Some Transition Metal Derivatives of Ferrocene

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Complexes of the general formulation LM–X–Fc and LMFc (L = η^5-C_5H_5, CO, PR_3; X = CO, CH_2, CH_2CO; Fc = $C_5H_4FeC_5H_5$; M = Fe, W, Mo, Mn) have been prepared using the salt elimination reaction between the appropriate transition metal carbonylate anion and halo-substituted ferrocenes. The spectral and chemical properties of the complexes have been studied. The mass spectral fragmentation data reveals several examples of ligand transfer from the ferrocene iron atom to the other metal and significant metal–metal bonding. Electrochemical studies indicate that redox properties of the two metal centers are independent of one another. The acyl derivatives LMCOFc readily decarbonylate thermally to LMFc, in the case of LM = $(\eta^5$-$C_5H_5)Fe(CO)_2$, this being one of the few such thermal decarbonylations observed.

Studies on the chemistry of the metal–carbon bond have occupied a central position in transition metal chemistry because of the intermediacy of such bonds in catalytic processes both industrial and biological.[1] Recently, it has become clear that new metal–carbon bonded complexes can be synthesized and studied using special alkyl ligands that impart a greater thermal and oxidative stability in comparison with the simple alkyl ligands, methyl, ethyl, etc.[2] Examples are the recent studies on the use of silylmethyl ligands to form many new complexes with very distinctive chemical characteristics.[3-5] The overall greater thermal and oxidative stability of the nonfunctionally substituted silylmethyl ligands (cf. methyl metal complexes) can, in part, be attributed to the steric bulk of the silylmethyl ligand partially protecting the central metal atom. We have sought to find other such ligands and report here on some initial studies using ferrocene as one such ligand. This potential ligand also has a large steric requirement and also offers the opportunity to study what interactions, if any, occur between the iron atom of the ligand and the central substituted metal atom. For example, McCleverty et al., have reported that the electrochemical oxidation of a ferrocenylcarbenechromium pentacarbonyl complex exhibits a single one-electron oxidation rather than the two single one-electron oxidations expected, i.e., $Cr^0 \rightarrow Cr^+$ and $Fe^{2+} \rightarrow Fe^{3+}$.[6] They suggested that this resulted from the highest occupied molecular orbital of the complex encompassing both metal centers. In the present paper we report the initial results of a study using the various substituted ferrocenes as ligands σ bonded to a central transition metal directly via the cyclopentadienyl ring of the ferrocene or via a bridging methylene, ketonic carbonyl, or ketenyl radical. While this work was in progress[7] the preparation of some of the complexes was reported by Nesmeyanov and co-workers.[8]

Experimental Section

All chemical manipulations were performed under a nitrogen atmosphere, using dry oxygen free solvents. Infrared data were obtained using a Perkin-Elmer 421 spectrometer, NMR data using a Perkin-Elmer R12 spectrometer, and mass spectra were recorded on a DuPont Double Focusing Instrument, Model 492. Chemical analyses were performed by Heterocyclic Chemical Corp. or Mr. and Mrs. A. Olney, University of Sussex, Sussex, England.

Starting transition metal complexes (non-ferrocene) were obtained from Strem Chemicals; the ferrocene complexes were obtained from Wind River Chemicals.

Preparation of $(\eta^5$-$C_5H_5)W(CO)_3CH_2COFc$. To a glyme solution of $(\eta^5$-$C_5H_5)W(CO)_3^-Na^+$ (5.0 mmol) prepared from $W(CO)_6$ and sodium cyclopentadienide was added chloroacetylferrocene (1.32 g, 5.0 mmol). The solution was stirred for 10 h at room temperature, and the solvent was then removed to leave crude products. This residue was extracted with a 50/50 mixture of diethyl ether/methylene chloride and the solution was placed upon an alumina column and the column developed with CH_2Cl_2. The first band collected was identified as the starting chloroacetylferrocene, and a second band, eluted with diethyl ether, was identified as the title complex (40%

yield), mp 124–127 °C. Anal. Calcd: C, 42.9; H, 2.87. Found: C, 41.7; H, 3.12.

