

Figure 4. Model for the photochemical behavior of $[\text{Rh}(\text{tren})\text{Cl}_2]^+$ based upon the formation of a trigonal-bipyramid intermediate.

tertiary amine. The ordering of these two steps is not important (Scheme I).

In summary, the distortions represented in Figure 4 account for the stereospecific photochemistry of $[\text{Rh}(\text{tren})\text{Cl}_2]^+$. The resulting conclusion that the ligands cis to the tertiary amine are photolabile, while those trans to the tertiary amine are photoinert, readily accounts for the photochemical behavior of α - and β - $[\text{Rh}(\text{tren})\text{Cl}(\text{OH}_2)]^{2+}$. Population of the antibonding e_g -derived orbitals would inhibit σ donation to the metal, so that Rh-Cl and Rh-N bond lengthening would result. Relief of intraligand repulsions within the tren ligand would be possible if Rh-Cl bond lengthening is accompanied by an opening of the amine-Rh-amine angles from ca. 90° (ground state) toward 120° (TBP). Such a concerted process would favor exclusion of the chlorine cis to the tertiary amine, for loss of the trans chloride would not significantly reduce intraligand repulsions. Work is currently in progress to determine whether a TBP model is useful in other, non-tren complexes.

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Registry No. $[\text{Rh}(\text{tren})\text{Cl}_2]^+$, 56026-84-7; α - $[\text{Rh}(\text{tren})\text{Cl}(\text{OH}_2)]^{2+}$, 67124-78-1; β - $[\text{Rh}(\text{tren})\text{Cl}(\text{OH}_2)]^{2+}$, 67179-21-9; $[\text{Rh}(\text{tren})\text{Cl}_2]\text{ClO}_4$, 67124-79-2; $[\text{Rh}(\text{tren})\text{Cl}_2]\text{Cl}$, 67124-80-5.

References and Notes

- (1) Abbreviations used throughout: tren = triethylenetetramine, $(\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NHCH}_2)_3$; tren = β, β', β'' -triaminotriethylamine, $\text{N}(\text{CH}_2\text{C}-\text{H}_2\text{NH}_2)_3$.
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Photochemistry of Cyclopentadienyliron Dicarbonyl Halide Complexes¹

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The primary photochemical process (366 or 436 nm) for $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$ and $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ is dissociation of carbon monoxide. Photolysis of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ (X = Cl, Br, I) in benzene solutions saturated with ^{13}CO yields $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(^{13}\text{CO})\text{X}$. Irradiation of the bromo or iodo derivatives in the presence of triphenylphosphine leads to the formation of the covalent complexes $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)\text{X}$ (X = Br, I) with a high quantum efficiency. Quantum yields for the substitution processes increase with increasing triphenylphosphine concentration and decrease with increasing concentration of carbon monoxide. The linkage isomers $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{NCS}$ and $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SCN}$ interconvert upon 366- or 436-nm irradiation in tetrahydrofuran. They undergo thermal and photochemical substitution reactions with triphenylphosphine to produce the new compounds $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)\text{NCS}$ and $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)\text{SCN}$. $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{NCS}$ reacts with triphenylarsine under photochemical conditions to yield $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{AsPh}_3)\text{NCS}$.

Introduction

A variety of photochemical deactivation pathways are available to cyclopentadienylmetal carbonyl complexes containing one-electron-donor ligands (X). These include dissociation of carbon monoxide,²⁻⁵ homolytic⁶⁻¹⁰ or heterolytic^{11,12} cleavage of the metal-X bond, intramolecular isomerization^{1,2} and intraligand rearrangements.^{13,14} The photochemistry of the dinuclear compounds $[\text{CpMo}(\text{CO})_3]_2$,^{6,9} $[\text{CpW}(\text{CO})_3]_2$,^{6,8} and $(\text{CO})_3\text{CpMo-WCp}(\text{CO})_3$,¹⁵ (Cp = $\eta^5\text{-C}_5\text{H}_5$) is dominated by homolytic cleavage of the metal-metal bond yielding the reactive radical species $\text{CpM}(\text{CO})_3\cdot$ (M = Mo, W). The

tetranuclear complex $[\text{CpFe}(\text{CO})]_4$ undergoes photooxidation in the presence of halocarbons to $[\text{CpFe}(\text{CO})]_4^{+16}$.

Although the synthetic utility of irradiation of the mononuclear complexes $\text{CpM}(\text{CO})_3\text{X}$,^{3,17-20} (M = Mo, W) and $\text{CpFe}(\text{CO})_3\text{X}$,^{3,18,19,21,22} has been recognized for some time, information regarding mechanistic aspects of their photochemical reactions is severely limited. Photolysis of $\text{CpM}(\text{CO})_3\text{CH}_3$ (M = Cr, W) in the presence of triphenylphosphine or trimethyl phosphite yields a mixture of the mono- and disubstituted methyl compounds $\text{CpM}(\text{CO})_2(\text{L})\text{CH}_3$ and $\text{CpM}(\text{CO})(\text{L})_2\text{CH}_3$ as well as the acetyl complexes CpM -

(CO)₂(L)COCH₃ (L = PPh₃, P(OCH₃)₃).¹⁰ Irradiation of CpFe(CO)₂CH₃ with EPh₃ (E = P, As, Sb) results exclusively in the formation of CpFe(CO)(EPh₃)CH₃.²³ Products of photolysis of CpFe(CO)₂Cl include [CpFe(CO)₂]₂,²⁴ Fe²⁺, Cl⁻, and ferrocene,⁹ depending upon experimental conditions.

In the present paper we report the results of a quantitative study of the photochemistry of the cyclopentadienyliron dicarbonyl halides CpFe(CO)₂Br and CpFe(CO)₂I and a more extensive examination of the previously reported¹ photolinkage isomerization of CpFe(CO)₂NCS and CpFe(CO)₂SCN. The results for the halide complexes are discussed in terms of the molecular orbital calculations and photoelectron spectra²⁵ of these complexes.

