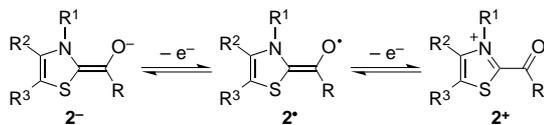


thiazolium ring. Therefore, the oxidative electron transfer processes of the active aldehyde can be described as shown in Scheme 1. The highly negative oxidation potentials of active



Scheme 1. Oxidation of active aldehydes  $2^-$  by two electron transfer steps.

aldehydes and the spin distribution of the intermediate radicals determined for the first time in this study provide the energetic basis for the ThDP-dependent electron transport systems as well as valuable mechanistic insight into the enzymatic reactions.

### Experimental Section

Thiazoles, benzyl bromide, acetaldehyde, and benzaldehyde were purchased from Tokyo Chemical Industry and used as received. MeCN was purified and dried with  $\text{CaH}_2$  by the standard procedure.<sup>[15]</sup> TBAP was recrystallized from ethanol and dried in vacuum at  $40^\circ\text{C}$  prior to use. 3-Benzylthiazolium bromide was prepared by the reaction of the corresponding thiazole with benzyl bromide at  $80^\circ\text{C}$ , and purified by recrystallization from acetone. Cyclic voltammetry measurements were performed on a BAS 100B electrochemical analyzer with solutions in deaerated MeCN containing 0.10M TBAP as supporting electrolyte. The Pt working electrode (BAS) was polished with a BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to the Ag/AgNO<sub>3</sub> (0.01M) reference electrode and converted into values versus SCE by adding 0.29 V.<sup>[16]</sup> All electrochemical measurements were carried out under an atmospheric pressure of argon. EPR spectra were recorded on a JEOL JES-RE1XE instrument under nonsaturating microwave power conditions. The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The g values and hyperfine splitting (hfs) constants were calibrated with a  $\text{Mn}^{2+}$  marker. Computer simulations of the EPR spectra were carried out with the program Calleo ESR Version 1.2 (Calleo Scientific) on a Macintosh personal computer.

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## Generation of “Naked” Fluoride Ions in Unprecedentedly High Concentrations from a Fluoropalladium Complex\*\*

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Since the discovery of the first reliable sources of weakly solvated (“naked”) fluoride ions,<sup>[1,2]</sup> a number of intriguing reactivity patterns and applications of the F<sup>-</sup> ion in synthesis have been reported which clearly indicate its extraordinarily strong basicity and nucleophilicity in media of low polarity.<sup>[1–8]</sup> However, the number of sources for “genuinely naked” F<sup>-</sup>

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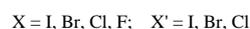
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ions known to date is limited to five "onium" compounds which contain no  $\beta$ -hydrogens as to avoid Hofmann elimination.<sup>[1, 2, 6–8]</sup> All of these salts are highly hygroscopic, and some are only sparingly soluble. Here we describe a totally different, novel approach to the generation of highly reactive naked fluoride ions in unprecedentedly high concentrations. An easily accessible, robust, air- and moisture-stable, non-hygroscopic organometallic fluoro complex can be efficiently used as the carrier of a naked fluoride ion that is easily displaced by a chloride ion.

Our recent study demonstrated that the preference of the metal center in  $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{X})\text{Ph}]$  for halide anions in anhydrous  $\text{CH}_2\text{Cl}_2$  [Eq. (1)] follows the order  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ .<sup>[9]</sup>

Once the equilibrium shown in Equation (1) had been established within the time of mixing at room temperature, the system remained unchanged in all cases except for  $\text{X} = \text{F}$ .



When  $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{F})\text{Ph}]$ <sup>[10]</sup> and  $[\text{Et}_3\text{NCH}_2\text{Ph}]\text{Cl}$  were dissolved in  $\text{CH}_2\text{Cl}_2$ , the equilibrium in Equation (1) was unstable and drifted slowly (within 5–8 h at 20 °C) toward  $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Cl})\text{Ph}]$ . This observation suggested that naked  $\text{F}^-$  ions are generated and cause Hofmann elimination of the ammonium cation. Indeed, NMR spectroscopic analysis of the reaction mixture confirmed the presence of the chloro complex (<sup>31</sup>P NMR:  $\delta = 24.1$  (s)) and  $\text{HF}_2^-$  (<sup>19</sup>F NMR:  $\delta = -150$  (d),  $J(\text{H},\text{F}) = 121$  Hz).<sup>[11]</sup> Benzyltriethylammonium bromide and iodide reacted similarly.<sup>[12]</sup>

To avoid Hofmann eliminations,  $[\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3]\text{Cl}$  ([PPN]Cl) was employed instead of the benzyltriethylammonium salts. A typical run was monitored by <sup>19</sup>F NMR spectroscopy (Table 1). The reaction between

