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Nineteen-Electron Adducts in the Photochemistry of $Cp_2Fe_2(CO)_4$ ($Cp = \eta^5\text{-}C_5H_5$)

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$Cp_2Fe_2(CO)_4$ is apparently different from the other metal–metal-bonded carbonyl dimers in that irradiation of this dimer in the presence of ligands does not lead to disproportionation: $Cp_2Fe_2(CO)_4 + L + h\nu \nrightarrow CpFe(CO)_2^- + CpFe(CO)_{3-n}L_n^+$. However, it was demonstrated that with most ligands the disproportionation reaction does occur but the back-reaction of the products is facile. The back-reaction can be prevented by reacting further one of the products. For example, in CH_2Cl_2 solution, $CpFe(CO)_2^-$ reacts with the solvent to give $CpFe(CO)_2CH_2Cl$ and the back-reaction is prevented. The mechanism of the disproportionation reaction is proposed to be a chain mechanism involving 19-electron adducts formed by the reaction of a 17-electron metal radical with a ligand, e.g. $CpFe(CO)_2 + L \rightarrow CpFe(CO)_2L$. It is demonstrated that the 19-electron adducts are powerful reductants. The following organometallic, organic, and inorganic substrates were reduced by the 19-electron species, thereby demonstrating the versatility of these species as reducing agents: $CpMo(CO)_3Cl$, $Fe(CN)_6^{3-}$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Ru_3(CO)_{12}$, $Fe(CO)_5$, *N*-*n*-butylpyridinium, and Cp_2Co^+. Experiments involving the reduction of Cp_2Co^+ demonstrated several mechanistic points concerning the reactivity of 19-electron species.

The reported photochemical reactivity of $Cp_2Fe_2(CO)_4$ with various ligands consists primarily of substitution reactions.[1,2] For many other transition-metal carbonyl dimers, e.g. $Cp_2Mo_2(CO)_6$, $Cp_2W_2(CO)_6$, $Mn_2(CO)_{10}$, and $Co_2(CO)_8$, photochemical reactivity with ligands, L, frequently results in disproportionation to afford ionic products of the type $[M(CO)_{n-m+1}L_m]^+[M(CO)_n]^-$.[1b] The only such reaction reported for $Cp_2Fe_2(CO)_4$ has been the thermal reaction with the bidentate ligand $Me_2PC_2H_4PMe_2$(dmpe), to give $[CpFe(CO)(dmpe)]^+[CpFe(CO)_2]^-$.[3] In this paper we examine the reasons for the (apparent) unreactivity of the $Cp_2Fe_2(CO)_4$ complex toward photochemical disproportionation.

We have previously demonstrated that the photoinduced disproportionations of $Cp_2Mo_2(CO)_6$ by phosphorus ligands proceed via the "19-electron" intermediates $CpMo(CO)_2(PR_3)_2$.[4,5] In this paper we demonstrate that analogous 19-electron complexes form when the $Cp_2Fe_2(CO)_4$ complex is irradiated in the presence of various ligands and we also explore the electron-transfer chemistry of these complexes.

Results and Discussion

Reactions in Inert Solvents. Addition in the dark of $R_2PC_2H_4PR_2$ (R = Et, depe; R = Bu, dbpe) (0.01–0.02 M) to a solution of $Cp_2Fe_2(CO)_4$ (15 mM) in a variety of solvents (benzene, acetone, THF) results in the immediate disproportionation of the iron dimer to give the salt $[CpFe(CO)L_2]^+[CpFe(CO)_2]^-$ (eq 1; L_2 = 1,2-bis(dialkylphosphino)ethane, dape),

$$Cp_2Fe_2(CO)_4 + L_2 \xrightarrow{h\nu \text{ or } \Delta} [CpFeL_2(CO)]^+[CpFe(CO)_2]^- \qquad L_2 = \text{dape} \tag{1}$$

a result similar to that reported by King.[3] The products were identified by infrared (IR) spectroscopy (Table I, ref 3). Solutions of $Cp_2Fe_2(CO)_4$ and monodentate tertiary phosphorus ligands (PBu_3, PPh_3, $P(OEt)_3$; 0.01–0.02 M) as well as $Ph_2PC_2H_4PPh_2$ (dppe) and $(c\text{-}C_6H_{11})_2PC_2H_4P(c\text{-}C_6H_{11})_2$ (dcype) in the above solvents are quite stable in the dark. Upon prolonged irradiation ($\lambda > 560$ nm) in a closed vessel, such solutions undergo substitution reactions (eq 2) that do not proceed to completion; apparently

$$Cp_2Fe_2(CO)_4 + L \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} Cp_2Fe_2(CO)_3L + CO \tag{2}$$

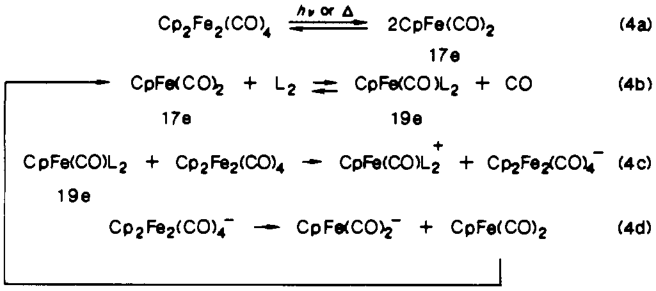
a photo steady state is reached in which the extent of substitution varies with the nature and concentration of L. The $Cp_2Fe_2(CO)_3L$ products were identified by IR spectroscopy.[2b] In no case, including that of the bidentate phosphines dppe and dcype, did irradiation of these closed systems result in the observation of disproportionation (eq 1) by analogy to that found with dape. King also noted[3] that thermal disproportionation did not occur with dppe.

The results above are similar to those we reported for the analogous molybdenum dimer $Cp_2Mo_2(CO)_6$,[4] which undergoes photochemical disproportionation in the presence of certain ligands (eq 3). In these reactions, we showed that three characteristics

$$Cp_2Mo_2(CO)_6 + 2L \xrightarrow{h\nu} [CpMo(CO)_2L_2]^+[CpMo(CO)_3]^- \tag{3}$$

of a ligand determined whether or not the ligand would induce disproportionation; small cone angles, good electron donors, and bidenticity favored disproportionation. Consistent with these criteria, and on the basis of other evidence,[4] it was shown that the mechanism of the disproportionation reaction 3 was a radical chain reaction. Apparently, the same criteria concerning the nature of the ligand are applicable to the iron dimer, although the requirements for disproportionation are more severe; i.e., only the most electron-rich, sterically unhindered, bidentate ligands lead to disproportionation. It is thus reasonable to hypothesize that the mechanism of reaction 1 is analogous to that of reaction 3 as shown in Scheme I.[7] Reaction 4a is known to proceed

Scheme I



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(1) (a) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187–218. (b) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217–240.

