Inorganica Chimica Acta, *96* (1985) 229–230

Sulfur Dioxide Insertion Reactions of Alkylruthenium Compounds

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Received May 2, 1984

Abstract

The compounds CpRuLL′R (L,L′ = CO, PPh_3; R = Me, $PhCH_2$) react with SO_2 in chloroform to form the corresponding S-sulfinato complexes. Consistent with the accepted S_E2 (inversion) mechanism, $CpRu(CO)_2Me$, which has a relatively high oxidation potential, is inert under these conditions.

Introduction

Reactions of the compounds CpFe(CO)LR (L = CO, tertiary phosphine; R = alkyl) with SO_2 to form S-sulfinates, *i.e.*

$$CpFe(CO)LR + SO_2 \longrightarrow CpFe(CO)L(SO_2R) \qquad (1)$$

have been long known [1] and are well studied mechanistically [1, 2]. Both kinetic and stereochemical data are consistent with a mechanism involving an S_E2 (inversion) process which is retarded by bulky substitutents on R, but accelerated by ligands L which are good electron donors.

To date, however, relatively little research has been carried out on the analogous ruthenium complexes, the only report being by Jacobson and Wojcicki [3], who found that the compounds $CpRu(CO)_2R$ (R = Me, $PhCH_2$) react with liquid SO_2 more slowly than do their iron counterparts.

We have been carrying out a survey of the chemistry and electrochemistry of compounds of the type CpRuLL′R (L,L′ = CO, PPh_3; R = Me, $PhCH_2$) [4], and thus the opportunity was presented to study the SO_2 insertion reactions as well. In doing so, we have extended the known chemistry of the alkylruthenium compounds, and have made comparisons with the iron analogues.

Experimental

The compounds $CpRu(CO)_2Me$ (**I**), CpRu(CO)(PPh_3)R (R = Me (**II**), $PhCH_2$ (**III**)) and $CpRu(PPh_3)_2R$ (R = Me (**IV**), $PhCH_2$ (**V**)) were prepared as reported previously [4]. All SO_2 insertion reactions were carried out by bubbling SO_2 through chloroform solutions of the alkyl compounds at room temperature for 15 min. In all cases except **I**, which showed no reaction (IR) after 1 hr, the yellow solutions turned slightly pale. In each case the solvent and unreacted SO_2 were removed at reduced pressure, and the

TABLE I. Analytical and Spectroscopic Data for the Compounds $CpRuL(PPh_3)SO_2R$.

L	R	Analytical Data[a]		ν_{CO} (cm^{-1})[b]	ν_{SO} (cm^{-1})[c]	$\delta(^1H)$[d]	$\delta(^{31}P)$[e]
		C	H				
CO	Me	56.35(56.01)	4.38(4.34)	1980	1175, 1040	2.74(s, Me), 5.04 (s, Cp), 7.44(m, Ph)	47.9
CO	$PhCH_2$	60.29(60.87)	4.41(4.46)	1980	1175, 1041	3.90, 4.30 (AB quartet, J = 12 Hz, CH_2), 0.56(s, Cp), 7.41(m, Ph)	47.8
PPh_3	Me	64.79(65.33)	5.31(4.98)[f]		1160, 1035	2.42(s, Me), 4.53(s, Cp), 7.20(m, Ph)	40.1
PPh_3	$PhCH_2$	67.36(68.15)	5.56(5.00)[g]		1155, 1030	3.74(s, CH_2), 4.62(s, Cp), 7.21(m, Ph)	40.0

[a] Calc'd in parentheses. [b] CH_2Cl_2. [c] Nujol. [d] $CDCl_3$, int. TMS ref. [e] $CDCl_3$, ext. H_3PO_4 ref. [f] S: 3.91(4.16). [g] S:4.30(3.79).

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0020-1693/85/$3.30

TABLE II. $^{13}C\{^1H\}$ NMR Data.

Compound	Chemical Shifts $(J_{P-C})^a$			
	CH_2	CO	Cp	Ph
$CpRuCO(PPh_3)CH_2Ph$	4.5(7.5)	207.3(19.7)	88.6	121–137
$CpRuCO(PPh_3)SO_2CH_2Ph$	78.5	203.1(17.1)	89.2	127–135
$CpRu(PPh_3)_2CH_2Ph$	3.9(11)		84.3	120–140
$CpRu(PPh_3)SO_2CH_2Ph$	74.5		85.7	126–138

[a]In $CDCl_3$, int. TMS ref.

residue was recrystallized from CH_2Cl_2–hexane to give pale yellow crystals of the product in about 90% yield. Elemental analyses and spectroscopic data for the new compounds CpRuLL′(SO_2R), are listed in Table I.

IR spectra were run on a Beckman IR 4240 spectrometer, ^1H NMR spectra on a Bruker HX 60 spectrometer, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra on a Bruker CXP 200 spectrometer. Elemental analyses were carried out by Canadian Microanalytical Services, Vancouver, B.C.

Results and Discussion

The SO_2 insertion reactions of the phosphine-containing complexes, **II**–**V**, proceeded quickly and cleanly to give the S-bonded sulfinato products. The compounds can be readily differentiated from the possible O-sulfinato isomers on the basis of the sulfur–oxygen stretching frequencies [1]. Thus ν_{asym} (SO_2) and ν_{sym} (SO_2) are found in the ranges 1155–1175 cm^{-1} and 1030–1040 cm^{-1}, respectively, rather than the lower values normally encountered for O-sulfinates. The ^1H NMR spectrum of $CpRu(PPh_3)_2(SO_2CH_2Ph)$ provides further evidence for S-bonding, as the two methylene protons are magnetically equivalent. O-sulfinato compounds contain a chiral sulfur atom, which would lead to magnetic nonequivalence of the benzyl methylene hydrogen atoms [1]. On the other hand, the magnetic nonequivalence observed for the methylene hydrogen atoms of $CpRu(CO)(PPh_3)(SO_2CH_2Ph)$ arises because of the chiral metal atom.

We include in Table II $^{13}C\{^1H\}$ NMR data for the benzyl and benzylsulfonyl compounds; to our surprise, few such data appear to exist in the literature [5]. Interestingly the changes on SO_2 insertion appear to parallel those on CO insertion [7, 8] *i.e.* small upfield and downfield shifts of the CO and Cp resonances, respectively, and a large downfield shift (70–75 ppm) for the α-carbon resonance.

As mentioned above, **I** and $CpRu(CO)_2CH_2Ph$ are reported to react slowly with liquid SO_2 at low temperatures [3]. We find that **I** is inert to SO_2 in chloroform solution at room temperature, conditions under which the phosphine-substituted compounds **II**–**V** react quickly. The results are entirely consistent with the generally accepted S_E2 mechanism [1, 2], as **I**, at least, exhibits an oxidation potential in methylene chloride which is about 0.5 V higher than those **II** and **III**, about 1.15 V higher than those of **IV** and **V**, and about 0.3 V higher than that of $CpFe(CO)_2Me$ [4]. Thus **I** must be considerably less electron rich than the other compounds, and thus less susceptible to electrophilic attack.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council for financial support, Queen's University for a scholarship to M.F.J., and The International Nickel Company of Canada for a loan of ruthenium trichloride.

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