kinetically very inert ruthenium(II) halo complexes.

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Registry No. **2a**, 90742-37-3; **2a**$^+$, 90742-46-4; **2b**, 90742-38-4; **2b**$^+$, 90742-47-5; **2c**, 90742-39-5; **2c**$^+$, 90742-48-6; **2d**, 90742-40-8; **2d**$^+$, 90742-49-7; **2e**, 90742-41-9; **2e**$^+$, 90742-50-0; **2f**, 90742-42-0; **2f**$^+$, 90742-51-1; **2g**, 90742-43-1; **3a**, 90821-16-2; **3a**$^+$, 90821-21-9; **3b**, 90821-17-3; **3b**$^+$, 90821-22-0; **3c**, 90821-18-4; **3c**$^+$, 90821-23-1; **3f**, 90821-19-5; **3f**$^+$, 90821-24-2; **3g**, 90821-20-8; **4**, 90742-45-3; $Ru(C_6H_5CN)_4Cl_2$, 21503-87-7.

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Reactions of Aziridine, Oxirane, and Thiirane with Carbonyl and Thiocarbonyl Ligands in Complexes of Iron, Manganese, and Ruthenium: Syntheses of Cyclic Carbene Compounds

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The 3-membered heterocycles aziridine ($\overline{HNCH_2CH_2}$) and oxirane ($\overline{OCH_2CH_2}$) react with one CO group in each of the cationic carbonyl complexes $Cp(OC)_3Fe^+$, $Cp(OC)_3Ru^+$, $Cp(OC)_2(ON)Mn^+$, and $Cp(OC)_2(Ph_3P)Fe^+$ in the presence of a halide ion at 25 °C or below to form the corresponding 5-membered cyclic amino oxy $M{=}\overline{COCH_2CH_2NH}^+$ and dioxy $M{=}\overline{COCH_2CH_2O}^+$ carbene complexes (M = $Cp(OC)_2Fe$, $Cp(OC)_2Ru$, $Cp(OC)(ON)Mn$, $Cp(OC)(Ph_3P)Fe$). Aziridine and thiirane ($\overline{SCH_2CH_2}$) also react with the CS ligand in the mixed carbonyl thiocarbonyl complex $Cp(OC)_2(CS)Fe^+$ to give the corresponding aminothiocarbene ($M{=}\overline{CSCH_2CH_2NH}$) and dithiocarbene ($M{=}\overline{CSCH_2CH_2S}$) products. In the reactions $M{-}C{\equiv}Z^+ + \overline{YCH_2CH_2} \xrightarrow{X^-} M{=}\overline{CZCH_2CH_2Y}^+$ (Z = O, Y = NH and O; Z = S, Y = NH and S), the role of the halide ion X^- as a catalyst has been demonstrated. Prolonged reactions of oxirane with $Cp(OC)_2LM^+$ (M = Fe, L = CO; M = Mn, L = NO) in the presence of Br^- ion generate bis(dioxycarbene) derivatives $CpLM(\overline{COCH_2CH_2O})_2^+$. Mechanisms for these reactions have been proposed. Reactions of $Cp(OC)_2LM^+$ (M = Fe, L = CO; M = Mn, L = NO) with $[BrCH_2CH_2CH_2NH_3]Br$ and the bases azetidine ($\overline{HNCH_2CH_2CH_2}$) or oxirane and Br^- yield 6-membered aminooxycarbene compounds $Cp(OC)LM(\overline{COCH_2CH_2CH_2NH})^+$. The basic behavior of oxiranes $R{-}\overline{CHCH_2O}$ in the presence of a halide catalyst is demonstrated by the isolation of the 5-membered dioxycarbene compound $Cp(CO)_2Fe(\overline{COCH_2CH_2O})^+$ from the reaction of $\overline{RCHCH_2O}$ with $Cp(OC)_3Fe^+$ in $BrCH_2CH_2OH$. IR and ^1H and ^{13}C NMR spectra of the compounds are discussed.

Introduction

There has been considerable interest in the reactions of the 3-membered heterocycles $\overline{YCH_2CH_2}$, where Y = NH (aziridine), O (oxirane), and S (thiirane), with transition-metal complexes. Simple coordination of aziridine through the N atom to metal ions has been observed.[3] One O-bonded oxirane compound, namely $[Cp(OC)_3Mo(\overline{OCH_2CH_2})]^+$, was also reported.[4] Aziridine and oxirane are also known to react with metal hydrido carbonyls[5,6] or with carbonyl anions[5,7] according to

$$LMH + \overline{YCH_2CH_2} \rightarrow LM{-}CH_2CH_2YH$$

$$LMH = Co(CO)_4H,\ Mn(CO)_5H,\ CpMo(CO)_3H,\ CpW(CO)_3H$$

$$LM^- + \overline{YCH_2CH_2} \rightarrow LM{-}CH_2CH_2Y^-$$

$$LM^- = Co(CO)_4^-,\ CpFe(CO)_2^-$$

Thiirane with hydrido carbonyls,[8,9] however, undergoes "desulfurization"

$$LMH + \overline{SCH_2CH_2} \rightarrow LM{-}SH + (LM)_2S + LM(SCH_2CH_2S)_2ML$$

In these and other reactions of metal carbonyl complexes,[4] the heterocycles $\overline{YCH_2CH_2}$ are observed to react at the metal centers. Recently, studies of the reactivity of CO ligands in metal carbonyl complexes have been stimulated by the search for catalytic reactions that convert CO into hydrocarbons, alcohols, and other organic products. Taking advantage of the tendency of highly strained 3-membered rings $\overline{YCH_2CH_2}$

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to undergo ring opening and using the known reactivity of electrophilic CO or CS ligands, we sought to initiate, under suitable catalytic conditions, the reaction of heterocycles at the carbon center of carbonyl or thiocarbonyl ligands. We have found that, indeed, such novel reactions do occur in the presence of a halide ion catalyst and that these reactions lead to the formation of cyclic carbene compounds in high yields. In this paper, we describe the results of studies of these reactions and the spectroscopic (IR and ^1H and ^{13}C NMR) characterization of the reaction products. Preliminary results of this study have been published as a communication.[10]

Experimental Section

General Information. Unless otherwise mentioned, reagent grade chemicals were used without further purification. All reactions and manipulations were performed under N_2 by using standard Schlenk techniques. Methylene chloride was dried over CaH_2 and distilled under N_2. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2. Predried (CaH_2) acetonitrile was distilled first from anhydrous P_2O_5 and then from CaH_2 before final collection under N_2. Acetone was dried and distilled from P_2O_5 under N_2 before use. Diethyl ether predried with CaH_2 was distilled from sodium benzophenone ketyl under N_2. Hexane was distilled from CaH_2 and stored under N_2 over molecular sieves, type 4Å. Infrared spectra were recorded on Perkin-Elmer 281 and 681 instruments. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer; $Cr(acac)_3$ was added to the solutions to reduce ^{13}C data collection time. Tetramethylsilane was employed as the internal standard for the ^1H and ^{13}C spectra. Melting points (uncorrected) of the compounds were determined in air on a Thomas hot-stage apparatus. As aziridine, oxirane, and thiirane are toxic substances, all preparations were performed in an efficient hood.

Starting Complexes. The compounds $[Cp(OC)_2Fe(CZ)]CF_3SO_3$ were prepared from $[Cp(OC)_2FeC(Z)ZMe]$ (Z = O, S) by known methods[11-13] using CF_3SO_3H in benzene. They, as well as $[Cp(OC)_3Ru]CF_3SO_3$, were recrystallized from acetone–ether before use. Other compounds, $[Cp(OC)_2(ON)Mn]PF_6$,[14] $[Cp(OC)_2(Ph_3P)Fe]^+$,[15,16] and $[Cp(OC)_3Ru]PF_6$,[17] were all prepared according to literature methods. The salt $[Cp(OC)_2(Ph_3P)Fe]CF_3SO_3$ was formed by the reaction of $[Cp(OC)_3Fe]CF_3SO_3$ (0.17 g, 0.48 mmol) with a stoichiometric amount of PPh_3 (0.13 g, 0.49 mmol) in acetone for 20 min followed by evaporation and recrystallization from CH_2Cl_2–Et_2O; yield 0.21 g (75%). This compound was characterized by its IR and ^1H and ^{13}C NMR spectra.[15,16]

$[Cp(OC)_3Fe]PF_6$. Though mentioned in the literature,[18] details of this preparative method were not given. The dimer $Cp_2(OC)_4Fe_2$ (0.50 g, 1.4 mmol) was dissolved in 20 mL of 1:1 CH_2Cl_2:CH_3CN. A rapid stream of CO gas was bubbled through the solution, and excess (~1.5 g) $NOPF_6$ was added in several portions. The solution color changed from deep brown to yellow brown, and yellow crystals of $[Cp(OC)_3Fe]PF_6$ began to precipitate. After removal of the solvents, the residue was washed with ether, extracted with acetone, filtered in air, and precipitated with Et_2O as yellow crystals at −20 °C. The compound was characterized by IR and NMR spectra;[11] yield 0.78 g (79%).