(2) (a) Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1981; Vol. 4, pp 520–522. (b) Haines, R. J.; DuPreez, A. L. *Inorg. Chem.* **1969**, *8*, 1459–1464.

(3) King, R. B.; Pannell, K. H.; Eggers, C. A.; Houk, L. W. *Inorg. Chem.* **1968**, *7*, 2353–2356.

(4) (a) Stiegman, A. E.; Steiglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037. (b) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 4066–4067.

(5) The phrase "19-electron complex" is used to describe the adducts that form when 17-electron metal radicals react with 2-electron ligands. It is conceptually helpful to define three limiting classes of structures for the 19-electron adducts. Class I comprises σ^* complexes; the 19th electron is in a M–L antibonding oribtal, e.g. $Mn(CO)_5Br^-$.[6] Class II comprises complexes that have a metal electron count lower than 19 due to slipped Cp rings, bent CO ligands, phosphoranyl radical formation, etc., e.g. $(\eta^4\text{-}Cp)Mo(CO)_3L$.[7] Class III ($\pi^*$ complexes) comprises complexes where the 19th electron is primarily in a ligand orbital. The metal is thus an 18-electron center, e.g. $Mo(CO)_4(bpy)^-$ and $CpMo(CO)_2$(c-hexDAB).

(6) (a) Lionel, T.; Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1981**, *81*, 17–20. (b) Anderson, O. P.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1972**, 1020–1021.

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Table I. Relevant Spectroscopic Data

complex	IR ν(CO), cm^{-1}	^{1}H NMR, δ
$Cp_2Fe_2(CO)_4$	1998 s, 1950 ms, 1780 s^a	4.94^b
	1992 s, 1952 m, 1779 s^c	4.23^d
	1998 s, 1956 ms, 1769 s^e	
[CpFe(CO)(dppe)]Cl	1981 s,^{e} 1970 s^g	
[CpFe(CO)(dppe)]PF_6	1978 s^c	5.14 (t, J_{PH} = 1.34 Hz)^{d,i}
[CpFe(CO)(depe)]Cl	1957 s^c	
[CpFe(CO)(dbpe)][$CpFe(CO)_2$]	1951 s, 1864 s, 1782 s^f	
[CpFe(CO)(dppe)][$CpFe(CO)_2$]	1972 ms, 1861 s, 1782 s^g	
[CpFe(CO)(depe)]Cl	1958 s^e	
[$CpFe(CO)(PBu_3)_2$]PF_6	1957 s^c	
[$CpFe(CO)(P(OEt)_3)_2$]PF_6	1994 s^c	
[$CpFe(CO)(P(OEt)_3)_2$]Cl	1997 s^e	
[$CpFe(CO)_2(P(OEt)_3)$][$FeCl_4$]	2069 s, 2026 s^e	
[$CpFe(CO)_2(P(OEt)_3)$]Cl	2065 s, 2021 s^e	
[$CpFe(CO)_2$(depe)]PF_6	2050 s, 2001 s^c	
[$CpFe(CO)_2(PBu_3)$]PF_6	2049 s, 2003 s^c	
$CpFe(CO)_2(CH_2Cl)$	2023 s, 1966 vs^e	5.07, 4.25^d
$CpFe(CO)_2Pr$	2001 s, 1941 vs^f	
[Bu_4N][$CpFe(CO)_2$]	1864 s, 1787 s^f	
Na[$CpFe(CO)_2$]	1887 s, 1864 m, 1809 s, 1768 m^f	
Cp_2Co		−51^{d,h}
[Cp_2Co]PF_6		−5.92
N-*n*-butylpyridinium dimer		0.93 (2 H), 1.40 (4 H), 2.8,^{i} 4.23 (2 H), 5.80 (2 H)

^{a}Benzene. ^{b}Benzene-d_6. ^{c}Acetone. ^{d}Acetone-d_6. ^{e}Dichloromethane. ^{f}THF. ^{g}Me_2SO. ^{h}Peak is averaged with peak due to Cp_2Co^+ if present. Literature value is δ = −53.8. ^{i}Peaks overlapped with peaks due to coordinated dppe.

thermally, although at a very slow rate at room temperature.[10] Thus the chain lengths must be quite long to account for the rapidity of the dape-induced disproportionation observed even in the rigorous absence of light. Alternatively, the chain reaction may be initiated by attack of dape on $Cp_2Fe_2(CO)_4$. Recently it was shown that phosphines can induce the homolytic cleavage of the Mn–Mn bond in $Mn_2(CO)_8(PPh_3)_2$.[11]

Reactions in CH_2Cl_2. Addition in the dark of depe (20 mM) to a solution of $Cp_2Fe_2(CO)_4$ (15 mM) in CH_2Cl_2 immediately results in reaction 5 (L_2 = depe). The products were identifieid

$$Cp_2Fe_2(CO)_4 + L_2 + CH_2Cl_2 \rightarrow [CpFe(CO)L_2]^+Cl^- + CpFe(CO)_2(CH_2Cl) \quad (5)$$

$$L_2 = \text{depe}$$

by ^{1}H NMR and IR spectroscopy (Table I).[12] CH_2Cl_2 solutions of $Cp_2Fe_2(CO)_4$ (15 mM) and dppe (40 mM) or monodentate phosphines or phosphites were found to be stable in the dark. However, irradiation of a solution of $Cp_2Fe_2(CO)_4$ (15 mM) and dppe (40 mM) results in reaction 5 (L_2 = dppe). Similarly, reaction 5 efficiently proceeds photochemically with L = $P(OEt)_3$ (0.2 M). Irradiation of $Cp_2Fe_2(CO)_4$ (15 mM) and PBu_3 (0.2 M) also results in the formation of $CpFe(CO)_2CH_2Cl$; however, the initially observed cationic complex is the monosubstituted $CpFe(CO)_2PBu_3^+$. Continued irradiation of this solution results in loss of the remaining $Cp_2Fe_2(CO)_4$, loss of the $CpFe(CO)_2PBu_3^+$, further formation of $CpFe(CO)_2CH_2Cl$, and the appearance of the disubstituted cation $CpFe(CO)(PBu_3)_2^+$. Irradiation of a CH_2Cl_2 solution of $Cp_2Fe_2(CO)_4$ (15 mM) and PPh_3 (0.2 M) results only in the slow and incomplete (ca. 25%) substitution of the dimer to give $Cp_2Fe_2(CO)_3(PPh_3)$. No $CpFe(CO)_2CH_2Cl$ was observed.

