Organometallics **1984**, *3*, 1749–1754

Oxidative Cleavage Reactions of Compounds of the Type CpRuLL′R (L, L′ = CO, PPh$_3$; R = Me, PhCH$_2$)

Michael F. Joseph, John A. Page, and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Received May 4, 1984

The compounds CpRuLL′R (Cp = η^5-C$_5$H$_5$; L, L′ = CO, PPh$_3$; R = Me, PhCH$_2$) have been prepared, some by improved routes. Alkyl cleavage reactions with halogens, hydrogen chloride, mercury(II) halides, and copper(II) halides are investigated, and the stoichiometries of the reactions are compared with those of the iron analogues. Electrochemical studies show that the ruthenium compounds are less susceptible to oxidation than are the corresponding iron compounds, but the data are consistent with all cleavage reactions being oxidative in nature.

Introduction

Reactions involving the formation and cleavage of metal–carbon bonds are central to organometallic chemistry and hence are of great interest mechanistically.[1] We have earlier presented evidence that many electrophilic cleavage reactions of compounds of the type CpFeCOLR (L = CO, tertiary phosphine; R = alkyl) with halogens, mercury(II) salts, and copper(II) salts are oxidative in nature and occur via formally iron(III) and iron(IV) intermediate species.[2] We were, however, unable to provide firm, direct evidence for the proposed intermediates and decided to explore the chemistry of analogous complexes of ruthenium. It is well established that higher oxidation states are often more stable for compounds of second- and third-row transition metals than for their first-row counterparts,[3–5] and a report that (η^5-C$_5$Me$_4$Et)Ru(CO)$_2$Br adds bromine to form (η^5-C$_5$Me$_4$Et)Ru(CO)Br$_3$[6] gave reason for optimism that alkylruthenium(III) or -(IV) species might be stable.

While our original hopes eventually proved misplaced, however, we have successfully explored and herein report a survey of a variety of electrophilic cleavage reactions of compounds of the type CpRuLL′R (L, L′ = CO, PPh$_3$). A preliminary account has appeared.[7]

Experimental Section

Preparation of Ruthenium Compounds. The compounds Ru$_3$(CO)$_{12}$,[8] [CpRu(CO)$_2$]$_2$,[9] CpRu(CO)$_2$ X (X = Cl,[10] Br,[11] I,[11] Me[12]), CpRu(CO)PPh$_3$X (X = Cl, Br, I),[13] CpRu(PPh$_3$)$_2$X (X = Cl,[14] Br,[15] I[15]), and CpRu(PPh$_3$)$_2$R (R = Me, PhCH$_2$)[16] were prepared essentially as described in the literature. All experiments described below were carried out under nitrogen unless otherwise stated.

CpRu(CO)$_2$R (R = Me, PhCH$_2$). A solution of 1.0 g of [CpRu(CO)$_2$]$_2$ in 15 mL of THF was treated with 15.0 mL of 1.5 M K[BHEt$_3$] (Aldrich). The mixture was stirred for 3 h, 2 mL of methyl iodide or benzyl chloride was added, and the solution was stirred a further 2 h. The solvent was then removed under reduced pressure, the resulting residue was extracted with petroleum ether (bp 30–60 °C), and the solution was eluted through an alumina column to give colorless (methyl) or pale orange (benzyl) solutions. Evaporation of the solvent gave pure alkyl compounds (IR, NMR[12,17]) in 30–40% yields.

CpRu(CO)(PPh$_3$)Me. (a) A solution of 0.7 g of CpRu(CO)$_2$Me and 2.3 g of PPh$_3$ in petroleum ether (bp 30–60 °C) was irradiated with a Hanovia lamp for 36 h. The solvent was removed at reduced pressure, and the resulting brown residue was dissolved in a minimum volume of methylene chloride and poured onto an alumina column. Elution with petroleum ether removed unreacted starting materials, and then elution with a 5:1 petroleum ether–CH$_2$Cl$_2$ mixture removed a pale yellow band containing the product contaminated with some CpRu(PPh$_3$)$_2$Me. After recrystallization from CH$_2$Cl$_2$–heptane, 0.50 g of CpRu(CO)(PPh$_3$)Me (40% yield) and about 0.20 g of CpRu(PPh$_3$)$_2$Me (10% yield) were obtained. The overall yield could be increased by recycling recovered starting materials. (b) Carbon monoxide was bubbled for 30 h through a solution of 1.0 g of CpRu(PPh$_3$)$_2$Me in 70 mL of toluene maintained at 80 °C. The solution was cooled and passed through an alumina column. Evaporation of the solvent followed by recrystallization of the yellow residue from CH$_2$Cl$_2$–heptane gave 0.50 g of product (75% yield). The compound was characterized by IR and NMR spectroscopy.[18]

CpRu(CO)(PPh$_3$)CH$_2$Ph. (a) Carbon monoxide was bubbled for 1 h through a solution of 1.0 g of CpRu(PPh$_3$)$_2$CH$_2$Ph in 50 mL of toluene at 80 °C. The solution was cooled, passed through an alumina column, and taken to dryness. The residue was then recrystallized from CH$_2$Cl$_2$–heptane to give 0.54 g of product (75% yield). (b) A solution of 1.5 g of CpRu(CO)(PPh$_3$)Cl in 100 mL of toluene was treated with 10.0 mL of 1.5 M PhCH$_2$MgCl in ethyl ether (Alfa). The reaction mixture was stirred for 4 h and then hydrolyzed, and the organic layer was separated and dried. Subsequent workup as above gave 1.25 g of the product (75% yield), shown to be pure by IR and NMR spectroscopy.[19]

In many of the studies to be described below, the course of a reaction was monitored spectroscopically. Pertinent data are therefore collected in Table I.

