited by the <sup>F</sup>PNP ligand to the environment at the metal, particularly with respect to the amido-metal or amine-metal nature of the N donor.<sup>34</sup> In 3a, the <sup>19</sup>F NMR resonance was detected at -111.7 ppm, which is consistent with a protonated amine form of the PNP ligand.

Similar reactions run in fluorobenzene or toluene resulted in mixtures of products. Each of these products displayed general NMR spectroscopic features that are similar to those of **3a**, including downfield NH signals,  $C_{\rm s}$  symmetry at RT, and <sup>19</sup>F NMR chemical shifts around -111.3 to -111.7 ppm that can be assigned to the <sup>F</sup>PNP ligand. For fluorobenzene, only the *ortho*-fluorophenyl isomer was detected, but two spectroscopically distinct rotamers were seen (F either *syn* or *anti* with respect to NH). Deprotonation of **3e** with KO<sup>t</sup>Bu led to a single neutral Pt-aryl isomer (**2e**).

For toluene, three structural isomers were formed (8% *ortho* and 92% *meta* + *para*<sup>37</sup>). The benzyl isomer **3g** was not detected.<sup>38</sup> This set of conditions yielded a higher, albeit still small, proportion of the *ortho*-isomer **3b** than the **1**/Et<sub>3</sub>N reaction in Scheme 3. However, the regio-discriminating step may not be identical for these two reactions. Deprotonation (Scheme 4) of this product mixture resulted in a corresponding mixture of neutral *ortho-*, *meta-* and *para-*tolyl–Pt isomers. Each of these isomers **2b–d** was independently synthesized (Scheme 5), and protonation of **2b–d** with  $[H(OEt_2)_2][B(C_6F_5)_4]$  yielded pure samples of each corresponding (<sup>F</sup>PN(H)P)Pt–tolyl isomer **3b–d**. Analogous protonation and deprotonation reactions were also carried out for other Pt–aryls and for the Pt–benzyl complex **2g** (Schemes 4 and 5).

We were able to obtain an X-ray quality single crystal of **3e**. The solid-state structure supported the proposed assignment of fluorine in the *ortho*-position (Fig. 1). Moreover, the F atom of



Scheme 4 1,2-Addition of arenes.



Scheme 5 Synthesis and protonation of (FPNP)Pt-R compounds.



Fig. 1 ORTEP drawings (50% probability ellipsoids) of **3e** (left) and **3c/d** (right) showing selected atom labeling. Hydrogen atoms (except for N–H) and the BARF counter-ion are omitted for clarity. Only one of the two disordered orientations is shown for the fluorophenyl (**3e**) and tolyl (**3d** shown) groups. Selected bond distances (Å) and angles (°) for **3e**: N1–Pt1 2.159(2), P1–Pt1 2.2828(8), P2–Pt1 2.2780(8), Pt1–C44 2.012(3); P1–Pt1–P2 160.96(3), N1–Pt1–C44 170.46(11), C44–Pt1–P1 95.22(8), C44–Pt1–P2 99.05(8), N1–Pt1–P1 83.34(7), N1–Pt1–P2 84.59(7), C29–N1–Pt1 108.82(18), C31–N1–Pt1 116.10(18), C31–N1–C29 119.5(2). Selected bond distances (Å) and angles (°) for **3d**: N1–Pt1 2.183(7), P1–Pt1 2.288(2), P2–Pt1 2.270(2), Pt1–C25 2.072(6); P1–Pt1–P2 161.35(8), N1–Pt1–C25 166.8(3), C25–Pt1–P1 93.9(3), C25–Pt1–P2 100.9(3), N1–Pt1–P1 83.13(17), N1–Pt1–P2 84.81(17), C1–N1–Pt1 107.4(5), C7–N1–Pt1 115.1(5), C1–N1–C7 119.9(6).

the  $FC_6H_4$  ligand was found to be disordered over the *syn-/anti*positions (*vs.* NH), consistent with the observation of these rotamers in solution. An X-ray quality single crystal was also obtained from the product mixture of the reaction of **1** with K-BARF in toluene (Fig. 1). Remarkably, in this case as well, we saw solid-state disorder between the two major isomers observed in solution: **3c** and **3d**. The structure was successfully modeled with a *para* (**3d**) to *meta* (**3c**) isomer ratio of 53 : 47. Both the structure of **3e** and that of **3c/d** showed a distorted square-planar environment about Pt and a tetrahedral one about N.