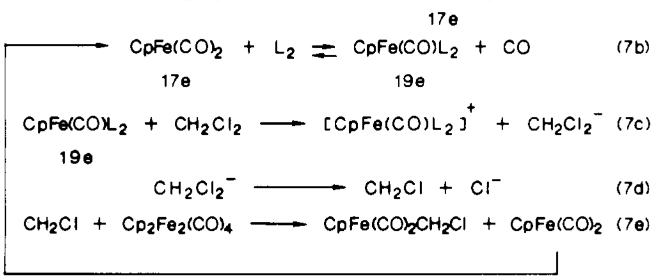
It is logical to propose that reaction 5 proceeds via the disproportionation pathway in Scheme I that is then followed by reaction 6. Indeed, when either [CpFe(CO)depe$^+$][$CpFe(CO)_2^-$]

$$CpFe(CO)_2^- + CH_2Cl_2 \rightarrow CpFe(CO)_2CH_2Cl + Cl^- \quad (6)$$

or [Bu_4N^+][$CpFe(CO)_2^-$] was dissolved in CH_2Cl_2, reaction 6 proceeded quickly as evidenced by the immediate loss of color due to the $CpFe(CO)_2^-$ anion. The $CpFe(CO)_2CH_2Cl$ complex was identified by IR spectroscopy (Table I).

An alternative pathway for reaction 5 is shown in Scheme II. According to this scheme, reduction of CH_2Cl_2 by the 19-electron complexes $CpFeL_n(CO)_{3-n}$ results in formation of the radical CH_2Cl, which then undergoes an S_H2 reaction with $Cp_2Fe_2(CO)_4$.

Scheme II



$$Cp_2Fe_2(CO)_4 \xrightarrow{h\nu} \underset{17e}{2CpFe(CO)_2} \quad (7a)$$

$$\underset{17e}{CpFe(CO)_2} + L_2 \rightleftharpoons \underset{19e}{CpFe(CO)L_2} + CO \quad (7b)$$

$$\underset{19e}{CpFe(CO)L_2} + CH_2Cl_2 \longrightarrow [CpFe(CO)L_2]^+ + CH_2Cl_2^- \quad (7c)$$

$$CH_2Cl_2^- \longrightarrow CH_2Cl + Cl^- \quad (7d)$$

$$CH_2Cl + Cp_2Fe_2(CO)_4 \longrightarrow CpFe(CO)_2CH_2Cl + CpFe(CO)_2 \quad (7e)$$

To test this pathway we needed to react CH_2Cl with $Cp_2Fe_2(CO)_4$ (eq 7e) and therefore a means of generating CH_2Cl in the presence of $Cp_2Fe_2(CO)_4$ in the dark was required. This test was accomplished as follows. Photolysis of $Mn_2(CO)_{10}$ in the presence of bidentate phosphines, L_2, results in the facile formation of long-lived radicals $Mn(CO)_3L_2$.[13] These radicals can be used to

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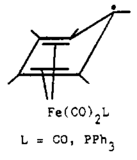
(7) Work by Blaha and Wrighton[8] strongly suggests that 19-electron complexes of the type $CpFe(CO)_{3-n}(PPh_3)_n$ (n = 0, 1; Cp = $C_5(CH_3)_5$ or C_5H_5) have an η^4-Cp structure:



Similar structures are proposed for the 19-electron complexes generated in this study; i.e., these species are class II complexes (see ref 5). Nineteen-electron complexes with an η^4-Cp structure might be expected to couple through the carbon based radical on the rings. (For example, the 19-electron Cp_2Rh complex dimerizes in this fashion.[9]) However, neither Blaha and Wrighton nor we observed any ring-coupled products of this type.

(8) Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694–2702.

(9) (a) Fisher, E. O.; Wawersik, H. *J. Organomet. Chem.* **1966**, *5*, 559–567. (b) Watts, W. E. In *Comprehensive Organometallic* Chemistry, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 1039.

(10) Cutler, A. R.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *120*, 87–96.

(11) Poë, A.; Sekhar, C. V. *J. Am. Chem. Soc.* **1985**, *107*, 4874–4883.

(12) Green, M. L. H.; Ishaq, M.; Whitely, R. N. *J. Chem. Soc. A* **1967**, 1508–1515.

generate organic radicals by halogen abstraction from the appropriate organic halide.[13] Thus, addition in the dark of a benzene solution of $Mn(CO)_3(dppe)$ to a CH_2Cl_2 solution of $Cp_2Fe_2(CO)_4$ (15 mM) resulted in the formation of $Mn(CO)_3(dppe)Cl$, as observed by IR spectroscopy, and presumably the CH_2Cl radical. However, neither the formation of $CpFe(CO)_2CH_2Cl$ nor the disappearance of $Cp_2Fe_2(CO)_4$ was observed. The pathway in Scheme II thus seems unlikely.

Back-Reactions. Why does disproportionation occur with numerous phosphines in CH_2Cl_2 but not in other solvents? Our initial hypothesis was that solvent polarity promoted the disproportionation reaction, and we therefore attempted the irradiation of $Cp_2Fe_2(CO)_4$ (15 mM) and dppe (20 mM) in Me_2SO. To our surprise, merely purging such a solution with argon in the dark resulted in complete disproportionation to give $[CpFe(CO)dppe]^+[CpFe(CO)_2]^-$ (eq 8). Bubbling CO through the resulting solution quickly resulted in a back-reaction to regenerate $Cp_2Fe_2(CO)_4$. This result and the results described below in less polar inert solvents suggested that the occurrence of disproportionation is not related to the polarity of the solvent. Rather, we propose that the disproportionation reaction is reversible and the equilibrium lies far to the left; only by removing one of the products from the system can the other products be observed. In the case of reaction 5, this is accomplished by a facile reaction of $CpFe(CO)_2^-$ with CH_2Cl_2. Although the equilibrium lies to the left in the Me_2SO reaction above, the polar solvent stabilizes the ionic products enough to allow the Ar purge to remove CO from the solution at a significant rate, preventing a back-reaction.

$$Cp_2Fe_2(CO)_4 + dppe \underset{\text{(in Me}_2\text{SO)}}{\overset{\text{Ar purge}}{\underset{\text{CO}}{\rightleftharpoons}}} CpFe(CO)dppe^+ + CpFe(CO)_2^- + CO \quad (8)$$

Consistent with the hypothesis above is the observation that solutions of *n*-propyl bromide (2.0 M) in THF displayed reactivity similar to that observed with CH_2Cl_2 solutions. Thus, irradiation of $Cp_2Fe_2(CO)_4$ (15 mM) and either dppe (40 mM) or $P(OEt)_3$ (0.2 M) resulted in the formation of $CpFe(CO)_2Pr$ and $[CpFe(CO)L_2]Br$ (eq 9, see Table I). (Recall that no net disproportionation occurred with these ligands in THF in the absence of PrBr.) With PPh_3 (0.2 M), the only observed reaction was incomplete (ca. 20%) substitution. *n*-Propyl bromide is, of course, an electrophile much more reactive than CH_2Cl_2 toward most substrates. This fact and the fact that the $Cp_2Fe_2(CO)_4/PPh_3/h\nu$ system gives identical results in CH_2Cl_2 and THF/PrBr solutions (i.e. no disproportionation-derived products are formed) may be an indication that CH_2Cl_2 efficiently traps all or most of the $CpFe(CO)_2^-$ generated in the disproportionation reactions. If this is the case then the $PPh_3/Cp_2Fe_2(CO)_4$ system does not give disproportionation products, as opposed to the case where disproportionation occurs but the back-reaction is so facile that the products are not trapped.