Instrumentation. IR spectra were run on a Beckman 4240 spectrometer, ^{1}H NMR spectra on a Bruker HX 60 spectrometer,

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0276-7333/84/2303-1749$01.50/0

Table I. Spectroscopic Data for the Compounds CpRuLL′X

compd	ν_{CO}, cm^{-1}	$\delta_{^{31}P}$^{a}	$\delta_{^1H}$^{b}
L = L′ = CO, X = Me	2020, 1963^c		0.34 (s, Me), 5.24 (s, Cp)
PhCH$_2$	2020, 1963^c		2.96 (s, CH$_2$), 5.09 (s, Cp), 7.13 (m, Ph)
Cl	2058, 2008^c		5.45 (s, Cp)
Br	2055, 2005^c		5.45 (s, Cp)
I	2048, 2000^c		5.45 (s, Cp)
L = CO, L′ = PPh$_3$, X = Me	1928^d	64.0	0.07 (d, J_{PH} = 5.3 Hz, Me), 4.81 (d, J_{PH} = 0.5 Hz, Cp), 7.36 (m, Ph)
CH$_2$Ph	1917^d	62.5	2.22 (q, J_{PH} = 8.5 Hz, J_{HH} = 8.9 Hz, CH$_2$), 2.85 (q, J_{PH} = 4.5 Hz, CH$_2$), 4.62 (s, Cp), 7.03 (m, C*Ph*), 7.39 (m, P*Ph*)
Cl	1960^d	49.2	4.88 (s, Cp), 7.40 (m, Ph)
Br	1962^d	48.4	4.88 (s, Cp), 7.40 (m, Ph)
I	1962^d	47.6	4.88 (s, Cp), 7.40 (m, Ph)
L = L′ = PPh$_3$, X = Me		55.4	0.40 (t, J_{PH} = 5.7 Hz, Me), 4.15 (s, Cp), 7.19 (m, Ph)
PhCH$_2$		51.3	2.66 (t, J_{PH} = 7.0 Hz, CH$_2$), 3.96 (s, Cp), 6.87 (m, C*Ph*), 7.19 (m, P*Ph*)
Cl		39.3	4.10 (s, Cp), 7.16 (m, Ph)
Br		38.4	4.10 (s, Cp), 7.16 (m, Ph)
I		37.4	4.10 (s, Cp), 7.16 (m, Ph)

^{a} CDCl$_3$, relative to external H$_3$PO$_4$. ^{b} CDCl$_3$, relative to internal Me$_4$Si. ^{c} CH$_2$Cl$_2$. ^{d} Cyclohexane.

Table II. Cleavage Reactions of CpRuLL′R with HgX$_2$

					products (% yields)	
L	L′	R	HgX$_2$	solv	CpRuLL′X	RHgX^a
CO	CO	Me	HgCl$_2$	(CD$_3$)$_2$CO	CpRu(CO)$_2$Cl (100)	MeHgCl (100)
			HgBr$_2$	(CD$_3$)$_2$CO	CpRu(CO)$_2$Br (100)	MeHgBr (100)
			HgCl$_2$	CD$_2$Cl$_2$	no reaction after 4 h	
CO	PPh$_3$	Me	HgCl$_2$	CD$_2$Cl$_2$	CpRu(CO)(PPh$_3$)Cl (80)	MeHgCl (100)
			HgBr$_2$	CD$_2$Cl$_2$	CpRu(CO)(PPh$_3$)Br (100)	MeHgBr (100)
CO	PPh$_3$	CH$_2$Ph	HgCl$_2$	CD$_2$Cl$_2$	CpRu(CO)(PPh$_3$)Cl (100)	PhCH$_2$HgCl (100)
			HgBr$_2$	CD$_2$Cl$_2$	CpRu(CO)(PPh$_3$)Br (100)	PhCH$_2$HgBr (100)
PPh$_3$	PPh$_3$	Me	HgCl$_2$	CD$_2$Cl$_2$	CpRu(PPh$_3$)$_2$Cl (100)	MeHgCl (100)
			HgBr$_2$	CD$_2$Cl$_2$	CpRu(PPh$_3$)$_2$Br (100)	MeHgBr (80)
PPh$_3$	PPh$_3$	CH$_2$Ph	HgCl$_2$	CD$_2$Cl$_2$	CpRu(PPh$_3$)$_2$Cl (100)	PhCH$_2$HgCl (100)
			HgBr$_2$	CD$_2$Cl$_2$	CpRu(PPh$_3$)$_2$Br (100)	PhCH$_2$HgBr (100)

^{a} Alkylmercury compounds recognized by their chemical shifts and ^{1}H–^{199}Hg coupling constants.[20,21]

and ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra on a Bruker CXP 200 spectrometer. T_1 measurements for some of the compounds were run on the CXP 200 using a computer-accessed standard T_1 inversion decay program. UV–visible spectra were run on a Perkin-Elmer 552 spectrometer.