Syntheses of Complexes. $[Cp(OC)_2Fe(\overline{COCH_2CH_2N}H)]PF_6$ (Ia). Aziridine (0.05 mL, 1 mmol) was added with a microsyringe to a solution of 0.35 g (1.0 mmol) of $[Cp(OC)_3Fe]CF_3SO_3$ and 0.20 g (0.98 mmol) of $[BrCH_2CH_2NH_3]Br$ in 20 mL of CH_3CN. After the mixture stirred for 10 min, excess KPF_6 (~2 g) was added to the mixture, which was stirred for an additional 5 min. The solvent was then removed under vacuum, and the residue was washed twice with 2-mL portions of Et_2O. It was then extracted with 20 mL of CH_2Cl_2 and filtered through anhydrous $MgSO_4$, and the volume of the light yellow filtrate was reduced under vacuum until crystallization began. To this solution was added 10 mL of Et_2O, and the solution was allowed to stand at −20 °C overnight. Cream yellow needles formed and were collected, washed with Et_2O, and finally vacuum dried: yield 0.40 g (99%); mp 134 °C. Anal. Calcd for $C_{10}H_{10}F_6NO_3PFe$: C, 30.56; H, 2.56; N, 3.56. Found: C, 31.00; H, 2.78; N, 3.78. Using 0.22 g (1.0 mmol) of $[BrCH_2CH_2CH_2NH_3]Br$ instead of $[BrCH_2CH_2NH_3]Br$ in the above procedure yielded 0.35 g (89%) of Ia from 0.35 g (1.0 mmol) of $[Cp(OC)_3Fe]CF_3SO_3$. When the same method was used but with 0.18 g (1.0 mmol) of $[Et_3NH]Br$ in place of $[BrCH_2CH_2NH_3]Br$, 0.25 g (64%) of Ia was isolated.

$[Cp(OC)_2Ru(\overline{COCH_2CH_2N}H)]PF_6$ (Ib). The same procedure as for the preparation of Ia was followed. The metathesis with KPF_6 was not required. Starting from 0.20 g (0.57 mmol) of $[Cp(OC)_3Ru]PF_6$, 0.03 mL (0.6 mmol) of aziridine, and 0.10 g (0.50 mmol) of $[BrCH_2CH_2NH_3]Br$, 0.19 g (87%) of the colorless snow white crystalline product was obtained; mp 119 °C. Anal. Calcd for $C_{10}H_{10}F_6NO_3PRu$: C, 27.41; H, 2.30; N, 3.20. Found: C, 27.74; H, 2.44; N, 3.24. Ib was also prepared from $[Cp(OC)_3Ru]CF_3SO_3$ by using KPF_6 for anion exchange.

$[Cp(OC)(ON)Mn(\overline{COCH_2CH_2N}H)]PF_6$ (Ic). The same method of preparation as for Ia was followed. The anion exchange with KPF_6 was not required. From 0.35 g (1.0 mmol) of $[Cp(OC)_2(ON)Mn]PF_6$ was obtained 0.34 g (85%) of orange yellow crystals of Ic, mp 136 °C. Anal. Calcd for $C_9H_{10}F_6N_2O_3PMn$: C, 27.43; H, 2.56; N, 7.10. Found: C, 27.40; H, 2.48; N, 7.20.

$[Cp(OC)(Ph_3P)Fe(\overline{COCH_2CH_2N}H)]PF_6$ (Id). With the use of a microsyringe, 0.03 mL (0.6 mmol) of aziridine was added to a stirring mixture of 0.26 g (0.50 mmol) of $[Cp(OC)_2(Ph_3P)Fe]BF_4$ and 0.10 g (0.50 mmol) of $[BrCH_2CH_2NH_3]Br$ in 10 mL of CH_3CN. The bromide salt disappeared during the reaction, but a whitish sticky residue formed in the reaction flask. The progress of the reaction was monitored by IR spectroscopy, and after 1.5 h an additional amount of aziridine (0.03 mL) was introduced. After 6 h the disappearance of ν(CO) bands at 2062 and 2017 cm^{-1} due to the starting complex and the simultaneous appearance of a strong band at 1980 cm^{-1} indicated that the reaction was complete. Addition of excess aziridine accelerated the reaction. The solution was evaporated to dryness under reduced pressure, and the residue was extracted with 20 mL of CH_3CN and filtered. The filtrate was treated with ~1 g of KPF_6 for anion exchange. After evaporation, the yellow residue was extracted with CH_2Cl_2; the solution was filtered and evaporated to 2 mL, and crystallization was induced by adding Et_2O at −20 °C. Yellow flaky crystals were collected the next day, washed with Et_2O, and dried under vacuum: yield 0.23 g (70%); mp 228 °C. Anal. Calcd for $C_{27}H_{25}F_6NO_2P_2Fe$: C, 51.71; H, 4.02; N, 2.23. Found: C, 51.74; H, 3.94; N, 2.09. This compound was also prepared from $[Cp(OC)_2(Ph_3P)Fe]CF_3SO_3$ by following the same method.

$[Cp(OC)_2Fe(\overline{COCH_2CH_2N}H)]CF_3SO_3$ (Ie). To an ice-cold stirring mixture of 8 mL of oxirane and 0.21 g (1.0 mmol) of $[BrCH_2CH_2NH_3]Br$ was added 0.35 g (1.0 mmol) of $[Cp(OC)_3Fe]CF_3SO_3$. The mixture was stirred at 0 °C (ice bath) for 45 min and was then taken to dryness under vacuum. The residue was washed once with Et_2O and then extracted with CH_2Cl_2. The solution was filtered through anhydrous $MgSO_4$, the filtrate was concentrated under vacuum, Et_2O was added, and the solution was allowed to stand at −20 °C overnight when light yellow crystals of Ie precipitated; yield 0.35 g (90%). Anal. Calcd for $C_{11}H_{10}F_3NO_6SFe$: C, 33.27; H, 2.54; N, 3.53. Found: C, 33.22; H, 2.48; N, 3.40. When 3 mL of thiirane instead of oxirane in the above procedure, 0.35 g (1.0 mmol) of $[Cp(OC)_3Fe]CF_3SO_3$, and 0.20 g (0.98 mmol) of $[BrCH_2CH_2NH_3]Br$ were used and the reaction mixture was treated with KPF_6 for the exchange of the anion, a 0.35 g (90%) yield of Ia was obtained.

$[Cp(OC)_2Fe(H\overline{NCH_2C}H_2)]PF_6$ (If). To a solution of 0.06 mL (1 mmol) of aziridine in 10 mL of CH_3CN was added 0.35 g (1.0 mmol) of $[Cp(OC)_3Fe]CF_3SO_3$. Immediately, evolution of gas was noticed, and a brown solution was obtained. An excess of KPF_6 (~2 g) was added, and the mixture was stirred for 5 min. The solution was taken to dryness, and the residue was washed several times with Et_2O and then extracted with 20 mL of CH_2Cl_2. After filtering through anhydrous $MgSO_4$, the brown solution (a difference from the filtrate of Ia) was concentrated to about 2 mL, and 10 mL of Et_2O was added carefully to form two layers. When the mixture was allowed to stand

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for several days at −20 °C, yellow needlelike crystals formed: yield 0.24 g (66%); mp 180 °C dec. Anal. Calcd for $C_9H_{10}F_6NO_2PFe$: C, 29.62; H, 2.76; N, 3.78. Found: C, 29.89; H, 2.44; N, 3.77.

