exchange. The loss of the coupling $^3J(\mathrm{HPt^APt^BP^X})$ at high temperature favors the latter interpretation. A ^{31}P NMR spectrum in the high-temperature limit should distinguish between the possible mechanisms unambiguously, but we have been unable to obtain such a spectrum.

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Stereochemistry and Mechanisms of Cleavage of Compounds of the Type $(\eta^5\text{-}C_5H_5)Fe(CO)_2$(alkyl) with Copper(II) Reagents and Halogens. Possible Roles of Solvent Cage Processes in Organometallic Cleavage Reactions

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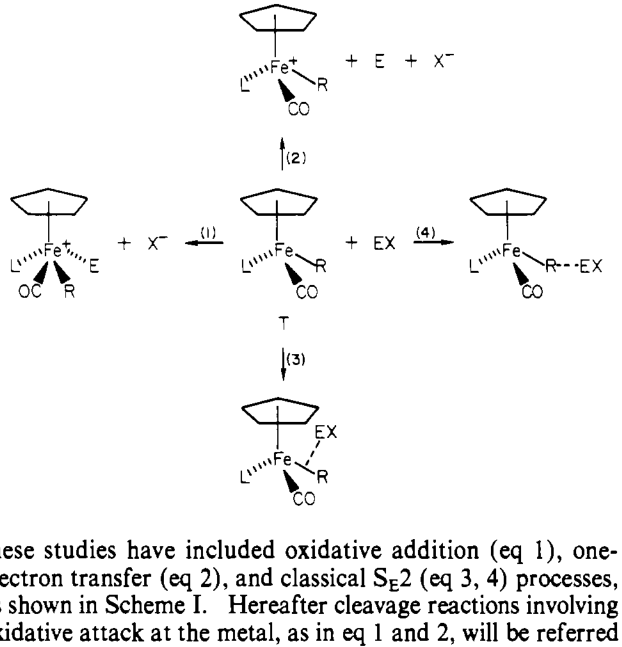
Cleavage reactions by a variety of copper(II) reagents of the compounds FpR (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$; R = Me, Et, *n*-Bu, $PhCH_2CH_2$, *threo*-PhCHDCHD, $PhCH_2{}^{13}CH_2$, $Me_3CCH_2CH_2$, $PhCH_2$, (*R*)-(−)-PhCHD, Me_3CCH_2, *s*-Bu) and $(\eta^5\text{-}C_5H_5)FeCOPPh_3R$ (R = $PhCH_2$, (*R*)-(−)-PhCHD) are studied and compared with similar electrochemical and halogen cleavage reactions. In general, reaction of FpR with a copper(II) halide, CuX_2, yields $[FpR^+][CuX_2^-]$ via a one-electron-transfer process. When R = Me or $PhCH_2$, the ion pair breaks down within the solvent cage via nucleophilic attack by halide ion on the α-carbon atom of R, the products being RX (inversion of configuration) and the iron radical Fp·. The latter then abstracts halogen from copper(II) halide or halogenated solvent. When R = *n*-Bu on $Me_3CCH_2CH_2$, the components of $[FpR^+][CuX_2^-]$ diffuse from the solvent cage and the cation undergoes homolysis of the iron–carbon bonds to give Fp^+ and R·; the latter abstracts halogen from copper(II) halide or halogenated compound. The major difference between the two series appears to be the proclivity of R to undergo S_N2-type processes, i.e., $PhCH_2$, Me > *n*-Bu, $Me_3CCH_2CH_2$, although the benzyl system will also undergo homolysis to yield benzyl radicals when good nucleophiles are absent. Reactions of $FpCH_2CH_2Ph$ proceed by a third route, dissociation of phenonium ions. It is also shown that halogen cleavage reactions of the compounds FpR in nonprotic solvents probably proceed via a two-electron-transfer process. The presumed intermediates, $[FpRX^+][X^-]$, appear to undergo more facile nucleophilic attack by halide ion on the α-carbon atom of R than do the species FpR^+, yielding RX (inversion of configuration) and FpX.

Introduction

Reactions involving cleavage of transition-metal–carbon σ bonds are central to much of the more interesting chemistry of organo transition-metal compounds, although mechanistic features are, in many cases, still rather controversial.[1] Cleavage reactions by electrophilic reagents EX (E = H, HgX, CuX, TlX_2, X; X = Cl, Br, I) have been much studied,[2] in particular of compounds of the general formula $(\eta^5\text{-}C_5H_5)$-Fe(CO)LR (I) (L = CO, tertiary phosphine; R = alkyl), which are both easy to prepare and relatively stable to heat and to air oxidation.

The compounds I are generally cleaved by electrophiles EX to yield RE and $(\eta^5\text{-}C_5H_5)Fe(CO)LX$, and mechanistic investigations to date have involved kinetic and stereochemical (at iron and the α-carbon) studies of cleavage by protic acids,[3-7] mercury(II) halides,[3-5,8-12] copper(II) halides,[13] and the halogens.[3-5,10,14-16] Mechanisms proposed on the basis of these studies have included oxidative addition (eq 1), one-electron transfer (eq 2), and classical S_E2 (eq 3, 4) processes, as shown in Scheme I. Hereafter cleavage reactions involving oxidative attack at the metal, as in eq 1 and 2, will be referred to as S_E(oxidative) processes.[17]

Scheme I



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[1] Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.
[2] Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57.
[3] Attig, T. G.; Wojcicki, A. *J. Am. Chem. Soc.* **1974**, *96*, 262.
[4] Flood, T. C.; Miles, D. L. *J. Organomet. Chem.* **1977**, *127*, 33.
[5] Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619.
[6] Rogers, W. N.; Baird, M. C. *J. Organomet. Chem.* **1979**, *182*, C65.
[7] DeLuca, N.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *193*, 359.
[8] Dodd, D.; Johnson, M. D. *J. Chem. Soc. B* **1971**, 662.
[9] Bock, P. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2826.
[10] Flood, T. C.; DiSanti, F. J. *J. Chem. Soc., Chem. Commun.* **1975**, 18.
[11] Dizikes, L. J.; Wojcicki, A. *J. Am. Chem. Soc.* **1977**, *99*, 5295.
[12] Dong, D.; Slack, D. A.; Baird, M. C. *Inorg. Chem.* **1979**, *18*, 188.
[13] Nicholas, K. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 4449
[14] Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814.
[15] Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539.
[16] Brunner, H.; Wallner, G. *Chem. Ber.* **1976**, *109*, 1053.
[17] See ref 12, footnote 27.

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Table I. Voltammetric and Coulometric Data for the Compounds $(\eta^5\text{-}C_5H_5)FeCOLR$

expt no.	R, L	$(E_p)_a$, V[a]	$n \pm 10\%$ (no. of expts)	electrolysis products (% yields)[b]
1	Me, CO	+1.23	0.91 (3)	FpCl (72); MeCl not analyzed
2	Et, CO	+1.30		
3	*n*-Bu, CO	+1.28		
4	$PhCH_2CH_2$, CO	+1.38	0.93 (3)	FpCl (82); $PhCH_2CH_2Cl$ (86)
5	*threo*-PhCHDCHD, CO		1.04 (1)	FpCl (83); *threo*-PhCHDCHDCl (79) with 77% retention of configuration
6	$PhCH_2{}^*CH_2$, CO		0.92 (1)	FpCl (79); $PhCH_2CH_2Cl$ (84) with complete scrambling of methylene groups
7	$PhCH_2$, CO	+1.28	0.93 (2)	FpCl (79); $PhCH_2Cl$ (76)
8	Me_3SiCH_2, CO	+1.37		
9	Me, $P(OPh)_3$	+1.06		
10	$PhCH_2$, $P(OMe)_3$	+0.92		
11	$PhCH_2$, PPh_3	+0.80		
12	$PhCH_2$, $PMePh_2$	+0.82		

[a] Scan rate 0.050 V s^{-1}. [b] Bu_4NCl supporting electrolyte.