Preparation of $(\eta^5$-$C_5H_5)Fe(CO)_2CH_2COFc$. A solution of $(\eta^5$-$C_5H_5)Fe(CO)_2^-Na^+$ (12 mmol) was prepared by cleavage of $[(\eta^5$-$C_5H_5)Fe(CO)_2]_2$ with excess Na/Hg in THF. Subsequent to removal of the amalgam the THF solvent was removed in vacuo. To the dry sodium salt was added 50 ml of cyclohexane. To the resulting slurry was added 11 mmol of chloroacetylferrocene and the mixture was stirred for 10 h at which time the solvent was removed. The residue was extracted twice with 15 ml of CH_2Cl_2 and the crude products were placed upon an alumina column. Elution with hexane/diethyl ether (70/30) separated a product that was identified as acetylferrocene, while a second product eluted with diethyl ether was identified as the title complex (10% yield), mp 112–115 °C. Anal. Calcd: C, 55.5; H, 3.72. Found: C, 56.3; H, 3.77. Attempts to make the complex using THF solvent were uniformly unsuccessful, the main isolated product being acetylferrocene. η^5-Cyclopentadienyliron dicarbonyl chloride was the other product isolated in this reaction indicating that metal halogen exchange took place in the more polar THF. An exactly analogous reaction occurred when we attempted to synthesize the related cyclopentadienylmolybdenum tricarbonyl complex. Even using cyclohexane as solvent none of the desired molybdenum acetylferrocene complex could be obtained, only acetylferrocene and cyclopentadienylmolybdenum tricarbonyl chloride were isolated.

Preparation of $(\eta^5$-$C_5H_5)W(CO)_3COFc$. To a dimethoxyethane solution of $(\eta^5$-$C_5H_5)W(CO)_3^-Na^+$ (20 mmol) was added dropwise chlorocarbonylferrocene, 20 mmol, in 20 ml of THF. The resulting mixture was stirred for 12 h and the solvent was removed in vacuo. The residue was recrystallized from CH_2Cl_2/hexane solution to yield 20% of the title product, mp 147 °C dec. Also prepared by the same general technique were: $(\eta^5$-$C_5H_5)Fe(CO)_2COFc$, 18%, mp = 155 °C dec; $(\eta^5$-$C_5H_5)Mo(CO)_3Fc$, 16%, mp = 140 °C dec (thermal decarbonylation takes place in the reaction medium, no acylferrocene derivative of molybdenum was ever observed).

Preparation of $(\eta^5$-$C_5H_5)Fe(CO)_2Fc$. **(a) Photochemical.** A solution of $(\eta^5$-$C_5H_5)Fe(CO)_2COFc$ (0.7 mmol) in 25 ml of benzene was irradiated for 24 h in a quartz flask. The solvent was removed and the crude product was placed upon an alumina column. The title product was obtained by eluting with a 50/50 CH_2Cl_2/hexane mixture in 36% yield, mp 100–106 °C.

(b) Thermal. A solution of $(\eta^5$-$C_5H_5)Fe(CO)_2COFc$ (0.7 mmol) in 45 ml of 2,2,4-trimethylpentane (bp 99.2 °C) was refluxed for 45 h. The solvent was removed and the crude product was placed upon an alumina column. A first yellow band was eluted with CH_2Cl_2/hexane (20/80) and identified as the starting acyl complex. A second orange band was obtained eluting with CH_2Cl_2 and identified as $(\eta^5$-$C_5H_5)Fe(CO)_2Fc$, 23% yield. Also prepared by the same techniques (a) and (b) above from $(\eta^5$-$C_5H_5)W(CO)_3COFc$ was $(\eta^5$-$C_5H_5)W(CO)_3Fc$, 20%, mp 170–173 °C dec.

Preparation of $(\eta^5$-$C_5H_5)Fe(CO)_2CH_2Fc$. To a THF solution of $(\eta^5$-$C_5H_5)Fe(CO)_2^-Na^+$ prepared from 3.2 mmol of $[(\eta^5$-$C_5H_5)Fe(CO)_2]_2$ was added slowly 5.9 mmol of freshly prepared[16] chloromethylferrocene in 20 ml of THF. The resulting solution was stirred for 24 h and the solvent was removed. The crude product was extracted with CH_2Cl_2 and purified by column chromatography to give the title product in 16% yield, mp 119–123 °C. Anal. Calcd: C, 56.4; H, 3.98. Found: C, 55.7, H, 3.77. A considerable amount

Table I. Infrared Data of LMXFc

LM	X	(C≡O)	(C=O)
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2$		2017; 1970	
	CH₂	2004; 1952	
	CO	2014; 1954	(1596)[a]
	CH₂CO	2022; 1965	(1626)
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3$		2025; 1938; 1930	
	CH₂	2014; 1930; 1922	
	CO	2020; 1937; 1922	(1588)[a]
	CH₂CO	2030; 1918 bd	(1615)
Mn(CO)₅	CH₂	2040 (w); 2104 (w); 1987 (w); 2010 (s); 2004 (s)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3$		2025; 1948; 1941	

[a] CH₂Cl₂ solution.

of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$ was also found. Also prepared by the same general technique were: $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{CH}_2\text{Fc}$, mp = 139–42 °C dec; $(\text{CO})_5\text{MnCH}_2\text{Fc}$, mp = 74–76 °C.