$$Cp_2Fe_2(CO)_4 + L_2 \text{ or } 2L + PrBr \xrightarrow{h\nu} [CpFe(CO)L_2]Br + CpFe(CO)_2Pr \quad (9)$$

We propose that reaction 8 takes place in the dark because of a chain reaction that is highly efficient, yet reversible. In order to test this hypothesis, an experiment was performed that utilized the "labeled" dimer $(MeCp)_2Fe_2(CO)_4$ (MeCp = η^5-$CH_3C_5H_4$). A control solution of $(MeCp)_2Fe_2(CO)_4$ (15 mM) and $Cp_2Fe_2(CO)_4$ (15 mM) in acetone-d_6 was found to be stable for 24 h at room temperature in the dark,[10] showing only very slight "scrambling" (eq 10). As expected, irradiation of such a solution does induce reaction 10, as determined by monitoring the ^1H NMR C_5H_5 resonance ($\delta_{Cp,Cp_2Fe_2(CO)_4} = 4.945$, $\delta_{Cp,(MeCp)(Cp)Fe_2(CO)_4} = 4.922$). Addition in the dark of dppe (30 mM) to an unscrambled solution results in the quick (<5 min) completion of reaction 10; i.e., a 2:1 ratio of $[(MeCp)(Cp)Fe_2(CO)_2]$:$[Cp_2Fe_2(CO)_4]$ is obtained. PCy_3 (0.2 M) and PPh_3 (0.2 M) do not bring about this scrambling to any significant extent as determined by comparison with the control solution containing no phosphine. Our interpretation of reactions 8 and 10 is that the slight rate of homolytic cleavage of the Fe–Fe bond at room temperature is sufficient to initiate the disproportionation chain reaction with L_2 = dppe; this is also the case with L_2 = dape. The key difference between these ligands is that in the case of dppe, unless the CO reaction product is removed, the resulting ionic products are unstable with respect to the back-reaction. As a result of the back-reaction, if the dimers are labeled, then the net reaction is scrambling. Note that the failure of PPh_3 and PCy_3 to catalyze reaction 10 is consistent with the result that these ligands do not lead to disproportionation upon homolysis of the metal–metal bond.

$$(MeCp)_2Fe_2(CO)_4 + Cp_2Fe_2(CO)_4 \rightleftharpoons 2(MeCp)(Cp)Fe_2(CO)_4 \quad (10)$$

The recombination reactivity of ions of the type $[CpFe(CO)L_2]^+$ with $CpFe(CO)_2^-$ was verified directly for the case of L = $P(OEt)_3$. An acetonitrile solution of $[CpFe(CO)(P(OEt)_3)_2^+][PF_6^-]$ (15 mM) was prepared from the reaction of $Cp_2Fe_2(CO)_4$ (7.5 mM) and $P(OEt)_3$ (15 mM) with $Cp_2Co^+PF_6^-$ (15 mM) (see the next section). To this solution was added an equal volume of a 15 mM solution of $[CpFe(CO)(depe)^+][CpFe(CO)_2^-]$ prepared via disproportionation of $Cp_2Fe_2(CO)_4$ (15 mM) with depe (15 mM). The mixing resulted in the immediate and complete disappearance of both $CpFe(CO)_2^-$ and $[CpFe(CO)(P(OEt)_3)_2]^+$.[14] $Cp_2Fe_2(CO)_4$ (3.7 mM) formed upon mixing along with some $Cp_2Fe_2(CO)_3P(OEt)_3$ (approximately 1.5 mM). This result is consistent with the hypothesis of reversible disproportionation. In addition, it illustrates the fact that substitution (eq 2) can proceed via ionic intermediates, although there is no reason to believe disproportionation is an exclusive or even important substitution pathway.

Photochemical Reductions Using the 19-Electron Adducts. Because the 19-electron complexes formed in the disproportionation reactions are capable of reducing $Cp_2Fe_2(CO)_4$ ($E_{1/2} = -2.2$ V vs. Ag/Ag^+),[15] they must be powerful reducing agents, and they should be capable of reducing substrates with reduction potentials less negative than $Cp_2Fe_2(CO)_4$, if present. We have previously shown[16] that irradiation of $Cp_2Fe_2(CO)_4$ in the presence of dppe and a variety of substrates results in reduction of the substrate and formation of $CpFe(CO)(dppe)^+$:

$$^1/_2Cp_2Fe_2(CO)_4 + dppe + S \xrightarrow{h\nu} CpFe(CO)(dppe)^+ + S^- \quad (11)$$

Some of the substrates, S, and their reduction potentials ($E_{1/2}$ or E_{pc} vs. Ag/Ag^+) for which reaction 11 proceeds include $CpMo(CO)_3Cl$ (the product is $CpMo(CO)_3^-$) (−1.4 V),[17] $[Ph_4P]_3[Fe(CN)_6]$ ($E_{1/2} > 0$),[18] $Mn_2(CO)_{10}$ (the product is $Mn(CO)_5^-$) (−1.7 V),[15] and $Re_2(CO)_{10}$ (−2.3 V).[15] These reactions proceed similarly when dape is used in place of dppe. Note, however, that in reaction 11 with dape, irradiation is required; the reaction solutions are stable in the dark. This result is noteworthy in that in the absence of these substrates the addition of dape to a solution of $Cp_2Fe_2(CO)_4$ results immediately in the disproportionation reaction 1. The substrate is thus acting as an inhibitor of the disproportionation chain reaction.

We have also demonstrated that systems of $Cp_2Fe_2(CO)_4$ and phosphorus ligands have utility as initiators of electron-transfer-catalyzed (ETC) chain reactions.[16,19,20] Thus, for example,

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(13) Goldman, A. S.; Tyler, D. R. *J. Organomet. Chem.* **1986**, *311*, 349–355.

(14) The concentration of $[CpFe(CO)(depe)]^+$ after mixing was approximately 10 mM as determined by IR spectroscopy (the expected concentration after dilution was 7.5 mM; it seems likely that a small amount of excess depe was present in the solution and reacted with the iron dimer or radicals formed upon mixing of the solutions).

(15) Dessy, R. E.; Stary, F. E.; King, R. B.; Walpdrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471–476.