While we have argued previously[15] that S_E2 mechanisms (eq 3, 4) are unlikely for electronic reasons,[18] we were not able, while considering possible mechanisms for halogen cleavage reactions, to distinguish between the types of one- and two-electron-transfer processes represented by eq 1 and 2. In an effort to correlate oxidative cleavage reactions of compounds of the type I by the various oxidants discussed above, we have investigated the products of electrochemical cleavage and cleavage by typical one-electron oxidants, copper(II) salts. By comparison of the nature of the products of electrochemical cleavage reactions with those of the copper(II) and halogen (expected two-electron oxidants) cleavage reactions, it was hoped that a unifying theme might become apparent. We report herein the story as it has unfolded. Aspects have been communicated previously;[20,21] others have reported similar cleavage reactions in alcohols as solvents.[13,14,22] Hereafter, the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ moiety will be designated Fp.

Experimental Section

Preparation of Iron Alkyl Compounds. The compounds FpR (R = Me,[23] Et,[24] *n*-Bu,[25] CH_2Ph,[26] CH_2CH_2Ph,[15] *threo*-CHDCHDPh,[15] $^{13}CH_2CH_2Ph$,[15] *s*-Bu,[27] CH_2CMe_3,[28] CH_2SiMe_3[29]), $(\eta^5\text{-}C_5H_5)FeCO[P(OPh)_3]Me$,[30] and $(\eta^5\text{-}C_5H_5)FeCOLCH_2Ph$[31] (L = $PMePh_2$, $P(OMe)_3$, PPh_3) were prepared essentially as reported in the literature. (*R*)-(−)-FpCHDPh ($[\alpha]^{25.2}{}_D$ −0.676°, CH_2Cl_2) was prepared by treating (*S*)-(+)-PhCHDOTs[32] with $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$. The tosylate ($[\alpha]^{28.2}{}_D$ +2.69°, CH_2Cl_2) was prepared from the corresponding monodeuterio alcohol[33] ($[\alpha]^{30}{}_D$ +1.27°, neat, ~80% optical purity); the latter was prepared from benzaldehyde-d_1.[34] (*R*)-(−)-$(\eta^5\text{-}C_5H_5)FeCOPPh_3CHDPh$ ($[\alpha]_D$ −0.245°, CH_2Cl_2) was prepared by the same procedure as for the perhydro analogue (see above).

The copper(II) salts $Cu(OAc)_2\cdot H_2O$ (AnalaR), $CuCl_2\cdot 2H_2O$ (AnalaR), $CuBr_2$ (AnalaR), and $Cu(NO_3)_2\cdot 3H_2O$ (Mallinckrodt) were used as received. Anhydrous $CuCl_2$[35] and $CuX_2(OPPh_3)_2$ (X = Cl,[36] Br,[36] NO_3[37]) were prepared as in the literature.

Bu_4NCl (Eastman) was dried in vacuo over P_2O_5, Bu_4NBF_4 and Bu_4NPF_6 (Aldrich) were crystallized from 1:1 ethyl acetate/petroleum ether (bp 40–60 °C), and Et_4NClO_4 was prepared by acidifying a saturated aqueous solution of Et_4NBr with 70% perchloric acid. The precipitated perchlorate salt was recrystallized from hot water and dried in vacuo at 100 °C. Bu_4NF was prepared by the method of Corey.[38]

Instrumentation. Voltammetric experiments were carried out with use of an E and G Princeton Applied Research Model 170 system. Triangular-wave voltammograms were routinely run over the potential cycle 0.0 → +1.6 → 0.0 V scan rates of 0.02–200 V s^{-1}. In some cases, i.e., very fast scans and/or low-temperature studies, data were also collected in the range −1.9 to 0 V. In the case of the fast scans, the data were recorded on a Hewlett-Packard Model 1201A storage oscilloscope or a Biomation Model 1015 waveform recorder. The voltammetry involved a glassy carbon working electrode, a Pt auxiliary electrode, and a Ag/AgCl/0.10 M Et_4NCl/CH_2Cl_2 reference. Measurements at lower than room temperature were achieved by passing cold gas, released from liquid N_2 by a controlled heat input, through a jacket surrounding the cell. The lowest temperature achieved was −62 °C with a temperature control of ±2 °C.

The electrochemical oxidations were carried out by using a Wenking Model 68 FR 0.5 potentiostate for control of electrode potential and an E and G Princeton Applied Research Model 370 coulometer for measurement of the quantity of electricity used. A two-compartment cell was employed with a graphite-rod working electrode, the same Ag/AgCl reference electrode mentioned above, and a Pt auxiliary electrode. The solution in the working compartment (100 mL) was well stirred, and the electrolyses were carried out at +1.40 V. Electrolyses were monitored by following changes in the IR spectra in the carbonyl region (1600–2200 cm^{-1}).

IR spectra were run on Perkin-Elmer 180 and Beckman 4240 spectrometers, and routine ^1H NMR spectra were run on Varian EM360 and HA100 spectrometers. ^{13}C and deuterium-decoupled ^1H NMR spectra were run on a Bruker HX60 spectrometer and ESR spectra on a Varian E3 spectrometer. Gas–liquid chromatography experiments were carried out on a Hewlett-Packard F and M Scientific 700 gas chromatograph and optical rotations on a Perkin-Elmer 141 polarimeter using a 1-cm quartz cell.

Electrochemical Cleavage Reactions. All electrochemical experiments utilized purified and freshly dried (over sodium wire or P_2O_5, as appropriate) solvents and supporting electrolytes; iron complexes were purified by chromatography on alumina just prior to use. All experiments were conducted under a nitrogen atmosphere at room temperature unless otherwise stated. Concentrations of iron compound and supporting electrolyte were generally ~3 × 10^{-3} M and 0.05–0.2 M, respectively. In both triangular-wave voltammetry and coulometry experiments, all data for the iron compounds were corrected for

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(18) The HOMO of a compound of type I, which is of essentially metal d character, lies some 30 kcal mol^{-1} above the Fe–C bonding orbital[19] (L = CO).

(19) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

(20) Rogers, W. N.; Page, J. A.; Baird, M. C. *J. Organomet. Chem.* **1978**, *156*, C37.

(21) Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chim. Acta* **1979**, *37*, L539.

(22) Anderson, S. N.; Fong, C. W.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1973**, 163.

(23) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(24) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58.

(25) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291.

(26) Bibler, J. P.; Wojcicki, A. *J. Am. Chem. Soc.* **1966**, *88*, 4862.

(27) Johnson, R. W.; Pearson, R. G. *J. Chem. Soc. D* **1970**, 986.

(28) Jacobson, S. E.; Wojcicki, A. *J. Am. Chem. Soc.* **1973**, *95*, 6962.

(29) King, R. B.; Pannell, K. H.; Bennett, C. R.; Ishaq, M. *J. Organomet. Chem.* **1969**, *19*, 327.

(30) Su, S. R.; Wojcicki, A. *J. Organomet. Chem.* **1971**, *27*, 231.

(31) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292.

(32) Kochi, J. K.; Hammond, G. S. *J. Am. Chem. Soc.* **1953**, *75*, 3443.

(33) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 2352.

(34) Burgstahler, A. W.; Walker, D. E.; Kuebrich, J. P.; Schowen, R. L. *J. Org. Chem.* **1972**, *37*, 1272.

(35) Pray, A. R. *Inorg. Synth.* **1957**, *5*, 153.

(36) Goodgame, D. M. L.; Cotton, F. A. *J. Chem. Soc.* **1961**, 2298.

(37) Bannister, A.; Cotton. F. A. *J. Chem. Soc.* **1960**, 2276.

(38) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

(39) Treichel, P. M.; Molzahn, D. C. *J. Organomet. Chem.* **1979**, *179*, 275.