[Cp(OC)$_2$Fe(CSCH$_2$CH$_2$NH)]PF$_6$ (Ig). Aziridine (0.05 mL, 1 mmol) was added to a stirring solution of 0.37 g (1.0 mmol) of [Cp(OC)$_2$(CS)Fe]CF$_3$SO$_3$ and 0.21 g (1.0 mmol) of [BrCH$_2$CH$_2$NH$_3$]Br in 40 mL of THF. After 2 min, about 2 g of KPF$_6$ was added, and the mixture was stirred for an additional 10 min. The volatiles were removed under reduced pressure, the residue was extracted with 20 mL of CH_2Cl_2 and filtered through anhydrous $MgSO_4$, and the CH_2Cl_2 filtrate was evaporated to an oil. It was dissolved in 1 mL of acetone, and Et_2O was added slowly to form two layers. Slow diffusion of Et_2O overnight at −20 °C induced the formation of light yellow-brown crystals of the product, yield 0.34 g (83%). This aminothiocarbene compound was characterized by its IR and ^{1}H and ^{13}C NMR spectra.[19]

[Cp(CO)$_2$Fe(COCH$_2$CH$_2$CH$_2$NH)]PF$_6$ (IIa). Azetidine, HNCH$_2$CH$_2$CH$_2$ (0.07 mL, 1 mmol), was added to a solution of 0.35 g (1.0 mmol) of [Cp(OC)$_3$Fe]CF$_3$SO$_3$ in 20 mL of CH_3CN containing 0.22 g (1.0 mmol) of [BrCH$_2$CH$_2$CH$_2$NH$_3$]Br. After 20 min of stirring, another portion of 0.07 mL (1 mmol) of azetidine was added and the mixture was stirred for 2 h. Then, ~2 g of KPF$_6$ was added. After the mixture was stirred for 10 min, the solvents were removed, and the residue was washed with Et_2O several times. Extraction with CH_2Cl_2 and subsequent evaporation produced an oil in 90% yield. When it was allowed to stand under Et_2O for 4 weeks, the oil changed to long yellow-brown needlelike crystals: yield 0.22 g (54%); mp 116 °C. Anal. Calcd for $C_{11}H_{12}F_6NO_3PFe$: C, 32.46; H, 2.97; N, 3.44. Found: C, 32.84; H, 3.20; N, 3.69.

The same compound was also prepared in 30% yield by using oxirane (8 mL) and [BrCH$_2$CH$_2$CH$_2$NH$_3$]Br (0.44 g, 2.0 mmol) at 0 °C by a method analogous to that described for the preparation of Ie from oxirane and [BrCH$_2$CH$_2$NH$_3$]Br. These crystals gave the same IR and NMR spectra as IIa.

[Cp(OC)(ON)Mn(COCH$_2$CH$_2$CH$_2$NH)]PF$_6$ (IIb). The procedure used for the preparation of Ie was employed. When 8 mL of oxirane, 0.24 g (1.1 mmol) of [BrCH$_2$CH$_2$CH$_2$NH$_3$]Br, and 0.33 g (0.94 mmol) of [Cp(OC)$_2$(ON)Mn]PF$_6$ were used, 0.20 g (52%) of IIb was obtained as brown-red crystals, mp 105 °C. Anal. Calcd for $C_{10}H_{12}F_6N_2O_3PMn$: C, 29.43; H, 2.96; N, 6.86. Found: C, 29.57; H, 3.16; N, 6.64.

[Cp(OC)$_2$Fe(COCH$_2$CH$_2$O)]PF$_6$ (IIIa). To a cooled (0 °C) suspension of 0.19 g (0.53 mmol) of [Cp(OC)$_3$Fe]CF$_3$SO$_3$ in 1 mL of BrCH$_2$CH$_2$OH was added 0.06 g (0.5 mmol) of NaBr followed by 4 mL of oxirane at 0 °C. The mixture was stirred for 3 h at 0 °C. After the removal of volatiles under reduced pressure, 5 mL of CH_3CN was added followed by excess KPF$_6$ (~2 g). After stirring for 15 min, the solution was evaporated to dryness, and the residue was washed once with 1–2 mL of Et_2O and extracted with 30 mL of CH_2Cl_2. After the solution was filtered through anhydrous $MgSO_4$, the volume was reduced to one-tenth, and Et_2O was added dropwise. Cooling of this mixture at −20 °C overnight produced the light yellow crystalline compound: yield 0.17 g (81%); mp 123–126 °C. Anal. Calcd for $C_{10}H_9F_6O_4PFe$: C, 30.40; H, 2.30. Found: C, 30.85; H, 2.30. The same compound was also prepared similarly but replacing 2-bromoethanol with 3-bromopropanol. Thus, with 0.19 g (0.54 mmol) of [Cp(OC)$_3$Fe]CF$_3$SO$_3$, 3 mL of oxirane, 1.5 mL of BrCH$_2$CH$_2$CH$_2$OH, and 0.10 g (0.97 mmol) of NaBr, 0.17 g of IIIa (yield 80%) was obtained. Repeating the procedure using NaCl (0.06 g, 1 mmol) and 1 mL of ClCH$_2$CH$_2$OH instead of NaBr and BrCH$_2$CH$_2$OH and starting with 0.36 g (1.0 mmol) of [Cp(OC)$_3$Fe]CF$_3$SO$_3$, 0.24 g (60%) of IIIa was isolated. Similarly, when NaBr was replaced by NaI (0.29 g, 0.96 mmol) in this method, 0.14 g (18%) of IIIa was produced from 0.7 g (2 mmol) of [Cp(OC)$_3$Fe]CF$_3$SO$_3$ and 2 mL of BrCH$_2$CH$_2$OH.

[Cp(OC)$_2$Ru(COCH$_2$CH$_2$O)]PF$_6$ (IIIb). The same procedure as for IIIa was employed. When 0.10 g (0.25 mmol) of [Cp(OC)$_3$Ru]CF$_3$SO$_3$ was stirred for 30 min with 4 mL of oxirane in 1 mL of BrCH$_2$CH$_2$OH containing 0.10 g (0.97 mmol) of NaBr, followed by treatment with ~1 g of KPF$_6$ in CH_3CN, 0.080 g (73%) of IIIb was isolated as colorless long needles, mp 125 °C. Anal. Calcd for $C_{10}H_9F_6O_4PRu$: C, 27.35; H, 2.06. Found: C, 27.44; H, 2.10.

[Cp(OC)(ON)Mn(COCH$_2$CH$_2$O)]PF$_6$ (IIIc). With 0.20 g (0.57 mmol) of [Cp(OC)$_2$(ON)Mn]PF$_6$, 2 mL of BrCH$_2$CH$_2$OH, 3 mL of oxirane, and 0.05 g (~0.5 mmol) of NaBr and from the same procedure as for the preparation of IIIa but without employing KPF$_6$ for metathesis, 0.18 g (80%) of orange-yellow crystals were obtained; mp 128 °C. Anal. Calcd for $C_9H_9F_6NO_4PMn$: C, 27.36; H, 2.30; N, 3.54. Found: C, 27.43; H, 2.40; N, 3.51.

[Cp(OC)(Ph$_3$P)Fe(COCH$_2$CH$_2$O)]PF$_6$ (IIId). Similarly, with 0.21 g (0.40 mmol) of [Cp(OC)$_2$(Ph$_3$P)Fe]BF$_4$, 0.06 g (0.6 mmol) of NaBr, 2 mL of BrCH$_2$CH$_2$OH (or BrCH$_2$CH$_2$CH$_2$OH), and 8 mL of oxirane and when KPF$_6$ in CH_3CN was used for anion exchange, IIId was isolated as light yellow crystals: yield 0.21 g (84%); mp 210 °C. Anal. Calcd for $C_{27}H_{24}F_6O_3P_2Fe$: C, 51.61; H, 3.85. Found: C, 51.53; H, 4.02. The same compound was also prepared from [Cp(OC)$_2$(Ph$_3$P)Fe]CF$_3$SO$_3$ by following the same procedure and employing KPF$_6$ for anion metathesis. The IR and NMR data were used to identify the compounds as IIId.

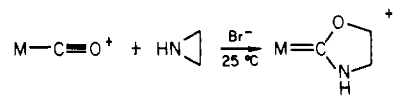
[Cp(OC)Fe(COCH$_2$CH$_2$O)$_2$]PF$_6$ (IIIe). Through a suspension of 0.07 g (0.2 mmol) of IIIa in 1 mL of BrCH$_2$CH$_2$OH containing 0.02 g (0.2 mmol) of NaBr were passed oxirane vapors at room temperature for 24 h. The solvent was removed under vacuum, and excess Et_2O was added to the brown mass. After the mixture was allowed to stand overnight at −20 °C, the Et_2O was decanted off, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated, Et_2O was added, and the light yellow crystalline compound was obtained upon standing at −20 °C overnight: yield 0.020 g (26%); mp 180 °C. Anal. Calcd for $C_{12}H_{13}F_6O_5PFe$: C, 32.90; H, 2.99. Found: C, 32.13; H, 3.02.