Triangular wave voltammetric experiments (TWV) were carried out by using Princeton Applied Research Corp. (PARC) Model 170 and 174A polarographic analyzers. At slow scan rates ($\leq$0.1 V s^{-1}), the voltammograms were recorded on a Hewlett-Packard (HP) Model 7040A recorder, while at faster scan rates the voltammograms were recorded on a PARC HP Model 7618 storage oscilloscope. Controlled potential electrolyses were carried out by using the 174A analyzer as a potentiostat in conjunction with a PARC Model 379 digital coulometer.

Analyses of organic products were done primarily by gas chromatography using a HP Model 5880A gas chromatograph and terminal.

Chemical Cleavage Reactions. Mercury(II) Halides. The mercury(II) halide cleavage reactions listed in Table II were carried out by adding a slight molar excess of the mercury compound to a solution of the alkylruthenium compound in CD$_2$Cl$_2$ that had been spiked with a known amount of *p*-dioxane. The yellow solutions generally turned orange as the mercury(II) halide dissolved, and yields of the various products were determined by integrations of the ^{1}H NMR spectra. Spectra for these reactions and those that are described below were generally run with pulse delays of 7–10 s in order to obtain accurate integrations. This was found to be necessary because Cp proton resonances generally have longer values of T_1 ($\geq$1 s) than do alkyl and phenyl resonances. IR and ^{31}P NMR spectra were run in most cases to confirm the identities of the ruthenium-containing products. Reaction products and yields are listed in Table II.

Most reactions proceeded rapidly and cleanly in spite of the low solubility of the mercury halides in the solvent used. The sole exception was CpRu(CO)$_2$Me, which was inert in CD$_2$Cl$_2$ and hence was run under totally homogeneous conditions in acetone-d_6.

A brief competition study to determine the relative rates of reactions of two complexes was performed by addition of a deficiency of HgCl$_2$ to a solution containing equimolar amounts of CpRu(CO)$_2$Me and CpRu(CO)(PPh$_3$)Me in acetone-d_6. The reaction was totally homogeneous and was monitored by ^{1}H NMR spectroscopy. The monosubstituted compound reacted about 20 times faster than did the dicarbonyl compound.

Halogens. Halogen cleavage reactions were carried out by adding slightly in excess of a 1 molar equiv of bromine or iodine to a solution of an alkylruthenium compound in CDCl$_3$. The reactions, which were invariable rapid, were monitored by ^{1}H NMR spectroscopy and, in some cases, by gas chromatography. Carbonyl-containing ruthenium compounds were also identified by IR spectroscopy. Results are listed in Table III.

In some cases where excess halogen was added, the ^{1}H NMR spectra exhibited broadened resonances, although no new species could be isolated or identified.

Hydrogen Chloride. Treatment of CpRu(CO)(PPh$_3$)CH$_2$Ph with excess anhydrous HCl in CDCl$_3$ gave CpRu(CO)(PPh$_3$)Cl and toluene in 100% and 85% yields, respectively.

Copper(II) Halides. Weighed amounts of copper(II) compounds were added to solutions or suspensions of alkylruthenium compounds as indicated in Table IV. Solvents were chosen so that either the ruthenium compound (CH$_2$Cl$_2$) or the copper compound (MeCN) was in solution. Reaction products were monitored by a combination of gas chromatography, IR, and ^{1}H

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Table III. Halogen Cleavage Reactions of CpRuLL'R

L	L'	R	X_2	products (% yields)	
				CpRuLL'X	RX
CO	CO	Me	Br_2	$CpRu(CO)_2Br$ (70)	MeBr (100)
			I_2	$CpRu(CO)_2I$ (100)	MeI (100)
CO	PPh_3	Me	Br_2	$CpRu(CO)(PPh_3)Br$ (45)	MeBr (27)
			I_2	$CpRu(CO)(PPh_3)I$ (100)	MeI (100)
CO	PPh_3	CH_2Ph	Br_2	$CpRu(CO)(PPh_3)Br$ (45)	$PhCH_2Br$ (65)
			I_2	$CpRu(CO)(PPh_3)I$ (100)	$PhCH_2I$ (100)
PPh_3	PPh_3	Me	Br_2	$CpRu(PPh_3)_2Br$ (20)	MeBr (75)
			I_2	$CpRu(PPh_3)_2I$ (98)	MeI (87)
PPh_3	PPh_3	CH_2Ph	Br_2	$CpRu(PPh_3)_2Br$ (20)	$PhCH_2Br$ (45)
			I_2	$CpRu(PPh_3)_2I$ (90)	$PhCH_2I$ (69)