Table II. Chemical Cleavage Reactions of FpR in CH_2Cl_2

expt no.	R	Cu(II) compd	products (% yields)[a]	comments
1	Me	$CuCl_2 \cdot 2H_2O$	MeCl (80), FpCl (88), CuCl (85)	
2	Me	$CuBr_2$	MeBr (90), FpBr (81), CuBr (100)	
3	Et	$CuCl_2 \cdot 2H_2O$	EtCl (>80), FpCl (7), CuCl (79)	
4	Et	$CuCl_2$	EtCl (>80), FpCl (87), CuCl (95)	
5	Et	$CuBr_2$	EtBr (85), FpBr (83), CuBr (80)	
6	*n*-Bu	$CuCl_2 \cdot 2H_2O$	*n*-BuCl (53), FpCl (10), CuCl (72)	no butenes
7	*n*-Bu	$CuCl_2$	*n*-BuCl (85), FpCl (86), CuCl (91)	
8	*n*-Bu	$CuBr_2$	*n*-BuBr (76), FpBr (74), CuBr (92)	no butenes
9	$PhCH_2CH_2$	$CuCl_2 \cdot 2H_2O$	$PhCH_2CH_2Cl$ (80), FpCl (5), CuCl (86)	
10	$PhCH_2CH_2$	$CuCl_2$	$PhCH_2CH_2Cl$ (81), FpCl (75)	
11	$PhCH_2CH_2$	$CuBr_2$	$PhCH_2CH_2Br$ (60), FpBr (74), CuBr (85)	
12	*threo*-PhCHDCHD	$CuCl_2 \cdot 2H_2O$	PhCHDCHDCl (77), FpCl (6), CuCl (73)	87% retention of configuration
13	*threo*-PhCHDCHD	$CuBr_2$	PhCHDCHDBr (67), FpBr (67), CuBr (82)	68% retention of configuration
14	$PhCH_2{}^*CH_2$	$CuCl_2 \cdot 2H_2O$	$PhCH_2CH_2Cl$ (82), FpCl (9), CuCl (79)	methylene label completely scrambled
15	$PhCH_2{}^*CH_2$	$CuBr_2$	$PhCH_2CH_2Br$ (69), FpBr (68), CuBr (74)	methylene label completely scrambled
16	$PhCH_2$	$CuCl_2 \cdot 2H_2O$	$PhCH_2Cl$ (87), FpCl (82), CuCl (76)	no change in products under 1 atm CO or on addition of up to 1000× excess MeOH
17	$PhCH_2$	$CuBr_2$	$PhCH_2Br$ (70), FpBr (66), CuBr (89)	
18	(*R*)-(−)-PhCHD	$CuCl_2 \cdot 2H_2O$	(*S*)-(+)-PhCHDCl	>90% inversion
19	(*R*)-(−)-PhCHD	$CuBr_2$	(*S*)-(+)-PhCHDBr	>90% inversion
20	$PhCH_2$	$CuCl_2(OPPh_3)_2$	$PhCH_2Cl$ (82), FpCl (92)	
21	$PhCH_2$	$CuBr_2(OPPh_3)_2$	$PhCH_2Br$ (85), FpBr (90)	
22	Me_3CCH_2	$CuCl_2 \cdot 2H_2O$	$Me_3CCH_2CO_2H$ (82), CuCl (56)	no FpCl, Me_3CCH_2Cl, or rearranged products; gas evolved
23	Me_3CCH_2	CiBr $CuBr_2$	$Me_3CCH_2CO_2H$ (67), FpBr (13), CuBr (58)	no Me_3CCH_2Br or rearranged products; gas evolved
24	*s*-Bu	$CuBr_2$	*s*-BuBr (30), FpBr (67), CuBr (83)	+ unidentified acyl species
25	$Me_3CCH_2CH_2$	$CuCl_2 \cdot 2H_2O$	$Me_3CCH_2CH_2Cl$ (87), FpCl (6), CuCl (85)	
26	$Me_3CCH_2CH_2$	$CuBr_2$	$Me_3CCH_2CH_2Br$ (78), FpBr (87), CuBr (87)	

[a] Based on the stoichiometry of eq 6.

Table III. Chemical Cleavage Reactions of FpR in Solvents Other Than CH_2Cl_2

expt no.	R	Cu(II) compd	solvent	products (% yields)	comments
1	Me	$CuCl_2 \cdot 2H_2O$	CH_2I_2	FpCl (27), FpI (51)	no MeI
2	Me	$CuBr_2$	CH_2I_2	FpBr (16), FpI (65)	no MeI
3	*n*-Bu	$CuCl_2 \cdot 2H_2O$	CH_2Br_2	*n*-BuCl (66), FpCl (6)	no *n*-BuBr, FpBr
4	*n*-Bu	$CuCl_2 \cdot 2H_2O$	CH_2I_2	*n*-BuCl (73), *n*-BuI (11), FpCl (12)	no FpI
5	*n*-Bu	$CuBr_2$	CH_2I_2	*n*-BuBr (61), *n*-BuI (12), FpBr (77)	no FpI
6	$PhCH_2CH_2$	$CuCl_2 \cdot 2H_2O$	CH_2I_2	$PhCH_2CH_2Cl$ (80), FpCl (9)	no $PhCH_2CH_2I$, FpI
7	$PhCH_2CH_2$	$CuBr_2$	CH_2I_2	$PhCH_2CH_2Br$ (74), FpBr (78)	no $PhCH_2CH_2I$, FpI
8	$PhCH_2CH_2$	$CuCl_2 \cdot 2H_2O$	MeOH	$PhCH_2CH_2CO_2Me$ (83)	1 atm CO
9	$PhCH_2$	$CuCl_2 \cdot 2H_2O$	CH_2Br_2	$PhCH_2Cl$ (88), FpCl (89)	no FpBr
10	$PhCH_2$	$CuCl_2 \cdot 2H_2O$	CH_2I_2	$PhCH_2Cl$ (56), FpCl (28), FpI (56)	no $PhCH_2I$
11	$PhCH_2$	$CuBr_2$	CH_2I_2	$PhCH_2Br$ (70), FpBr (17), FpI (65)	no $PhCH_2I$
12	$PhCH_2$	$CuCl_2 \cdot 2H_2O$	MeOH	$PhCH_2CO_2Me$ (39), FpCl (36), CuCl (70)	ester yield 86% under 1 atm CO
13	$PhCH_2$	$CuCl_2 \cdot 2H_2O$	*t*-BuOH	$PhCH_2CO_2$-*t*-Bu (22), FpCl (45), CuCl (64)	1 atm CO
14	$PhCH_2$	$Cu(NO_3)_2(OPPh_3)_2$	$ClCH_2CH_2Cl$	$(PhCH_2)_2$ (93)	at 56 °C; trace of iron complex possibly $FpNO_3$
15	$Me_3CCH_2CH_2$	$CuCl_2 \cdot 2H_2O$	CH_2I_2	$Me_3CCH_2CH_2Cl$ (65), $Me_3CCH_2CH_2I$ (18), FpCl (6)	no FpI
16	$Me_3CCH_2CH_2$	$CuBr_2$	CH_2I_2	$Me_3CCH_2CH_2Br$ (58), $Me_3CCH_2CH_2I$ (14), FpBr (85)	no FpI

background contributions from the supporting electrolyte. The resulting data are shown in Table I.

Cleavage Reactions by Copper(II) Compounds. An extensive series of cleavage reactions involving various combinations of the above-mentioned alkyliron compounds and copper(II) reagents were carried out at room temperature, under nitrogen, in methylene chloride. These generally involved treatment of (2–5) × 10^{-3} mol of iron compound in 50–100 mL of CH_2Cl_2 with 3 molar equiv of copper compound, either in solution or as the powdered solid. The course of a reaction could be readily followed by monitoring the IR spectrum of the reaction solution (1600–2200 cm^{-1}). Workup of reaction mixtures depended to some extent on the nature of the expected products, but in general involved filtration of any precipitated copper(I) halides. In many cases, yields of copper(I) halides were determined gravimetrically after washing well with methanol (to remove unreacted copper(II) salt) and drying. Yields of iron carbonyl products such as FpX (X = Cl, Br) were readily obtained from intensities of the carbonyl bands in the IR spectrum of a reaction mixture, and yields of organic products were determined with use of a combination of GLC and NMR techniques. The reactions studied and the yields of the products are listed in Table II. Yields of copper(I) salts are calculated on the assumption that 2 mol of copper(II) was consumed for every mole of iron alkyl compound reacted (see Results and Discussion).