Cyclic voltammetry experiments were performed on 2.1×10^{-4} M solutions in acetonitrile with 0.1 M tetraethyl ammonium perchlorate as supporting electrolyte. All solutions were degassed prior to, and maintained under a nitrogen atmosphere during, the experiment. Sweep rates were varied from 0.1 to 0.01 V/s. Since the oxidations associated with the substituted metal (non-ferrocene) were non-reversible both electrochemically and chemically the potentials measured by the cyclic voltammetry varied considerably with both concentration and scan rate. In this initial exploratory investigation the data cited were obtained mainly to illustrate the qualitative aspects of the system and the specific potentials obtained should not be assigned too great a significance.

Results and Discussion

The present work has illustrated that the general techniques of salt elimination between transition metal carbonylate anions and various chloro-substituted ferrocenes may be used satisfactorily to prepare transition metal derivatives of ferrocene. The thermal and oxidative stability of the resulting complexes more closely resemble those characteristic of the ferrocene portion of the complex than the carbonylate metal portion. For example, while most alkyl complexes of the cyclopentadienyliron dicarbonyl system are low melting, relatively oxygen sensitive waxes, the ferrocene derivatives described here are high melting, air stable complexes. The acyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{–CO–Fc}$ may be readily decarbonylated thermally to the corresponding complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Fc}$. This thermal decarbonylation is in direct contrast to the inability to thermally decarbonylate the unsubstituted complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{COCH}_3$, which only yields the related methyl complex via photochemical reaction. It has been shown that the steric bulk of ligands plays a very important role in ligand dissociation leading to decarbonylations,[10] and this is probably the cause of the observed thermal decarbonylation of the ferrocenoyl iron complex. The tungsten ferrocenoyl complex readily decarbonylates thermally as does the corresponding acetyl complex, while the molybdenum ferrocenoyl complex decarbonylates thermally so rapidly that no evidence for its existence could be obtained in this study, and only the resulting ferrocenyl complex, $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{Fc}$, has been isolated.
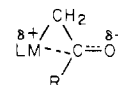
Spectral Properties

The infrared and ^{1}H NMR spectral properties of the complexes are recorded in Tables I and II and are totally in accord with the proposed structures. Although many of the complexes contain three distinct cyclopentadienyl groups the analysis of the ^{1}H NMR data is not problematical. The protons of the substituted cyclopentadienyl ring, $\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5$, occur as a pair of broad triplets except in the case of the methylferrocenyl complexes, LMCH₂Fc, where resonances for these protons and those of the unsubstituted cyclopentadienyl ring of the ferrocenyl ligand are observed as one single resonance. In all the other complexes the unsubstituted cyclopentadienyl protons of the ferrocene appear as a sharp singlet around τ 6.0, while the protons of the cyclopentadienylmetal carbonyl system uniformly occur as a singlet at considerably lower field.

For the complexes LMFc the terminal carbonyl stretching frequencies are at high frequency compared to the corresponding methyl complexes LMCH₃, although the methylferrocenyl complexes LMCH₂Fc do not exhibit such a shift. This indicates that a mesomeric effect is removing electron density from the central metal into the aromatic ferrocene cyclopentadienyl ring and no inductive electron withdrawal is operating. The ketenyl- and carbonylferrocenyl complexes, LMCH₂COFc and LMCOFc, also exhibit higher stretching frequencies for the terminal carbonyl groups. This effect has been noted before for the acyl complexes, LMCOCH₃, and is due to the removal of electron density from the central metal by the contribution of the resonance form

$$\text{LM}^+=\text{C}-\text{O}^-$$
$$\underset{R}{|}$$
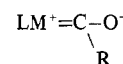
which restricts retrodative π bonding into the antibonding orbitals of the terminal carbon monoxide ligands, thus increasing the C≡O bond order and stretching frequency. For the ketenyl system, LMCH₂COFc, the increase in terminal stretching frequency is even higher, and the ketonic stretching frequency is also appreciably lowered in comparison with acetyl ferrocene, i.e., $\nu(\text{C}=\text{O})$ for LMCH₂COFc = 1620 cm^{-1}, cf., for CH₃COFc = 1684 cm^{-1}. These two observations indicate a considerable electron withdrawal from the central metal to the ketonic group. This can either be an inductive effect or possibly a 1,3 π interaction placing some d-orbital electron density directly into the π-antibonding orbital of the ketonic group, i.e.