Experimental Section

Materials. CpFe(CO)₂X²⁶ (X = Cl, Br, I), CpFe(CO)₂NCS,²⁷ and CpFe(CO)₂SCN²⁷ were prepared by methods previously described in the literature. Spectroscopic grade solvents were used after drying over molecular sieves. Tetrahydrofuran was distilled from CaH₂ under argon immediately prior to use. ¹³CO (90% enriched) was purchased from Monsanto Chemical Co. NaPPh₄, hydroquinone, PPh₃, AsPh₃, CBr₄, and Ph₃CCl are commercially available and were used as received. Elemental analyses were performed by Galbraith Microanalytical Laboratories.

Spectra. Infrared spectra were recorded with Perkin-Elmer 337 or 521 grating spectrophotometers using matched 0.1- or 1.0-mm KBr solution cells. Proton NMR and UV-visible spectra were obtained with Varian T-60 and Beckman Acta MVI spectrophotometers, respectively. Mass spectra were recorded using an AEI MS-1201B spectrometer at 70-eV ionizing voltage.

Photolysis Procedures. Solutions of the iron complexes (1 × 10⁻³ M, 366 nm; 2 × 10⁻³ M, 436 nm) were degassed by three freeze-pump-thaw cycles or by purging with prepurified argon in matched 10-mm i.d. Pyrex tubes. The tubes were placed in a merry-go-round apparatus²⁸ of our own design. A 200-W Hanovia medium-pressure mercury-arc lamp was situated in an immersion well surrounded by two concentric, cylindrical Pyrex jackets containing appropriate aqueous filter solutions to isolate the desired mercury emissions (336 nm: 0.125 M NiSO₄, 0.50 M CoSO₄ (l = 20 mm) and 6.4 × 10⁻⁴ M 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (l = 10 mm); 436 nm: 5.4 M NaNO₂ (l = 20 mm) and 0.18 M CuSO₄, 2.7 M NH₃ (l = 10 mm)). Light intensities (366 nm, 4.4 × 10⁻⁸ einstein/s; 436 nm, 5.5 × 10⁻⁸ einstein/s) were measured by ferrioxalate actinometry.²⁹ Photoproducts were characterized by infrared, proton NMR, and UV-visible spectroscopy and were identified by comparison to spectra of authentic samples. Quantum yields were determined by monitoring UV-visible absorption spectral changes and are reported as the average of triplicate determinations. Conversions were limited to 15% or less and were linear with irradiation time. Thermal dark reactions were monitored and were negligible within the times required for irradiation and analysis.

ESR Experiments. Benzene solutions of the iron complexes (2 × 10⁻³ M) and Ph₃CCl (1 × 10⁻¹ M) were degassed in 3-mm o.d. Pyrex ESR tubes which were then sealed. The solutions were irradiated in the cavity of a Varian E-12 ESR spectrometer with a water-cooled 200-W medium-pressure mercury-arc lamp. The 366- and 436-nm emission lines were isolated using Oriol G-522-3650 (29%T) and Oriol G-522-4358 (55%T) narrow-band-pass glass interference filters, respectively.

Synthesis of CpFe(CO)(PPh₃)NCS. CpFe(CO)₂NCS (0.60 g, 2.5 mmol) and PPh₃ (0.68 g, 2.6 mmol) were dissolved in 100 mL of benzene and the solution was refluxed under argon for 2.5 h. The brown solution was allowed to cool and its volume reduced to ~5 mL by rotary evaporation. Chromatography on neutral alumina (Brockman Activity Grade I, 3 × 25 cm column), using benzene as eluant, afforded a red-brown band and a green band which remained on the upper portion of the column. The red band was collected under argon, and the solvent removed by rotary evaporation to leave a brown solid. This was recrystallized from CHCl₃/hexane, washed with hexane, and dried to yield 0.61 g of CpFe(CO)(PPh₃)NCS (51%), mp 141–143 °C dec.

Anal. Calcd for C₂₅H₂₀FeOPNS: C, 64.0; H, 4.27; P, 6.61; S, 6.83. Found: C, 63.65; H, 4.55; P, 6.45; S, 6.79. ¹H NMR (CDCl₃ solvent, TMS internal standard): δ(Cp) 4.52 (d, J_{P-H} = 2 Hz), δ(Ph) 7.4 (m). IR (CHCl₃ solution): ν(CN) 2120 cm⁻¹, ν(CO) 1980 cm⁻¹. The

Table I. Electronic Absorption Bands for CpFe(CO)(L)X Complexes

X	L	λ _{max} , nm (ε, M ⁻¹ cm ⁻¹)	solvent
Cl	CO	388 (565) sh; 336 (935)	C ₆ H ₆
Br	CO	386 (700) sh; 350 (1028)	C ₆ H ₆
		385 (674) sh	CH ₃ NO ₂
		385 (717) sh; 346 (922)	CH ₃ CN
I	CO	342 (2090)	C ₆ H ₆
		323 (2300)	CH ₃ CN
NCS	CO	418 (795); 340 (1590); 270 (4650) sh	THF
SCN	CO	525 (1094); 345 (1604); 278 (7420)	THF
Br	PPh ₃	614 (160); 444 (775); 360 (785) sh	C ₆ H ₆
		615 (162); 440 (780)	CH ₃ NO ₂
		617 (164); 440 (772); 360 (628) sh	CH ₃ CN
I	PPh ₃	619 (168); 440 (784); 326 (2510) sh	C ₆ H ₆
		617 (165); 438 (770)	CH ₃ NO ₂
		618 (188); 437 (781); 320 (2355) sh	CH ₃ CN
NCS	PPh ₃	550 (362); 435 (948); 308 (2430)	THF

integrated absorption intensity of the CN stretching band, determined by the method of Ramsay,³⁰ was found to be 10.0 × 10⁴ M⁻¹ cm⁻², diagnostic of an M–NCS linkage.³¹