Table IV. Copper(II) Halide Cleavage Reactions of CpRuLL'R

L	L'	R	Cu(II) compd	Cu:Ru ratio	solv	products (% yields)
CO	CO	Me	$CuBr_2$	2:1	$(CD_3)_2CO$	$CpRu(CO)_2Br$ (100), MeBr (100)
			$CuBr_2$	>4:1	CH_2Cl_2	no reaction after 1 h
			$CuCl_2{\cdot}2H_2O$	>4:1	$(CD_3)_2CO$	no reaction after 5 h
CO	PPh_3	Me	$CuBr_2$	>4:1	CH_2Cl_2	$CpRu(CO)(PPh_3)Br$ (100), MeBr (>29)
			$CuCl_2{\cdot}2H_2O$	>4:1	$CDCl_3$	$CpRu(CO)(PPh_3)Cl$ (38), MeCl (>10)
CO	PPh_3	CH_2Ph	$CuBr_2$	3.2:1	CH_2Cl_2	$CpRu(CO)(PPh_3)Br$ (76), $PhCH_2Br$ (79)
			$CuCl_2{\cdot}2H_2O$	3.6:1	CH_2Cl_2	$CpRu(CO)(PPh_3)Cl$ (93), $PhCH_2Cl$ (91)
PPh_3	PPh_3	CH_2Ph	$CuCl_2{\cdot}2H_2O$	2.0:1	CH_2Cl_2	$CpRu(PPh_3)_2Cl$ (85), PhMe (22), $PhCH_2Cl$ (7), $(PhCH_2)_2$ (28)
			$CuCl_2{\cdot}2H_2O$	3.6:1	MeCN	$CpRu(PPh_3)_2Cl$ (80), PhMe (10), $PhCH_2Cl$ (55), $(PhCH_2)_2$ (6)
			$CuCl_2{\cdot}2H_2O$	5.3:1	MeCN	$CpRu(PPh_3)_2Cl$ (85), PhMe (7), $PhCH_2Cl$ (77), $(PhCH_2)_2$ (7)
			$CuCl_2{\cdot}2H_2O$	10:1	MeCN	$CpRu(PPh_3)_2Cl$ (91), PhMe (3), $PhCH_2Cl$ (75), $(PhCH_2)_2$ (4)
			$CuBr_2$	2.1:1	CH_2Cl_2	$CpRu(PPh_3)_2Br$ (94), PhMe (18), $PhCH_2Br$ (21), $(PhCH_2)_2$ (28)
			$CuBr_2$	2.6:1	MeCN	$CpRu(PPh_3)_2Br$ (93), PhMe (4), $PhCH_2Br$ (90), $(PhCH_2)_2$ (6)

Table V. Voltammetric Peak Potentials

compd	$(E_p)_a/V^a$	comments[b]
$CpRu(CO)_2Me$	1.55	irreversible
$CpRu(CO)(PPh_3)Me$	1.02	irreversible
$CpRu(CO)(PPh_3)CH_2Ph$	1.03	irreversible
$CpRu(CO)(PPh_3)Cl$	1.37	quasi-reversible
$CpRu(PPh_3)_2Me$	0.39	quasi-reversible
$CpRu(PPh_3)_2CH_2Ph$	0.40	irreversible
$CpRu(PPh_3)_2Cl$	0.72	quasi-reversible

[a] $(E_p)_a$ = anodic peak potential vs. Ag/AgCl/aqueous KCl/reference, 0.1 V s^{-1}, CH_2Cl_2 solvent, 0.05 M Bu_4NBF_4 supporting electrolyte. [b] Irreversible—no cathodic process on TWV at scan rates up to 0.5 V s^{-1}. Quasi-reversible—cathodic peak current ≈ anodic peak current at 0.1 V s^{-1} but $(E_p)_a - (E_p)_c > 0.057$ V.

and ^{31}P NMR spectroscopy, as appropriate.

The reactions typically turned from yellow to orange, with the formation of fine gray precipitates of copper(I) halides. Attempts to determine the yields of copper(I) halides by gravimetric procedures, as done previously,[2] gave very erratic results because of the small scale involved. In one case, however, the reaction of $CpRu(CO)(PPh_3)CH_2Ph$ with a 3.2 molar ratio of $CuBr_2$ in MeCN, spectrophotometric determination of unreacted $CuBr_2$ indicated that the Cu:Ru ratio for the reaction was 2.1:1.

Electrochemical Studies. All experiments were run by using rigorously deaerated and anhydrous conditions. The CH_2Cl_2 used was distilled directly from P_2O_5 under nitrogen prior to use, and the supporting electrolytes were recrystallized, dried, and stored under vacuum. Solutions used in the studies were typically 0.05–0.10 M in supporting electrolyte.

The TWV experiments were carried out by using approximately 10^{-4} M solutions of alkylruthenium substrate in CH_2Cl_2. A three-electrode system consisting of a polished glassy carbon working electrode, a platinum counter electrode, and a Ag/AgCl/saturated aqueous KCl reference electrode was used. The reference electrode was well isolated from the working compartment by a Luggin capillary junction filled with anhydrous electrolyte; the working electrode surface was cleaned prior to each run with a soft cloth. The voltammetry was investigated over a range of positive potentials and sweep rates, with results as given in Table V.