[Cp(ON)Mn(COCH$_2$CH$_2$O)$_2$]PF$_6$ (IIIf). The initial steps in this preparation were the same as for the synthesis of IIIc with the exception that the stirring of the reaction mixture was continued until no ν(CO) bands were seen in the IR spectrum of the mixture. Oxirane was added from time to time to replace that which evaporated. Following the crystallization procedure for IIIa, 0.12 g (27%) of orange-brown crystals were obtained from 0.35 g (1.0 mmol) of [Cp(OC)$_2$(ON)Mn]PF$_6$. This compound was characterized by its IR and ^{1}H and ^{13}C NMR spectra.[20]

[Cp(OC)$_2$Fe(CSCH$_2$CH$_2$S)]PF$_6$ (IV). To a stirring solution of 0.37 g (1.0 mmol) of [Cp(OC)$_2$(CS)Fe]CF$_3$SO$_3$ in 10 mL of CH_3CN containing 0.10 g (0.97 mmol) of NaBr was added 0.11 mL (2.0 mmol) of thiirane. Stirring was continued for 2 h. An examination of the IR spectrum of the mixture at this stage did not reveal any ν(CO) bands due to the starting complex. Then, ~2 g of KPF$_6$ was added, and after the mixture was stirred for an additional 20 min, the solvent was evaporated. The residue was washed with Et_2O, extracted with CH_2Cl_2, and filtered through anhydrous $MgSO_4$. The filtrate was concentrated, and Et_2O was added very carefully so that no oil separated out. This mixture on standing at −20 °C for 1 week gave yellow crystals: yield 0.32 g (75%); mp 87 °C. The compound was recrystallized from a CH_2Cl_2–Et_2O mixture at −20 °C. This compound was characterized by its IR and ^{1}H and ^{13}C NMR spectra.[21]

Results and Discussion

Reactions of Aziridine with Metal Carbonyl Cations. Syntheses of 5-Membered Aminooxycarbene Complexes. Aziridine is observed to react (eq 1) with one CO group in each of the cationic carbonyl complexes in acetonitrile solvent in the presence of a bromide salt at room temperature to form the corresponding cyclic aminooxycarbene compounds (I) in high yields (70–99%). The products Ia,b are prepared from the corresponding Cp(OC)$_3$M$^+$ cations (M = Fe, Ru) and are



(1)

Ia, M = Cp(OC)$_2$Fe
b, M = Cp(OC)$_2$Ru
c, M = Cp(OC)(ON)Mn
d, M = Cp(OC)(Ph$_3$P)Fe

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(19) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 1231.

(20) Motschi, H.; Angelici, R. J. *Organometallics* **1982**, *1*, 343.

(21) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1111.

isolated as highly crystalline air-stable PF_6^- salts via anion exchange with excess KPF_6. The $CF_3SO_3^-$ salt of Ia[22] has also been prepared as a yellow crystalline compound (Ie) in equally good yields (90%) by a different route (vide infra). The use of salts with different anions such as BF_4^-, PF_6^-, or $CF_3SO_3^-$ do not seem to affect noticeably the overall yields of the end products. Highest isolated yields of Ia,b have been obtained by reacting for 5–10 min equimolar quantities of aziridine and $[BrCH_2CH_2NH_3]Br$ as the bromide salt in reaction 1.

The preparations of Ia by other methods[19,20] have been described. However, the present method affords very high yields of Ia in a considerably shorter reaction time. Since Ia may be prepared from the reaction of $Cp(OC)_3Fe^+$ with a mixture of $[BrCH_2CH_2NH_3]Br$ and NaH in CH_3CN,[20] it is necessary to consider the possibility that reaction 1 using $[BrCH_2CH_2NH_3]Br$ as the halide catalyst involves deprotonation of $BrCH_2CH_2NH_3^+$ by aziridine to give the reactive $BrCH_2CH_2NH_2$. That the $BrCH_2CH_2NH_3^+$ cation is not essential to reaction 1 is shown by the fact that other halide salts also catalyze the reaction. Thus, it is found that the salts $[Et_4N]Br$, $[Et_3NH]Br$, $[(n\text{-}Bu)_4N]I$, NaBr, and $[BrCH_2CH_2CH_2NH_3]Br$ also catalyze the formation of Ia from aziridine in the yields 56, 64, 52, 53, and 89%, respectively. The lower yields are due to the formation of significant amounts of side products such as $Cp(OC)_2FeX$ (X = Br, I) and $[Cp(OC)_2Fe(\overline{HNCH_2CH_2})]PF_6$. Moreover, difficulties were experienced in crystallizing and subsequently isolating the compound when tetra- or trialkylammonium salts were used. One side product, namely $Cp(OC)_2FeBr$, can be separated from the carbene product by washing with Et_2O. When $[Et_4N]Br$ is used, $Cp(OC)_2FeBr$ can actually be isolated from the Et_2O washings and characterized as such. IR [ν(CO) ($CHCl_3$)]: 2050 vs, 2006 vs cm^{-1}. ^1H NMR (CD_3CN): δ_{Cp} 5.12. ^{13}C NMR: δ_{CO} 214.17, δ_{Cp} 86.33.[23,24] The other side product $[CpFe(CO)_2(\overline{HNCH_2CH_2})]^+$ has been prepared and characterized as the PF_6^- salt (If). In fact, $Cp(OC)_3Fe^+$ reacts rapidly with an equimolar amount of aziridine in CH_3CN in the absence of halide salt, evolving CO gas and forming If as the only isolable product.

Although reactions 1 were commonly performed with equimolar bromide salt, high yields of the carbene product are also obtained when much lower concentrations of Br^- are used (see below).

$$[Cp(OC)_3Fe]^+ + [BrCH_2CH_2NH_3]Br \xrightarrow[CH_3CN\ (10\ ml),\ 25\ °C]{\overline{HNCH_2CH_2}\ (1\ mmol)} Ia$$

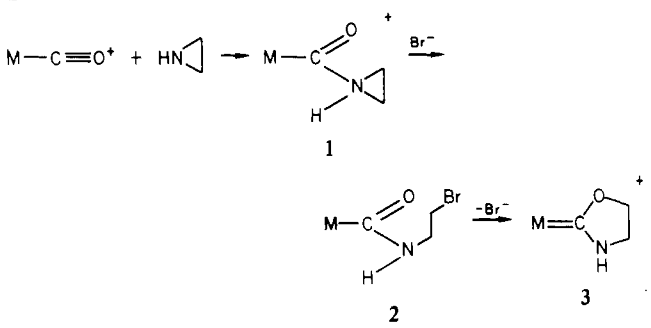
1 mmol	1 mmol	98.7%
1 mmol	0.5 mmol	98.0%
1 mmol	0.1 mmol	80.0%
1 mmol	0.05 mmol	74.0%

This clearly demonstrates that Br^- is a catalyst for the reaction and may be used in lower than equimolar concentrations.

The cationic manganese complex $[Cp(OC)_2(ON)Mn]PF_6$ also reacts with an equimolar amount of aziridine in the presence of a bromide salt to form Ic in high yield (85%). Compound Ic was previously prepared by another method[20] though in slightly lower yield. When $[Cp(OC)_2(ON)Mn]PF_6$ reacts with aziridine in CH_3CN solvent in the absence of a halide catalyst, it forms a deep brown solution that decomposes without yielding any well-defined compound.

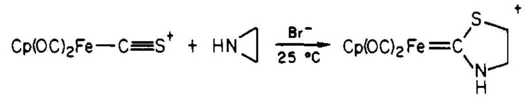
One CO group in $Cp(OC)_2(Ph_3P)Fe^+$ is converted to the aminooxycarbene Id according to reaction 1. This reaction,

Scheme I



however, takes 6 h to complete at 25 °C and consumes excess aziridine. The slowness of this reaction probably allows the partial polymerization[25] of aziridine, thus requiring the use of excess aziridine.

In order to compare the reactivity of the CO and CS ligands, the reaction of the mixed carbonyl thiocarbonyl complex cation $Cp(OC)_2(CS)Fe^+$ with equimolar aziridine and a bromide salt in THF was examined. Here, aziridine attacks preferentially the CS ligand and within 10–12 min gives the aminothiocarbene derivative (Ig), which is isolated as the PF_6^- salt in high yield (83%).