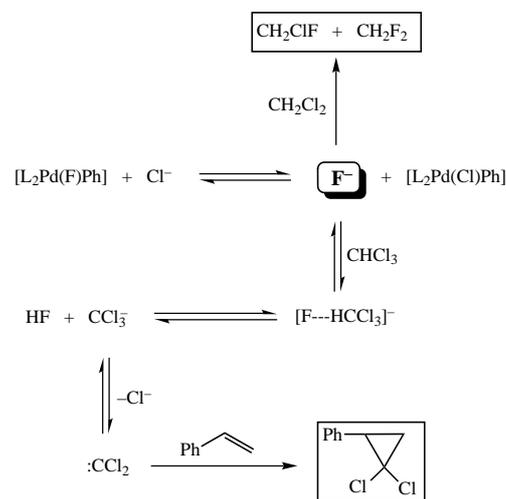
Table 1. Fluorination of  $\text{CH}_2\text{Cl}_2$  (0.7 mL) with  $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{F})\text{Ph}]$  (0.065 mmol) and [PPN]Cl (0.093 mmol), as monitored by <sup>19</sup>F NMR spectroscopy.

<i>t</i> [min]	Product distribution [mol %]				
	$[(\text{Ph}_3\text{P})_2\text{Pd}(\text{F})\text{Ph}]$	$\text{F}^-$	$\text{HF}_2^-$	$\text{CH}_2\text{ClF}$	$\text{CH}_2\text{F}_2$
10	75	18	4	3	–
35	62	10	5	16	7
90	46	7	5	27	15
180	25	traces	6	38	31
420	traces	–	7	52	41

$[(\text{Ph}_3\text{P})_2\text{Pd}(\text{F})\text{Ph}]$  and [PPN]Cl in  $\text{CH}_2\text{Cl}_2$  gave rise to  $\text{CH}_2\text{ClF}$  ( $\delta = -170$  (t),  $J(\text{H},\text{F}) = 48$  Hz) and  $\text{CH}_2\text{F}_2$  ( $\delta = -143$  (t),  $J(\text{H},\text{F}) = 52$  Hz) as main products. At early stages the  $\text{F}^-$  ion was present in considerable quantities ( $\delta = -109$  (s),  $\Delta\nu_{1/2} = 30$ –45 Hz), and only small amounts of  $\text{HF}_2^-$  were formed. Resonances from both the  $\text{F}^-$  ion and the fluoropalladium complex rapidly diminished in intensity as the selective fluorination of the solvent readily occurred under *exceedingly mild conditions*. Nucleophilic substitution

reactions of  $\text{CH}_2\text{Cl}_2$  are rare,<sup>[13]</sup> and the fluorination of  $\text{CH}_2\text{Cl}_2$  with metal fluorides, a process of potential industrial importance,<sup>[14]</sup> normally requires very high temperatures (180–300 °C) and pressures.<sup>[15, 16]</sup> As anticipated, no fluoromethanes were formed when the fluoropalladium complex and [PPN]Cl were allowed to react in  $\text{CH}_2\text{Cl}_2$  saturated with water (ca. 0.2%;  $\text{H}_2\text{O}:\text{F}$  molar ratio = 2:1).

A totally different reactivity pattern was observed when chloroform was used instead of dichloromethane (Scheme 1). The <sup>19</sup>F NMR spectrum measured five minutes after



Scheme 1.  $\text{L} = \text{PPh}_3$ .

$[(\text{Ph}_3\text{P})_2\text{Pd}(\text{F})\text{Ph}]$  (0.067 mmol) and [PPN]Cl (0.096 mmol) were dissolved in dry  $\text{CHCl}_3$  (0.7 mL) revealed the presence of the starting fluoro complex ( $\delta = -276$  (br t),  $J(\text{F},\text{P}) = 13$  Hz, 37%),  $\text{HF}_2^-$  ( $\delta = -164$  (d),  $J(\text{H},\text{F}) = 126.6$  Hz, 3%), and  $\text{F}^-$  ( $\delta = -141$  (s),  $\Delta\nu_{1/2} = 9$  Hz, 60%). No significant changes were observed in this pattern within the next 2–3 h; one day later minute amounts (ca. 1%) of  $\text{CHF}_3$  ( $\delta = -79$  (d),  $J(\text{H},\text{F}) = 79.2$  Hz) and  $\text{CHCl}_2\text{F}$  ( $\delta = -81$  (d),  $J(\text{H},\text{F}) = 53.3$  Hz)<sup>[11]</sup> were detected. The increase in bifluoride content to about 15% occurred concomitant to the proportional slight decrease in intensity of the Pd–F and  $\text{F}^-$  resonances. When complete conversion of the fluoropalladium complex was achieved in five days, only sharp singlets from  $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Cl})\text{Ph}]$  ( $\delta = 24.1$ ) and  $[\text{PPN}]^+$  ( $\delta = 21.5$ ) were observed in the <sup>31</sup>P NMR spectrum of the pale yellow, clear solution.