Controlled potential electrolyses were carried out by using various substrates and supporting electrolytes with the results given in Table VI. A two-compartment cell was used with a

Table VI. Controlled Potential Electrolysis Experiments

compd	E/V^a	n	supporting electrolyte	products (% yields)
$CpRu(CO)_2Me$	1.68	1.05	0.05 M Bu_4NBF_4	$CpRu(CO)_2Cl$ (79)
$CpRu(CO)(PPh_3)Me$	1.08	1.02	0.05 M Bu_4NBF_4/0.10 M Et_4NCl	$CpRu(CO)(PPh_3)Cl$ (75)
$CpRu(CO)(PPh_3)CH_2Ph$	0.93	0.95	0.05 M Et_4NClO_4/0.10 M Et_4NCl	$CpRu(CO)(PPh_3)Cl$ (83) $PhCH_2Cl$ (50)
$CpRu(PPh_3)_2Me$	0.60	0.97	0.05 M Bu_4NBF_4/0.02 M Bu_4NCl	$CpRu(PPh_3)_2Cl$ (60)
$CpRu(PPh_3)_2CH_2Ph$	0.60	0.85	0.05 M Bu_4NBF_4/0.02 M Bu_4NCl	$CpRu(PPh_3)_2Cl$ (87) $PhCH_2Cl^c$
$CpRu(PPh_3)_2CH_2Ph^b$	0.60	0.84	0.05 M Bu_4NBF_4/0.02 M Bu_4NCl	$CpRu(PPh_3)_2Cl$ (60) PhCHO (32), $(PhCH_2)_2$ (15)

[a] Graphite electrode potential vs. Ag/AgCl/saturated aqueous KCl reference; CH_2Cl_2 solvent. [b] Air present. [c] Yield not determined.

platinum basket counterelectrode, a large graphite working electrode, and a Ag/AgCl/aqueous KCl reference electrode. It was found that the working electrode became coated with a film during electrolysis, and it was necessary to clean it periodically to maintain a good current flow. Electrolyses were run with 100-mL volumes of 10^{-3} M solutions of the alkylruthenium compounds and took 6–10 h.

Volatile electrolysis products were determined directly by gas chromatography, while the ruthenium-containing products were isolated by taking the solutions to dryness and extracting the residues with petroleum ether to remove organic products. Subsequent extraction with ethyl ether removed the ruthenium products from the bulk of the solid supporting electrolyte; subsequent removal of the ether and dissolution in $CDCl_3$ then permitted analysis of the metal-containing products by ^1H NMR spectroscopy. In the case of $CpRu(CO)_2Me$, the halo product was shown to be $CpRu(CO)_2Cl$, rather than $CpRu(CO)_2F$, by precipitation of AgCl on treatment with $AgNO_3$ in acetonitrile.

The number of electrons involved in the charge-transfer process, *n*, was estimated by a Faraday law calculation after correction of the total quantity of electricity for a background based on the final constant residual current.

Results and Discussion

Syntheses. It had been anticipated that compounds of the type $CpRu(CO)_2R$ would be readily synthesized via reactions of $Na[CpRu(CO)_2]$, prepared by reduction of $[CpRu(CO)_2]_2$ with sodium amalgam, with alkyl halides or tosylates. Similar procedures certainly work well for the analogous iron compounds.[22]

While we have confirmed that the methyl compound can be prepared in 40% yield by treating $Na[CpRu(CO)_2]$ with methyl iodide,[12] we have also confirmed an earlier report[17] that the benzyl analogue cannot be readily prepared by this approach. Presumably the reduced nucleophilicity of $[CpRu(CO)_2]^-$ relative to $[CpFe(CO)_2]^-$ [23] is responsible for the lowered yields of the benzylruthenium compound, although we find that isolation of the compound is also hampered by the presence of the byproducts ruthenocene and $Hg[CpRu(CO)_2]_2$.

A superior route to the desired benzylruthenium compound involved treatment of $[CpRu(CO)_2]_2$ with $K[BHEt_3]$, a procedure pioneered by Gladysz[24] for several carbonylate anions and which presumably involves formation of $K[CpRu(CO)_2]$. Treatment of the solution with benzyl chloride gave $CpRu(CO)_2CH_2Ph$ in about 30% yield, much superior to a previously reported yield.[17] While the stoichiometry and mechanism of the reaction are not known, hydride attack on a carbonyl group to form a formyl species is a likely step; there are many precedents for such behavior,[25] and a singlet appeared at δ 14.0, indicative of a formyl group,[25] in the NMR spectrum of the $[CpRu(CO)_2]_2$–$K[BHEt_3]$ reaction mixture. It is interesting to note that the best yields of the compounds $CpRu(CO)_2R$ (R = Me, $PhCH_2$) were obtained by using $K[BHEt_3]$ rather than either the corresponding lithium or sodium salts or $Na[CpRu(CO)_2]$ prepared by sodium amalgam cleavage of the dimer. The results are probably to be attributed to decreased ion pairing in the potassium system, with thereby enhanced nucleophilicity of the carbonylate anion.[26]

While the monosubstituted compounds $CpRu(CO)(PPh_3)R$ had been reported previously,[18,19,27] procedures were lengthy and sometimes gave low yields. We therefore sought more facile routes and have found that the monosubstituted methyl compound can readily be obtained by the photochemical decarbonylation of $CpRu(CO)_2Me$ in the presence of triphenylphosphine. This method is well-known for the analogous iron compounds[28,29] but had surprisingly not been reported for ruthenium. Interestingly, and in contrast to the iron system, some of the disubstituted ruthenium compound $CpRu(PPh_3)_2Me$ was also obtained. The corresponding iron compound has not been observed, possibly because of steric hindrance around the smaller iron atom.