(2)

Ig

Ig was previously prepared in lower yield by another route.[19] This reactivity of the CS ligand toward aziridine demonstrates the higher electrophilicity of the thiocarbonyl carbon in comparison to that of the CO in $Cp(OC)_2(CS)Fe^+$; this is a reactivity pattern that has been observed previously in the reactions of the CS ligand in $Cp(OC)_2(CS)Fe^+$ with organic amines and alkoxides.[26]

A possible mechanism for reactions 1 and 2 involves initial attack by aziridine on the electrophilic carbon of the CO (or CS) ligand to form intermediate **1**, which may then be attacked by Br^- ion at an aziridine ring carbon, resulting in ring opening to yield carbamoyl intermediate **2**. Then, **2** could undergo intramolecular cyclization by carbonyl oxygen displacement of Br^- ion to give the carbene product, **3** (Scheme I). Neither the acyl adduct **1** nor the intermediate carbamoyl species **2** could be detected in reactions 1 or 2. Nevertheless, aziridine attack at the carbonyl (or thiocarbonyl) carbon is supported by examples of primary and secondary amine reactions with relatively positive CO or CS ligands in electron-deficient metal–carbonyl (and thiocarbonyl) systems to form carbamoyl derivatives M—C(=O)NHR.[27] Such reactions have been reported for the complexes used in reactions 1 and 2: $Cp(OC)_3Fe^+$,[11] $Cp(OC)_2(Ph_3P)Fe^+$,[11] $Cp(OC)_3Ru^+$,[17] $Cp(OC)_2(ON)Mn^+$,[28] and $Cp(OC)_2(CS)Fe^+$.[26]

Syntheses of 6-Membered Cyclic Aminooxycarbene Complexes. Previous attempts[20] to generate 6-membered aminooxycarbenes $M{=}\overline{COCH_2CH_2CH_2NH}^+$ from either $Cp(OC)_3Fe^+$ or $Cp(OC)_2(ON)Mn^+$ using $[BrCH_2CH_2CH_2NH_3]Br$ and a strong base were unsuccessful. Now we find that treatment of a cationic carbonyl complex with 2 equiv of azetidine ($\overline{HNCH_2CH_2CH_2}$) and equimolar $[BrCH_2CH_2CH_2NH_3]Br$ in CH_3CN solvent leads to the isolation of crystals

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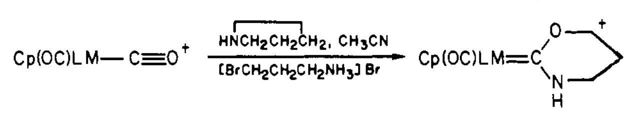
[22] McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1118.
[23] Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406.
[24] Sloan, T. E.; Wojcicki, A. *Inorg. Chem.* **1968**, *7*, 1268.
[25] Dermer, O. C.; Ham, G. E. "Ethyleneimine and Other Aziridines"; Academic Press: New York, 1969.
[26] Busetto, L.; Graziani, M.; Belluco, U. *Inorg. Chem.* **1971**, *10*, 78.
[27] Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.
[28] Busetto, L.; Palazzi, A.; Pietropaolo, D.; Dolcetti, G. J. *J. Organomet. Chem.* **1974**, *66*, 453.

of 6-membered aminooxycarbenes (II) in 52–54% (eq 3) yields.



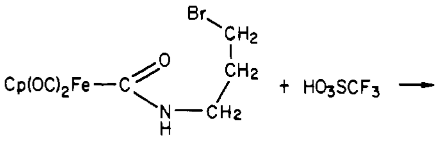
IIa, M = Fe, L = CO
b, M = Mn, L = NO

(3)

However, unlike the reactions of aziridine (eq 1), those of azetidine do not involve ring opening of the 4-membered heterocycle. Thus, the reaction of $Cp(OC)_3Fe^+$ with equimolar $[BrCH_2CH_2NH_3]Br$ in the presence of excess azetidine results in the formation of the 5-membered aminooxycarbene Ia instead of IIa. Moreover, compounds II are also obtained by treating the $Cp(CO)_2LM^+$ (M = Fe, Mn and L = CO, NO, respectively) compounds with $[BrCH_2CH_2CH_2NH_3]Br$ in oxirane at 0 °C, where $BrCH_2CH_2O^-$ acts as the base. These results indicate that the 3-bromopropylamine is the reactant that is incorporated in the 6-membered carbene ligand, not azetidine.

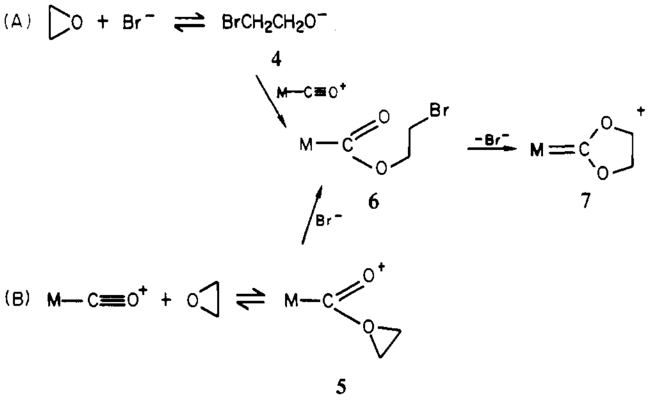
This difference in reactivity between aziridine and azetidine in the presence of haloalkylamine hydrobromide salts may be understood, first, in terms of the increasing basicities[29] of the cyclic and acyclic amines in the order $HNCH_2CH_2$ (pK_a = 8.04) < $H_2NCH_2CH_2Br$ (pK_a = 8.43) < $H_2NCH_2CH_2CH_2Br$ (pK_a = 8.93) < $HNCH_2CH_2CH_2$ (pK_a = 11.29). Azetidine, being the strongest base, initiates the reaction between haloammonium salts $[Br(CH_2)_nNH_3]Br$ and $M—C≡O^+$ by deprotonating the ammonium nitrogen in the same manner as proposed for reactions of $[BrCH_2CH_2NH_3]Br$ with cationic carbonyl complexes in the presence of NaH.[20] Second, the lower strain energy[30] of azetidine makes it less susceptible to ring opening as compared with aziridine. Third, the imine nitrogen of aziridine is more nucleophilic than would be predicted from its base strength,[31] thus making attack at the CO carbon atom in $M—C≡O^+$ more favorable.

As pointed out above, the proposed carbamoyl intermediate **2** (Scheme I) could not be detected. However, in the case of reaction 3, the formation of the intermediate carbamoyl derivative, i.e. $Cp(OC)_2Fe—C(=O)NHCH_2CH_2CH_2Br$, was observed in an IR spectrum run immediately after mixing the reactants $Cp(OC)_3Fe^+$, $[BrCH_2CH_2CH_2NH_3]Br$, and $HNCH_2CH_2CH_2$ in CH_3CN. This IR spectrum shows two strong ν(CO) absorptions at 2020 and 1965 cm^{-1} and a medium—strong band at 1597 cm^{-1} due to ν(C=O) of the carbamoyl group. As the reaction progresses, the intensities of the acyl carbonyl bands decrease while two new strong absorptions at high wavenumbers (2058 and 2012 cm^{-1}) for $CpFe(CO)_2(COCH_2CH_2CH_2NH)^+$ grow. An additional piece of evidence for the intermediacy of the carbamoyl complex is obtained by acidifying with CF_3SO_3H a part of the reaction mixture containing the carbamoyl species; immediately $Cp(OC)_3Fe^+$ is regenerated, as expected,[11] according to

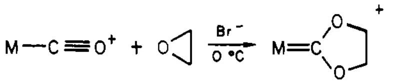


$$\rightarrow [Cp(OC)_3Fe]CF_3SO_3 + BrCH_2CH_2CH_2NH_2 \quad (4)$$

Scheme II



Reactions of Oxiranes with Metal Carbonyl Cations. Syntheses of 5-Membered Cyclic Dioxycarbene Complexes. In the presence of bromide ion, oxirane reacts with a CO ligand in each of the following cationic carbonyl complexes at 0 °C in 1–2 mL of 2-bromoethanol to form air-stable 5-membered cyclic dioxycarbene complexes (III). IIIa and IIIb are obtained in high yields (IIIa, 81%; IIIb, 73%) as crystalline PF_6^- salts from the corresponding $[Cp(OC)_3M]CF_3SO_3$ compounds; KPF_6 is used for the anion exchange.



(5)

IIIa, M = $Cp(OC)_2Fe$
b, M = $Cp(OC)_2Ru$
c, M = $Cp(OC)(ON)Mn$
d, M = $Cp(OC)(Ph_3P)Fe$

When 3-bromopropanol is used as the solvent in lieu of 2-bromoethanol in reaction 5, IIIa is isolated in yields (80%) comparable to those obtained when $BrCH_2CH_2OH$ is employed in the reaction. When oxirane is used both as reactant and solvent, the dioxycarbene IIIa is also formed but in lower yields (<30%). The reaction of $Cp(OC)_3Fe^+$ with oxirane in the presence of NaCl and 2-chloroethanol also leads to the isolation of IIIa in 60% yield. When NaI is employed in the reaction 5, an 18% yield of the carbene complex IIIa is obtained; the formation of a significant amount of $Cp(OC)_2FeI$ is responsible for the reduced yield. It is important to note that in the absence of a halide ion, oxirane alone or a mixture of oxirane plus 2-bromoethanol fails to convert the carbonyl group into the carbene ligand. These results, thus, demonstrate that (i) reaction 5 is catalyzed by a halide ion and (ii) it is the oxirane rather than the solvent that is involved in the formation of the carbene ligand. These observations are relevant to mechanistic aspects of the reaction discussed below.