$$\overset{\text{CH}_2}{\underset{R}{\overset{\delta+}{\text{LM}}\cdots\overset{\delta-}{\underset{}{\text{C}}}=\text{O}}}$$

We are investigating the physical and chemical properties of other more orthodox ketenyl metal systems LMCH₂COR, R = Me, Ar, etc., to obtain more information concerning this possible 1,3 interaction.

Mass Spectra

The mass spectral fragmentation patterns of the cyclopentadienyl metal carbonyl complexes were recorded and the

Table II. ^{1}H NMR Data LMXFc

LM	X	$(\eta^5\text{-C}_5\text{H}_5)\text{M}$	$(\eta^5\text{-C}_5\text{H}_5)\text{Fc}$		$\text{C}_5\text{H}_4\text{Fc}$		Other
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2$		5.17	6.02		5.87	6.20	
	CH₂	5.30		5.85			7.40 (CH₂)
	CO	5.10	5.80		5.44	5.70	
	CH₂CO	5.26	5.89		5.34	5.64	7.93 (CH₂)
$(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3$		4.65	6.02		5.80	6.02	
	CH₂	4.65		5.85			7.15 (CH₂)
	CO	4.42	5.95		5.68	5.78	
	CH₂CO	4.50	5.86		5.32	5.62	6.81 (CH₂)
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3$		4.72	6.08		5.80	6.12	
(CO)₅Mn	CH₂			5.80			7.75 (CH₂)

Table III

m/e	Ion	Rel intensity
546	$C_5H_5W(CO)_3COC_5H_4FeC_5H_5^+$	7
518	$C_5H_5W(CO)_2COC_5H_4FeC_5H_5^+$	57
490	$C_5H_5W(CO)COC_5H_4FeC_5H_5^+$	28
462	$C_5H_5WCOC_5H_4FeC_5H_5^+$	57
434	$C_5H_5WC_5H_4FeC_5H_5^+$	100
432	$C_5H_4WC_5H_4FeC_5H_4^+$	100
408	$C_5H_4WC_5H_2FeC_5H_5^+$	21
406	$C_5H_4WC_3H_2FeC_5H_4^+$	21
378	$W(C_5H_4)(C_5H_5)_2^+$	14
369	$W(C_5H_4)FeC_5H_5^+$	11
352	$(C_3H_3)W(C_5H_5)_2^+$	11
350	$C_3H_3W(C_5H_4)_2^+$	11
343	$C_5H_5WFeC_3H_2^+$	14
305	$C_5H_5W(CO)_2^+$	7
287	$C_5H_5WC_3H_3^+$	7
277	$C_5H_5W(CO)^+$	11
186	$C_5H_5FeC_5H_5^+$	27
560	$C_5H_5W(CO)_3CH_2COC_5H_4FeC_5H_5^+$	7
532	$C_5H_5W(CO)_2CH_2COC_5H_4FeC_5H_5^+$	30
504	$C_5H_5W(CO)CH_2COC_5H_4FeC_5H_5^+$	7
476	$C_5H_5WCH_2COC_5H_4FeC_5H_5^+$	100
448	$C_5H_5WCH_2C_5H_4FeC_5H_5^+$	25
432	$C_5H_4WC_5H_4FeC_5H_4^+$	6
383	$WCH_2C_5H_4FeC_5H_5^+$	13
372	$C_5H_5FeC_5H_5C_5H_5FeC_5H_5^+$	10
333	$C_5H_5W(CO)_3^+$	10
305	$C_5H_5W(CO)_2^+$	10
277	$C_5H_5WCO^+$	7
228	$CH_3COC_5H_4FeC_5H_5^+$	60
518	$C_5H_5W(CO)_3C_5H_4FeC_5H_5^+$	62
490	$C_5H_5W(CO)_2C_5H_4FeC_5H_5^+$	27
462	$C_5H_5W(CO)C_5H_4FeC_5H_5^+$	31
434	$C_5H_5WC_5H_4FeC_5H_5^+$	100
432	$C_5H_4WC_5H_4FeC_5H_4^+$	100
408	$C_3H_3WC_5H_4FeC_5H_5^+$	20
378	$WC_5H_4(C_5H_5)_2^+$	17
376	$W(C_5H_4)_3^+$	17
369	$(C_5H_5)^+WC_5H_4Fe$	21
352	$C_3H_3WC_5H_4(C_5H_5)^+$	13
329	$C_5H_5WC_6H_6^+$	13
305	$WC_5H_5(CO)_2^+$	10
277	$WC_5H_5(CO)^+$	13
186	$C_5H_5FeC_5H_5^+$	6