In a similar experiment styrene (threefold excess) was added to the sample after the equilibrium between the fluoropalladium complex,  $\text{HF}_2^-$ , and  $\text{F}^-$  in  $\text{CHCl}_3$  was reached (< 10 min; [PPN]Cl: $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{F})\text{Ph}] = 3.3:1$ ) and the system exhibited no significant changes for the following hour. As a result, the  $\text{F}^-$  and Pd–F resonances immediately started to diminish in intensity, while the  $\text{HF}_2^-$  doublet resonance became stronger.<sup>[17]</sup> The reaction was complete in about 8 h and furnished 1,1-dichloro-2-phenylcyclopropane, which was identified and quantified by <sup>1</sup>H NMR spectroscopy (ca. 40% yield). It is clear that dichlorocarbene was produced in the reaction.

These results are summarized in Scheme 1. As can be concluded from the molar ratio of  $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{F})\text{Ph}]$  to

$\text{CH}_2\text{Cl}_2$  (ca.  $6 \times 10^{-4}$ ) employed and the data in Table 1,  $\text{CH}_2\text{ClF}$  was at least three orders of magnitude more reactive toward the  $\text{F}^-$  ion than  $\text{CH}_2\text{Cl}_2$ . In comparison with  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  is much more acidic while being insufficiently electrophilic to undergo efficacious nucleophilic displacement by  $\text{F}^-$ .<sup>[18]</sup> Our system is somewhat similar to the phase transfer catalyzed generation of  $:\text{CCl}_2$  from  $\text{CHCl}_3$  and alkali metal.<sup>[19]</sup> Adding styrene to the reaction mixture shifts all equilibria toward the formation of  $:\text{CCl}_2$ , which is irreversibly trapped by the olefin present to furnish the cyclopropane derivative.

According to  $^{31}\text{P}$  NMR spectra, in all reactions the corresponding organopalladium halide  $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{X})\text{Ph}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ) was the only product that contained phosphorus and palladium. Remarkably, the Pd–C bond remained intact in the presence of such reactive species as naked  $\text{F}^-$ ,  $\text{HF}$ ,  $\text{HF}_2^-$ ,  $\text{CCl}_3^-$ , and  $:\text{CCl}_2$ . The role of palladium in our system seems to be limited to the carrier of the  $\text{F}^-$  ion, which upon release may react as a strong nucleophile or base. Uncommonly high concentrations of the fluoride ion can be easily generated by simply dissolving the two *nonhygroscopic* reagents in a dry solvent of low polarity. Moreover, the fluoride concentration can be finely tuned by simply varying the ratio of the fluoropalladium complex to  $[\text{PPN}]\text{Cl}$ .

Significant conclusions may be drawn: 1) A novel strategy has been developed for the generation of highly reactive naked  $\text{F}^-$  ions. 2) Care should be exercised when conducting anion-metathesis studies with fluorometal complexes in chlorinated aliphatic solvents. 3) The reactivity of naked fluoride depends on the nature of its counterion. Thus, anhydrous  $[\text{Me}_4\text{N}]\text{F}$  readily fluorinates  $\text{CHCl}_3$ , but reacts with  $\text{CH}_2\text{Cl}_2$  more slowly to give  $\text{CH}_2\text{ClF}$ .<sup>[11]</sup> The  $\text{HF}_2^-$  ion is the only species detectable by  $^{19}\text{F}$  NMR spectroscopy in solutions of methylurotropinium fluoride in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ .<sup>[8]</sup> Our Pd–F/ $[\text{PPN}]\text{Cl}$  system readily fluorinates  $\text{CH}_2\text{Cl}_2$  to a mixture of  $\text{CH}_2\text{ClF}$  and  $\text{CH}_2\text{F}_2$ , whereas only minor amounts of fluorinated methanes are formed in the sluggish reaction with  $\text{CHCl}_3$ .

## Experimental Section

Chlorinated solvents were transferred under vacuum from  $\text{P}_2\text{O}_5$  to a 5-mm glass NMR tube charged with the fluoropalladium complex and  $[\text{PPN}]\text{Cl}$ . The tube was sealed under nitrogen and placed into the probe of a Varian VXR-200 NMR spectrometer. In one of the experiments, after complete conversion of the fluoropalladium complex had been achieved, the pure chloro complex  $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{Cl})\text{Ph}]$  was isolated from the mixture in 96% yield and found to be identical with an authentic sample ( $^1\text{H}$  and  $^{31}\text{P}$  NMR).

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