The Et_2O washings obtained during the workup of IIIa prepared according to eq 5 using NaBr are always brown in color. Removal of the Et_2O followed by fractional crystallization with CH_2Cl_2–pentane at −20 °C produces two kinds of crystalline compounds. The first is obtained as dark brown long needles characterized by IR and NMR spectra as $Cp(OC)_2FeBr$. IR [ν(CO)] ($CHCl_3$): 2050 vs, 2006 cm^{-1}. ^1H NMR (CD_3CN): δ_{Cp} 5.12. ^{13}C NMR: δ_{CO} 214.17, δ_{Cp} 86.33. The second crystals are the bromonium salt $[Cp(OC)_2Fe–Br–Fe(CO)_2Cp]Br$. IR [$\nu$(CO)]: 2069 vs, 2027 vs cm^{-1}, (no PF_6^- band). ^1H NMR: δ_{Cp} 5.02.[32,33]

Oxirane is also observed to react with one CO group in each of the cationic complexes $Cp(OC)_2(Ph_3P)Fe^+$ and $Cp(OC)_2(ON)Mn^+$ to form the corresponding cyclic dioxycarbene compounds IIIc,d in yields of 80 and 84%, respectively.

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(29) Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solutions"; Butterworths: London, 1965.
(30) Moore, A. J. "Heterocyclic Compounds"; Weissberger, A. Ed.; Interscience: New York, 1964; Part II, p 885.
(31) Fedor, L. R.; Bruice, T. C.; Kirk, K. L.; Meinwald, J. *J. Am. Chem. Soc.* **1966**, *88*, 108.
(32) Fischer, E. O.; Moser, E. *J. Organomet. Chem.* **1965**, *3*, 16.
(33) Haines, R. J.; du Preez, A. L. *J. Chem. Soc. A* **1970**, 2341.

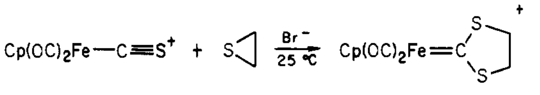
The preparation of IIId (yield 80%) was also carried out in $BrCH_2CH_2CH_2OH$ instead of $BrCH_2CH_2OH$.

Two mechanisms for the reaction of oxirane with the carbonyl ligand may be considered (Scheme II). The first (A), involving initial Br^- attack on oxirane to produce the haloalkoxide ion, is supported by other studies in which the halide ion acts as a catalyst to promote ring opening in certain organic reactions.[34,35] As noted earlier, the bromoalkoxide ion **4** can act as a nucleophile and attack the electrophilic CO ligand in cationic carbonyl complexes to form the bromoalkoxy carbonyl intermediate **6**.[20] This then undergoes intramolecular cyclization to yield dioxycarbene compound **7**. The alternative mechanism (B) involves the formation of the adduct **5** and is analogous to that suggested for the aziridine reaction; however, oxirane is less basic than aziridine and would form a less stable adduct **5** with CO. All attempts to detect intermediate **6** during the reaction failed. However, it is found that when IIIa is treated with equimolar NaI in acetone solution at room temperature, a mixture of $Cp(OC)_2FeI$ and $Cp(OC)_2Fe{-}C({=}O)OCH_2CH_2I$ is formed. The alkoxy carbonyl compound was characterized by its IR and NMR spectra. IR [ν(CO)] (CH_2Cl_2): 2038 vs, 1985 vs, 1640 ms cm^{-1} (acyl carbonyl). ^1H NMR (CD_3CN): δ_{Cp} 4.88, δ_{OCH_2} 3.68 (t), δ_{ICH_2} 3.24 (t). Though the pure compound could not be isolated free from other species, its spectral data compare well with those of $Cp(OC)_2Fe{-}C({=}O)CH_2CH_2CH_2Cl$[36] and $(OC)_5Mn{-}C({=}O)OCH_2CH_2I$.[37]

If the reaction of $Cp(OC)_3Fe^+$ with excess oxirane is allowed to proceed for more than 24 h or if oxirane vapors are passed through a solution of IIIa in $BrCH_2CH_2OH$ at 50–60 °C in the presence of NaBr for 2 h, the bis(dioxycarbene) derivative $[Cp(OC)Fe(\overline{COCH_2CH_2O})_2]PF_6$ (IIIe) is obtained in 26% yield. Similarly, by extending the reaction time (overnight, 16 h) one can prepare $Cp(ON)Mn(\overline{COCH_2CH_2O})_2]PF_6$ (IIIf) from $[Cp(OC)(NO)Mn(\overline{COCH_2CH_2O})]PF_6$. IIIf was also prepared earlier[20] by treatment of $[Cp(OC)_2(ON)Mn]PF_6$ with $BrCH_2CH_2OH$ and NaH, though the mono(dioxycarbene) compound IIIc could not be isolated. Most likely, under the exothermic reaction conditions used in the $BrCH_2CH_2OH$ and NaH system,[20] both CO ligands in $Cp(OC)_2(ON)Mn^+$ were converted into dioxycarbenes. When the reaction of $Cp(OC)_3Fe^+$ with $BrCH_2CH_2OH$ and NaH is repeated according to the published method[20] but if the reaction vessel is not cooled, IR and NMR spectra of the product mixture show that both the mono(dioxycarbene) IIIa and bis(dioxycarbene) IIIe are formed. Relative intensities of the carbonyl bands and NMR signals indicate that IIIe is the principal constituent of the mixture.

The reaction of other oxiranes such as styrene oxide or 1,2-epoxybutane with $Cp(OC)_3Fe^+$ or $Cp(OC)_2(ON)Mn^+$ in the presence of 2-bromoethanol and the Br^- ion results in the isolation of IIIa and IIIc instead of the desired substituted dioxycarbene products. In the presence of halide ions, oxiranes $R\overline{CHCH_2O}$ also act as bases in the dehydrohalogenation of β-haloalcohols.[35] The basic behavior of oxirane is also demonstrated by the isolation of 5- and 6-membered aminooxycarbene derivatives Ie and IIa from the reaction of $Cp(OC)_3Fe^+$ and $[Br(CH_2)_nNH_3]Br$ (n = 2 or 3) in excess oxirane. Presumably, in these reactions the haloalkoxide ion (**4**, Scheme II) produced by halide attack on the oxirane ring acts as a base.[35]

Reactions of Thiirane. In the presence of Br^- ion, thiirane does not react with $Cp(OC)_3Fe^+$ and $Cp(OC)_2(ON)Mn^+$ to form cyclic oxythiocarbene $M{=}\overline{COCH_2CH_2S}^+$ complexes; similarly, the reaction between the mixed thiocarbonyl cation $Cp(OC)_2(CS)Fe^+$ and oxirane fails to give an oxythiocarbene derivative. The known instability of acyclic analogues such as $Cp(OC)_2Fe[{=}C(SMe)(OMe)]^+$[21] and of $PtCl(PPh_3)_2[C(SMe)(OMe)]^+$[38] suggests that the cyclic oxythiocarbene derivative may be unstable. However, treatment of $Cp(OC)_2(CS)Fe^+$ with thiirane in the presence of NaBr in CH_3CN solvent at room temperature does produce the expected dithiocarbene complex IV in 75% yield:



(6)

IV

A mechanism similar to that described for the oxirane reactions (Scheme II) may be suggested for reaction 6.