Synthesis of CpFe(CO)(PPh₃)SCN. CpFe(CO)₂SCN (0.33 g, 1.4 mmol) and PPh₃ (0.37 g, 1.4 mmol) were dissolved in 100 mL of tetrahydrofuran and the solution was refluxed for 9 h under argon. After the mixture was cooled, the solvent was removed by rotary evaporation leaving a brown solid. This was extracted with three 5-mL portions of CH₂Cl₂ and chromatographed on Florisil (3 × 20 cm column) using 1:1 CH₂Cl₂/hexane as eluant. Three bands developed: the first red-brown, the second olive-brown, and the third orange. The bands were collected under argon and the solvents removed by rotary evaporation. The residues from the first and third fractions were identified as CpFe(CO)(PPh₃)NCS and a mixture of CpFe(CO)₂NCS and CpFe(CO)₂SCN, respectively. The residue of the second eluate was crystallized from CHCl₃/hexane, washed with hexane, and dried to yield 0.065 g of a mixture of CpFe(CO)(PPh₃)SCN and triphenylphosphine. Repeated attempts to remove the phosphine by chromatography and fractional crystallization proved to be unsuccessful, prohibiting characterization of the product by elemental analysis.

¹H NMR (CDCl₃ solvent, TMS internal standard): δ(Cp) 4.60 (d, J_{P-H} = 2 Hz), δ(Ph) 7.4 (m). IR (CHCl₃ solution): ν(CN) 2115 cm⁻¹, ν(CO) 1975 cm⁻¹. Taking into account the percentage of triphenylphosphine present in the sample (determined by integration of the phenyl and Cp resonances in the ¹H NMR spectrum), we found the upper limit for the integrated absorption intensity of the CN stretching band to be 6 × 10⁴ M⁻¹ cm⁻², indicative of an M–SCN linkage.³¹

Synthesis of CpFe(CO)(AsPh₃)NCS. CpFe(CO)₂NCS (1.00 g, 4.3 mmol) and AsPh₃ (1.22 g, 4.0 mmol) were dissolved in 100 mL of tetrahydrofuran under argon. The solution was photolyzed for 6 h at 28 °C in a Rayonet Type RS-5 Reactor fitted with four Ru1-3500 lamps. The solvent was removed by rotary evaporation leaving a brown solid. The benzene solubles were extracted and chromatographed on neutral alumina (Brockman Activity Grade I, 3 × 30 cm column). Elution with 1:1 benzene/hexane afforded an olive-brown band followed by an orange band. They were each collected under argon and the solvents removed by rotary evaporation. The orange residue of the second eluate was identified as a mixture of CpFe(CO)₂NCS and CpFe(CO)₂SCN. The oil from the first eluate was crystallized from CHCl₃/hexane, washed with hexane, and dried to yield 0.022 g of brown CpFe(CO)(AsPh₃)NCS (1%).

Anal. Calcd for C₂₅H₂₀FeOAsNS: C, 58.50; H, 3.92; S, 6.25; As, 14.60. Found: C, 52.02; H, 3.90; S, 6.17; As, 14.37. IR (CHCl₃ solution): ν(CN) 2115 cm⁻¹, ν(CO) 1975 cm⁻¹. The integrated absorption intensity³⁰ of the CN stretching band was found to be 11.7 × 10⁴ M⁻¹ cm⁻², representative of M–NCS bonding.³¹ Attempts to prepare CpFe(CO)(AsPh₃)NCS by thermal substitution of CpFe(CO)₂NCS were unsuccessful.

Results and Discussion

Electronic absorption spectral data for the CpFe(CO)₂X and CpFe(CO)(PPh₃)X complexes are given in Table I. The spectra of the dicarbonyl halides exhibit an intense absorption band in the UV-visible region (λ_{max} ~ 340 nm) which overlaps

Table II. Carbonyl Infrared Spectral Data for $\text{CpFe}(^{12}\text{CO})_2\text{X}$ and $\text{CpFe}(^{12}\text{CO})(^{13}\text{CO})\text{X}^a$

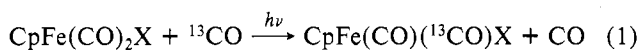
X	$\text{CpFe}(\text{CO})_2$	$\text{CpFe}(^{12}\text{CO})\text{-}(^{13}\text{CO})\text{X}$ (obsd) ^b	$\text{CpFe}(^{12}\text{CO})\text{-}(^{13}\text{CO})\text{X}$ (calcd) ^c
Cl	2050, 2005	2035, 1978	2037, 1973
Br	2045, 2003	2030, 1975	2035, 1972
I	2038, 2005	2025, 1968	2028, 1968

^a Cyclohexane solution; matched 0.1-mm KBr cells. ^b $\pm 2 \text{ cm}^{-1}$; average of three determinations. ^c Calculated using the secular equations $\lambda_1 = \mu(k - k_1)$ and $\lambda_2 = \mu(k + k_1)$.

with a weaker absorption band in the visible spectral region ($\lambda_{\text{max}} \sim 400 \text{ nm}$). The spectra of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$ ($\text{X} = \text{Br}, \text{I}$) display an additional visible absorption ($\lambda_{\text{max}} \sim 615 \text{ nm}$).

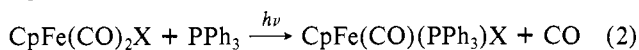
Photolysis of $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) at 366 or 436 nm in benzene, acetonitrile, nitromethane, or tetrahydrofuran solutions results in no observable changes in the infrared or UV-visible spectra of the complexes. Thus, there is no detectable photochemical reaction in the absence of added nucleophiles in these solvents. The report by Giannotti and Merle⁹ that photolysis (300–700 nm) of $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) in benzene or chloroform produces ferrocene, Fe^{2+} , and X^- would seem to be the result of using high light intensities (2500-W xenon-arc lamp) and possibly lack of temperature control.