(16) Stiegman, A. E.; Goldman, A. S.; Leslie, D. B.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1984**, 632–633.

(17) Dessy, R. E.; King, R. B.; Walpdrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112–5117.

(18) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974.

irradiation of a THF solution of $Ru_3(CO)_{12}$ (4 mM) ($E_{1/2} = -0.82$ V vs. Ag/AgCl),[21] PMe_2Ph (4 mM), and only a catalytic amount of $Cp_2Fe_2(CO)_4$ (0.5 mM), initiates the ETC substitution[16] in reaction 12. (Note that $Cp_2Fe_2(CO)_4$ is the only species in solution which absorbs light at the wavelengths used.)

$$\mathrm{Ru_3(CO)_{12} + PMe_2Ph \xrightarrow{Cp_2Fe_2(CO)_4,\ h\nu\ (\lambda > 525\ nm)} Ru_3(CO)_{11}(PMe_2Ph)} \quad (12)$$

Similar results were obtained with $Os_3(CO)_{12}$ (3.0 mM) ($E_{1/2} = -1.16$ V vs. Ag/AgCl)[21a] although a higher concentration of PMe_2Ph (0.5 M) was required for a clean reaction. The ETC substitution of $Fe(CO)_5$ was initiated with $Cp_2Fe_2(CO)_4$ and dppe and afforded the "dangling-ligand" species $Fe(CO)_4(\eta^1\text{-dppe})$ identified by IR spectroscopy:[20]

$$\mathrm{Fe(CO)_5 + dppe \xrightarrow{Cp_2Fe_2(CO)_4,\ h\nu\ (\lambda > 560\ nm)} Fe(CO)_4(\eta^1\text{-}dppe)} \quad (13)$$

As only negligible amounts of $Cp_2Fe_2(CO)_4$ were consumed, in none of these catalyses was an oxidized $Cp_2Fe_2(CO)_4$ derivative identified.

The reduction of anthracene (anthr) with the photogenerated 19-electron species was unsuccessful. A control experiment showed the following reaction:

$$\mathrm{2Na^+anthr^- + Cp_2Fe_2(CO)_4 \rightarrow 2NaCpFe(CO)_2 + 2anthr} \quad (14)$$

Thus, the inability of the $Cp_2Fe_2(CO)_4$/depe system to reduce anthracene cannot necessarily be taken as an indication of a lack of electrochemical potential of the CpFe(CO)depe reductant. Rather, it is likely either that these species reduce anthracene, which then in turn reduces $Cp_2Fe_2(CO)_4$, or that $Cp_2Fe_2(CO)_4$ is reduced directly in preference to anthracene.

In another example of the 19-electron adducts acting as reducing agents, we found that irradiation of $Cp_2Fe_2(CO)_4$ (15 mM), dppe (40 mM), and *N*-*n*-butylpyridinium chloride (Bu-py$^+$) (50 mM) in CH_2Cl_2 results in the efficient reduction of the Bu-py$^+$ ($E_{1/2} = -1.30$ V vs. SCE)[21b,c] and the formation of CpFeCO(dppe)$^+$:

$$\mathrm{Cp_2Fe_2(CO)_4 + 2dppe + 2Bu\text{-}py^+ \xrightarrow{h\nu} 2CpFe(CO)(dppe)^+ + (Bu\text{-}py)_2} \quad (15)$$

The reduce butylpyridiniumyl dimer was identified by ^{1}H NMR (Table I).

Reaction 15 also proceeds smoothly in Me_2SO. Recall that an argon purge of a Me_2SO solution of $Cp_2Fe_2(CO)_4$ and dppe in the dark results in the disproportionation reaction 8. However, extended (60 min) purging of a Me_2SO solution of $Cp_2Fe_2(CO)_4$ (15 mM), dppe (40 mM), and Bu-py$^+$ (50 mM) in the dark results in no observable reaction. Once again the reducible substrate is acting to quench the disproportionation reaction.

It should be noted that all of the substrates discussed above that were successfully reduced by the $Cp_2Fe_2(CO)_4$/phosphorus ligand systems could also be reduced by $[Bu_4N]^+[CpFe(CO)_2]^-$:

$$\mathrm{CpFe(CO)_2^- + S \rightarrow {}^1/_2Cp_2Fe_2(CO)_4 + S^-} \quad (16)$$

Reaction 16 also proceeded with S = Cp_2Co^+ (PF_6^- salt) ($E_{1/2} = -1.15$ V vs. NHE, CH_3CN)[22] (vide infra) although not with S = anthracene. This result raises the possibility that the actual reducing agent in the above reactions is $CpFe(CO)_2^-$, formed via the disproportionation reaction. However, results below demonstrate, at least in some cases, that the reductions do not proceed via the intermediate formation of $CpFe(CO)_2^-$ but rather that the substrates are directly reduced by the 19-electron species $CpFe(CO)_{3-n}L_n$.

Experiments with Cp_2Co^+. Irradiation of acetone solutions of $Cp_2Fe_2(CO)_4$ (15 mM) and $[Cp_2Co]^+[PF_6]^-$ (30 mM) and either dppe (40 mM) or $P(OEt)_3$ (0.2 M) results in the reduction of Cp_2Co^+ to cobaltocene as identified by ^{1}H NMR (Table I).[23]

$$\mathrm{{}^1/_2Cp_2Fe_2(CO)_4 + 2L\ or\ L_2 + Cp_2Co^+ \xrightarrow{h\nu} CpFe(CO)L_2^+ + Cp_2Co} \quad (17)$$

$$\mathrm{L_2 = dppe;\ L = P(OEt)_3}$$

Note that disubstituted cationic products are formed in these reactions. The use of PPh_3 (0.1 M) as the ligand in a solution otherwise identical with those above also led to the reduction of Cp_2Co^+ (eq 18), although the reaction only proceeded to ca. 15% completion under steady-state irradiation conditions.

$$\mathrm{{}^1/_2Cp_2Fe_2(CO)_4 + PPh_3 + Cp_2Co^+ \xrightarrow{h\nu} CpFe(CO)_2PPh_3^+ + Cp_2Co} \quad (18)$$

Note that the cationic product of reaction 18 contains one phosphine while the disubstituted cation forms in eq 17 with $P(OEt)_3$. A thorough discussion of this point is postponed until the last section. In that section we show that the reducing ability of the 19-electron adducts increases as *n* increases in the formula $CpFe(CO)_{3-n}L_n$. The steric bulk[24] of PPh_3 only allows *n* = 1, and the consequence is the incomplete reaction in eq 18. $P(OEt)_3$, however, is considerably smaller than PPh_3,[24] so the formation of $CpFe(CO)(P(OEt)_3)_2$ is possible. This species has a greater reducing ability than $CpFe(CO)_2PPh_3$, and eq 17 goes to completion.