The reaction with  $C_6H_5Cl$  (Scheme 4) ultimately produced a single *ortho* isomer<sup>39</sup> (and a single rotamer) of **3f**. However, an intermediate was observed in the initial stages of the reaction that we tentatively assigned as **4**. Although we do not have firm structural evidence, we believe it is more likely to be the  $\kappa^1$ -Cl chlorobenzene complex than a  $\pi$ -complex (*i.e.*, an  $\eta^2$ -C,C–arene complex), because similar intermediates were not observed in reactions with benzene, toluene or fluorobenzene. In addition, we observed what we believe to be a similar  $\kappa^1$ -Br adduct in the reaction with  $C_6D_5Br$ , which will be discussed in another section. Halocarbon (CH<sub>2</sub>Cl<sub>2</sub>, PhBr and PhI, but not PhCl) adducts of cationic Pt<sup>II</sup> fragments have been studied by Kubas *et al.*<sup>40</sup>

#### Rotamerism

The observation of two rotamers by NMR spectroscopy suggests slow (on the NMR timescale) rotation about the Pt–C bond in **3e**. On the timescale of experimental handling, however, these two rotamers are in apparent equilibrium; the ratio changes reversibly with temperature, and recrystallization does not change the ratio of rotamers. One would expect even slower rotation about the Pt–C bond in the analogous compounds **3b** and **3f**, which have larger *ortho* substituents, but in both of these cases, only a single rotamer was observed.

This was interpreted to mean that the larger substituent size perturbs the equilibrium constant far away from unity. In compounds that have a hydrogen atom at both *ortho* positions (**3a**, **3e** and **3d**), we did not observe resolved rotamers, but the aromatic signals were broad, which is consistent with a rotation rate about the Pt–C bond that is on the order of the NMR timescale. Restricted rotation about a metal–phenyl bond is common in complexes where an aryl ligand is *cis* to two phosphine ligands of this or greater size.<sup>41,42</sup> However, in pincer complexes containing P<sup>i</sup>Pr<sub>2</sub> groups and an aryl substituent of comparable size to a phenyl ring, this is usually observed only when the aryl group is also *cis* to the central pincer atom.<sup>43</sup>

In contrast, the neutral (<sup>F</sup>PNP)Pt–aryl complexes **2a–f** do not display any evidence of separately observable rotamers, showing only one sharp set of signals for each compound at ambient temperature. It is likely that the puckering of the PNP ligand upon quaternization of the N atom exacerbates the steric interactions between the isopropyl groups and the Pt–aryl bond, leading to a lower rate of rotation about Pt–C<sub>aryl</sub> in the protonated complexes.

#### Probing inter- and intramolecular exchange

We designed several experiments to probe whether the C–H addition across N–Pt is reversible. The first set of experiments involved thermolysis of isolated arene addition products **3a-D** and **3b–e** in a different arene (Scheme 6). We did not observe arene exchange for any of the combinations, indicating that the complete reversal of arene addition (including liberation of the free arene) is not kinetically accessible. However, heating **3a-D** in neat acetonitrile for 24 h at 80 °C did result in the formation of the cationic acetonitrile adduct [(<sup>F</sup>PNP)Pt(NCMe)][BARF] (6) and loss of  $C_6D_6$  from **3a-D**. It is unclear whether the apparent elimination of  $C_6D_6$  is simply faster in MeCN as solvent rather than arenes, or if it involves a more direct interaction of MeCN with **3a-D** that makes benzene elimination kinetically accessible.