Photolysis of $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in ^{13}CO -saturated benzene solutions leads to the formation of $\text{CpFe}(\text{CO})(^{13}\text{CO})\text{X}$ (eq 1) as evidenced by infrared and mass



spectral analysis of the photolyzed complexes. Infrared spectral changes accompanying photolysis include a decrease in intensity of the carbonyl stretching bands of $\text{CpFe}(\text{CO})_2\text{X}$ as the corresponding bands of $\text{CpFe}(\text{CO})(^{13}\text{CO})\text{X}$ appear and grow in intensity. Observed and calculated $\nu(\text{CO})$ bands for $\text{CpFe}(\text{CO})(^{13}\text{CO})\text{X}$ are given in Table II.

Photolysis at 366 or 436 nm of $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Br}, \text{I}$) in degassed solutions containing triphenylphosphine results in efficient formation of the monosubstituted complexes $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$.



The disubstituted complexes $\text{CpFe}(\text{PPh}_3)_2\text{X}$ are not observed (^1H NMR) upon 366- or 436-nm irradiation of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$ with PPh_3 . King et al. have reported²² that ultraviolet irradiation of $\text{CpFe}(\text{CO})_2\text{X}$ with an excess of the stronger π -acceptor phosphorus ligand $\text{C}_3\text{H}_{10}\text{NPF}_2$ yields the disubstituted products $\text{CpFe}(\text{PF}_2\text{NC}_3\text{H}_{10})_2\text{X}$.

UV-visible spectral changes observed during photolysis of $\text{CpFe}(\text{CO})_2\text{I}$ and PPh_3 are shown in Figure 1. Clean isosbestic points are observed at 402 and 405 nm for the bromo and iodo derivatives, respectively, indicating the absence of secondary thermal or photochemical reactions. $\text{CpFe}(\text{CO})_2\text{Cl}$ reacts rapidly with PPh_3 in the dark at room temperature to produce a mixture of the covalent $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$ and ionic $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]\text{Cl}$ derivatives, precluding a study of the photochemical substitution reactions of this complex.

The 366- and 436-nm quantum yields obtained for appearance of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$ ($\text{X} = \text{Br}, \text{I}$) in several solvents are given in Table III. The values are essentially independent of irradiation wavelength but do vary as a function of triphenylphosphine concentration (Figure 2). The quantum yield for substitution of $\text{CpFe}(\text{CO})_2\text{I}$ increases with increasing ligand concentration until triphenylphosphine is present in about threefold molar excess of $\text{CpFe}(\text{CO})_2\text{I}$. Maximum values of 0.77 ($\Phi_{366 \text{ nm}}$) and 0.80 ($\Phi_{436 \text{ nm}}$) are then obtained. Additional phosphine has no further effect on the quantum yield for

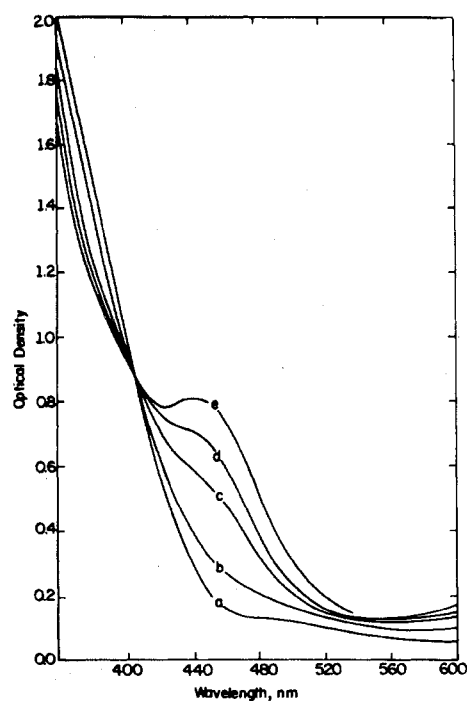


Figure 1. UV-visible spectral changes upon 366-nm irradiation of $\text{CpFe}(\text{CO})_2\text{I}$ in benzene solution containing triphenylphosphine. Curve a corresponds to the initial spectrum; $[\text{CpFe}(\text{CO})_2\text{I}] = [\text{PPh}_3] = 1 \times 10^{-3} \text{ M}$. Curves b, c, and d correspond to 1-, 5-, and 13-min irradiation times, respectively. Curve e is the spectrum of $1 \times 10^{-3} \text{ M}$ $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$ in benzene.

Table III. Quantum Yields for the Reaction $\text{CpFe}(\text{CO})_2\text{X} + \text{PPh}_3 \rightarrow \text{CpFe}(\text{CO})(\text{PPh}_3)\text{X} + \text{CO}^a, b$

X	irradn $\lambda, \text{ nm}$	solvent	Φ ($\pm 10\%$)
Br	366	C_6H_6	0.72
Br	366	$\text{C}_6\text{H}_6/\text{CO}^d$	0.18
Br	366	CH_3CN	0.89
Br	366	$\text{CH}_3\text{CN}/\text{NaBPh}_4$	0.86
Br	366	$\text{CH}_3\text{CN}/\text{C}_6\text{H}_6\text{O}_2^e$	0.75
Br	436	C_6H_6	0.82
Br	436	$\text{C}_6\text{H}_6/\text{CO}^d$	0.58
Br ^c	436	C_6H_6	0.68
Br ^c	436	$\text{C}_6\text{H}_6/\text{CO}^d$	0.17
Br	436	CH_3NO_2	0.40
Br	436	$\text{CH}_3\text{NO}_2/\text{NaBPh}_4$	0.46
Br	436	$\text{CH}_3\text{NO}_2/\text{C}_6\text{H}_6\text{O}_2^e$	0.34
I	366	C_6H_6	0.63
I	366	$\text{C}_6\text{H}_6/\text{CO}^d$	0.14
I	366	CH_3CN	0.21
I	366	$\text{CH}_3\text{CN}/\text{NaBPh}_4$	0.19
I	366	$\text{CH}_3\text{CN}/\text{C}_6\text{H}_6\text{O}_2^e$	0.23
I	436	C_6H_6	0.69
I	436	$\text{C}_6\text{H}_6/\text{CO}^d$	0.40
I ^c	436	C_6H_6	0.75
I ^c	436	$\text{C}_6\text{H}_6/\text{CO}^d$	0.21
I	436	CH_3NO_2	0.40
I	436	$\text{CH}_3\text{NO}_2/\text{NaBPh}_4$	0.48
I	436	$\text{CH}_3\text{NO}_2/\text{C}_6\text{H}_6\text{O}_2^e$	0.38

