

## Electron-Transfer induced by Salt Effect: Disproportionation of Fe<sup>I</sup> Complexes

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The first electron transfer in an organometallic reaction induced by the addition of a salt to a solution is reported.

Since their recognition in solvolysis reactions,<sup>1</sup> salt effects<sup>2</sup> have found practical use in organic synthesis,<sup>3</sup> organometallic reactions, and catalysis.<sup>4</sup> Their role in photochemically induced electron transfer (ET) has been recently emphasized.<sup>5</sup> However, most salt effects are counter-ion effects and the induction of ET by addition of a salt to a neutral species is unprecedented. We wish to indicate that the presence of a simple sodium salt can completely change the course of organotransition metal reactions by double exchange of ions in ion pairs. Therefore, we report that disproportionation<sup>6</sup> of Fe<sup>I</sup> sandwiches with several P donors only occurs in the presence of a sodium salt.<sup>7</sup>

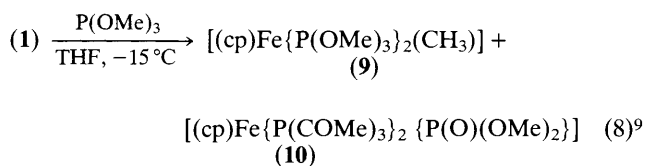
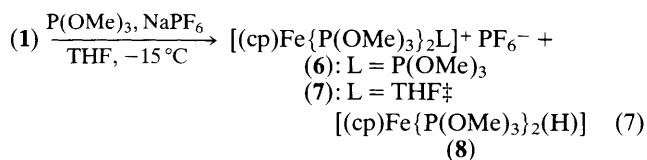
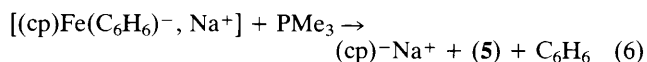
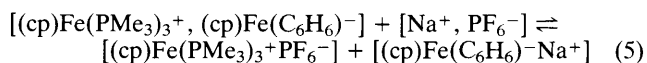
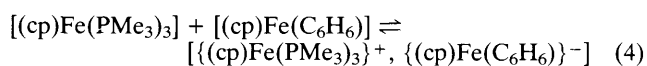
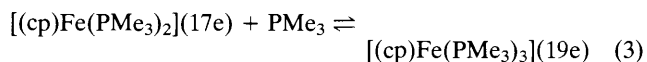
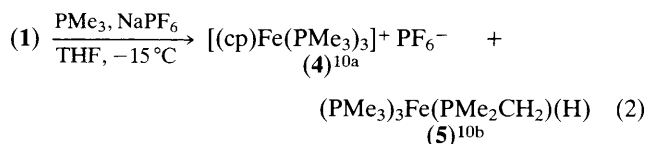
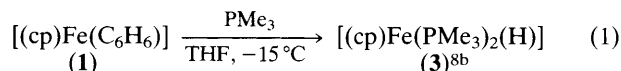
The 19 electron (19e) complex [(cp)Fe(C<sub>6</sub>H<sub>6</sub>)], (1), cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>, reacts in tetrahydrofuran (THF) with CO to give [(cp)Fe(CO)<sub>2</sub>]<sub>2</sub>, (2),<sup>8a</sup> a reaction on which the presence of NaPF<sub>6</sub> has no influence. However, in the reaction with PMe<sub>3</sub>, disproportionation occurs in the presence of 1 equiv. NaPF<sub>6</sub>, compare equations 1 and 2.† This salt effect is consistently

subjected to variation of magnitude as a function of the relative sizes of cations and anions; the yields of [(cp)Fe(PMe<sub>3</sub>)<sub>3</sub>]<sup>+</sup> are: 50% [NaPF<sub>6</sub>, yield of (5) also 50%], 36% (KPF<sub>6</sub>), 17% (KPF<sub>6</sub> stoichiometry 18-crown-6), 35% (NaBF<sub>4</sub>), 30% (Bu<sup>n</sup><sub>4</sub>NBF<sub>4</sub>), 26% (KBF<sub>4</sub>), and 0% (no salt).

The exchange of the benzene ligand by PMe<sub>3</sub> gives rise to the species in equation 3, the interconversion between 17e and 19e species being well established.<sup>6</sup> H Atom abstraction from the medium is a characteristic reaction of 17e radicals<sup>11</sup> such as [Fe(C<sub>5</sub>Me<sub>5</sub>)L<sub>2</sub>]<sup>•</sup> and ML<sub>5</sub><sup>•</sup> (L = CO or phosphine, M = Mn or Re; here, THF and PMe<sub>3</sub> are good H donors). The key step of the disproportionation observed in the presence of NaPF<sub>6</sub> should be electron transfer (ET) from the extremely electron-rich 19e species (cp)Fe(PMe<sub>3</sub>)<sub>3</sub>. This ET process is slightly exergonic [*E*<sup>o</sup> values; (cp)Fe(PMe<sub>3</sub>)<sub>3</sub><sup>+0</sup>: -2.06 V vs. standard calomel electrode (SCE); CH<sub>2</sub>Cl<sub>2</sub>, Pt, -80 °C; (cp)FeC<sub>6</sub>H<sub>6</sub><sup>0/-</sup>: -1.95 V vs. SCE]. In the presence of NaPF<sub>6</sub>, the large ion pair can be metathesized to two new ion pairs as shown in equation 5. The 20e anion [(cp)Fe(C<sub>6</sub>H<sub>6</sub>)]<sup>-</sup> is presumably much more unstable as a Na<sup>+</sup> salt than as a (cp)Fe(PMe<sub>3</sub>)<sub>3</sub><sup>+</sup> salt. Thus the decomposition of [(cp)Fe(C<sub>6</sub>H<sub>6</sub>)<sup>-</sup>, Na<sup>+</sup>] (equa-

