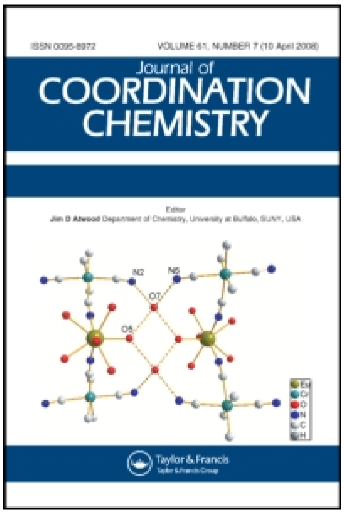

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NEW RUTHENIUM(II) COMPLEXES CONTAINING ORGANODISULFIDE LIGANDS

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NEW RUTHENIUM(II) COMPLEXES CONTAINING ORGANODISULFIDE LIGANDS

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The new complexes [CpRu(PPh$_3$)$_2$(RSSR)PF$_6$ R = CH$_3$, iso-Pr, CH$_2$C$_6$H$_5$ and C$_6$H$_5$ have been prepared from the reaction of CpRu(PPh$_3$)$_2$Cl with RSSR in CH$_3$OH in presence of NH$_4$Cl. This result contrasts with the oxidative additions of RSSR to CpFe(dppe)l dppe = PPh$_2$ (CH$_2$)$_2$PPh$_2$ to give [CpFe(dppe)SR]PF$_6$ (C. Diaz *et al.*, *J. Organomet. Chem.* **516**, 59 (1996)). Huckel calculations on model fragments CpFe(PPh$_3$)$_2$ and CpRu(PPh$_3$)$_2$ suggest that the higher electron density of iron could explain the differences observed in reactivity. Possible biological implications are discussed.

Keywords: Organodisulfide complexes; Ruthenium; S-S cleavage; Sulfur; MO calculations

INTRODUCTION

Disulfide complexes of metal [1] are unusual due to the tendency of S—S bond cleavage to give metal-thiolate complexes.

$$\mathrm{RSSR} + 2\mathrm{MLn} \longrightarrow 2\mathrm{LnM} - \mathrm{SR} \qquad (1)$$

This behavior is favored by organometallic fragments with metals in low oxidation states [2].

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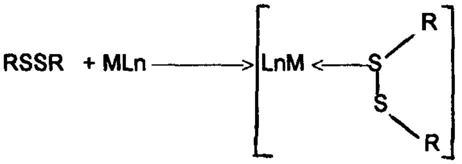
The activation of the S—S bond probably involves coordination of RSSR to MLn [3]



(2)

leading to an intermediate which with metals in low oxidation state, produces a great back-donation metal(π) → S(π) interaction. This back-bonding produces an electron-donation from metal toward S—S antibonding levels producing a destabilization of the S—S bond and a consequent S—S cleavage.

The characteristics of the MLn fragments, which cause S—S cleavage, with exception of the low oxidation of the metal, are not clear. For instance we have found that CpFe(dppe)I cleaves RSSR to give the iron(III)-thiolate complexes [3] [CpFe(dppe)SR]PF_6. On the contrary reaction of CPRu (dppe)Cl with RSSR affords the disulfide complexes [$CpRu(PPh_3)_2R_2S_2$]PF_6 of interest to this paper.

EXPERIMENTAL

Infrared spectra were recorded on a FT-Bruker-66 V spectrometer in KBr pellets. NMR spectra were recorded on a Bruker AMX 300 spectrometer in dichloromethane-d_2 with TMS (H) $\delta = 0.0$ ppm as the internal standard or 85% H_3PO_4 (downfield positive to the reference) as external standard for the ^{31}P measurements.

Elemental analyses were performed on a Fisons-Carlo Erba EA 1108 apparatus by CEPEDEQ, Universidad de Chile.

All reactions were carried out under dinitrogen with standard Schlenk techniques. Solvents were purified by standard methods. $CpRu(PPh_3)_2Cl$ (Aldrich); $S_2(CH_3)_2$ (EGA-chemie), $S_2(iPr_2)$ (Fluka), $S_2(CH_2C_6H_5)_2$ (Fluka), $S_2(C_6H_5)_2$ (Fluka) were used as purchased. NH_4PF_6 was dried and maintained in a desiccator.