The photochemical reaction of $Cp_2Fe_2(CO)_4$ (15 mM) in the presence of PBu_3 (80 mM) and $[Cp_2Co]^+[PF_6]^-$ (35 mM) in acetone proceeded to completion as described in eq 19 (L = PBu_3).

$$\mathrm{{}^1/_2Cp_2Fe_2(CO)_4 + PBu_3 + Cp_2Co^+ \xrightarrow{\lambda > 500\ nm} CpFe(CO)_2PBu_3^+ + Cp_2Co} \quad (19)$$

The metal center of the reducing agent $CpFe(CO)_2(PBu_3)$ is more electron rich than the PPh_3 analogue and can quantitatively reduce Cp_2Co^+ as well as effect disproportionation (as evidenced in CH_2Cl_2 solution, eq 5). With a $[Cp_2Co]^+[PF_6]^-$ concentration of 28 mM the reaction initially proceeded as in eq 18. However, as the reaction neared completion (and the concentration of Cp_2Co^+ approached zero) the conversion of $CpFe(CO)_2(PBu_3)^+$ to $CpFe(CO)(PBu_3)_2^+$ was observed by IR spectroscopy:

$$\mathrm{CpFe(CO)_2(PBu_3)^+ + PBu_3 \xrightarrow{Cp_2Fe_2(CO)_4\ (\lambda > 500\ nm)} CpFe(CO)(PBu_3)_2^+} \quad (20)$$

These results can be explained as follows. In the presence of significant concentrations of Cp_2Co^+, formation of $CpFe(CO)_2(PBu_3)$ is quickly followed by electron transfer (Scheme III, eq 21c). In the absence of Cp_2Co^+, $CpFe(CO)_2(PBu_3)$ can be further substituted by PBu_3 to give $CpFe(CO)(PBu_3)_2$ (eq 21d). This disubstituted 19-electron complex can then reduce the monosubstituted cation (eq 21e), the result being a net ligand substitution reaction by an electron-transfer-catalyzed pathway.[19] A similar explanation accounts for the conversion of $CpFe(CO)_2PBu_3^+$ to $CpFe(CO)(PBu_3)_2^+$ in the disproportionation of $Cp_2Fe_2(CO)_4$ with PBu_3 (see the section on Reactions in CH_2Cl_2).

Evidence That $CpFe(CO)_2^-$ Is Not the Reducing Agent. Whereas the addition of depe to solutions of $Cp_2Fe_2(CO)_4$ results in im-

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(19) For recent reviews of ETC reactions, see: (a) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425–506. (b) Chanon, M. *Bull. Soc. Chim. Fr.* **1982**, 197–238.

(20) Goldman, A. S.; Tyler, D. R. *Inorg. Chim. Acta* **1985**, *98*, L47–L48.

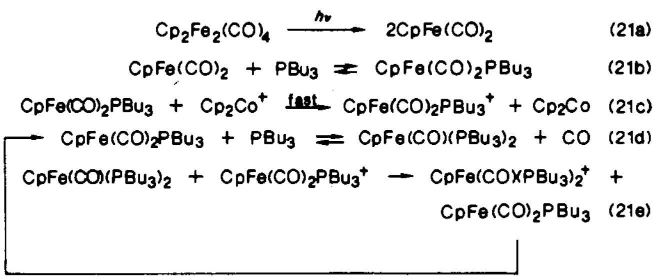
(21) (a) Bond, A. M.; Dawson, P. A.; Penke, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1977**, *16*, 2199–2206. (b) Volke, J.; Naarova, M. *Collect. Czech. Chem. Commun.* **1972**, *37*, 3361–3375. (c) Raghavan, R. A.; Iwamoto, R. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *92*, 101–114.

(22) Morriss, M. D.; Kok, G. L. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1979; Vol. 13, p 7.

(23) (a) Fritz, H. P.; Keller, H. J.; Schwarzhans, K. E. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1966**, *21B*, 809–810. (b) Fritz, H. P.; Keller, H. J.; Schwarzhans, K. E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1968**, *23b*, 298–302.

(24) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

Scheme III



mediate disproportionation of the dimer, an acetone solution of depe (40 mM), $Cp_2Fe_2(CO)_4$ (15 mM) and $[CpCo]^+[PF_6]^-$ (35 mM) appears completely stable in the dark. Irradiation of this solution results in reduction of the cobaltocenium, with the initial cationic product being the monosubstituted "dangling-ligand" complex (Table I):

$$^1/_2Cp_2Fe_2(CO)_4 + \text{depe} + Cp_2Co^+ \xrightarrow{h\nu} CpFe(CO)_2(\text{depe-}P)^+ + Cp_2Co \quad (22)$$

Continued irradiation results in conversion of this product to the disubstituted chelated cation, as well as the further disappearance of the remaining $Cp_2Fe_2(CO)_4$ and the reduction of Cp_2Co^+. If irradiation is discontinued early in the reaction, the $CpFe(CO)_2(\text{depe-}P)^+$ complex undergoes a slow thermal substitution to the chelated cation. For an acetone solution of $Cp_2Fe_2(CO)_4$ (3.0 mM), depe (8.0 mM), and $[Cp_2Co]^+[PF_6]^-$ (30 mM), the $Cp_2Fe_2(CO)_4$ disappearance quantum yield (λ = 545 nm) for reaction 22 was 0.14 ± 0.03. When the depe concentration was increased to 40 mM a value of 0.16 ± 0.03 was obtained.

Several key points can be illustrated with the above results obtained with depe. (1) Note that the presence of Cp_2Co^+ stabilizes a solution of depe and $Cp_2Fe_2(CO)_4$ with respect to disproportionation. This result strongly supports the hypothesis that the thermal (and photochemical) disproportionation reaction follows a chain pathway involving an intermediate capable of reducing Cp_2Co^+ and, thereby, being intercepted. (2) The $Cp_2Fe_2(CO)_4$ disappearance quantum yields for the Cp_2Co^+ reduction are much less than unity, consistent with a nonchain pathway for this reaction. In fact, the quantum yield is roughly that reported[25] for the photoreaction of the iron dimer with CCl_4, 0.2, (affording $CpFe(CO)_2Cl$) at $\lambda > 500$ nm. Also note that a 5-fold increase in depe concentration results in no significant increase of Φ, suggesting that the reaction proceeds with nearly unit efficiency upon occurrence of the primary photoprocess. Thus, in spite of the observation that $CpFe(CO)_2^-$ reduces Cp_2Co^+ (reaction 16), it can be concluded that the photochemical reduction of Cp_2Co^+ does not proceed via disproportionation and subsequent reaction of $CpFe(CO)_2^-$ with Cp_2Co^+ (reaction 23). Such a

$$CpFe(CO)_2^- + Cp_2Co^+ \rightarrow CpFe(CO)_2 + Cp_2Co \quad (23)$$

process would proceed with chain lengths at least as great as the disproportionation itself (>>100 for L = $^1/_2$depe), perhaps even more efficiently because the back-reaction of the ionic products would be prevented. In conclusion, the involvement of the 19-electron complexes in the reductions is strongly implicated.[26]