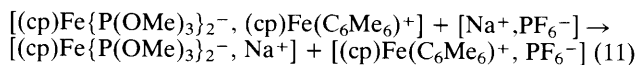
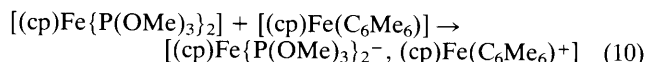
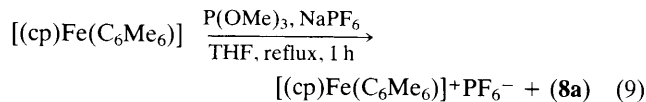
† Throughout this paper, the products obtained from reactions effected in the absence of NaPF<sub>6</sub> are stable in its presence.

tion 6) should displace equations 4 and 5 to the right. We believe this difference in stability of the 20e anion in the two ion pairs is a major factor responsible for the salt effect. The other one, ergonicity of the ET step in equation 4, directly depends on the electronic requirement of the phosphorous ligand. This is shown by the absence of the salt effect in the reaction of (1) with CO: the 19e species [(cp)Fe(CO)<sub>3</sub>] does not seem to be electron rich enough to reduce (1). The ET can, however, be endergonic to some extent as indicated by the quantitative salt effect also obtained with P(OMe)<sub>3</sub> ( $E^\circ$  [(cp)Fe{P(OMe)<sub>3</sub>}<sub>3</sub>]<sup>+0</sup> = -1.73 V vs. SCE, CH<sub>2</sub>Cl<sub>2</sub>, Pt, -80°C). In the absence of salt,<sup>9</sup> the transition metal mediated radical Arbusov reaction<sup>12</sup> is quantitative, compare equations 7 and 8,



Since (7) does not react rapidly with P(OMe)<sub>3</sub>, it can be concluded that [(cp)Fe{P(OMe)<sub>3</sub>}<sub>3</sub>]<sup>+</sup> PF<sub>6</sub><sup>-</sup> (equation 7) directly comes from the 19e intermediate [(cp)Fe{P(OMe)<sub>3</sub>}<sub>3</sub>] after ET as in equation 4. This emphasizes the role of the follow up chemistry occurring after the double ion exchange of equation 5. In order to investigate the role of the ergonicity in the salt effect induced ET of equation 4, we varied the number of Me groups on the benzene ligand of (1) between 0 and 6. We observe, with P(OMe)<sub>3</sub>, the same reactions (equations 1 and 2) with [(cp)Fe<sup>I</sup>(toluene)]<sup>13</sup> and [(cp)Fe<sup>I</sup>(mesitylene)]<sup>13</sup>. In the latter case, the endergonicity of equation 4 reaches 0.4 V. Beyond this limit, e.g. with [(cp)Fe(C<sub>6</sub>Me<sub>6</sub>)],<sup>13</sup> the ET of equation 4 is no longer observed. Instead, we obtain another salt induced ET according to equation 9, giving a 50% yield of each product.

‡ Ratio (7) : (6) : 0.2 [3 equiv. P(OMe)<sub>3</sub>]; 0 [10 equiv. P(OMe)<sub>3</sub>]. (7); 48% yield.



This disproportionation presumably follows ET from [(cp)Fe(C<sub>6</sub>Me<sub>6</sub>)] to [(cp)Fe{P(OMe)<sub>3</sub>}<sub>2</sub>], see equations 10 and 11. Similarly the salt effect appears to be due to both the fact that [(cp)Fe{P(OMe)<sub>3</sub>}<sub>2</sub>]<sup>-</sup> is more reactive as a Na<sup>+</sup> salt than as a [(cp)Fe(C<sub>6</sub>Me<sub>6</sub>)]<sup>+</sup> salt, and the ability of [(cp)Fe(C<sub>6</sub>Me<sub>6</sub>)] to act as a reducing agent in equation 10 ( $E^\circ$ , [(cp)Fe(C<sub>6</sub>Me<sub>6</sub>)]<sup>+0</sup>: -1.55 V vs. SCE<sup>13</sup>).

In all these reactions, the salt effect is quantitative with NaPF<sub>6</sub> only. The additional driving force provided by the precipitation of the organometallic PF<sub>6</sub> salt when the reactions are carried out in THF is not needed. Even in the case of P(OMe)<sub>3</sub>, the salt effect is identical when the reactions of equations 7 and 9 are performed without precipitation [in THF/MeCN: 1/1; 50% yield of (6) and of (8)]. In conclusion, NaPF<sub>6</sub> can very efficiently induce ET between neutral organometallic species.

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