Preparation of the Complexes

[$CpRu(PPh_3)_2\{S_2(CH_3)_2\}$]$PF_6$ (1): to a solution of $CpRu(PPh_3)_2Cl$ 0.141 g (0.19 mmol) in CH_3OH (20 mL) was added $(CH_3)_2S_2$ 0.018 g (0.19 mmol) and NH_4PF_6 0.03 g (0.18 mmol) and the mixture was stirred at room temperature for 20 h. The solvent was evaporated in *vacuo* and the resulting solid was extracted with CH_2Cl_2 and filtered through Celite. The solvent was again evaporated in *vacuo* and the solid washed twice with diethylether and dried in *vacuo*.

Anal. Found C 56.6 H 4.16 S 6.5.

Calc. for $C_{43}H_{41}F_6P_3S_2Ru$ C 55.49; H 4.40; S 6.8.

$[CpRu(PPh_3)_2\{S_2(iPr)_2\}]PF_6$ (2): A mixture of $CpRu(PPh_3)_2Cl$ 0.12 g (0.16 mmol) was and $S_2(iPr)_2$ 0.05 g (0.33 mmol) in the presence of NH_4PF_6 0.05 g (0.3 mmol) was stirred in CH_3OH (20 mL) at room temperature for 20 h. A similar separation and purification procedure to that for (1) affords yellow powder: yields 70%.

Anal: Calcd. for $C_{47}H_{49}F_6P_3S_2Ru \cdot 5CH_2Cl_2$ (%) C 44.26; H 4.18; S 4.5 Found C 44.57, H 4.41, S 4.6.

$[CpRu(PPh_3)_2S_2(CH_2C_6H_5)_2]PF_6$ (3): A solution of 0.122 g (0.16 mmol) of $CpRu(PPh_3)_2Cl$, 0.0501 g (0.21 mmol) of $(C_6H_5CH_2)_2S_2$ in 20 ml CH_3OH and 0.0614 g (0.37 mmol) NH_4PF_6 were stirred at room temperature for 20 h.

The solvent was evaporated under vacuum and the yellow solid was extracted with CH_2Cl_2 and filtered through Celite. The solution was concentrated to *ca.* 5 mL and n-hexane (5 mL) was added. The resulting solid residue was twice washed with n-hexane and dried in *vacuo*. Yield 60%.

Anal. Calcd. for $C_{55}H_{49}F_6P_3S_2Ru$(%)C61.58; H 4.57; S 5.90. Found C 62.42 H 4.59 S 5.4.

$[CpRu(PPh_3)_2(C_6H_5SSC_6H_5)]PF_6$ (4): In a similar way to the preparation of (1), the complex (4) was prepared from 0.12 g, (0.16 mmol) of $CpRu(PPh_3)_2Cl$, 0.04 g (0.33 mmol) of $(C_6H_5)_2S_2$ and 0.06 g (0.36 mmol) of NH_4PF_6 in 20 mL of CH_3OH and obtained as yellow powder. Yield 55%.

Anal. Found C 56.6; H 4.16;S 6.0

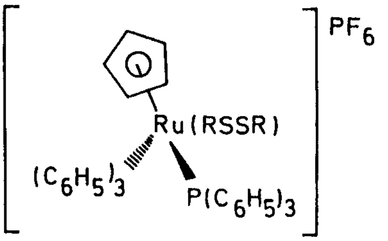
Calc. For $C_{53}H_{45}F_6S_2Ru \cdot CH_2Cl_2$ C 56.9; H 3.95; S 5.9.

MO calculations. EHMO calculations [4] were carried out using modified Wolfsberg-Helmholz with weighted H_{ij} values [5]. The atomic parameters for the elements involved in the calculations were taken from the literature [5, 6]. The geometrical parameters used were taken from the crystal structure of $[CpRu(L)_2L']^+$ [7] and $[CpFe(L_2)L']^+$ [8] (L, L′ = neutral ligands) complexes.