Both monosubstituted alkylruthenium compounds could also be readily prepared by carbonylation of the corresponding bis(phosphine) alkyl compounds, although there is a suggestion in the literature that such reactions require high carbon monoxide pressures.[27] Lehmkuhl et al.[30] have, however, postulated facile phosphine dissociation from compounds of the type $CpRu(PPh_3)_2R$ at 80 °C, and it seemed likely that the vacant site thus generated would readily coordinated carbon monoxide. We find that toluene solutions of the compounds $CpRu(PPh_3)_2R$ (R = Me, $PhCH_2$) react smoothly at 80 °C with carbon monoxide at atmospheric pressure. The monosubstituted benzyl compound can also be prepared in good yields by reactions of benzylmagnesium chloride with $CpRu(CO)(PPh_3)Cl$.

Electrophilic Cleavage Reactions. Although the reactions of compounds of the type CpFeLL′R with electrophilic reagents such as halogens, anhydrous hydrogen halides, mercury(II) salts, and copper(II) salts have been extensively studied,[2] we have found surprisingly little information in the literature pertaining to the corresponding chemistry of the analogous alkylruthenium compounds. We have therefore carried out a survey of the reactions of compounds of the type CpRuLL′R with the electrophilic reagents listed above and report below our findings. Although we have not as yet performed many experiments designed to elucidate the mechanisms of the cleavage reactions, we have found in many cases that similarity to the much better studied iron chemistry,[1,2] coupled with complementary electrochemical studies which are also described below, has allowed us to at least suggest reasonable mechanisms for the reactions studied.

Mercury(II) Halide Cleavage Reactions. The results of the mercury(II) cleavage reactions are listed in Table II. With one exception, all reactions proceeded to completion in CD_2Cl_2 as in eq 1 in spite of the low solubility of the mercury compounds.

$$\mathrm{CpRuLL'R} + \mathrm{HgX_2} \rightarrow \mathrm{CpRuLL'X} + \mathrm{RHgX} \qquad (1)$$

$$\mathrm{L, L'} = \mathrm{CO, PPh_3};\ \mathrm{X} = \mathrm{Cl, Br};\ \mathrm{R} = \mathrm{Me, PhCH_2}$$

The stoichiometries of the cleavage reactions are thus identical with those reported for many analogous iron compounds[31,32] and may be expected to involve the type of oxidative mechanism postulated previously for the iron system,[1,31,32] i.e., eq 2.

Consistent with the hypothesis of an oxidative mechanism, $CpRu(CO)_2Me$, which has the highest oxidation potential of the compounds studied (Table V; see below),

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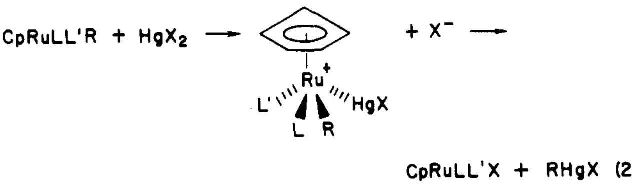
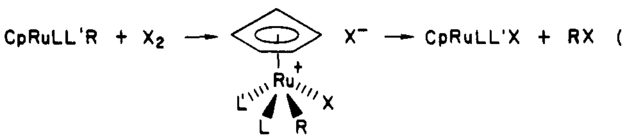


(2)

is also the least reactive. It alone failed to react with the mercury(II) salts under heterogeneous conditions; it also reacted with $HgCl_2$ some 20 times slower than did $CpRu(CO)(PPh_3)Me$ in a competition study run under homogeneous conditions. While the substituted compound would experience considerably more steric hindrance during the cleavage reaction, it also has a considerably lower oxidation potential.

Halogen Cleavage Reactions. The results of the halogen cleavage reactions (Table III) suggest a stoichiometry, and presumably a mechanism, similar to that of the iron system,[1,2] i.e., eq 3.



(3)

Yields of bromoruthenium products were low because of as yet unidentified side reactions in which the cyclopentadienyl groups underwent bromination. Additions of excess bromine in all cases led to disappearance of the cyclopentadienyl resonances from the NMR spectra and broadening and deshielding of the triphenylphosphine phenyl resonances (to about δ 7.4–7.7). In several cases, new resonances appeared at δ 6.15, 5.16, and 4.86; partial bromination of free cyclopentadiene results in multiplets having about the same chemical shifts.

Separate experiments showed that the halo compounds $CpRu(CO)_2Br$, $CpRu(CO)(PPh_3)Cl$, and $CpRu(PPh_3)_2X$ (X = Cl, Br, I) all react with bromine to give rather undistinguished NMR spectra, as described above. Broadening of resonances is generally observed, consistent with the presence of paramagnetic species, but attempted determinations of magnetic susceptibilities using the Evans method[33] were inconclusive. It would seem that any paramagnetic complexes formed are minor products; no new oxidized compounds were ever isolated.