^a Determined by appearance of a long-wavelength absorption band of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$. ^b At 366 nm, $[\text{CpFe}(\text{CO})_2\text{X}] = [\text{PPh}_3] = 1 \times 10^{-3} \text{ M}$. At 436 nm, $[\text{CpFe}(\text{CO})_2\text{X}] = 2 \times 10^{-3} \text{ M}$. ^c $[\text{CpFe}(\text{CO})_2\text{X}] = [\text{PPh}_3] = 1 \times 10^{-3} \text{ M}$. ^d One atmosphere CO pressure (see Experimental Section). ^e $\text{C}_6\text{H}_6\text{O}_2 = \text{hydroquinone}$.

substitution. A similar dependence of the quantum yield on ligand concentration is observed for triphenylphosphine substitution of $\text{CpFe}(\text{CO})_2\text{Br}^2$ and 1,1,1,1-tetracarbonyl-2,3,1-diazaferrole.³²

Quantum yields for triphenylphosphine substitution are decreased by addition of CO. The extent of this decrease is

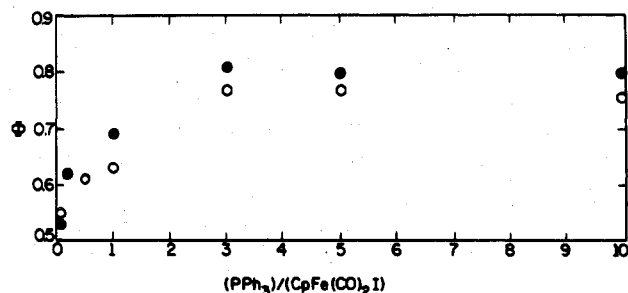
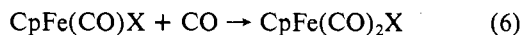
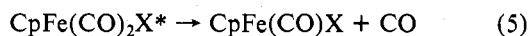


Figure 2. Effect of triphenylphosphine concentration on the quantum yield for the reaction $\text{CpFe}(\text{CO})_2\text{I} + \text{PPh}_3 \rightarrow \text{CpFe}(\text{CO})(\text{PPh}_3)\text{I} + \text{CO}$ in benzene solution: ○, 366-nm irradiation, $[\text{CpFe}(\text{CO})_2\text{I}]$ constant at 1×10^{-3} M; ●, 436-nm irradiation, $[\text{CpFe}(\text{CO})_2\text{I}]$ constant at 2×10^{-3} M.

dependent upon the relative ratio of $[\text{CO}]/[\text{CpFe}(\text{CO})_2\text{X}]$ to $[\text{PPh}_3]/[\text{CpFe}(\text{CO})_2\text{X}]$. For example, the decrease in Φ_a upon 436-nm irradiation of CO-saturated benzene solutions in which $[\text{CpFe}(\text{CO})_2\text{I}] = [\text{PPh}_3] = 2 \times 10^{-3}$ M is from 0.69 to 0.40. When $[\text{CpFe}(\text{CO})_2\text{I}] = [\text{PPh}_3] = 1 \times 10^{-3}$ M, the corresponding decrease in Φ_a is from 0.75 to 0.21. Similar data were obtained for $\text{CpFe}(\text{CO})_2\text{Br}$ (Table III).

These results, along with our observations concerning ^{13}CO incorporation, are best accounted for by eq 3–7.



Equation 4 represents all physical decay processes of the excited-state molecule. Dissociation of CO produces the coordinatively unsaturated intermediate $\text{CpFe}(\text{CO})\text{X}$ (eq 5) which may recombine with CO (eq 6) or react with triphenylphosphine (eq 7). At low phosphine concentrations, recombination of CO, which is expected to occur rapidly,^{12,32,33} is competitive with attack by triphenylphosphine. As the concentration of phosphine is increased, CO competes less effectively for the monocarbonyl intermediate and $\Phi_a(\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X})$ increases until a limiting value is obtained (Figure 2). The observed decrease in $\Phi_a(\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X})$ for CO-saturated solutions (Table III) is consistent with competition between CO and PPh_3 for the $\text{CpFe}(\text{CO})\text{X}$ intermediate.

The data could also be interpreted in terms of an associative reaction of the excited-state complex with the entering nucleophile. A bimolecular excited-state process has been considered in the photosubstitution of $\text{Mn}(\text{CO})_4\text{NO}$.³⁴ Although we cannot exclude this possibility, we consider it to be less likely than simple CO dissociation, which is the dominant process in metal carbonyl photochemistry.^{3–5}

Our results strongly suggest that rupture of the iron–halogen bond is not an important pathway of excited-state decay. The result of heterolytic cleavage would be formation of the ionic intermediate $[\text{CpFe}(\text{CO})_2]^+$. This intermediate is readily susceptible to nucleophilic attack by two-electron-donor ligands³⁵ and should efficiently react with CO or PPh_3 to produce $[\text{CpFe}(\text{CO})_3]^+$ and $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]^+$, respectively. The ionic complexes are not observed following photolysis of $\text{CpFe}(\text{CO})_2\text{X}$ with CO or PPh_3 . The 366- or 436-nm irradiation of saturated solutions of $[\text{CpFe}(\text{CO})_3]\text{X}$ or $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]\text{X}$ does not produce the covalent complexes $\text{CpFe}(\text{CO})_2\text{X}$ or $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$, thus excluding the ionic derivatives as intermediates in the observed

photosubstitution processes. Furthermore, increasing the ionic strength of the solutions by addition of NaBPh_4 has no significant effect on the quantum yields for triphenylphosphine substitution (Table III).