RESULTS AND DISCUSSION

Treatment of $CpRu(PPh_3)_2Cl$ with NH_4PF_6 in the presence of sulfides RSSR ($R = CH_3$; $(CH_3)_2CH$; $CH_2C_6H_5$; C_6H_5) gives the cationic complexes

1–4 Scheme 1. The yellow complexes were characterized by elemental analysis and IR, ^1H, ^{31}P and ^{13}C-NMR spectroscopic methods. The IR spectra exhibit, the characteristic bands of CpFe(dppe)$^+$ [9] as well as the $\nu(PF_6)$ bands typical of [CpFe(dppe)L]PF_6 complexes (Tab. I). The ^1H-NMR spectra of the complexes show the typical signals of Cp and C_6H_5 groups from the CpFe(dppe)$^+$ moiety as well as the signals of the ligand RSSR. Data are displayed in Table II. The ^{31}P-NMR signals of the groups dppe and PF_6 were clearly observed (Tab. II). The ^{13}C-NMR spectra



Nr	R
1	CH_3
2	i-Pr
3	CH_2-C_6H_5
4	C_6H_5

SCHEME 1

TABLE I IR data[a] for complexes 1–4

Complex	*C_5H_5*[b]	*$\nu(PF_6)$*	*(dppe)*[c]
(1)	1089	840	695
(2)	1118	841	695
(3)	1118	839	695
(4)	1087	839	695

[a] IR. Kbr pellet.
[b] $\delta(C_5H_5)$ bending in plane vibrations.
[c] Bending out-of-plane vibrations.

TABLE II ^1H, ^{31}P and ^{13}C NMR spectral data[a]

	^1H		*^{31}P*		*^{13}C*		
Complex	*RSSR*	*Cp*	*$P(Ph_3)$*	*PF_6*	*RSSR*	*C_5H_5*	*C_6H_5*
(1)	1.7(CH_3)	4.10	43.38	−139	23	81.8	134.18 132.28 128.83 127.88
(2)	1.1(CH) 0.9(CH_3)	4.08	32.87	−139	1.37(CH_3) 2.14(CH)	82	136.5 133, 131 129
(3)	1.68(CH_2)	4.11	43.4	−139.9	29(CH_2)	81.9	[b]
(4)	7.1–7.7 (C_6H_5)	4.11	43.4	−140	[b]	81.9	[b]

[a] In CD_2Cl_2 solution, at room temperature.
[b] Signal complex; signals of $(C_6H_5)_2S_2$ masked with those of $P(C_6H_5)_3$.

confirm the presence of Cp and C_6H_5 of dppe together with the signals of RSSR.

MO calculations. In order to shed some light on the different reactivity of $CpRu(PPh_3)_2Cl$ toward RSSR with respect to their CpFe(dppe)I analogue toward the same disulfide compounds [3], extended calculations [4] on the model fragments $CpFe(PPh_3)_2^+$ (5) and $CpRu(PPh_3)_2^+$ (6) were accomplished. The geometries of the fragments were pyramidal with angles close to the ideal *pseudo*-octahedral ML_5 coordination. The MO diagrams of the fragments are shown in Figure 1. The splitting pattern for both fragments are similar, with the HOMO-LUMO gap also very similar. The energy levels for the Ru fragment are somewhat shifted with respect to the Fe analogue. The only major differences are the atomic charges on the metallic atoms, −0.5 for the iron atom and +0.1 for the ruthenium. This can explain the different reactivities observed for the iron and ruthenium complexes. As