Spectroscopic Properties. Selected IR and ^1H and ^{13}C NMR data for all the complexes are given in Tables I–III, respectively. The dicarbonyl complexes, as expected, exhibit two very strong carbonyl absorptions of equal intensity in the regions 2084–2058 and 2010–2026 cm^{-1}; the monocarbonyl complexes show only one carbonyl band; the compounds containing the nitrosyl ligand (Ic, IIb, IIIc,f) have a ν(NO) band at ~1800 cm^{-1}. Apart from the carbonyl bands, the aminooxycarbene compounds also have two other characteristic bands, one occurring at ~1605 cm^{-1} and the other in the range 1570–1530 cm^{-1}. The high-frequency band that is weaker than the other is assigned to the NH deformation and the other to the C–N stretching vibration. These assignments are made by comparing IR spectra of the aminooxycarbene derivatives with that of the aziridine-substituted compound, If, which shows an NH deformation band at ~1605 cm^{-1} but no band at ~1530 cm^{-1}. An increase in the value of the ν(CN) band by 20–30 cm^{-1} is observed as one passes from the 5- to the 6-membered carbene ring. Similarly, ν(CN) of the 5-membered oxazoline $R{-}\overline{C{=}NCH_2CH_2O}$ (1652 cm^{-1}) is somewhat lower than that (1665 cm^{-1}) of the corresponding 6-membered oxazine $R{-}\overline{C{=}NCH_2CH_2CH_2O}$.[39]

By comparing ν(CO) force constants k(CO) (Table I) as a function of the N, O, or S atoms bonded to the carbene carbon in the series of complexes $Cp(OC)_2Fe{=}\overline{CZCH_2CH_2Y}^+$ (where Z, Y = O, O; S, S; O, NH; S, NH; NH, NH) and $Cp(OC)_2Ru{=}\overline{COCH_2CH_2Y}^+$ and $Cp(OC)(ON)Mn{=}\overline{COCH_2CH_2Y}^+$ (where Y = O, NH), one notes that the k(CO) values decrease in the order (Z, Y) O, O > S, S > O, NH > S, NH > NH, NH. This trend follows the increasing electron-donating ability of Z and Y.[19] Probably both the σ- and π-bonding abilities of the heteroatoms are important in determining the trend.

In comparison to acyclic compounds, k(CO) values of 5-membered cyclic carbenes are higher as may be noted in the following pairs of examples (k(CO) values in mdyn/Å are given in parentheses): $M{=}C(OMe)_2^+$ (16.85)[12,21] and $M{=}\overline{COCH_2CH_2O}^+$ (17.14); $M{=}C(SMe)_2^+$ (16.77)[19,21] and $M{=}\overline{CSCH_2CH_2S}^+$ (16.88); $M{=}C(OMe)(NH_2)^+$ (16.73)[22] and $M{=}\overline{COCH_2CH_2NH}^+$ (16.86); $M{=}C(SMe)(NMe_2)^+$ (16.54)[19] and $M{=}\overline{CSCH_2CH_2NH}^+$ (16.74), where M =

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Table I. Important Infrared Bands (cm^{-1}) of the Compounds in CH_2Cl_2

compd	ν(CO)	k(CO)[a]	δ_{NH}	ν(CN)	$\nu(PF_6)$
$[Cp(OC)_2Fe(\overline{COCH_2CH_2NH})]PF_6$ (Ia)	2064 (vs), 2018 (vs)	16.82	1603 (m)	1540 (m)	840 (vs)
$[Cp(OC)_2Ru(\overline{COCH_2CH_2NH})]PF_6$ (Ib)	2074 (vs), 2026 (vs)	16.97	1610 (w, br)	1547 (m)	847 (vs)
$[Cp(OC)(ON)Mn(\overline{COCH_2CH_2NH})]PF_6$ (Ic)	2045 (vs), 1805 (vs)[b]	16.89	1605 (w)	1535 (m)	830 (vs)
$[Cp(OC)(Ph_3P)Fe(\overline{COCH_2CH_2NH})]PF_6$ (Id)	1980 (vs)	15.83	1600 (w, br)	1524 (m) 1535 (sh)	850 (vs)
$[Cp(OC)_2Fe(\overline{COCH_2CH_2NH})]CF_3SO_3$ (Ie)	2066 (vs), 2020 (vs)	16.86	1607 (m)	1547 (m)	
$[Cp(OC)_2Fe(\overline{HNCH_2CH_2})]PF_6$ (If)	2064 (vs), 2016 (vs)	16.81	1605 (m)		843 (vs)
$[Cp(OC)_2Fe(\overline{CSCH_2CH_2NH})]PF_6$ (Ig)	2059 (vs), 2013 (vs)	16.74	1603 (m)	1533 (m)	840 (vs)
$[Cp(OC)_2Fe(\overline{COCH_2CH_2CH_2NH})]PF_6$ (IIa)	2058 (vs), 2012 (vs)	16.73	1600 (w)	1565 (m)	850 (vs)
$[Cp(OC)(ON)Mn(\overline{COCH_2CH_2CH_2NH})]PF_6$ (IIb)	2044 (vs), 1802 (vs)[b]	16.87	1606 (w)	1568 (m)	850 (vs)
$[Cp(OC)_2Fe(\overline{COCH_2CH_2O})]PF_6$ (IIIa)	2083 (vs), 2040 (vs)	17.16			850 (vs)
$[Cp(OC)_2Ru(\overline{COCH_2CH_2O})]PF_6$ (IIIb)	2084 (vs), 2036 (vs)	17.14			847 (vs)
$[Cp(OC)(ON)Mn(\overline{COCH_2CH_2O})]PF_6$ (IIIc)	2062 (vs), 1820 (vs)[b]	17.17			847 (vs)
$[Cp(OC)(Ph_3P)Fe(\overline{COCH_2CH_2O})]PF_6$ (IIId)	1993 (vs)	16.04			845 (vs)
$[Cp(OC)Fe(\overline{COCH_2CH_2O})_2]PF_6$ (IIIe)	2008 (vs)	16.28			837 (vs)
$[Cp(ON)Mn(\overline{COCH_2CH_2O})_2]PF_6$ (IIIf)	1787 (vs)[b]				850 (vs)
$[Cp(OC)_2Fe(\overline{CSCH_2CH_2S})]PF_6$ (IV)	2065 (vs), 2024 (vs)	16.88			847 (vs)
$[Cp(OC)_2Fe(\overline{CNHCH_2CH_2NH})]PF_6$[c]	2053 (vs), 2003 (vs)	16.61			

[a] In mdyn/Å. Calculated by the method in: Cotton F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* 1962, *84*, 4432. [b] ν(NO) band. [c] Reference 19.

Table II. ^1H NMR Data for the Carbene Complexes[a]

compd	Cp	$-OCH_2-$	$-NCH_2-$	NH and/or other
Ia	5.27	4.62 (t)	3.70 (t)	9.48[b]
Ib	5.63	4.64 (t)	3.72 (t)	9.04[b]
Ic	5.47	4.66 (t)	3.73 (t)	9.14[b]
Id	4.78 (d)	4.0 (m)	3.33 (m)	8.66,[b] 7.46 (m)[c]
Ie	5.28	4.62 (t)	3.71 (t)	*d*
If	5.29			1.3,[b] 2.1[e]
Ig	5.26	4.45 (t)[f]	3.69 (t)	*d*
IIa	5.21	4.34 (t)	3.30 (m)	9.04,[b] 2.13 (m)[g]
IIb	5.42	4.36 (t)	3.30 (m)	8.60,[b] 2.10 (m)[g]
IIIa	5.39	4.74		
IIIb	5.71	4.76		
IIIc	5.59	4.78		
IIId	4.90 (d)	4.20 (m)		7.50 (m)[c]
IIIe	5.06	4.62 (m)		
IIIf	5.35	4.66		
IV	5.40	3.90[f]		

[a] In CD_3CN solvent; chemical shifts (δ) downfield from Me_4Si; m = multiplet, d = doublet, t = triplet. [b] NH signals. [c] PPh_3 signals. [d] NH signal not observed. [e] Ring $-CH_2-$ signal in coordinated aziridine. [f] $-SCH_2-$ signal. [g] $-CH_2-$ signal.

$Cp(OC)_2Fe$. This indicates that the acyclic carbenes are better donors (lower π-acceptor/σ-donor ratio) than the 5-membered cyclic ones.

In the $Cp(OC)_2FeL^+$ complexes the electronic properties of the aminooxycarbene ligand L = $\overline{COCH_2CH_2NH}$ [k(CO) = 16.86] are similar to those of L = PPh_3 (16.70).[40] In $Cp(OC)LFe{=}\overline{COCH_2CH_2O}^+$, the π-acceptor/σ-donor ratio of the L ligand decreases in the order L = $=\overline{COCH_2CH_2O}$ (16.28) > PPh_3 (16.04). In the $Cp(OC)_2Fe{=}\overline{CO(CH_2)_nNH}^+$ complexes, the carbonyl stretching force constants decrease as n increases from 2 to 3. A similar trend has been observed in the case of cyclic dithio- and diaminocarbene complexes $Cp(OC)_2Fe{=}\overline{CS(CH_2)_nS}^+$ and $Cp(OC)_2Fe{=}\overline{CNH(CH_2)_nNH}^+$ (n = 2 and 3) and has been explained in terms of different ring conformations of the 5- and 6-membered cyclic carbene ligands.[21] Better π overlap between the heteroatoms and the carbene carbon in 6-membered rings causes a decrease in the k(CO) value as compared to that in 5-membered ring carbene compounds.