m/e	Ion	Rel intensity
390	$C_5H_5Fe(CO)_2COC_5H_4FeC_5H_5^+$	11
362	$C_5H_5FE(CO)COC_5H_4FeC_5H_5^+$	46
334	$C_5H_5FeCOC_5H_4FeC_5H_5^+$	15
306	$C_5H_5FeC_5H_4FeC_5H_5^+$	100
304	$C_5H_4FeC_5H_4FeC_5H_4^+$	100
279	$C_3H_3FeC_5H_4FeC_5H_4^+$	5
266	$C_2H_2FeC_5H_4FeC_5H_4^+$	5
250	$Fe(C_5H_5)_2C_5H_4^+$	11
212	$C_2H_2Fe(C_5H_5)_2^+$	33
186	$C_5H_5FeC_5H_5^+$	35
177	$Fe(CO)_2C_5H_5^+$	5
151	$C_3H_3Fe(CO)_2^+$	3
148	$C_5H_5FeCO^+$	3
121	$C_5H_5Fe^+$	33
248	$Fe(C_5H_4)^+$	12
404	$C_5H_5Fe(CO)_2CH_2COC_5H_4FeC_5H_5^+$	21
348	$C_5H_5FeCH_2COC_5H_4FeC_5H_5^+$	100
306	$C_5H_5FeC_5H_4FeC_5H_5^+$	37
304	$C_5H_4FeC_5H_4FeC_5H_4^+$	35
283	$FeCH_2COC_5H_4FeC_5H_5^+$	6
241	$C_5H_5FeC_5H_4Fe^+$	16
228	$C_5H_5FeC_5H_4COCH_3^+$	57
179	$C_5H_5Fe(CO)_2^+$	27
149	$C_5H_5Fe(CO)^+$	10
121	$C_5H_5Fe^+$	10
145	$[C_5H_5FeC_5H_4COCH_2-]_2^+$	6
362	$C_5H_5Fe(CO)_2C_5H_4FeC_5H_5^+$	100
306	$C_5H_5FeC_5H_4FeC_5H_5^+$	75
304	$C_5H_4FeC_5H_4FeC_5H_4^+$	75
279	$C_3H_3FeC_5H_4FeC_5H_4^+$	2
250	$FeC_5H_4(C_5H_5)_2^+$	52
248	$Fe(C_5H_4)_3^+$	52
224	$C_3H_3FeC_5H_4(C_5H_5)^+$	6
216	$C_3H_3FeC_5H_5(CO)_2^+$	20
186	$C_5H_5FeC_5H_5^+$	104
177	$Fe(CO)_2C_5H_5^+$	18
112	$FeFe^+$	100

data are collected in Table III. All the complexes exhibited parent ions confirming their structural assignments and exhibited those ions expected from loss of terminal carbonyl ligands. Subsequent to the loss of all terminal carbonyl groups some interesting fragmentations and migrations may be observed. The fragmentation pattern of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Fc$ is outlined in Scheme I as typical of the data compiled in Table III for all the complexes studied.

This particular complex loses both terminal carbonyl groups simultaneously as witnessed by a metastable peak at m/e 258.7 for the process $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}Fc]^+$ (m/e 362) → $[(\eta^5\text{-}C_5H_5)FeFc]^+$ (m/e 306). Although the simultaneous loss of both carbonyls has been observed for the general system $(\eta^5\text{-}C_5H_5)Mn(CO)_2L$, L = olefin, acetylene,[11] this is the first such observation for the $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ system. Normally such complexes are thermally unstable in the mass spectrometer and either ions related to various ferrocene derivatives are observed, or in one report, using special mass spectrometer conditions involving the presence of iodine, iodo derivatives of the iron complexes.[12] Parent ions and stepwise loss of carbonyl groups have, however, been observed for certain silylmethyl derivatives, e.g., $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_3$, under mild mass spectrometer operating conditions.[13] Both the iron ketenyl- and acylferrocene complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}CH_2COFc$ and $-COFc$ exhibit stepwise loss of the carbonyl groups, three in the case of the acyl complex. This latter observation indicates clearly that