Interestingly, treatment of $CpRu(CO)(PPh_3)Cl$ in $CDCl_3$ with iodine resulted in slow replacement of the Cp resonance at δ 4.88 with a new peak at δ 5.03. Removal of the solvent yielded an orange product that proved to be (^1H NMR, qualitative halide analysis) $CpRu(CO)(PPh_3)I$. This in turn was found to react rapidly and reversibly with iodine in $CHCl_3$ or $CDCl_3$ to form a new compound exhibiting a carbonyl stretching band at 1975 cm^{-1} and a Cp resonance at δ 5.02. The new species, which was deeply colored, was probably a charge-transfer complex involving interaction of molecular iodine with either the Cp ring or the halo ligands.[34] It is very unlikely that the products were oxidized ruthenium complexes, in part because of the ready reversibility of the reaction of iodine with $CpRu(CO)(PPh_3)I$ and also because much greater changes in ν_{CO} and δ_{Cp} would be anticipated.[35]

Cleavage by Hydrogen Chloride. Only a single HCl cleavage reaction was carried out, i.e., eq 4. The reaction went cleanly and in high yield and presumably involves protonation of the metal to give $[CpRu(H)(CO)(PPh_3)CH_2Ph]Cl$, followed by reductive elimination of toluene.[38,39]

$$CpRu(CO)(PPh_3)CH_2Ph + HCl \rightarrow CpRu(CO)(PPh_3)Cl + PhMe \quad (4)$$

Copper(II) Cleavage Reactions. The data listed in Table IV are complicated by the fact that the scale at which most of the reactions were run generally precluded satisfactory gravimetric determinations of the copper(I) halides being formed. However, in at least one case, the homogeneous reaction of $CpRu(CO)(PPh_3)CH_2Ph$ with $CuBr_2$, spectrophotometric determination of the copper(II) salt consumed showed that cleavage to give metal and alkyl halides proceeds as in the iron system,[2] i.e., eq 5.

$$CpRuLL'R + 2CuX_2 \rightarrow CpRuLL'X + RX + 2CuX \quad (5)$$

Thus the data are consistent with one-electron oxidations to form the 17-electron intermediates $[CpRuLL'R]^+$,[2] i.e., eq 6. Nucleophilic attack by X^- on the α-carbon atom

$$CpRuLL'R + CuX_2 \rightarrow [CpRuLL'R]^+ + X^- + CuX \quad (6)$$

of R would yield RX and the metal-based radical $CpRuLL'\cdot$, which would abstract a halogen atom from a second CuX_2 to complete the reaction.[2] One-electron oxidations of the type postulated have been demonstrated electrochemically (see below) and give chemical products consistent with eq 5 and 6. As with the mercury(II) reactions, $CpRu(CO)_2Me$ was inert except in a homogeneous system, probably because of its relatively high oxidation potential.

As demonstrated with the iron system,[2] the complexes $[CpRuLL'R]^+$ should also be able to undergo homolysis to yield radicals R·; when R = $PhCH_2$, dimerization would occur to yield bibenzyl. While $CpRu(CO)(PPh_3)CH_2Ph$ appears to react solely as in (5), it is interesting to note that the bis(phosphine) analogue $CpRu(PPh_3)_2CH_2Ph$ appears to react in both ways. Small but significant amounts of bibenzyl were observed for each reaction of this compound, while reactions in the presence of air also yielded benzyl alcohol and benzaldehyde, products which may arise from benzyl radical scavenging by oxygen.[40,41]

Reactions of the compound $CpRu(PPh_3)_2CH_2Ph$ were carried our in both methylene chloride and acetonitrile, the latter being a better solvent for the copper(II) salts. The data in Table IV show quite clearly that the formation of benzyl halides is much more preferred in the polar solvent, consistent with the relatively high concentration of halide ions in that solvent. The even greater preference for formation of benzyl halides from reactions of $CpRu(CO)(PPh_3)CH_2Ph$ is also consistent with the mechanism proposed,[2] as the monosubstituted species $[CpRu(CO)(PPh_3)CH_2Ph]^+$, should be more susceptible to nucleophilic attack at the α-carbon atom than is the disubstituted analogue.

The mode of formation of the toluene is not known; the yields of the gaseous methyl halides from the reactions of $CpRu(CO)(PPh_3)Me$ are lower limits based on estimates from integrations of the NMR spectra.

Electrochemical Cleavage Reactions. The TWV experiments showed oxidation peaks for each of the al-

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[34] For precedents, see: Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969.

[35] For instance, conversion of the compounds $CpM(CO)_3X$ to $CpM(CO)_2X_3$ (M = Mo, W; X = Cl, Br, I) results in increases of the averages of the carbonyl stretching frequencies of 50–60 cm^{-1}, while the Cp resonances are deshielded by 0.4–0.7 ppm.[36,37]

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kylruthenium compounds, with anodic peak potentials as in Table V. Those processes deemed irreversible showed no evidence of a cathodic wave on the reverse scan at scan rates up to 0.5 V s^{-1}, behavior which was independent of the switching potential for the triangular wave scan. Those processes deemed quasi-reversible did exhibit a cathodic process at 0.1 V s^{-1} with current comparable in magnitude to the anodic peak current, but only if the switching potential for the reverse scan was less than 0.1 V positive to the potential of the anodic peak. More positive switching potentials or faster scan rates resulted in disappearance of the cathodic peak, indicating short lifetimes for the initial products of the electrode reactions. Similar observations have been made for many of the analogous iron complexes.[2,42]

