

Preliminary communication

The reaction of $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with phosphines catalyzed by $[\text{CpFe}(\text{CO})_2]_2$: evidence for an electron transfer chain catalysis mechanism

Stephen L. Gipson^{a,*}, Ling-Kang Liu^{b,*}, Raul U. Soliz^a

^a Chemistry Department, Baylor University, PO Box 97348, Waco, TX 76798, USA

^b Institute of Chemistry, Academia Sinica, Taipei, 11529, Taiwan, Republic of China

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Abstract

The catalytic substitution of phosphines for halide on $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) has been shown to proceed through an electron transfer chain catalysis mechanism. The reaction may be initiated by $\text{CpFe}(\text{CO})_2(\text{PR}_3)^+$ generated by photochemical or thermal cleavage of $[\text{CpFe}(\text{CO})_2]_2$ or by addition of catalytic amounts of other strong reductants.

Keywords: Electron transfer; Catalysis; Iron; Substitution; Reduction

Treatment of equimolar FpX ($\text{Fp} = \text{CpFe}(\text{CO})_2$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and PR_3 ($\text{R} = \text{Ph}$ and/or Me) in THF at -78°C with $\text{R}'\text{Li}$ ($\text{R}' = \text{Me}, n\text{-Bu}, s\text{-Bu}, \text{Ph}$) produces primarily $(\eta^4\text{-exo-R}'\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PR}_3)$ [1,2]. This reaction has been demonstrated to be an R' anion addition to the Cp ring of the $[\text{Fp}(\text{PR}_3)]^+$ cation from an exo position, taking advantage of an initial conversion of the reactants FpX and PR_3 to the reactive intermediate $[\text{Fp}(\text{PR}_3)]^+$. The conversion has been proposed to be catalyzed by in situ generated Fp_2 [1,2]. We would like to address in this report the electron transfer chain catalyzed (ETC) [3–5] nature of the reactions of FpX and PR_3 when a catalytic amount of a reducing agent is present in the system.

Dimers of the type $[\text{CpM}(\text{CO})_n]_2$ ($\text{M} = \text{Fe}, \text{Ru}; n = 2$; $\text{M} = \text{Mo}, \text{W}; n = 3$) can catalyze numerous substitution reactions [6–13]. Since it appears necessary to break the metal-metal bond of the dimer catalyst either thermally or photochemically to initiate the substitution reactions, chain and/or non-chain radical mechanisms have generally been proposed. However, the necessity of metal-metal bond cleavage is also consistent with electron transfer mechanisms in which the 17-electron radicals,

e.g. Fp^{\cdot} , formed by the homolytic cleavage of the metal-metal bonds in dimeric organometallic complexes coordinate another ligand to form 19-electron complexes, e.g. $\text{Fp}(\text{PR}_3)^{\cdot}$, which are potent reducing agents [14–18].

In this investigation, controlled experiments were performed on solutions containing 20 mM FpI and 40 mM PPh_3 in THF with or without addition of 1 mM Fp_2 . (Reactions were performed at room temperature under nitrogen in distilled deoxygenated solvents. Typical reactions used 20 mM FpX and 40 mM ligand in 10 ml solvent. Reactions catalyzed by dexamethylmanganocene were initiated by addition of 0.1 ml of a 20 mM solution in THF. The presence or absence of light affected only the reactions catalyzed by Fp_2 . Reactions were followed and products were characterized by FTIR.) Under normal laboratory lighting at room temperature very little reaction occurred over a period of 21 h in the absence of Fp_2 , but within minutes the solution containing Fp_2 formed a precipitate of $[\text{Fp}(\text{PPh}_3)]\text{I}$. When the experiment was repeated with rigorous exclusion of light, no reaction occurred even in the presence of Fp_2 . Thus the catalyzed reaction depends on photochemical initiation, presumably to break the Fe-Fe bond of Fp_2 and generate Fp^{\cdot} . If the substitution reaction further depends on electron transfer from $\text{Fp}(\text{PPh}_3)^{\cdot}$ to FpI , then oxidants should inhibit the

* Corresponding author.

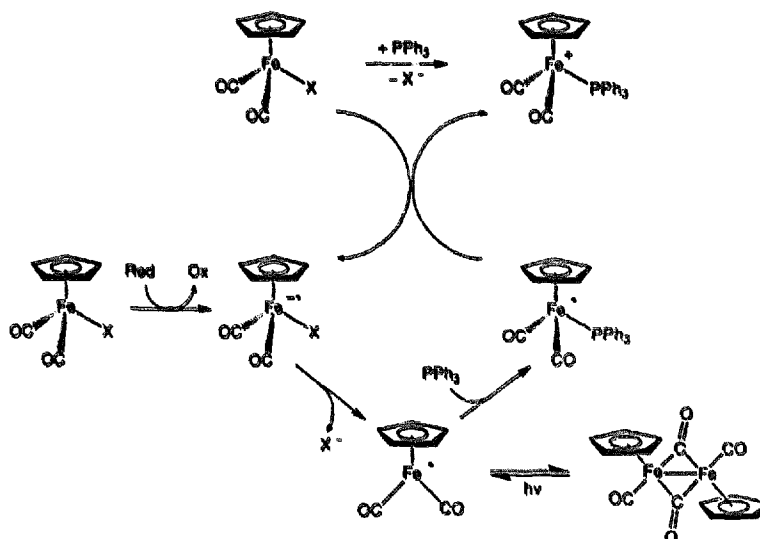
reaction by intercepting this reductant. In agreement with this prediction, when the reaction of FpI with PPh_3 in the presence of Fp_2 was repeated with the addition of 20 mM of the mild oxidants tetracyanoquinodimethane (in THF) or $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}]\text{BF}_4$ (in CH_2Cl_2), neither of which reacts with Fp_2 , no substitution occurred. Along the same line, yet from the reductive side, it is known that one-electron reduction of FpX complexes causes Fe-X bond cleavage to generate halide and the 17-electron Fp^\cdot fragment [19]. Should Fp_2 initiate the substitution reaction by forming a reducing agent, other strong homogeneous reductants would also be capable of initiating the reaction. The addition of small quantities (1–2 mM) of cobaltocene ($E_1 = -1.37\text{ V vs. Fc}^+/\text{Fc}$), bis(benzene)chromium ($E_1 = -1.25\text{ V}$) and decamethylmanganocene ($E_1 = -1.00\text{ V}$) to THF solutions of FpI and PPh_3 did indeed initiate rapid reaction to give the same products as the dimer-catalyzed reaction. Decamethylferrocene ($E_1 = -0.54\text{ V}$) did not initiate the reaction.