the mass spectral fragmentation pattern of the acyl complex does not involve the intermediacy of the decarbonylated product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Fc]^+$, i.e., the process involves loss of the two terminal CO groups prior to the migration of the ferrocene ligand to the other iron atom with final loss of the third CO group. For the ketenyl complex expulsion of ketene is observed, verified by the corresponding metastable ion, $[(\eta^5\text{-}C_5H_5)Fe(CH_2COFc)]^+$ (m/e 348) → $[(\eta^5\text{-}C_5H_5)FeFc]^+$ + CH_2CO (m/e 306, $m^* = 269.1$).

The ion resulting from the above expulsions, namely $[(C_5H_5)_2(C_5H_4)Fe_2]^+$, probably possesses the structure expected from the mode of formation, i.e.,
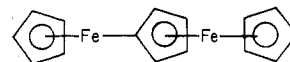
This ion is closely related to, but not identical with, the so-called triple decker ions observed by King in the mass spectrum of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$[12]
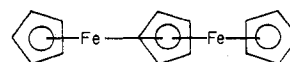
There are three major fragmentation routes for this new ion species; (a) loss of hydrogen, (b) loss of acetylene, and (c) loss of an iron atom.

(a) The loss of hydrogen is the most characteristic feature of the fragmentation pattern of the ion to form the novel ionic

Scheme I

Figure 1.
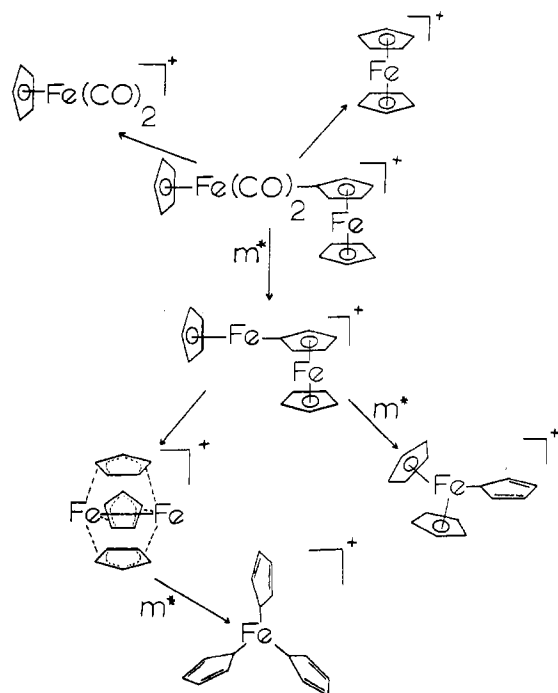
species $[(C_5H_4)_3Fe_2]^+$. The nature of this ion is uncertain; however, the great abundance, carrying up to 18% of the total ion current of the complexes, suggests some special stability. It is not insignificant that the C_5H_4 species can be thought of as comprising two 3-electron allyl ligands, and thus three bridging C_5H_4 groups coupled to a metal–metal bond will provide an inert gas configuration to the resulting ion and account for the apparent special stability. The expulsion of an iron atom from this species is observed accompanied by the appropriate metastable ion at 202.3. The resulting $[(C_5H_4)_3Fe]^+$ ion illustrates the overall transfer of one of the original cyclopentadienyl groups from one iron atom to the other. While it is not possible to state which iron atom of the original structure is the donor and which the acceptor in this migration process, the corresponding complexes (η^5-$C_5H_5)M(CO)_3Fc$, M = Mo, W, also exhibit such a transfer, exclusively resulting in the formation of $(C_5H_4)_3M$, i.e., showing that the ferrocenyl cyclopentadiene ligand is transferred to the other metal atom.

(b) The loss of acetylene from cyclopentadienyl iron complexes has been observed previously and is totally expected.[12]

(c) The loss of iron from the $[(C_5H_5)_2(C_5H_4)Fe_2]^+$ ion is closely related to that expulsion observed from $[(C_5H_4)_3Fe_2]^+$ and again examination of the related W and Mo spectra indicates that a transfer of the C_5H_5 group from ferrocene to the other metal has occurred.