Finally, note that the stabilization of $Cp_2Fe_2(CO)_4$/depe solutions by reagents other than Cp_2Co^+ (e.g., $Mn_2(CO)_{10}$) is also explained by the oxidative interception of the 19-electron species, which prevents perpetuation of the chain reaction. Also, the failure of an argon purge to promote the chain reaction disproportionation of $Cp_2Fe_2(CO)_4$ by dppe in Me_2SO in the presence of Bu-py$^+$ is accounted for, and the failure of reaction 5 to proceed in CH_2Cl_2 solutions of $Cp_2Fe_2(CO)_4$ and depe (thermally) or other ligands (photochemically) in the presence of Bu-py$^+$ is similarly explained.

Importance of n and L in $CpFe(CO)_{3-n}L_n$. An important assumption involved throughout this paper is that the ability of the 19-electron species $CpFe(CO)_{3-n}L_n$ to reduce Cp_2Co^+ or other substrates is dependent on the nature of L and the value of n. Thus, the failure of $P(OEt)_3$ to afford monosubstituted cations, $CpFe(CO)_2P(OEt)_3^+$, in contrast with the behavior of PBu_3, is attributed to the inability of the relatively electron-poor species $CpFe(CO)_2(P(OEt)_3)$ to reduce Cp_2Co^+. To test this hypothesis, the cations of $CpFe(CO)_2(P(OEt)_3)^+$ and $CpFe(CO)_2PBu_3^+$ were prepared from $Cp_2Fe_2(CO)_4$, the appropriate phosphorus ligand, and the commercially available ferrocenium salt, $[Cp_2Fe]^+[FeCl_4]^-$:

$$^1/_2Cp_2Fe_2(CO)_4 + L + [Cp_2Fe]^+[FeCl_4]^- \rightarrow [CpFe(CO)_2L]^+[FeCl_4]^- + Cp_2Fe \quad (24)$$

Addition of cobaltocene (18 mM) to a solution of $[CpFe(CO)_2(P(OEt)_3]^+[FeCl_4]^-$ (20 mM) and $P(OEt)_3$ (10 mM) resulted in the reduction of most of the $FeCl_4^-$ anion present, as evidenced by a definite counterion shift in the IR spectrum of $CpFe(CO)_2(P(OEt)_3)^+$ (ca. 4 cm^{-1}) and formation of a precipitate analyzed to contain Fe(II). Further addition of 50 mM Cp_2Co to the reaction solution resulted in the formation of additional precipitate and the reduction of the iron phosphite cation to $Cp_2Fe_2(CO)_4$ (eq 25) along with the formation of some $CpFe(CO)(P(OEt)_3)_2^+$. The occurrence of this reaction supports the

$$Cp_2Co + CpFe(CO)_2P(OEt)_3^+ \rightarrow Cp_2Co^+ + {}^1/_2Cp_2Fe_2(CO)_4 \quad (25)$$

hypothesis that the complex $CpFe(CO)_2P(OEt)_3$ lacks the potential necessary to reduce Cp_2Co^+; instead, the reverse reaction proceeds, as shown in eq 26.

$$Cp_2Co + CpFe(CO)_2P(OEt)_3^+ \rightarrow Cp_2Co^+ + CpFe(CO)_2P(OEt)_3 \quad (26a)$$

$$CpFe(CO)_2P(OEt)_3 \rightarrow CpFe(CO)_2 + P(OEt)_3 \quad (26b)$$

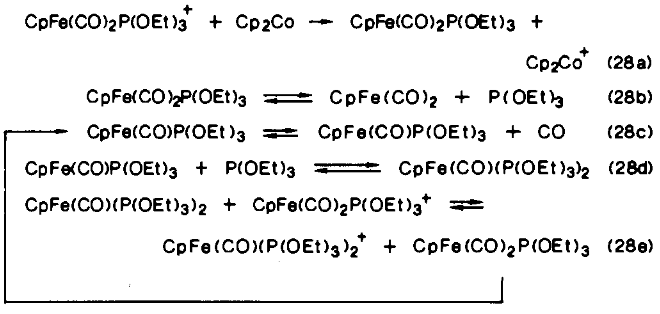
$$CpFe(CO)_2 \rightarrow {}^1/_2Cp_2Fe_2(CO)_4 \quad (26c)$$

In the presence of 0.1 M $P(OEt)_3$, the slow addition of cobaltocene (25 mM) to a solution of 20 mM $[CpFe(CO)_2P(OEt)_3]^+[FeCl_4]^-$ resulted in the formation of a precipitate containing Fe(II) and the virtually complete phosphite substitution of the organoiron cation (eq 27), with only negligible amounts

$$CpFe(CO)_2P(OEt)_3^+ + P(OEt)_3 \xrightarrow{Cp_2Co} CpFe(CO)(P(OEt)_3)_2^+ + CO \quad (27)$$

of $Cp_2Fe_2(CO)_4$ being formed. Cobaltocene thus induces the ETC substitution of $CpFe(CO)_2P(OEt)_3^+$.[19] The mechanism of this reaction and the various equilibria involved in reactions 25 and 27 are presumably as shown in Scheme IV. Note that the high concentration of $P(OEt)_3$ tends to push the equilibrium positions

Scheme IV



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[25] (a) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753–2755. (b) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 6018–6021.

[26] Consistent with the interpretation involving Cp_2Co^+ as a chain inhibitor, a solution of $Cp_2Fe_2(CO)_4$ (15 mM) and depe (40 mM) is stable even in the presence of a small concentration (5 mM) of Cp_2Co^+. Very brief (2 s, in an IR cell) irradiation of such a solution results only in the slight disappearance of $Cp_2Fe_2(CO)_4$ and the formation of $CpFe(CO)_2(\text{depe-}P)^+$. An additional 4-s irradiation results in the complete disproportionation of $Cp_2Fe_2(CO)_4$ according to eq 1. Presumably, during the second irradiation period the Cp_2Co^+ was virtually all consumed, allowing disproportionation to proceed.

of reactions 28b and 28d so as to favor formation of the cationic product rather than $Cp_2Fe_2(CO)_4$ from $CpFe(CO)_2$ dimerization. The slow addition of Cp_2Co to the mixture also favored substitution rather than net reduction by resulting in a lowered $CpFe(CO)_2$ concentration. Also note that the resulting $CpFe(CO)(P(OEt)_3)_2^+$ solution was stable even upon addition of another equivalent of cobaltocene.