In order to check literature reports and to complement the studies listed in Table II, we also carried out some cleavage reactions in other solvents. These experiments are listed in Table III. Listed in Table IV are cleavage experiments involving (η^5-C_5H_5)$FeCOPPh_3CH_2Ph$.

As many of the reactions studied either were heterogeneous in character or, when homogeneous, were too rapid to study kinetically by conventional techniques, kinetics studies were generally precluded as a route to mechanistic information. However, some conclusions could be reached on the basis of competition experiments. Procedures involved treating a solution containing equimolar amounts of two alkyl compounds, FpR and FpR′, with a deficiency of copper(II) compound.

Table IV. Cleavage Reactions of $(\eta^5\text{-}C_5H_5)FeCOPPh_3CH_2Ph$ in CH_2Cl_2

expt no.	Cu(II) compd	temp, °C	products (% yields)
1	$CuCl_2 \cdot 2H_2O$	23	$PhCH_2Cl$ (18), $(PhCH_2)_2$ (69), $(\eta^5\text{-}C_5H_5)FeCOPPh_3Cl$ (55), CuCl (70)
2	$CuCl_2 \cdot 2H_2O$	−78	$PhCH_2Cl$ (35), $(PhCH_2)_2$ (53), $(\eta^5\text{-}C_5H_5)FeCOPPh_3Cl$ (62), CuCl (77)
3	$CuBr_2$	23	$PhCH_2Cl$ (29), $(PhCH_2)_2$ (64), $(\eta^5\text{-}C_5H_5)FeCOPPh_3Br$ (63), CuBr (64)

Table V. Relative Rates of Cleavage Reactions from Competition Experiments in CH_2Cl_2 between Equimolar Amounts of FpR and FpR′

R	R′	Cu(II) compd	rel rates, $k_R:k_{R'}$
Me	Et	$CuCl_2 \cdot 2H_2O$	1:1
Me	*n*-Bu	$CuCl_2 \cdot 2H_2O$	1:1
Me	Et	$CuBr_2$	1.1:1
Me	*n*-Bu	$CuBr_2$	1.1:1
Me	$PhCH_2CH_2$	$CuCl_2 \cdot 2H_2O$	1.7:1

Table VI. Products of Bromination Reactions of $FpCH_2CH_2Ph$ in the Presence of Excess $n\text{-}Bu_4NF$ at 25 °C

	% yields	
solvent (*Z*)	$PhCH_2CH_2Br$	$PhCH_2CH_2F$
MeCN (71.3)	65	21
Me_2CO (65.7)	63	11
CH_2Cl_2 (64.2)	75	3
C_6H_6 (54.0)	77	2

The relative amounts of unreacted alkyl compounds were assessed with ^1H NMR spectroscopy, the relative rates of disappearance of FpR and FpR′ being deduced therefrom. The relevant data appear in Table V; in all cases, mass balances were satisfactory. Similar competition experiments between $FpCH_2Ph$ and $(\eta^5\text{-}C_5H_5)FeCOPPh_3CH_2Ph$ showed that the latter was 10 times more reactive with $CuCl_2 \cdot 2H_2O$ and 2 times more reactive with $CuBr_2$.

Halogen Cleavage Reactions of (*R*)-(−)-FpCHDPh. The reactions were carried out in CH_2Cl_2 with procedures similar to those employed for the corresponding cleavage reactions of the phenethyl system.[15] The products were the (*S*)-(+)-benzyl halides, in all cases in >90% yield and >75% stereospecificity.

Bromination Reactions of $FpCH_2CH_2Ph$ in the Presence of Bu_4NF. The reactions were carried out as before[15] but in the presence of a 10-fold excess of Bu_4NF. The results are shown in Table VI.

Results and Discussion

Electrochemical Cleavage Reactions. The triangular-wave voltammetric experiments with Bu_4NCl as supporting electrolyte indicated that at room temperature the oxidations of the FpR compounds were electrochemically irreversible over the range of scan rates studied (up to 200 V s^{-1}). In each case well-defined oxidation peaks were obtained on the forward scan over the range of scan rates, but there was no evidenced of a current peak on the reverse scan corresponding to a reduction of the product of the anodic process. (Reductions of the alkyl compounds were observed in the range −1.60 to −1.70 V but were not investigated further.) It was also observed that the peak anodic potential shifted to more positive potentials and the peak anodic current increased with scan rate. Other experiments using a chloride-free Et_4NClO_4 supporting electrolyte gave results with closely comparable peak currents and potentials, while experiments in EtOH with Bu_4NPF_6 as supporting electrolyte were similar except that the anodic peak potentials were shifted positively by ~0.15 V. Comparison experiments at 0.05 V s^{-1} in CH_2Cl_2 using ferrocene as a model compound, with a known[40] one-electron charge-transfer step, showed quasi-reversible behavior with a peak current for the ferrocene oxidation eight-tenths that for the oxidation of an equal concentration of $FpCH_2Ph$. This would indicate that the oxidation process with the compounds FpR also involves one electron; the nonunity relation between the peak currents can be explained in part by the fact that one process is quasi-reversible and the other irreversible, and in part by differences in the diffusion coefficients of the two compounds.

Low-temperature studies were also carried out by using the benzyl compound in CH_2Cl_2 with Bu_4NPF_6 as a chloride-free electrolyte. The choice of supporting electrolyte was determined in part by solubility considerations. The behavior at room temperature was as previously observed with the Bu_4NCl and Et_4NClO_4, but lowering the temperature and increasing the scan rate resulted in the appearance and growth of a peak on the reverse scan of the cyclic voltammogram. The cathodic peak evidently corresponded to a reduction of a product resulting from the anodic process on the forward scan. At −35 °C and 10 V s^{-1}, the anodic peak appeared at +1.40 V and the cathodic peak at +0.75 V; the height of the resolved cathodic peak appeared only marginally less than that of the anodic peak. However further lowering of the temperature and/or increase in the scan rate caused the cathodic peak to decrease relative to the anodic peak, and at −40 °C and 100 V s^{-1} it was no longer apparent. The growth of the cathodic peak is to a point consistent with the existence of a short-lived electrochemically active product formed in the initial anodic process, but the disappearance of the cathodic peak at high scan rates and low temperatures suggests a complex behavior.

The data in Table I show that, as expected, the ease of oxidation of the compounds tends to parallel the anticipated electron-donating abilities of the ligands. Thus the ease of oxidation of the compounds decreases in the order L = tertiary phosphine > phosphite > CO (R = $PhCH_2$). Somewhat similar trends have been noted previously for oxidation of the isoelectronic series $(\eta^5\text{-}C_5H_5)Fe(CNR)_2X$,[39] while reduction potentials of the series $(\eta^5\text{-}C_5H_5)FeCOLR$[40] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_{3-n}L_n]^+$[41] become more negative as the donor properties of the ligands increase.

The controlled-potential coulometric analyses involved (1.8–2.8) × 10^{-3} mol of FpR in 100 mL of electrolyte. The products and yields obtained on exhaustive electrolysis in the CH_2Cl_2 solvent with Et_4NCl as supporting electrolyte are listed in Table I; the reactions were monitored by following changes in the IR spectrum of the electrolyte in the carbonyl region (1600–2200 cm^{-1}), and there was no evidence of trace acyl intermediates. In general the electrolyses proceeded slowly but smoothly; ~6 h was required for the current to decay to a steady background value. The background correction was 5–10% of the total quantity of electricity consumed.