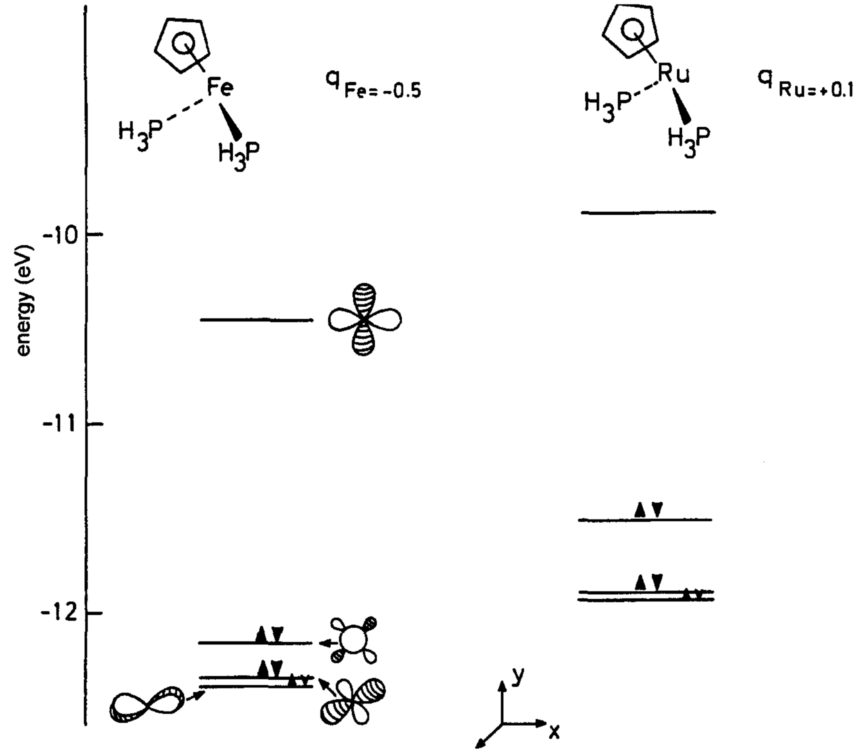


FIGURE 1 Simplified MO diagram for the fragments $CpFe(PPh_3)_2^+$ and $CpRu(PPh_3)_2^+$. Atomic charges on the metal are also indicated.

previously suggested [3] the S—S bond cleavage occur through the intermediate CpFe(dppe)(RSSR)$^+$. The more electron rich iron creates more effective π(metal)$-\pi^*$(RSSR) backbonding leading to an S—S destabilization and subsequently S—S cleavage. Consistent with this, the less electron rich fragment $\mathrm{CpFe(CO)}_2^+$ does not cleave the S—S bond and the $[\mathrm{CpFe(CO)_2(S_2R_2)}][\mathrm{PF_6}]$ complexes are stable [10].

As pointed out by Carrillo [1] the susceptibility of coordinated disulfide ligands to cleave *via* oxidative addition a difficulty inherent in the preparation and isolation of metal disulphide complexes. Our results suggest that the reactivity of RSSR with metal complexes may be modulated through the electron density of the metal fragment. This may have interesting biochemical implications in view of the relevancy of the redox process

$$\mathrm{RSSR} + 2\bar{e} \longrightarrow 2\mathrm{RS}^- \qquad (3)$$

in biological systems [1]. Experiments to probe this are in progress.

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References

[1] D. Carrillo, *Coord. Chem. Rev.* **119**, 137 (1992).

[2] (a) M. Cowie, R. L. Dekock, T. R. Wagenmaker, D. Seyferth, R. S. Henderson and M. K. Gallagher, *Organometallic* **8**, 119 (1989); (b) T. D. Ju, K. B. Cupps, R. F. Lang, G. C. Roper and C. D. Hoff, *Inorg. Chem.* **36**, 614 (1997).

[3] C. Díaz, C. Leal and N. Yutronic, *J. Organomet. Chem.* **516**, 59 (1996).

[4] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).

[5] J. H. Ammeter, H. B. Burgi, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.* **100**, 3686 (1978).

[6] C. Díaz, I. Izquierdo, F. Mendizábal and N. Yutronic, *Inorg. Chim. Acta.* **294**, 20 (1999).

[7] W. A. Schenk, J. Frish, M. Dürr, N. Burzalaff, D. Stalke, R. Fleischer, W. Adams, F. Prechtl and A. K. Smerz, *Inorg. Chem.* **36**, 2372 (1997).

[8] P. E. Riley, Ch. E. Capshew, R. Pettit and R. E. Daks, *Inorg. Chem.* **17**, 408 (1978).

[9] M. M. Campos, C. Díaz, K. Figueroa, L. Padilla, N. Lara and G. Díaz, *V. Spectroscopy* **7**, 61 (1994).

[10] N. Kuhn and H. Schumann, *J. Organomet. Chem.* **287**, 345 (1985).