Addition of 2 equiv of cobaltocene to a solution of $[CpFe(CO)_2PBu_3]^+[FeCl_4]^-$ resulted only in the reduction of the $FeCl_4^-$ as indicated by the formation of a precipitate and a small shift in the IR spectrum of the cation. Thus, reduction of Cp_2Co^+ by the 19-electron complex $CpFe(CO)_2PBu_3$ (eq 21c) does appear to be thermodynamically favorable.

Further evidence that ligand substitution can increase the reducing ability of the 19-electron species comes from the following considerations. Recall that by comparing the reactivity of PPh_3 with $Cp_2Fe_2(CO)_4$ in CH_2Cl_2 and PrBr/THF solutions, we concluded that PPh_3 does not induce reversible disproportionation of the $Cp_2Fe_2(CO)_4$ complex. We can thus infer that the $CpFe(CO)_2PPh_3$ complex does not have the necessary potential to reduce $Cp_2Fe_2(CO)_4$. Because PPh_3 is a better electron donor than $P(OEt)_3$,[24] we can also infer that $CpFe(CO)_2P(OEt)_3$ does not have the necessary potential to reduce $Cp_2Fe_2(CO)_4$. However, the 19-electron $CpFe(CO)(P(OEt_3)_2)$ complex does have the potential to reduce the dimer because the cationic product in reaction 5 is $CpFe(CO)(P(OEt_3))_2^+$. (Substitution of CO by PPh_3 in $CpFe(CO)_2PPh_3$ would give a 19-electron species capable of reducing $Cp_2Fe_2(CO)_4$, but presumably for steric reasons,[24] this substitution cannot occur and thus no disproportionation occurs.)

Conclusion. The $Cp_2Fe_2(CO)_4$ dimer, thought to be unreactive toward photochemical disproportionation, was shown to undergo this type of reactivity. In this regard, the $Cp_2Fe_2(CO)_4$ dimer is similar to the $Cp_2M_2(CO)_6$ (M = Cr, Mo, W), $M_2(CO)_{10}$ (M = Mn, Re), and $Co_2(CO)_8$ dimers. The apparent unreactivity of the $Cp_2Fe_2(CO)_4$ dimer can be attributed to a facile back-reaction of the cationic and anionic products. As in the disproportionation reactions of the other dimers, the key intermediate in the $Cp_2Fe_2(CO)_4$ reactions is a 19-electron species, $CpFe(CO)_{3-n}L_n$. This intermediate forms by the reaction of the 17-electron $CpFe(CO)_2$ species with a ligand. Formation of 19-electron species via this route is quite common: we have demonstrated that the $CpM(CO)_3$ and $Mn(CO)_{5-n}L_n$ radicals also react readily to form 19-electron species. Recent studies from our lab have also demonstrated that the reaction of a 17-electron species with a ligand to form the 19-electron species can be thermodynamically "downhill".[27] Given this result, our demonstration of the facile formation of 19-electron species, and the widespread occurrence of 17-electron metal radicals in organometallic chemistry, we feel that 19-electron intermediates should be considered as potential intermediates in numerous reaction systems. Our laboratory is actively investigating this point.

Experimental Section

Materials and Supplies. $Cp_2Fe_2(CO)_4$ was prepared by the method of King[28] and recrystallized from CH_2Cl_2/hexane. $(MeCp)_2Fe_2(CO)_4$ was obtained from Alfa and used as received. $[Bu_4N][CpFe(CO)_2]$ was prepared as described by Burlitch et al.[29] $[CpFe(CO)(depe)][CpFe(CO)_2]$ was prepared by the addition of depe to a benzene solution of $Cp_2Fe_2(CO)_4$ and collection of the resulting precipitate. $NaC_{14}H_{10}$ solutions were prepared by addition of an excess of freshly cut sodium to a THF solution of anthracene (50 mM), resulting in the formation of $Na_2C_{14}H_{10}$. Syringing the resulting solution into an equal volume of a 70 mM anthracene solution afforded a solution of $NaC_{14}H_{10}$ (50 mM) and neutral $C_{14}H_{10}$. $[CpFe(CO)_2(PBu_3)][FeCl_4]$ and $[CpFe(CO)_2(P(OEt)_3)][FeCl_4]$ were prepared by the method of Astruc.[30] All reactions were done under an argon or nitrogen atmosphere. All solvents were stored under inert gas. Benzene and acetone were distilled from $LiAlH_4$ and CaH_2, respectively. THF and CH_2Cl_2 were Aldrich "anhydrous Gold Label." All other chemicals were obtained commercially and used as received: depe, dbpe, dcype, PMe_2Ph, $[Cp_2Co][PF_6]$, cobaltocene, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe(CO)_5$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ (Strem); PPh_3, dppe, $P(OEt)_3$, PBu_3, PrBr, anthracene, and deuterated solvents (Aldrich); *N*-*n*-butylpyridnium chloride and $[Cp_2Fe][FeCl_4]$ (Alfa).

Instruments and Techniques. The reactions were generally monitored by infrared spectroscopy. Products were identified by comparison of their absorption bands to the values in Table I. The procedure typically used for IR-monitored experiments was as follows. The reaction solution was prepared and thoroughly degassed with a purge of argon. If required, CO was subsequently bubbled through the solution. An infrared cell was then filled via syringe; the cell was irradiated, and spectra were taken at given time intervals in the ν_{CO} region, 2200–1600 cm^{-1}.

The light source was a 200-W Oriel high-pressure mercury lamp. Unless stated otherwise a Corning CS 3-66 filter ($\lambda > 560$ nm) was used for all irradiations of $Cp_2Fe_2(CO)_4$. For $\lambda > 525$ nm, a CS 3-68 filter was used. The long wavelengths used made it unlikely that other species in solution absorbed light. Irradiations of 366-nm light utilized a CS 7-83 filter. All IR spectra were obtained with a Perkin-Elmer 983 spectrometer. NMR spectra were obtained with a Varian XL-200 FT spectrometer; screwcap-sealed NMR tubes (Wilmad) were used. Electronic spectra were recorded on a Cary 17 spectrophotometer.

A 545-nm interference filter was used for quantum yield measurements. Lamp intensities were measured by Reinecke's salt actinometry.[31] The concentration of $Cp_2Fe_2(CO)_4$ was monitored with a Beckman DU spectrophotometer at $\lambda = 525$ nm. The precipitate formed in the reaction of Cp_2Co with $FeCl_4^-$ was analyzed for Fe(II) with EM Quants Fe(II) test strips.

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(27) Philbin, C. E.; Granatir, C. A.; Tyler, D. R. *Inorg. Chem.*, in press.

(28) King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. 1, pp 114–116.

(29) Burlitch, J. M.; Leonowicz, M. E.; Petersen, R. B.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1097–1105.

(30) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094–1100.

(31) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394–403.