The coulometry experiments, coupled with the triangular-wave voltammetry comparison experiment, indicate that 1 faraday/mol is required for the oxidation, suggesting the intermediacy of the species FpR^+ in the overall process. However the lack of a characteristic IR spectrum and the previously observed voltammetric irreversibility suggest that the initial product formed in the charge-transfer process must undergo rapid rearrangement or decomposition with products, in the presence of chloride ion, consistent with the general process shown in eq 5.

$$FpR \xrightarrow{-e^-} FpR^+ \xrightarrow{2Cl^-} FpCl + RCl \qquad (5)$$

The observed electrochemical irreversibility suggests that the apparent oxidation products $[(\eta^5\text{-}C_5H_5)FeCOLR]^+$ un-

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(40) Denisovich, L. I.; Gubin, S. P.; Chapovskii, Y. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1967**, 2271.

(41) Connelly, N. G.; Kitchen, M. D. *J. Chem. Soc., Dalton Trans.* **1977**, 931.

dergo rapid rearrangement or decomposition. The results are in contrast to the reversibility reported for cyclic voltammetry studies of the systems (η^5-C_5H_5)Fe$(CNR)_2X$[39] and (η^5-C_5H_5)Fe(diphos)X,[42] although the observation of 17-electron products in the latter case lends credence to the suggestion of a cationic intermediate of the type $[(\eta^5\text{-}C_5H_5)FeCOLR]^+$. High lability with respect to CO loss seems reasonable for a cationic, 17-electron (formally iron(III)) complex, and the cathodic peak observed at +0.75 V at −35 °C and scan rates of 10–50 V s^{-1} is undoubtedly a short-lived intermediate in the conversion of $[FpR]^+$ to products. Similar studies on the cleavage of FpMe in acetonitrile have given IR and ESR evidence for the species $[C_5H_5FeCO(COMe)(MeCN)]^+$.[43] There is evidence in the literature that neutral 17-electron species are also labile.[44]

In the cases of the labeled phenethyl derivates, the reactions proceeded with predominant retention of configuration (Table I, expt 5) and with complete scrambling of the methylene groups (expt 6). Thus the product distributions are similar to those obtained from chlorination cleavage reactions,[15] possibly suggesting similarities in mechanism (see below).

A coulometry experiment on the benzyl compound, $FpCH_2Ph$, in the absence of chloride ion (Et_4NClO_4 supporting electrolyte) was also carried out. Again a one-electron transfer was observed, but the electrolysis proceeded very slowly (~35 h), and periodic cleaning of the graphite anode was required to maintain the process. IR monitoring of the reaction mixture showed that, as well as an acyl species with ν_{CO} at 1726 cm^{-1}, there were also FpCl (ν_{CO} 2055, 2005 cm^{-1}; 24% yield) and a second iron carbonyl compound with ν_{CO} 2072, 2028 cm^{-1} present in the solution. The latter could not be obtained sufficiently pure to be satisfactorily characterized, but was readily converted to FpCl on treatment with Bu_4NCl. Reasonable suggestions as to its identity include $FpClO_4$,[45] $[Fp(CH_2Cl_2)]^+ClO_4^-$,[45] and $[Fp_2Cl]^+ClO_4^-$.[49] Organic products included $PhCH_2Cl$ (8%), bibenzyl (55%), and, after chromatography on alumina, $PhCH_2CO_2H$ (29%). Possible routes to these will be discussed below in conjunction with the results of the chemical cleavage reactions.

Cleavage by Copper(II) Compounds. The results of an extensive series of copper(II) halide cleavage reactions in methylene chloride are listed in Table II. Although yields varied somewhat for unknown reasons, the stoichiometry generally appears to be

$$FpR + 2CuX_2 \rightarrow FpX + RX + 2CuX \qquad (6)$$

Exceptions are cleavage of the ethyl (Table II, expt 3), *n*-butyl (expt 6), phenethyl (expt 10, 12, 14), and 3,3-dimethylbutyl (expt 25) compounds by $CuCl_2 \cdot 2H_2O$ (low yields of FpCl) and of the neopentyl compound by $CuCl_2 \cdot 2H_2O$ and $CuBr_2$ (expt 22, 23). The *sec*-butyl compound (expt 24) also appears anomalous.

Anomalies aside, the results appear to be quite consistent with the results of both the electrochemical cleavage reactions (see above) and halogen cleavage reactions, suggesting the *possibility* of a common mechanism. Interestingly, the phenethyl system is cleaved both with retention of configuration and with complete scrambling of the methylene groups, as occurs during both electrochemical (Table I, expt 5, 6) and halogen cleavage[15] reactions.

Possible Mechanisms. At this point in the discussion, it is opportune to consider the various mechanistic possibilities. Although earlier work on halogen cleavage reactions of the iron alkyl compounds has been interpreted in terms of essentially a two-electron-transfer process (eq 1),[3-5,11,16] the coulometry experiments and stoichiometry of the copper(II) halide reactions with the compounds FpR clearly demonstrate that a one-electron-transfer process (eq 2) can also be operative. It seems likely that the initial step in both cases would be formation of a 17-electron cationic species, $[FpR]^+$. In the case of copper(II) halide cleavage in CH_2Cl_2, this would presumably involve formation of an ion pair within a solvent cage (i.e., eq 7).

$$FpR + CuX_2 \rightarrow [FpR]^+[CuX_2]^- \qquad (7)$$

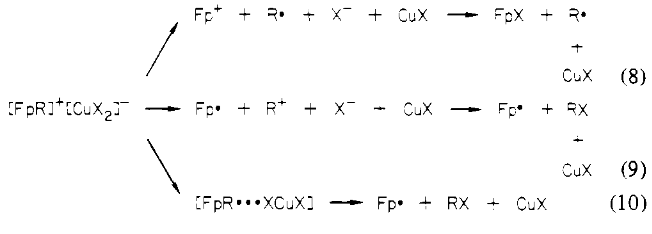
The cyclic voltammetry studies show that the cationic iron species is very labile, with a half-life $<2 \times 10^{-3}$ s at room temperature, and no paramagnetic species could be detected by ESR spectroscopy (dichloromethane solutions were allowed to proceed only partially to completion at −63 °C prior to freezing at −196 °C). Thus the ion pair must also decompose rapidly *and without significant loss of CO*, as judged by the observed stoichiometries. Several possible pathways are shown in Scheme II.

Reactions 8 and 9 involve homogeneous and heterogeneous cleavages, respectively, of the iron–carbon bond, followed by combination of cationic and anionic species. Both pathways would be expected to be consistent with the stoichiometry of eq 6. The alkyl radical would be readily scavenged by a second mole of copper(II) halide to give RX and a second mole of CuX,[50] and while ability of the iron radical, Fp·, to abstract halogen atoms from copper(II) salts is not known, abstractions of chlorine from chlorinated solvents have been reported.[44] In addition the metal-based radical $Mn(CO)_5$· apparently abstracts chlorine atoms from both copper(II) and chlorinated solvents.[51]

The third possibility, eq 10, resembles eq 9 but involves nucleophilic attack on the α-carbon atom of R by a halide ion, possibly within the solvent cage in an essentially S_N2 process, rather than via dissociation of a free carbenium ion.

Many of the experiments in Tables II and III were designed to test for one or more of the possibilities. Thus the experiments with the labeled phenethyl moiety (Table II, expt 12–15) appeared to provide evidence for the intermediacy of phenonium ions (eq 9) rather than phenethyl radicals (eq 8),[50] while the absence of 2-halo-2-methylbutenes and 2-methyl-1-butene

Scheme II



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(42) Treichel, P. M.; Molzahn, D. C.; Wagner, K. P. *J. Organomet. Chem.* **1979**, *174*, 191.

(43) Magnuson, R. H.; Zulu, S.; T'sai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887.

(44) Fabian, B. D.; Labinger, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 2239 and references therein.