Scheme 6 Reactions probing intramolecular isomerization.

The second set of experiments was based on the notion that the C-H addition process and its reverse should proceed *via* the intermediacy of a  $[({}^{F}PNP)Pt(arene)]^{+}$  adduct (7). Re-forming this arene adduct from a C-H addition product such as **3a** could hypothetically reverse C-H cleavage without liberating any free arene. In the case of **3b-d**, this would lead to an intramolecular scrambling of isomers. However, solutions of pure **3b**, **3c** or **3d** did not produce any other isomers in NMR-detectable concentrations after 2 weeks at ambient temperature (Scheme 6). The same was true for the benzyl isomer **3g** (not observed in the reactions of **1** with K-BARF in toluene). There was also no evidence of isomerization when **3c** or **3d** was exposed to ( ${}^{F}PNP$ ) Pt(*m*-C<sub>6</sub>H<sub>4</sub>Me), Me<sub>2</sub>S-BF<sub>3</sub> or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

On the other hand, treatment of **3b–d** in  $CD_2Cl_2$  with an HOTf–PhF solution did result in some isomerization and the formation of  $[({}^{F}PN(H)P)PtOTf]^{+}$  (**8**).<sup>44</sup> We propose that triflic acid can reversibly protonate **3b–d** and **3g** to give unobserved  $[({}^{F}PN(H)P)Pt(toluene)]^{2+}$  (**A**, Scheme 6), causing *ortho/meta/para* scrambling, and that the arene in **A** can be irreversibly but relatively slowly be replaced by triflate. Notably,  $[H(OEt_2)_2][BARF]$  or triflic acid in ether failed to induce the isomerization. Evidently, protonated Et<sub>2</sub>O is not a strong enough Brønsted acid. Related observations were made by Tilset *et al.*, who reported that protonation of a cationic  $[(diimine)Pt(Ph)(NCMe)]^+$  complex in acetonitrile was orders of magnitude faster with HOTf than with HBF<sub>4</sub>/Et<sub>2</sub>O.<sup>22</sup>  $[({}^{F}PN(H)P)PtOTf]^+$  appears to be unstable in dichloromethane, producing  $[({}^{F}PN(H)P)PtCl]^+$  (**9**) over time.

All in all, our observations imply that the C–H addition products **3a–f** are separated from the arene adducts **7** by a barrier that is insurmountable under 100 °C. This means that (in the absence of very strong acid, which can access a different pathway through **A**) the regioselectivity of the C–H addition is achieved under kinetic control. That is interesting, considering that the *ortho*-halophenyl isomers (**3e–f**) are almost certainly thermodynamically preferred as well,<sup>45</sup> but usually are not kinetically preferred.<sup>46</sup>

To probe the relative barriers to the activation of C-H bonds in various substrates, we set up a few competition experiments in which 1 was treated with K-BARF at 80 °C (3-24 h) in the presence of two different arenes. In all of these reactions, full conversion to the corresponding products 3a-e and 3a-D was observed. C<sub>6</sub>H<sub>6</sub> was activated three times as fast as C<sub>6</sub>D<sub>6</sub>, which may indicate the importance of the C-H/C-D breaking step. However, this apparent kinetic isotope effect of approximately 3 may be a composite value,13,47 and we do not have enough information for a more conclusive analysis. The ortho-C-H bond in fluorobenzene was decidedly more reactive than the C-H or C-D bonds of C<sub>6</sub>H<sub>6</sub> or C<sub>6</sub>D<sub>6</sub>. Based on prior studies, we would expect the activation of the ortho-C-H bond in fluorobenzene to be thermodynamically more favorable,45 but it is apparently also kinetically more facile than activation of a C-H bond in benzene. The fact that C<sub>6</sub>H<sub>6</sub> was approximately three times more competitive than C<sub>6</sub>D<sub>6</sub> against C<sub>6</sub>H<sub>5</sub>F is consistent with the 3 : 1 ratio for the  $C_6H_6-C_6D_6$  competition experiment. In the C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> competition reaction, the observed ratio of products was close to the ratio between the number of C-H bonds in  $C_6H_6$  and the number of meta + para C-H bonds in toluene.