The above results are in agreement with the original observation that in the absence of Fp_2 , the reaction between FpX and PR_3 could be initiated by $\text{R}'\text{Li}$ [1,2]. Alkyl lithium compounds are known to be able to function as reducing agents [20,21]. Thus, in the reaction initiated by $\text{R}'\text{Li}$, the initial step is now proposed to be electron transfer from $\text{R}'\text{Li}$ to FpX followed by cleavage of the Fe-X bond. The resulting Fp^\cdot would coordinate a phosphine ligand to yield a 19-electron fragment which would then be capable of reducing another molecule of FpX . The products of this reaction would be $[\text{Fp}(\text{PR}_3)]^+$ and $[\text{FpX}]^{\cdot-}$, which would initiate another cycle in the catalytic substitution reaction. Any reductant strong enough to reduce FpX can initiate the same catalytic cycle. The Fp_2 which is observed to form in the $\text{R}'\text{Li}$ -initiated reaction and which was previously

taken to be the catalyst is more likely formed by combination of two Fp^\cdot intermediates. The Fe-centered radicals are exceedingly reactive species, dimerizing at near diffusion-controlled rates [22].

The proposed mechanism is depicted in Scheme 1, exhibiting the ETC cycle [3–5,13]. Coville and coworkers [7] have proposed a radical chain mechanism for some substitutions catalyzed by Fp_2 , but as pointed out by Tyler [5], ETC is a viable alternative for virtually any reaction proposed to proceed through a radical chain mechanism. In fact, in substitution reactions which replace CO rather than halide, the ETC and radical chain mechanisms may be in competition. So while we cannot comment on all dimer-catalyzed substitution reactions, in this case we have produced conclusive evidence for the ETC mechanism. It should be noted that electrochemical measurements have shown very clearly that the closely related substitution reactions of $[\text{CpFe}(\text{CO})_3]^+$ proceed through an ETC mechanism [23]. However, because the cyclic voltammetric peak potentials for the irreversible reductions of the FpX complexes are more negative than those of the $[\text{Fp}(\text{PPh}_3)]^+$ cation, electrochemistry does not provide the same clear evidence for ETC in these systems [24].

The generality of the ETC substitution reaction was explored by varying the solvent and the reactants, with products identified by FTIR [8,16,25]. The reaction of FpI with PPh_3 catalyzed by 0.2 mM decamethylmanganocene was investigated in benzene, CH_3CN , and CH_2Cl_2 . In benzene, as in THF [2], the reaction produced detectable quantities of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$ in addition to a precipitate of $[\text{Fp}(\text{PPh}_3)]\text{I}$. In CH_3CN , $[\text{Fp}(\text{PPh}_3)]\text{I}$ was formed selectively and was soluble, but the reaction was significantly slower than in the other solvents. The best solvent was found to be CH_2Cl_2 , which selectively and rapidly (5–10 min) yielded



Scheme 1.

[Fp(PPh₃)I]. The reaction proceeded more quickly as the PPh₃ concentration was increased, but for PPh₃/FpI ratios between 1 and 5 the product remained unchanged. Other phosphines (PMePh₂, PMe₂Ph, and PBu₃) reacted similarly. The reactions of FpX (X = Cl, Br) with PPh₃ catalyzed by decamethylmanganocene in CH₂Cl₂ were found to yield the same product as the iodo complex with only small differences in rate (Cl ≥ Br ≥ I). Decamethylmanganocene failed to initiate the reaction of (η⁵-C₅Me₅)Fe(CO)₂Br with PPh₃ in CH₂Cl₂, but bis(benzene)chromium, a stronger reductant, succeeded in producing [(η⁵-C₅Me₅)Fe(CO)₂(PPh₃)Br], in accordance with the fact that the pentamethylcyclopentadienyl complex is more difficult to reduce than the Cp analog [24].

In conclusion, the catalytic substitution reactions of FpX with PR₃ replacing halide are initiated by strong reductants, including photochemically generated Fp(PR₃)', and are inhibited by oxidants. All three Fp-halide complexes react similarly, but the pentamethylcyclopentadienyl analog requires a stronger reductant. This evidence, and the lack of the radical chain product CpFe(CO)(PR₃)I, lead us to propose that the ETC mechanism operates for this reaction. The evidence is also strongly suggestive that ETC mechanisms are involved in other ligand substitution reactions catalyzed by dimeric organometallic compounds. Further work is in progress on the electrochemistry and redox-induced reactions of FpX-type complexes [24].

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