(45) $FpClO_4$ does not appear to have been characterized, although solvates of the type $[Fp(solvent)]^+ClO_4^-$ are known.[46] CH_2Cl_2 solvates have been postulated as intermediates on several occasions,[47] and it would seem reasonable that $[Fp(CH_2Cl_2)]^+$ should exhibit carbonyl stretching bands at slightly higher frequencies than does FpCl. The compound $FpNO_3$, which would be similar to $FpClO_4$, exhibits carbonyl stretching bands at higher frequencies than does FpCl.[48]

(46) Williams, W. E.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1329.

(47) Reger, D. L.; Coleman, C. J.; McElligott, P. *J. Organomet. Chem.* **1979**, *171*, 73 and references therein.

(48) Dombeck, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

(49) Fischer, E. O.; Moser, E. *Z. Anorg. Allg. Chem.* **1966**, *342*, 156. Nujol mull IR spectra of this type of ion exhibit ν_{CO} at ~2075, ~2055 (sh), and ~2020 cm^{-1}, although solution spectra do not appear to have been reported.

(50) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, p 591.

(51) Hallock, S. A.; Wojcicki, A. *J. Organomet. Chem.* **1979**, *182*, 521.

from the reactions of the neopentyl compound (Table II, expt 22, 23) appeared to rule out a carbenium ion path in this case, although the products of expt 22 and 23 were anomalous.

The first recognizably useful, positive mechanistic evidence obtained was that derived from the cleavage reactions of (R)-(−)-FpCHDPh (Table II, expt 18, 19). Reaction 10, unlike reactions 8 and 9, requires inversion of configuration at the α-carbon atom of R, and the observation of >90% inversion for reactions of the labeled benzyl compound appears to be consistent with only nucleophilic attack of halide ion (or CuX_2^-) on the benzylic carbon atom. Certainly free benzyl radicals and carbenium ions can be ruled out. The neutral iron radical, Fp·, would probably be a good leaving group and would react with a second copper(II) compound. Similar oxidative cleavage mechanisms have been reported for alkylcobaloxime complexes.[52]

Many of the experiments in Table III were designed to test for the presence of Fp·. Since the iron radical is known to abstract a chlorine atom from chlorinated solvents,[44] it was expected to exhibit even greater proclivity toward abstracting the heavier halogens from methylene bromide and iodide.[53] That this is at least partially so is shown by expt 10 and 11, in which considerable amounts of FpI were formed.[55] Some abstraction from the copper(II) halides was also observed, possibly reflecting diffusion of Fp· from the solvent cage, but clearly the solvent in these cases was behaving as a fairly efficient spin trap. Lack of abstraction from CH_2Br_2 presumably reflects the greater strength of carbon–bromine bonds.[53] Similarly the lack of $PhCH_2I$ is not indicative of an absence of benzyl radicals but is consistent with the relatively low bond strength of the benzyl–iodine bond.[50]

Benzyl radicals were formed, however, in those cases where the intermediate $[FpCH_2Ph]^+$ was produced in the absence of a Lewis base sufficiently nucleophilic to displace Fp·. Reaction of $FpCH_2Ph$ with the triphenylphosphine oxide complex $Cu(NO_3)_2(OPPh_3)_2$ was carried out in refluxing 1,2-dichloroethane because it was too slow in CH_2Cl_2. In this case, the reaction apparently proceeded as in eq 8, yielding benzyl radicals, which subsequently dimerized to give a nearly quantitative yield of bibenzyl. No iron carbonyl compound was obtained, but the 16-electron cation $[Fp]^+$ is known to be very substitution labile.[56]

The coulometry experiments on $FpCH_2Ph$, listed in Table I and discussed in the previous subsection, are readily understood on the basis of the above discussion. Electrolysis clearly yielded $[FpCH_2Ph]^+$, which reacted with the chloride ion of the supporting electrolyte (Bu_4NCl) to form $PhCH_2Cl$ and Fp·. The latter would abstract chlorine from the solvent. Alternate pathways, such as oxidation of the iron radical at the anode, seem to be ruled out on the basis of the coulometry data.

The coulometry experiment with $FpCH_2Ph$, in the presence of Et_4ClO_4 rather than Bu_4NCl as supporting electrolyte, was complicated by side reactions and is not totally understood. However, bibenzyl was the major organic product here also, consistent with a mechanism involving homolysis to benzyl radicals.

Cleavage reactions of FpMe in CH_2I_2 (Table III, expt 1, 2) also produced significant amounts of FpI but no MeI. The absence of alkyl iodide is significant in these cases, because the methyl radical would be expected to abstract iodine from CH_2I_2.[54] On this basis, we suggest that FpMe resembles $FpCH_2Ph$, in that both are cleaved by copper(II) halides predominantly via eq 9.

The mechanism of the reactions of the *n*-butyl and 3,3-dimethylbutyl compounds, however, appears to be quite different. While the stoichiometries of the cleavage reactions with copper(II) halides in CH_2Cl_2 were essentially identical with those of the methyl and benzyl compounds (Table II), the pattern of products in CH_2I_2 was quite different. In these cases (Table III, expt 4, 5), small but significant amounts of alkyl iodides were formed but no FpI; clearly alkyl radicals were produced and were trapped by the solvent, but Fp· radicals were not. Thus these primary alkyl compounds appear to be cleaved by copper(II) halides via eq 8 rather than eq 9. Furthermore, in contrast to the observed behavior of Fp·, discussed above, the alkyl radicals appear to be trapped much more efficiently by copper(II) halide than by CH_2I_2. While this seems reasonable, given that primary radicals react with $CuCl_2$ with rates almost at the diffusion-controlled limit,[50] abstraction from alkyl iodides is also very rapid,[54] and it seems likely that homolysis within the solvent cage would yield relatively large amounts of alkyl iodide. On this basis, it is probable that the components of $[FpR]^+[CuX_2]^-$ diffuse from the solvent cage prior to homolysis. Conversely, if Fp· radicals also react significantly faster with copper(II) halides than with alkyl iodides, then the high yields of FpI in expt 1, 2, 10, and 11 of Table III strongly suggest that Fp· displacement during eq 10 must occur within the solvent cage rather than after diffusion of $[FpCH_2Ph]^+$ from the solvent cage. While the potential importance of solvent cage effects on metal–carbon cleavage reactions does not appear to have been seriously considered prior to this study, communications appearing while this paper was in preparation have drawn attention to similar cage effects on the cleavage of carbon–silicon[57] and carbon–tin[58] bonds.

In summary of the above arguments, it would seem that a 17-electron cationic species, $[FpR]^+$, is formed initially in each case. When R is an alkyl group (Me, $PhCH_2$) that is normally susceptible to nucleophilic attack and when a good nucleophile (Cl^-, Br^-) is available, an S_N2 process occurs with concomitant formation of alkyl halide and Fp·. When R is an alkyl group that is less susceptible to nucleophilic attack (*n*-Bu, $Me_3CCH_2CH_2$, presumably Et) or when a good nucleophile is not present, a reaction pathway involving homolysis of the iron–carbon bond and yielding alkyl radicals becomes more competitive.[59]

Apparent confirmation of these suggestions is found in the chemistry of $(\eta^5\text{-}C_5H_5)FeCOPPh_3CH_2Ph$ (Table IV). As can be seen, cleavage reactions with $CuCl_2\cdot 2H_2O$ and $CuBr_2$ in CH_2Cl_2 at room temperature yielded both $PhCH_2Cl$, the expected product of "intermolecular" attack, and bibenzyl, the expected product of homolysis. In addition, cleavage of (*R*)-(−)-$(\eta^5\text{-}C_5H_5)FeCOPPh_3CHDPh$ with $CuCl_2\cdot 2H_2O$ yielded (*S*)-(+)-PhCHDCl with >80% inversion of configuration. The contrast with the reactions of $FpCH_2Ph$ is reasonable, since the bulky triphenylphosphine should make the substituted intermediate $[(\eta^5\text{-}C_5H_5)FeCOPPh_3CH_2Ph]^+$ less

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(52) Topich, J.; Halpern, J. *Inorg. Chem.* **1979**, *18*, 1339 and references therein.