#### Halogen atom abstraction

Although complexes **3** were stable when dissolved in dichloromethane for extended periods of time at ambient temperature, dichloromethane could not be used as a solvent for their synthesis. Treatment of **1** with K-BARF in dichloromethane led to the formation of a blue solution that clearly contained a paramagnetic product, which we assigned as **9a**. The addition of decamethylferrocene to this solution resulted in the formation of the diamagnetic compound **5**, which was observed in a 50% yield *vs.* an integration standard after filtration.

An alternative synthesis of the **9** cation was achieved *via* oxidation of a pure sample of **5** with Ag[HCB<sub>11</sub>Cl<sub>11</sub>]. This reaction allowed for the isolation of **9b** as an analytically pure solid in 44% (unoptimized) yield after work-up. An X-ray diffraction study on a single crystal of **9b** revealed its solid-state structure (Fig. 2). In this structure, Pt maintains an approximately square-planar environment, and the  $[HCB_{11}Cl_{11}]^-$  anion is well separated from the cation. Mindiola *et al.* previously studied the reversible oxidation of (<sup>Me</sup>PNP)NiCl and concluded that the oxidation takes place primarily on the ligand.<sup>48</sup> We made similar observations in collaboration with the Nocera group concerning the oxidation of (<sup>Me</sup>PNP)M(CO)<sub>3</sub> (M = Mn, Re).<sup>49</sup> Oxidation of **5** is expected to be a ligand-centered event as well, and so **9a/9b** should not be viewed as Pt<sup>III</sup> compounds, but rather as Pt<sup>II</sup> compounds with an oxidized <sup>F</sup>PNP ligand.

The reaction of **1** with K-BARF in  $C_6D_5Br$  led to the complete disappearance of **1** in 12 h at ambient temperature and the formation of a compound tentatively identified as **10**. Compound **10** is analogous to **4**, which is observed in the reaction with  $C_6H_5Cl$ , and showed a single <sup>19</sup>F NMR resonance at -122.9 ppm (along with three normal BARF resonances), which is nearly identical to the spectrum of **4**. In the <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} NMR spectra, **10** exhibited  $C_{2v}$ -symmetry, which is consistent with a  $\kappa^1$ -Br adduct. Treatment of **10** with acetonitrile resulted in the clean formation of **6** (<sup>19</sup>F NMR resonance at -125.1 ppm). After two weeks in a  $C_6D_5Br$  solution, the intensity



Fig. 2 ORTEP drawing (50% probability ellipsoids) of **9b** showing selected atom labeling. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): N1–Pt1 1.987(6), P1–Pt1 2.285(3), P2–Pt1 2.304(3), Pt1–Cl1 2.296(2); P1–Pt1–P2 166.72(7), N1–Pt1–Cl1 171.92(16), Cl1–Pt1–P1 93.99(7), Cl1–Pt1–P2 97.67(7), N1–Pt1–P1 85.20(16), N1–Pt1–P2 84.13(16), C1–N1–Pt1 119.9(4), C7–N1–Pt1 118.6(4), C1–N1–C7 121.2(6).

of the NMR resonances assigned to **10** were diminished (with no new <sup>19</sup>F NMR signals emerging), and broad resonances reminiscent of **11** were evident in the <sup>1</sup>H NMR spectrum. Addition of decamethylferrocene to this aged solution resulted in the appearance of NMR resonances indicative of **12** (20%). We propose that Br atom abstraction from the bound  $C_6D_5Br$  takes place over time, producing **11**. We have not yet attempted to establish the fate of the organic fragments after the abstraction of the Br atom from bromobenzene or of the Cl atom from dichloromethane.