^1H NMR spectra of complexes containing 5-membered aminooxycarbene ligands show $-OCH_2-$ triplets (~4.5 ppm) 1 ppm downfield from triplets (~3.5 ppm) with additional fine structure for the NCH_2 groups. Splitting of the OCH_2 groups follows a second-order AA′BB′ pattern. The additional splitting of the NCH_2 protons is due to coupling between the NH and $-NCH_2$ protons; this has been proven by spin decoupling the NH protons, which makes the splitting pattern of the NCH_2 protons that expected for an ideal AA′BB′ spin system. The 6-membered carbene compounds IIa and b exhibit three sets of methylene proton signals at 4.3 ppm (t, $-OCH_2-$), 3.3 ppm (m, $-NCH_2-$), and 2.1 ppm (m, $-CH_2-$); the splitting of the signal at 3.3 ppm is again more complicated due to NH coupling. The broad amine proton signals occur at low field (~9).

In all the mono(dioxycarbene) compounds one singlet methylene proton signal is observed at ~4.7 ppm, which is at slightly lower field than the $-OCH_2-$ resonance in the corresponding aminooxycarbene derivatives. The carbene and Cp proton resonances in $Cp(OC)(Ph_3P)Fe{=}\overline{COCH_2CH_2Y}^+$ (Y = NH, O) occur at higher field than in the corresponding $Cp(OC)_2Fe{=}\overline{COCH_2CH_2Y}^+$, indicating the stronger donor character of PPh_3 than CO. Moreover, in $Cp(OC)(Ph_3P)$-

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Table III. ^{13}C NMR Data for the Carbene Complexes[a]

compd	carbene C	CO	Cp	$-OCH_2-$	$-NCH_2-$	other
Ia	220.24	211.31	87.89	73.11	46.11	
Ib	206.28	196.49	90.14	73.15	45.85	
Ic	228.56	223.18	95.42	73.02	46.02	
Id	234.20 (d)	217.55	86.24	72.20	45.21	133.30 (m)[b]
Ie	220.08	211.24	87.89	73.24	46.20	
If	. . .	211.28	87.54			28.95[c]
Ig	234.36	211.31	88.23	56.77[d]	33.45	
IIa	218.76	212.09	87.71	70.98	42.05	20.71[e]
IIb	225.96	210.70	95.25	70.72	41.69	20.80[e]
IIIa	242.51	209.66	89.01	73.93		
IIIb	227.08	195.19	91.09	73.90		
IIIc	253.43	219.90	96.38	74.10		
IIId	254.73 (d)	217.20 (d)	87.37	72.46		131 (m)[b]
IIIe	251.00	216.51	87.70	72.54		
IIIf	262.53		96.29	72.89		
IV	295.40	209.92	89.88	48.54[d]		

[a] In CD_3CN solvent; chemical shifts in δ; d = doublet, m = multiplet. [b] PPh_3 carbon signal. [c] Ring $-CH_2-$ in coordinated aziridine. [d] $-SCH_2-$ signal. [e] $-CH_2-$ signal.

$Fe{=}\overline{COCH_2CH_2Y}^+$, the methylene proton resonances appear as multiplets as a result of chirality at the iron center when the $-CH_2-$ protons of the carbene ligand become nonequivalent.[41] In the $Cp(OC)_2Fe{=}\overline{CZCH_2CH_2NH}^+$ complexes, though the $-NCH_2-$ resonances appear at almost the same position, the $-ZCH_2-$ signal shifts to higher field as Z changes from O to S. Similarly, the $-CH_2-$ resonance for $Cp(OC)_2Fe{=}\overline{CSCH_2CH_2S}^+$ occurs at higher field than that of the analogous dioxycarbene derivative. The same trend is observed if one compares the $-CH_2-$ proton signal position in acyclic dithio- and dioxycarbene compounds $Cp(OC)_2Fe{=}C(ZMe)_2^+$ (Z = S or O).[21] The $-CH_2-$ singlet signal in the ^1H NMR spectrum of the dithiocarbene complex $[Cp(OC)_2Fe{=}\overline{CSCH_2CH_2S}]PF_6$ in $(CD_3)_2CO$ does not change even at −80 °C.[42]

Conclusive evidence for the presence of carbene ligands in these complexes is the very low-field (206–295 ppm) carbene ^{13}C NMR signal (Table III). The position of the carbene ^{13}C resonance in the cationic complexes containing $={\overline{CZ(CH_2)_nY}}$ ligands can be broadly classified according to the heteroatoms in the carbene ligands: (i) Y = Z = NH and n = 2 or 3, values are at the highest field[21] in the range $\delta_{carbene}$ 190–200; (ii) Y = NH, Z = O, and n = 2 or 3, values lie in the range $\delta_{carbene}$ 206–234; (iii) Z = Y = O and n = 2, values lie in the range $\delta_{carbene}$ 240–260; (iv) Y = Z = S and n = 2 or 3,[21] values appear at the lowest field in the range $\delta_{carbene}$ 283–295. For $Cp(CO)_2Fe{=}C(ZR)(YR)^+$ complexes containing acyclic carbene ligands, $\delta_{carbene}$ moved to lower field as Z and Y changed in the order Z = O, Y = NR (δ 220–227) < Z = Y = O (δ 250) < Z = Y = S (δ 300).[12,21] When PPh_3 is substituted for one of the CO groups in $Cp(OC)_2Fe{=}\overline{COCH_2CH_2Y}^+$ (Y = NH, O), $\delta_{carbene}$ shifts to lower field by about 12–13 ppm; a similar trend was noted for $Cp(OC)LFe{=}C(SMe)_2^+$[43] and $Cp(ON)LMn{=}\overline{COCH_2CH_2NH}^+$.[20]

As one passes from iron to ruthenium, the ^{13}C resonances (Table III) of the carbene and carbonyl ligands move to higher field; this upfield shift on descending the group is typical of other metal carbene[44] and carbonyl complexes.[45] The ^{13}C chemical shifts δ_{CO} of the CO ligands in the same types of complexes shift much less widely than $\delta_{carbene}$, but they do show a trend of shifting downfield as a function of the heteroatoms in the order O,N ~ S,N > O,O ~ S,S. It appears that slight changes in the electronic environment at the carbene carbon cause greater shifts in $\delta_{carbene}$ than in δ_{CO}. In the cases of Id and IIId, which contain a Ph_3P ligand, the carbene carbon signals appear as doublets; the ^{13}CO signal in IIId is also split, and these splittings are due to coupling with the ^{31}P of the phosphine ligand.

Registry No. Ia, 69532-52-1; Ib, 84433-09-0; Ic, 79664-11-2; Id, 84433-11-4; Ie, 76136-60-2; If, 90858-53-0; Ig, 69532-54-3; IIa, 90858-55-2; IIb, 90858-57-4; IIIa, 79664-09-8; IIIb, 84433-14-7; IIIc, 84433-12-5; IIId, 84433-16-9; IIIe, 90858-59-6; IIIf, 79664-14-5; IV, 76136-38-4; $[Cp(OC)_3Fe]CF_3SO_3$, 76136-47-5; $[BrCH_2CH_2NH_3]Br$, 2576-47-8; $[BrCH_2CH_2CH_2NH_3]Br$, 5003-71-4; $[Et_3NH]Br$, 636-70-4; $[Cp(OC)_3Ru]PF_6$, 31741-71-6; $[Cp(OC)_3Ru]CF_3SO_3$, 90858-60-9; $[Cp(OC)_2(ON)Mn]PF_6$, 31921-90-1; $[Cp(OC)_2(Ph_3P)Fe]BF_4$, 32614-25-8; $[Cp(OC)_2(Ph_3P)Fe]CF_3SO_3$, 90858-61-0; $[Cp(OC)_2(CS)Fe]CF_3SO_3$, 60817-01-8; $\overline{HNCH_2CH_2CH_2}$, 503-29-7; $BrCH_2CH_2OH$, 540-51-2; NaBr, 7647-15-6; NaCl, 7647-14-5; NaI, 7681-82-5; $Cp_2(OC)_4Fe_2$, 12154-95-9; $NOPF_6$, 16921-91-8; aziridine, 151-56-4; oxirane, 75-21-8; 3-bromopropanol, 627-18-9; thiirane, 420-12-2.

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