(53) Methyl radicals abstract halogen atoms from alkyl compounds with relative rates RI > RBr > RCl, as expected on the basis of relative carbon–halogen bond strengths.[54]

(54) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, p 37.

(55) Although FpCl, FpBr, and FpI have virtually identical IR and ^1H NMR spectra, their ^{13}C NMR spectra do exhibit distinguishable cyclopentadienyl resonances (84.94, 84.65, and 84.26 ppm, respectively, in $CDCl_3$).

(56) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967.

(57) Tamao, K.; Yoshida, J.; Murata, M.; Kumada, M. *J. Am. Chem. Soc.* **1980**, *102*, 3267.

(58) Eaton, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 3278.

(59) The low yields of FpCl from reactions of primary alkyl compounds with $CuCl_2\cdot 2H_2O$ (Table II, expt 3, 6, 9, 12, 14; Table III, expt 3, 4, 6) may be the result of a decreasing of the nucleophilicity of the chloride ion by hydrogen bonding to the water molecules within the solvent cage. Note that very good yields are obtained with anhydrous $CuCl_2$.

susceptible to nucleophilic attack for both steric and electronic reasons.

These results provided a test for the suggestion that the benzyl chloride was formed within the solvent cage. If the organic product of one of the two competing pathways is formed during the reaction within the solvent cage, while that from the other pathway is formed only after diffusion from the solvent cage, the relative yields of the two should be temperature dependent because of changes in solvent viscosity.[60] As can be seen, the ratio of $PhCH_2X$ to $(PhCH_2)_2$ increased dramatically on going from +23 to −78 °C, consistent with their being the products of reactions occurring within the solvent cage and after diffusion from the solvent cage, respectively.

Competition Studies. As mentioned in the Experimental Section, satisfactory kinetic characterization of the chemistry studied here could not be carried out for a variety of reasons. It seemed imperative, however, that the possibility, however slight, of direct, bimolecular attack of copper(II) salts on the iron–carbon σ-bonding orbitals (S_E2 mechanisms, as in eq 3 or 4) be ruled out as unequivocally as possible. The competition studies listed in Table V were therefore carried out with the expectation that the relative rates of disappearance of the compounds FpR (R = Me, Et, *n*-Bu) would vary considerably if a common S_E2 mechanism were operative.[62] The fact that the rates are almost independent of R is thus consistent with the postulated S_E (oxidative) mechanism, and it is interesting to note that the slight variations in rates correlate with the oxidation potentials of the compounds (Table I), suggesting that the electron-transfer step may be rate determining. The competition studies also appear to argue against an oxidative mechanism (eq 1) as has been postulated for mercury(II) halide cleavage reactions,[11] for which relative rates vary over 3 orders of magnitude.

As expected on the basis of the relative oxidation potentials, the substituted compound (η^5-C_5H_5)$FeCOPPh_3CH_2Ph$ is more reactive than its dicarbonyl analogue, $FpCH_2Ph$. The differences are not great, possibly suggesting some steric hindrance to the postulated outer-sphere electron transfer, but the results are clearly inconsistent with an S_E2 mechanism. A bimolecular process would certainly be adversely affected by the presence of the bulky phosphine.

Cleavage Reactions of $FpCH_2CH_2Ph$. We have previously shown that $FpCH_2CH_2Ph$ is generally cleaved by halogens as in eq 11.[15]

$$FpCH_2CH_2Ph + X_2 \rightarrow PhCH_2CH_2X + FpX \quad (11)$$

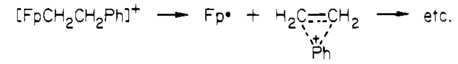
Reactions of the D-labeled analogue *threo*-FpCHDCHDPh proceeded predominantly with retention of configuration in a variety of solvents, while reactions of the ^{13}C-labeled analogue $Fp^*CH_2CH_2Ph$ yielded the phenethyl halides with complete scrambling of the methylene groups. Interestingly, chlorination and bromination reactions in methanol gave the phenethyl methyl ethers with retention of configuration and complete methylene scrambling.

The results were interpreted tentatively in terms of an S_E(oxidative) mechanism involving a two-electron transfer as in eq 1 (i.e., eq 12).

$$FpCH_2CH_2Ph + X_2 \rightarrow [Fp(CH_2CH_2Ph)X]^+X^- \quad (12)$$

It was suggested that the iron(IV) intermediate could be fluxional in a manner that would exchange the methylene groups and that it would eliminate phenethyl halide with retention of configuration. A one-electron transfer to give $[FpCH_2CH_2Ph]^+$ was ruled out because its yielding products with retention of configuration seemed unlikely without invoking dissociation of a free phenonium ion, and the latter in turn seems unlikely because reactions in the presence of equimolar amounts of "naked" fluoride ion[64] yielded no phenethyl fluoride.

However, as shown in Tables I (expt 4–6), II (expt 11–17), and III (expt 6–8), electrochemical and copper(II) cleavage reactions generally yield the same products as do the halogen cleavage reactions. The electrochemical data show unequivocally that a one-electron-transfer process is operative, and thus the results for the D- and ^{13}C-labeled compounds (Tables I–III) seem interpretable *only* in terms of a phenonium ion mechanism (i.e., eq 13).



$$[FpCH_2CH_2Ph]^+ \longrightarrow Fp\bullet + H_2C\overset{+}{\underset{Ph}{\cdots}}CH_2 \longrightarrow \text{etc.} \quad (13)$$

Consistent with this hypothesis, cleavage reactions in CH_2I_2 (Table III, expt 6, 7) produced no $PhCH_2CH_2I$, showing that the phenethyliron compound differed from the other primary alkyl compounds, FpEt and FpBu, in not undergoing homolysis to form alkyl radicals. However, it is interesting that no FpI is formed, suggesting that the presumed Fp• radicals are scavenged much more readily by copper(II) during the reactions than by solvent. This may be taken as evidence for diffusion from the solvent cage of the components of $[FpCH_2CH_2Ph]^+[CuX_2]^-$ prior to disengagement of Fp• and phenonium ion (cf. FpBu, above).

Correlations with Studies of Halogen Cleavage Reactions. A systematic study of the stoichiometry of halogen cleavage reactions of various Fp(alkyl) compounds in various solvents has not been carried out. Aside from our previous study of the phenethyl system,[15] the only general investigation reported has been that of Whitesides et al.[14] on the 3,3-dimethylbutyl system, which gives the alkyl halides in many solvents but the methyl ester of 4,4-dimethylpentanoic acid in methanol (as in eq 11).

As we have shown previously,[15] the apparent similarity between halogen and copper(II) cleavage reactions of $FpCH_2CH_2Ph$ disappears when the reactions are carried out in methanol. While halogen cleavage reactions in methanol yielded phenethyl methyl ether,[15] copper(II) salts yielded the methyl ester of 3-phenylpropionic acid[13] in a reaction that almost certainly involved $[FpCH_2CH_2Ph]^+$. Thus the ether formation provides indirect evidence that the halogenation reactions may proceed via a pathway other than a one-electron transfer, presumably one involving two electrons. Indeed, the reactions observed are well accommodated by a sequence of one-electron-transfer steps (i.e., eq 14).

$$FpR + X_2 \rightarrow [FpR]^+[X_2]^- \rightarrow [FpRX]^+[X]^- \rightarrow \text{etc.} \quad (14)$$

The first step resembles the copper(II) halide reactions (eq 7) in involving transfer of one electron to give a caged ion pair. The similarity ends here, however, because in contrast to the copper systems, the X_2^- anion in the solvent cage retains considerable oxidizing power and a second electron can be transferred *within the solvent cage*.[65,66]

Halogen cleavage reactions of *threo*- and *erythro*-$FpCHDCHDCMe_3$ to give the alkyl halides generally proceed stereospecifically with inversion of configuration,[14] results which appear to rule out the one-electron homolytic pathway

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[60] Lowering the temperature increases the viscosity of the solution; viscosity effects on reactions in solvent cages have been discussed.[61]

[61] Koenig, T.; Fischer, H. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, p 157.