Homolytic cleavage of the iron–halogen bond would produce the paramagnetic species $\text{CpFe}(\text{CO})_2\cdot$ and $\text{X}\cdot$. Cross-coupling of these radicals would yield the dimeric complex $[\text{CpFe}(\text{CO})_2]_2$ and X_2 . Ali, Cox, and Kemp have reported²⁴ that the principal product of irradiation ($\lambda > 280$ nm) of $\text{CpFe}(\text{CO})_2\text{Cl}$ in the donor solvents pyridine and dimethyl sulfoxide is $[\text{CpFe}(\text{CO})_2]_2$; they observed no reaction in cyclohexane or diethyl ether. The dimer is not observed as a photoproduct of $\text{CpFe}(\text{CO})_2\text{X}$ under our reaction conditions. This observation is not compelling evidence against radical formation, however, since secondary thermal or photochemical reactions of $[\text{CpFe}(\text{CO})_2]_2$ with X_2 should rapidly regenerate the starting complexes.²⁶

A variety of metal carbonyl radicals efficiently react with halogen donors such as CCl_4 , CBr_4 , and Ph_3CCl to produce the corresponding metal carbonyl halides.^{6–8,36} In the latter instance, the resultant $\text{Ph}_3\text{C}\cdot$ radical may be detected by ESR spectroscopy. The characteristic spectrum of the trityl radical³⁷ is not observed during photolysis of $\text{CpFe}(\text{CO})_2\text{X}$ with Ph_3CCl , suggesting that $\text{CpFe}(\text{CO})_2\cdot$ is not generated. When $[\text{CpMo}(\text{CO})_3]_2$ or $\text{Mn}_2(\text{CO})_{10}$ are photolyzed with Ph_3CCl under the same conditions, we observe the ESR spectrum of the $\text{Ph}_3\text{C}\cdot$ radical as previously reported by other workers.^{6,36} Furthermore, irradiation of $\text{CpFe}(\text{CO})_2\text{X}$ in the presence of CX'_4 ($\text{X} = \text{Cl}$, $\text{X}' = \text{Br}$; $\text{X} = \text{Br}$, I , $\text{X}' = \text{Cl}$) does not lead to formation of $\text{CpFe}(\text{CO})_2\text{X}'$. Addition of the radical scavenger hydroquinone³⁸ does not affect the quantum yields for triphenylphosphine substitution (Table III), further indicating that homolytic cleavage of the Fe–X bond is not an important process of excited-state decay.

The photochemistry of $\text{CpFe}(\text{CO})_2\text{Br}$ and $\text{CpFe}(\text{CO})_2\text{I}$ correlates with photoelectron spectral data and molecular orbital calculations reported for these complexes by Lichtenberger and Fenske.²⁵ They have shown that the highest occupied molecular orbitals are a doubly degenerate set of iron–halogen π -antibonding orbitals. The consequence of one-electron excitation from this level, regardless of the orbital which is populated, is a net increase in the metal–halogen bond order. Thus, scission of the iron–halogen bond is neither expected nor observed to be an important photochemical process for the subject complexes. The character of the lowest unoccupied molecular orbitals in these complexes is not revealed by the molecular orbital calculations.²⁵ However, excitation to orbitals antibonding with respect to the σ framework or to CO π -antibonding orbitals is expected to cause labilization of the CO ligands. Luminescence and excited-state quenching studies are needed to determine the nature of the low-lying excited states of these complexes and will be the subject of future investigations.

The photochemistry of the thiocyanato complexes $\text{CpFe}(\text{CO})_2\text{NCS}$ and $\text{CpFe}(\text{CO})_2\text{SCN}$ is of additional interest. Electronic spectral data for these complexes are given in Table I. The linkage isomers are interconverted upon 366- or 436-nm irradiation in degassed tetrahydrofuran solutions, photostationary states being reached after 2 h.¹ Infrared spectra of each isomer and the product mixture obtained following 436-nm irradiation are shown in Figure 3.

When $\text{CpFe}(\text{CO})_2\text{NCS}$ is photolyzed in tetrahydrofuran solutions saturated with CO, no reaction is observed. In contrast, the photolinkage isomerization of $\text{CpFe}(\text{CO})_2\text{SCN}$ is not completely inhibited by CO. Irradiation of $\text{CpFe}(\text{CO})_2\text{NCS}$ in the presence of ^{13}CO or PPh_3 results exclusively in the formation of $\text{CpFe}(\text{CO})(^{13}\text{CO})\text{NCS}$ or $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{NCS}$, respectively, with no evidence of linkage isom-

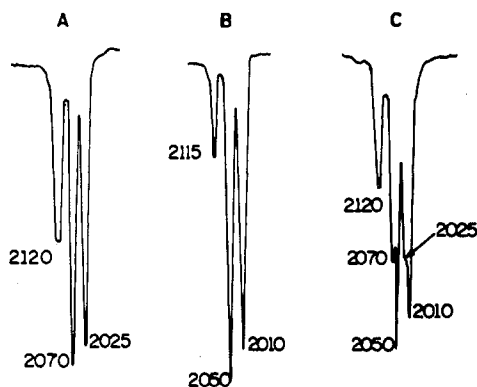
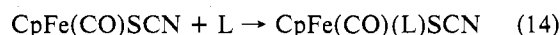
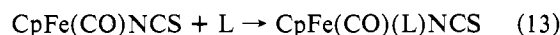
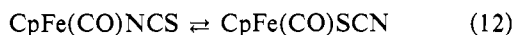
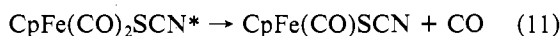
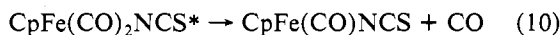
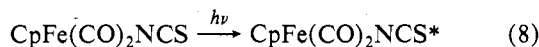