Ions resulting from the cleavage of the ferrocene iron bond to produce $[(C_5H_5)Fe(CO)_2]^+$ and $[(C_5H_4)Fe(C_5H_5)]^+$ are observed in some abundance as might be expected. These ions fragment in a fashion that has previously been observed.[12] The mass spectra of the ketenyl ferrocene complexes, $LMCH_2COFc$, all exhibit ions resulting from an instrument catalyzed reduction by water of the ketenyl complex to yield acetylferrocene. Such behavior has been previously reported for organic haloacetyl compounds, i.e., $[XCH_2COR]^+ \rightarrow [CH_3COR]^+$,[14] $[CH_3COFc]^+$ representing 20% of the ion current.

The spectral properties of the other ferrocenyl complexes were essentially the same as those commented on above for the iron complex, with the important exception that only trace
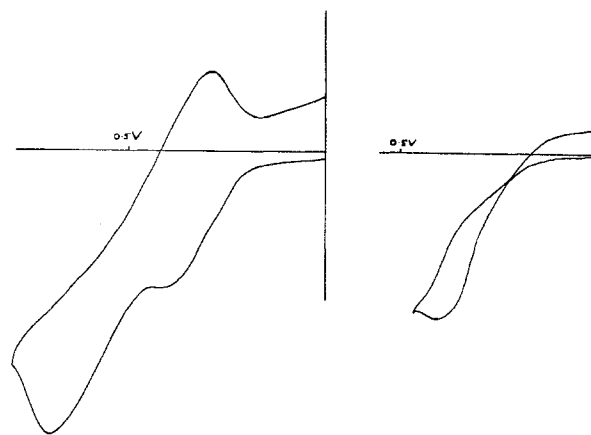
abundances of ions representing a simple diatomic metal–metal bonded ion were observed, whereas in the case of the iron ferrocene complexes the ion $[Fe_2]^+$ m/e 112 is a very important contribution to the total ion current, 25% of the base ion.

Electrochemical Studies

The observation of possible metal–metal bonding in the mass spectral fragmentation patterns of the new ferrocenyl complexes, coupled to the published observation by McCleverty and co-workers mentioned in the introduction, led us to perform an exploratory electrochemical redox investigation of the new complexes. The cyclic voltammogram of (η^5-$C_5H_5)Fe(CO)_2CH_2Fc$ is illustrated in Figure 1, showing the anodic sweep.

Two distinct oxidation waves are observed, contrary to the single wave observed by McCleverty for the ferrocenyl-carbenechromium pentacarbonyl complex. It is further apparent that only one of the two oxidation waves is reversible. Cyclic voltammograms run in our laboratories on other cyclopentadienyliron dicarbonyl complexes uniformly exhibit one single irreversible oxidation wave, similar to those reported by Dessy et al.[15] We can thus separate the two observed oxidation waves into the expected reversible wave for the ferrocene iron oxidation, $Fe^{II} \rightarrow Fe^{III}$, and the irreversible wave for the cyclopentadienyl iron oxidation process. The acyl complexes (η^5-$C_5H_5)Fe(CO)_2COFc$ and (η^5-$C_5H_5)Fe(CO)_2Fc$ were also investigated and showed similar two-wave cyclics. For the acyl complex one again was reversible and one irreversible as for the illustrated example. The complex (η^5-$C_5H_5)Fe(CO)_2Fc$ possesses two irreversible waves, and it is clear from the cyclic on this complex that a new species forms which possesses a completely reversible oxidation wave at lower potential. Further examination of this system indicates that ferrocene is formed by the destructive oxidation of the complex, accounting for this observed pattern. We have attempted to synthesize charge transfer complexes of the corresponding ferrocenium ion using tetracyanoethylene; however, this technique has not as yet been successful. The chemical and electrochemical oxidation studies on the complexes are incomplete, and work will continue on this aspect of ferrocene metal complexes. However, the work does illustrate the lack of any significant metal–metal interactions related to those postulated for the ferrocenylcarbenechromium complex. The reasons for the difference in behavior must await a more detailed and instructive electrochemical investigation.

voltammetry equipment and explanation and assistance on its use.