[62] Steric effects on rates of S_E2-type reactions have been discussed in some detail.[63]

[63] Sayre, L. M.; Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 6001.

[64] KF solubilized with 18-crown-6; ratio of $FpCH_2CH_2Ph$ to KF ~1:1.

[65] For similar considerations of iodine cleavage of tin–carbon bonds, see: Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141.

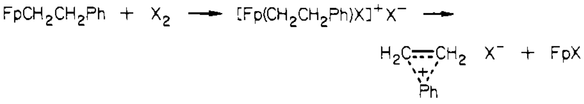
[66] Thornton, A. T.; Laurence, G. S. *J. Chem. Soc., Dalton Trans.* **1973**, 804, 1632.

(eq 8) (Table II, expt 25, 26; Table III, expt 15, 16). However, while nucleophilic displacement of Fp· from the bulky $[FpCH_2CH_2\text{-}t\text{-}Bu]^+$ by halide ion (eq 10) may not be a facile process, FpX should be a much better leaving group than Fp·, and nucleophilic displacement of the iron(II) compound from $[Fp(CH_2CH_2\text{-}t\text{-}Bu)X]^+$ by halide ion seems the best general rationale for the halogen cleavage reactions. On this basis, halogen cleavage reactions of (*R*)-(−)-FpCHDPh should be even more likely to proceed with inversion of configuation, and it was reassuring to find that chlorination and bromination reactions in CH_2Cl_2 produced the corresponding (*S*)-(+)-benzyl halides in high yields and with >75% inversion of configuration.

Finally, the idea that the chemistry of an intermediate, $[FpRX]^+[X]^-$, might occur solely within a solvent cage had not occurred to us during our earlier work on bromination of the phenethyl system. We expected that formation of a free phenonium ion in the presence of equimolar amounts of fluoride and bromide ions would result in formation of both phenethyl fluoride and bromide, but did not consider the possibility that the phenonium ion might be formed in a solvent cage in close promixity to bromide ion and not come into contact with significant amounts of fluoride ion (the amount of fluoride available in solution was limited by the rather low solubility of the 18-crown-6 complex of potassium fluoride that was used).

In retrospect, while the present investigation was winding down, it seemed possible that the competition experiments carried out were not as conclusive as had been hoped, and further experiments were carried out with the much more soluble $n\text{-}Bu_4NF$. The results of several bromination reactions of $FpCH_2CH_2Ph$ in the presence of a tenfold excess of fluoride ion are listed in Table VI, along with the *Z* values for each solvent.[67]

As can be seen, $PhCH_2CH_2F$ was formed in yields that correlated reasonably well with the extent to which ion pairs might be expected to diffuse from a solvent cage, as indicated by the *Z* values. In C_6H_6 and CH_2Cl_2, phenethyl bromide was the predominant product, presumably formed within the solvent cage. In MeCN and Me_2CO, however, formation of phenethyl fluoride became more competitive, presumably in a process that involved diffusion of the phenethyl moiety or of the components of $[FpRX]^+[X]^-$ from the solvent cage. Since, as argued above, the normal pathway for collapse of $[FpRX]^+[X]^-$ to RX presumably involved nucleophilic attack of X^- on the α-carbon atom of R (inversion of configuration), the data for the phenethyl system now seem explicable in terms of only the phenonium ion path (i.e., eq 15).



$$FpCH_2CH_2Ph + X_2 \longrightarrow [Fp(CH_2CH_2Ph)X]^+X^- \longrightarrow H_2C{=}CH_2(Ph^+)\ X^- + FpX \quad (15)$$

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Registry No. FpMe, 12080-06-7; FpEt, 32611-65-7; Fp-*n*-Bu, 69661-74-1; $FpCH_2CH_2Ph$, 32760-31-9; Fp-*threo*-CHDCHDPh, 55102-02-8; $FpCH_2Ph$, 12093-91-3; $FpCH_2SiMe_3$, 32963-17-0; (*R*)-(−)-FpCHDPh, 77944-67-3; $FpCH_2CMe_3$, 43157-77-3; Fp-*s*-Bu, 69661-73-0; $FpCH_2CH_2CMe_3$, 43157-76-2; $(\eta^5\text{-}C_5H_5)FeCO[P(OPh)_3]Me$, 12290-98-1; $(\eta^5\text{-}C_5H_5)FeCO[P(OMe)_3]CH_2Ph$, 54496-25-2; $(\eta^5\text{-}C_5H_5)FeCO(PPh_3)CH_2Ph$, 33135-99-8; $(\eta^5\text{-}C_5H_5)FeCO(PMePh_2)CH_2Ph$, 54496-24-1; $CuCl_2{\cdot}2H_2O$, 13933-17-0; $CuBr_2$, 7789-45-9; $CuCl_2$, 7447-39-4; $CuCl_2(OPPh_3)_2$, 31240-85-4; $CuBr_2(OPPh_3)_2$, 58618-32-9; $Cu(NO_3)_2(OPPh_3)_2$, 22578-21-8.

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(67) Griffiths, T. R.; Pugh, D. C. *Coord. Chem. Rev.* **1979**, *29*, 129 The *Z* values are derived from the energies of charge-transfer transitions of 1-ethyl-4-(carbomethoxy)pyridinium iodide in a range of solvents. They are a potentially useful measure of solvent polarity in the present context because they are believed to provide a measure of the extent of ion-pair association in a particular solvent.[68,69]

(68) Reference 1, Chapter 15.

(69) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3267.

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Photochemical Reaction of $Mn_2(CO)_{10}$ with Pyridine: Evidence for a Radical Pathway[1a]

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The photochemical reaction of $Mn_2(CO)_{10}$ with pyridine and several alkyl- and halogen-substituted pyridines as neat solvents has been studied. Initial products of the reaction are $Mn_2(CO)_9py$ and $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$, formed concurrently in roughly comparable amounts. Continued photolysis leads eventually to $[Mn(py)_6^{2+}][Mn(CO)_5^-]_2$ as final product. Addition of CO results in a shift in initial product distribution toward the nonionic product. Addition of galvinoxyl results in a slower rate of conversion of $Mn_2(CO)_{10}$ to products. The rate of conversion of $Mn_2(CO)_{10}$ to products is increased slightly for 4-alkyl-substituted pyridines and decreased markedly for 3-chloro- or 3-bromopyridine. In addition, the relative amount of ionic product is slightly higher for the alkylpyridines and markedly lower for the halogen-substituted compounds. The results support a mechanism involving a homolytic cleavage of the metal–metal bond, followed by rapid pyridine substitution into the $Mn(CO)_5\cdot$ radical. There follows an electron transfer, probably from $Mn(CO)_3(py)_2\cdot$, to $Mn_2(CO)_{10}$, leading to the formation of $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$.

Introduction

In recent years there has been a growing interest in the formation and reactivity of metal-centered radicals. One widely employed means of producing transition-metal carbonyl radicals involves photolysis of a dinuclear metal carbonyl compound.[2] Gray and co-workers have assigned the strong absorption in the UV spectrum of $M_2(CO)_{2n}$ complexes as a $\sigma \rightarrow \sigma^*$ transition characteristic of the metal–metal bond.[3]

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(1) (a) This research was supported by the National Science Foundation through Research Grant CHE76-17570. (b) Eli Lilly Fellowship, 1977–1978; Sohio Fellowship, 1980–1981.

(2) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 3533.

(3) Levenson, R. A.; Gray, H. B.; Ceasar, G. P. *J. Am. Chem. Soc.* **1970**, *92*, 3653.

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