Figure 3. Infrared spectra of (A) $\text{CpFe}(\text{CO})_2\text{NCS}$, (B) $\text{CpFe}(\text{CO})_2\text{SCN}$, and (C) the isomeric mixture at the photostationary state (436 nm). Irradiations were conducted in THF solution, and spectra were recorded in chloroform.

erization. However, the corresponding photoreaction with AsPh_3 yields the substitution product $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{NCS}$ and an isomeric mixture of the dicarbonyl complexes. Photolysis of $\text{CpFe}(\text{CO})_2\text{SCN}$ with PPh_3 results in a mixture of $\text{CpFe}(\text{CO})_2\text{SCN}$ and $\text{CpFe}(\text{CO})_2\text{NCS}$ and their respective substitution products $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCN}$ and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{NCS}$. Neither $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCN}$ nor $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{NCS}$ isomerizes upon 366- or 436-nm irradiation in degassed tetrahydrofuran solutions for periods of up to 4 h.

Unfortunately, quantum yields for the linkage isomerization and substitution processes could not be obtained owing to a substantial increase in light absorption over the entire 350–500-nm spectral range following photolysis of either $\text{CpFe}(\text{CO})_2\text{NCS}$ or $\text{CpFe}(\text{CO})_2\text{SCN}$. This phenomenon is observed in a variety of solvents including tetrahydrofuran, nitromethane, diethyl ether, chloroform, acetonitrile, and acetone. Attempts to isolate and identify the species responsible for the observed light absorption have been unsuccessful.

The data at hand indicate that the photolinkage isomerization and substitution processes are competitive and depend upon both the mode of attachment of the thiocyanato ligand to the metal and the nature of the entering nucleophile. Observations concerning ^{13}CO incorporation and PPh_3 substitution parallel those made for the halide complexes and strongly suggest dissociation of CO as the primary photochemical process for the thiocyanate complexes. The results may be rationalized as follows:



Equations 10 and 11 represent dissociation of CO from the excited-state molecules $\text{CpFe}(\text{CO})_2\text{NCS}^*$ and $\text{CpFe}(\text{CO})_2\text{SCN}^*$. Rearrangement of the thiocyanato ligand (eq 12) and nucleophilic attack by CO or PPh_3 on the coordinatively unsaturated intermediates (eq 13 and 14) are likely to be competitive secondary processes. The total inhibition of $\text{Fe-NCS} \rightarrow \text{Fe-SCN}$ but not $\text{Fe-SCN} \rightarrow \text{Fe-NCS}$ isomerization by CO or PPh_3 may be a consequence of the expected³⁹ Fe-N-C and Fe-S-C bond angles of ~ 180 and

$\sim 105^\circ$, respectively. If these geometries persist in the excited states, then, following loss of CO, competition by external ligands for the vacant-metal coordination site of $\text{CpFe}(\text{CO})\text{NCS}$ would be more effective than that for $\text{CpFe}(\text{CO})\text{SCN}$. While this scheme is consistent with our observations, it remains speculative in the absence of quantum-yield data for the photoisomerization and -substitution processes.⁴⁰

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Registry No. $\text{CpFe}(\text{CO})_2\text{Cl}$, 12107-04-9; $\text{CpFe}(\text{CO})_2\text{Br}$, 12078-20-5; $\text{CpFe}(\text{CO})_2\text{I}$, 12078-28-3; $\text{CpFe}(\text{CO})_2\text{NCS}$, 12317-60-1; $\text{CpFe}(\text{CO})_2\text{SCN}$, 12317-59-8; $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Br}$, 12099-12-6; $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$, 12099-18-2; $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{NCS}$, 61113-76-6; $\text{CpFe}^{(12)\text{CO}}(^{13}\text{CO})\text{Cl}$, 67351-00-2; $\text{CpFe}^{(12)\text{CO}}(^{13}\text{CO})\text{Br}$, 67351-01-3; $\text{CpFe}^{(12)\text{CO}}(^{13}\text{CO})\text{I}$, 67351-02-4; $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCN}$, 64784-33-4; $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{NCS}$, 67351-03-5.

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cyclopentadienyl proton resonance for the complex assigned as $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCN}$ but did not influence the chemical shift of this resonance for $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{NCS}$. This behavior is characteristic of thiocyanato organometallic compounds since the N atom of the

S-bonded ligand readily coordinates to europium but the S atom of the N-bonded ligand does not.⁴¹

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Mass Spectra of Organometallic Compounds. 7.¹ Electron-Impact Study of Some Cyclopentadienylmetal Thiocarbonyl-Bridged Dimers

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Mass spectra of the thiocarbonyl-bridged dimers $[\text{QMn}(\text{CS})(\text{NO})]_2$ ($\text{Q} = \eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-MeC}_5\text{H}_4$), $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CS})(\text{CO})]_2$, and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CS})(\text{CO})_3$ have been examined, and appearance potentials of most of the metal-containing fragment ions, especially those with intact ligands, have been determined. The primary fragmentations in the mass spectra of these complexes have been assigned and compared. Fragment ions resulting from the loss of CO or NO are much more abundant than those resulting from the loss of CS. In fact, a large fraction of the total ion current in the mass spectra of those complexes arises from $\text{M}_2(\text{CS})_n$ -containing ions.