Abstraction of a halogen atom is not a reaction associated with low-spin, closed-shell transition-metal complexes. Metalloradicals with odd numbers of electrons such as (porphyrin)Rh or (porphyrin)Ir species are known to abstract halogen atoms from halocarbons.<sup>50</sup> In contrast, Bullock's [(PCP)Pt]<sup>+</sup> or Peters'[(SiP<sub>3</sub>)Pt]<sup>+</sup> simply coordinated dichloromethane and did not show chlorine atom abstracting reactivity.<sup>25,51</sup> Since Pt<sup>II</sup> is reliably low-spin in its complexes, the halogen-atom abstraction observed with [(<sup>F</sup>PNP)Pt]<sup>+</sup> appeared likely related to the non-innocence of the <sup>F</sup>PNP ligand (Scheme 7). To probe this further, we initiated a theoretical study.

### DFT studies

The contrast between the typical low-spin reactivity for Pt in C–H activation and the apparent metalloradical-type reactivity in halogen atom abstraction led us to consider the nature of the ground state of [(<sup>F</sup>PNP)Pt]<sup>+</sup>. Although we have not observed this species directly, we thought that a comparison of the singlet and triplet energies might assist in understanding the divergent reaction pathways that can formally be defined as reactions of [(<sup>F</sup>PNP)Pt]<sup>+</sup> with a substrate. We turned to DFT calculations using either the PBE0<sup>52</sup> or the M06-L<sup>53</sup> functionals with Gaussian 09,<sup>54</sup> which predicted that the singlet state is more stable than the triplet. However, the triplet was calculated to be higher in energy



**Scheme 7** Halogen atom abstraction and redox chemistry of [(<sup>F</sup>PNP)PtX]-[(<sup>F</sup>PNP) PtX]<sup>+</sup> complexes.



Fig. 3 Depictions of the frontier orbitals of the singlet (left) and triplet (right) states of [(PNP)Pt]<sup>+</sup> calculated with the PBE0 functional.

by a relatively small margin (PBE0: by 12.6 kcal mol<sup>-1</sup> in enthalpy and by 11.0 kcal mol<sup>-1</sup> in free energy; M06-L: by 10.7 and 10.2 kcal mol<sup>-1</sup>, respectively). The triplet can be best described as arising from the promotion of an electron from the lone pair of N to the empty orbital at Pt (see Fig. 3). We do not interpret the singlet/triplet difference as evidence that the triplet [<sup>F</sup>(PNP)Pt]<sup>+</sup> is ever present in a kinetically competent concentration in solution; indeed, we do not know whether free [<sup>F</sup>(PNP)Pt]<sup>+</sup> in any spin state is an intermediate at all. However, this modest difference indirectly suggests that [<sup>F</sup>(PNP)Pt]<sup>+</sup> and its singlet four-coordinate adducts may have reaction pathways accessible to them that lead to products of apparent triplet reactivity.

## Conclusions

In summary, we have described the reactivity taking place upon removal of one of the ligands from a square-planar complex of Pt<sup>II</sup>. The putative [<sup>F</sup>(PNP)Pt]<sup>+</sup> fragment reacted with aromatic C-H bonds by net heterolytic C-H addition across the N-Pt bond when only C-H and strong C-Hal bonds were present in the substrate. When weaker C-Hal bonds were present, such as in bromobenzene or dichloromethane, the  $[^{F}(PNP)Pt]^{+}$  fragment exhibited a tendency to abstract a halogen atom, a reaction quite unexpected of a Pt<sup>II</sup> complex. The key to understanding the divergent reactivity of [F(PNP)Pt]<sup>+</sup> is the non-innocence of the supporting FPNP ligand, which can function as an intramolecular component of a frustrated Lewis pair, or as a source of a single electron. This work was originally conceived with the thought of using  $[^{F}(PNP)Pt]^{+}$  as a scaffold for forming hydrocarbon complexes. It is now clear that a different pincer ligand is necessary to achieve this goal, namely one with much lower Bronsted basicity and with lesser tendency to give up an electron.

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