The number of electrons involved in the oxidation process was evaluated by using ferrocene as an internal standard representing a one electron reversible charge-transfer process.[43] Experiments with a solution containing equimolar concentrations of $CpRu(CO)_2Me$ and Cp_2Fe in the CH_2Cl_2/Bu_4NBF_4 electrolyte gave the same peak current for each of the anodic waves at 0.1 V s^{-1}, indicating $n = 1.0$ for the oxidation of the $CpRu(CO)_2Me$. However, experiments with the PPh_3-substituted Ru substrates gave anodic peak currents less than those of the equimolar Cp_2Fe standard, with $n = 0.5$–0.6. The unexpectedly low apparent n values probably result from the assumption that the diffusion coefficients for the substrates are comparable to that of the standard. However, the PPh_3-substituted substrates have significantly higher molecular weights and size than does Cp_2Fe and would be expected to have significantly lower diffusion coefficients.

Values of n were also determined by using controlled potential coulometry (Table VI). Values of $n \approx 1$ were found for all the compounds studied, consistent with previous results on the iron system,[2] while the products of electrolyses in CH_2Cl_2 in the presence of chloride ion were invariably the ruthenium and alkyl chlorides. The compound $CpRu(CO)_2Me$ required a relatively positive electrode potential and could not be electrolyzed in the presence of chloride ion because of the likelihood of oxidation of the chloride. Electrolysis was therefore carried out by using Bu_4NBF_4 as supporting electrolyte, and the product was shown to be $CpRu(CO)_2Cl$ rather than $CpRu(CO)_2F$ or $CpRu(CO)_2BF_4$. The results are as anticipated for a mechanism involving a metal-based radical,[2] although identities and yields of methyl-containing products could not be determined. Dry nitrogen was bubbled continuously through the solutions during the coulometric experiments, and thus volatile organic products were swept away as they formed.

While oxidation of $CpRu(PPh_3)_2CH_2Ph$ in the presence of chloride ion yielded no bibenzyl, oxidation in the presence of air did yield bibenzyl and benzaldehyde, indicative of benzyl radical intermediates. The presumed source of the benzaldehyde, the benzylperoxy radical, should give some benzyl alcohol (see above), but it is possible that the latter is oxidized at the anode.

Several trends in the oxidation potentials in Table V should be noted. Firstly, comparison with earlier work shows that the compounds $CpRu(CO)_2Me$ and $CpRu(CO)(PPh_3)CH_2Ph$ are not easier to oxidize than their iron analogues, as had been hoped, but are actually more difficult by 0.1–0.3 V.[2] Secondly, there is a drop in oxidation potential of 0.5–0.6 V on substituting carbon monoxide for triphenylphosphine and an increase of about 0.3 V on substituting alkyl by chloro ligands. These trends have been noted previously for other systems[2,44-46] and reflect the net charge on the metal atom.

Summary

Complexes of the type CpRuLL′R are somewhat less prone to undergo oxidative cleavage reactions than their iron counterparts, but cleavage reactions with halogens, hydrogen chloride, mercury(II) halides, and copper(II) halides nonetheless appear to involve one- and two-electron-transfer processes.

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada (J.A.P. and M.C.B.) and Queen's University (scholarship to M.F.J.) is gratefully acknowledged, as are loans of ruthenium trichloride from the International Nickel Co. of Canada, Ltd. and Johnson Matthey Ltd.

Registry No. $CpRu(CO)_2Me$, 53449-90-4; $CpRu(CO)_2(PhCH_2)$, 53449-91-5; $CpRu(CO)_2Cl$, 32611-12-4; $CpRu(CO)_2Br$, 32613-75-5; $CpRu(CO)_2I$, 31781-83-6; $CpRu(CO)(PPh_3)Me$, 71438-17-0; $CpRu(CO)(PPH_3)(PhCH_2)$, 70586-96-8; $CpRu(CO)(PPh_3)Cl$, 32613-25-5; $CpRu(CO)(PPh_3)Br$, 32611-27-1; $CpRu(CO)(PPh_3)I$, 32611-25-9; $CpRu(PPh_3)_2Me$, 34692-09-6; $CpRu(PPh_3)_2(PhCH_2)$, 59568-94-4; $CpRu(PPh_3)_2Cl$, 32993-05-8; $CpRu(PPh_3)_2Br$, 32993-06-9; $CpRu(PPh_3)_2I$, 34692-10-9; MeHgCl, 115-09-3; MeHgBr, 506-83-2; $PhCH_2HgCl$, 2117-39-7; $PhCH_2HgBr$, 4109-72-2; MeBr, 74-83-9; MeI, 74-88-4; $PhCH_2Br$, 100-39-0; $PhCH_2I$, 620-05-3; PhMe, 108-88-3; $(PhCH_2)_2$, 103-29-7; $PhCH_2Cl$, 100-44-7; PhCHO, 100-52-7; $[CpRu(CO)_2]_2$, 12132-87-5; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; Br_2, 7726-95-6; I_2, 7553-56-2; $CuBr_2$, 7789-45-9; $CuCl_2$, 7447-39-4; HCl, 7647-01-0.

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