Registry No. (η^5-C$_5$H$_5$)W(CO)$_3$CH$_2$COFc, 60349-55-5; (η^5-C$_5$H$_5$)Fe(CO)$_2$CH$_2$COFc, 54804-00-1; (η^5-C$_5$H$_5$)W(CO)$_3$COFc, 52680-31-6; (η^5-C$_5$H$_5$)Fe(CO)$_2$COFc, 52462-21-2; (η^5-C$_5$H$_5$)-Mo(CO)$_3$Fc, 60349-56-6; (η^5-C$_5$H$_5$)Fe(CO)$_2$Fc, 11067-36-0; (η^5-C$_5$H$_5$)Fe(CO)$_2$CH$_2$Fc, 60349-57-7; (η^5-C$_5$H$_5$)W(CO)$_3$CH$_2$Fc, 60349-58-8; (CO)$_5$MnCH$_2$Fc, 60349-59-9; W(CO)$_6$, 14040-11-0; chloroacetylferrocene, 51862-24-9; [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$, 12154-95-9; (η^5-C$_5$H$_5$)W(CO)$_3^-$Na$^+$, 12107-36-7; chlorocarbonylferrocene, 1293-79-4; chloromethylferrocene, 12093-15-1; (η^5-C$_5$H$_5$)W(CO)$_3$Fc, 52472-04-5.

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(16) In our hands the use of chloromethylferrocene that had been stored at −10 °C for periods in excess of a week was less than satisfactory. The synthetic technique used was that of ref 9.

Reactivity of Cyclopalladated Compounds. 4.[1] Crystal and Molecular Structures of Tetra-*n*-butylammonium Chlorobromo(*N*-(phenylamino)-α-methylbenzylidenimino-2-*C,N*)palladate(II) and *trans*-Chloro(*N*-(phenylamino)-α-methylbenzylidenimino-2-*C,N*)bis-(triethylphosphine)palladium(II)

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The crystal structures of [(*n*-Bu)$_4$N]$^+$[Pd(C–N)ClBr]$^-$ and [Pd(C–N)(PEt$_3$)$_2$Cl] where (C–N) is the ligand *N*-(phenylamino)-α-methylbenzylidenimino-2-*C,N*, have been determined by single-crystal diffraction methods. The first structure exhibits slight disorder: the halide trans to the carbon atom is 80% bromide and 20% chloride with the reverse proportions trans to the nitrogen atom. A proton of the [(*n*-Bu)$_4$N]$^+$ cation belongs to the coordination sphere of the metal atom. The second structure shows that in this compound the direct coordination polyhedron of the palladium atom is not planar and that the ligand is distorted relative to the first structure. The relations between these distortions and the great reactivity of this compound are discussed.

Introduction

The synthesis of metallocyclic compounds and study of their chemical properties have undergone considerable development over the last few years.[4] We are interested in the reactivities of cyclopalladated dimers of the type
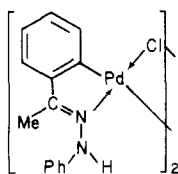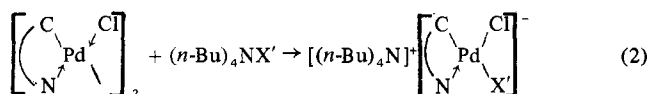

and of the monomers obtained by bridge-cleavage reactions on these dimers.[1,5-7]

According to reactions 1 and 2, addition of tetraalkyl-
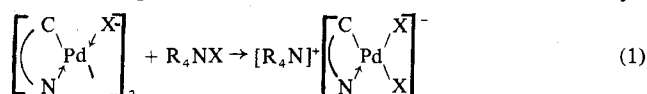

$$X = Cl, Br, I$$
$$R = Et, n\text{-Bu}$$

$$X' = Br, I$$

ammonium halides to cyclopalladated dimers [Pd(C–N)X]$_2$ leads to two types of compounds.[6] Compounds of the second type are mixed anionic species which can also be synthesized by making use of the lability of pyridine,[8] according to reaction 3. The complexes obtained by reaction 3 are the same as those
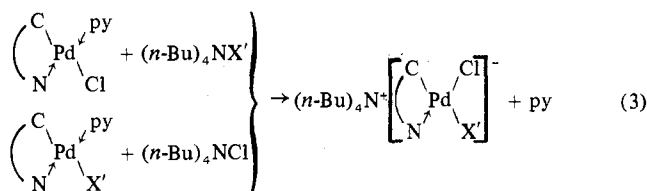
obtained by reaction 2.

Similar results have recently been reported for the compounds[9,10]
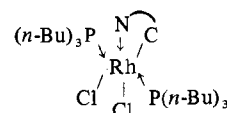
where (C–N) = 2-vinylpyridine or benzo[*h*]quinoline.

In these cases also, addition of lithium bromide or lithium iodide causes substitution of the chlorine trans to the carbon while the chlorine trans to the nitrogen cannot be displaced.