Introduction

In recent years, a considerable amount of information has become available on the behavior of organometallic compounds under electron-impact conditions.² Despite the large volume of mass spectral data on such systems, relatively little effort has been made to examine in detail proposed fragmentation modes. In general, under electron-impact conditions most metal-containing ions exhibit one detectable appearance potential, and this probably suggests the existence of a single primary precursor for each of these ions. An accurate description of a fragmentation pathway should contain viable information concerning predominant processes by which fragment ions are being produced. As a matter of convenience, such processes will henceforth be referred to as primary fragmentations, and this in order to distinguish them from minor processes to be termed secondary. In a primary fragmentation sequence, subsequent ions are expected to exhibit higher appearance potentials due to the endothermicity of the breaking processes involved. Generally, metal-containing ions with all ligands account for most of the ion current in the majority of the mass spectra of organometallic compounds. This feature indicates that under electron-impact conditions the cleavage of metal-to-ligand bonds is greatly favored over processes involving the decay of coordinated ligands. Detailed studies of the energetics of metal-to-ligand bond-breaking fragmentations have so far been reported for relatively few organometallic systems.^{1,3}

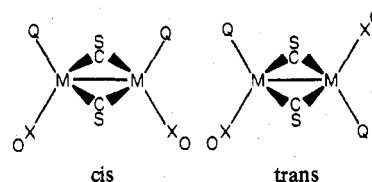
Recently, we have reported a comprehensive mass spectral study⁴ on the well-known cyclopentadienylmetal dimers $[\text{CpCr}(\text{CO})_2]_2$, $[\text{Me}_5\text{C}_5\text{Cr}(\text{CO})_2]_2$, $[\text{CpFe}(\text{CO})_2]_2$, and $[\text{CpNi}(\text{CO})_2]_2$. A related class of the novel binuclear complexes $[\text{MeC}_5\text{H}_4\text{Mn}(\text{CS})(\text{NO})]_2$,⁵ $[\text{CpMn}(\text{CS})(\text{NO})]_2$,⁵ $[\text{CpFe}(\text{CS})(\text{CO})]_2$,⁶ and $\text{Cp}_2\text{Fe}_2(\text{CS})(\text{CO})_3$,^{7a} is of considerable interest in view of the remarkably high tendency of the coordinated thiocarbonyl to engage in carbon-bridging geometries.^{7b} Incidentally, this tendency is dramatically greater than that of either the carbonyl or the nitrosyl ligands. A detailed analysis of the mass spectra of the carbon-bridged thiocarbonyl derivatives, described in the current paper, was undertaken in order to ascertain their primary fragmentation modes under electron-impact conditions and, more specifically,

Table I. Intensities (*I*) (at 80 eV) and Appearance Potentials (AP) of Metal-Containing Ions in the Mass Spectra of $\text{Q}_2\text{Mn}_2(\text{CS})_2(\text{NO})_2$ [$1: \text{Q} = \text{C}_5\text{H}_5, \text{CH}_3\text{C}_5\text{H}_4$]

ion	$\text{Q} = \text{C}_5\text{H}_5$			$\text{Q} = \text{CH}_3\text{C}_5\text{H}_4$	
	<i>m/z</i>	<i>I</i> , ^a %	AP, ^b eV	<i>m/z</i>	<i>I</i> , ^a %
Metal-Containing Ions with All Ligands					
$\text{Q}_2\text{Mn}_2(\text{CS})_2(\text{NO})_2^+$	388	40	6.77 ± 0.02	416	61
$\text{Q}_2\text{Mn}_2(\text{CS})_2(\text{NO})^+$	358	10	7.90 ± 0.02	386	12
$\text{Q}_2\text{Mn}_2(\text{CS})_2^+$	328	69	8.99 ± 0.02	356	100
$\text{Q}_2\text{Mn}_2(\text{CS})(\text{NO})^+$	314	2		342	9
$\text{QMn}_2(\text{CS})_2(\text{NO})^+$	293	11	11.97 ± 0.02	307	1
$\text{Q}_2\text{Mn}_2(\text{CS})^+$	284	18	12.64 ± 0.02	312	6
$\text{QMn}_2(\text{CS})_2^+$	263	77	12.89 ± 0.02	277	36
$\text{QMn}(\text{CS})_2(\text{NO})^+$	238	35	9.03 ± 0.04	252	34
$\text{QMn}_2(\text{CS})^+$	219	8	16.18 ± 0.07	233	8
$\text{QMn}(\text{CS})_2^+$	208	9	16.02 ± 0.05	222	8
$\text{Mn}_2(\text{CS})_2^+$	198	8	20.92 ± 0.04	198	5
$\text{QMn}(\text{CS})(\text{NO})^+$	194	8	11.04 ± 0.03	208	6
Q_2Mn^+	185	49	16.16 ± 0.03	213	11
$\text{QMn}(\text{CS})^+$	164	27	13.00 ± 0.02	178	12
$(\text{C}_5\text{H}_5)\text{Mn}_2^+$				175	29
QMn^+	120	73	21.33 ± 0.16^c	134	20
Mn_2^+	110	7	28.38 ± 0.02	110	3
$\text{Mn}(\text{CS})^+$	99	5		99	2
Mn^+	55	100	26.71 ± 0.03	55	17
Metal-Containing Ions with Partial Ligands (<i>I</i> ≥ 4%)					
$(\text{Q}-\text{H})\text{Mn}_2(\text{CS})_2^+$	262	60	11.87 ± 0.03	276	62
$(\text{Q}-\text{H})\text{Mn}(\text{CS})_2^+$	207	10	15.61 ± 0.16		
$(\text{C}_5\text{H}_4)\text{Mn}_2^+$	174	23		174	9

^a Conditions: SHT, $200 \pm 2^\circ\text{C}$; ICT, $200 \pm 2^\circ\text{C}$. ^b Conditions: SHT, $165 \pm 2^\circ\text{C}$; ICT, $200 \pm 2^\circ\text{C}$. ^c Nitrogen used as calibrant.

to examine the influence of this unique bridging ligand on the fragmentation pattern of the complexes. The complexes investigated are known to exist in both cis and trans isomeric forms and have the general structures shown:



1, $\text{M} = \text{Mn}$; $\text{X} = \text{N}$; $\text{Q} = \text{C}_5\text{H}_5, \text{CH}_3\text{C}_5\text{H}_4$
2, $\text{M} = \text{Fe}$; $\text{X} = \text{C}$; $\text{Q} = \text{C}_5\text{H}_5$

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