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Preparation and Properties of Ruthenium(II) Mercapto Complex, $RuH(SH)(PPh_3)_3 \cdot PhCH_3$

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Despite the recent interest in the complexes that contain SH^- or S^{2-} ligand [1–3], little is known about the reaction of sulfur or hydrogensulfide with metal hydrido complexes [4, 5] compared with those with other low valent transition metal complexes [6–8]. In this paper we report the preparation of a new ruthenium(II) mercapto complex $RuH(SH)(PPh_3)_3 \cdot PhCH_3$ **1** by the reaction of both H_2S and S_8 with $RuH_2(PPh_3)_4$ and the properties of **1** such as NMR behavior and hydrogen exchange with MeOD.

The reaction of $RuH_2(PPh_3)_4$ with equimolar H_2S in toluene gave complex **1** in a high yield (74%) accompanied by evolution of a quantitative amount of H_2, similarly to the reaction of thiols with $RuH_2(PPh_3)_4$ [9].

$$RuH_2(PPh_2)_4 + H_2S \xrightarrow[PhCH_3]{-PPh_3} RuH(SH)(PPh_3)_3 \cdot PhCH_3 + H_2$$

1

Complex **1** was also obtained independently from the reaction of S_8 with $RuH_2(PPh_3)_4$. Experimentally, addition of a toluene solution of S_8 to $RuH_2(PPh_3)_4$ at −50 °C, followed by standing the reaction mixture at −20 °C for five days, gave purple microcrystals of **1**. Although the yield of the complex is low (10%), it can be obtained in pure form.

$$RuH_2(PPh_3)_4 + \tfrac{1}{4}S_8 \xrightarrow[PhCH_3]{} RuH(SH)(PPh_3)_3 \cdot PhCH_3 + S{=}PPh_3$$

1

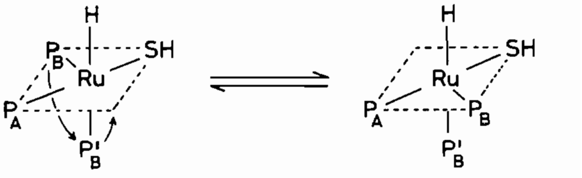
This reaction appears to proceed through insertion of sulfur atom to the ruthenium hydrogen bond. A similar insertion process is proposed to elucidate the formation of H_2S in the reaction of S_8 with $MH_2(C_5H_5)_2$ (M = Mo, W) [4]. Although formation of mercapto complexes from metal hydrido complexes and tiirans or carbonyl sulfide is known [10, 11], this is the first example to our knowledge of the preparation of a mercapto complex from the reaction of elemental sulfur with a hydrido complex.

TABLE I. IR, ^1H NMR and Analytical Data of **1**.

IR[a]	$\nu(Ru{-}H)$	$1971\ cm^{-1}$	
	$\nu(S{-}H)$	$2525\ cm^{-1}$	
^1H NMR[b]	C_6H_5[c]	7.7–7.0 ppm broad 50H	
	CH_3[c]	2.3 ppm s 3H	
	SH	1.6 ppm dq 1H J_{HH} = 1 Hz J_{PH} = 16 Hz	
	RuH	−16.7 ppm dq 1H J_{HH} = 1 Hz J_{PH} = 26 Hz	
Analyses	C(%)	H(%)	S(%)
Found	71.8	5.3	3.1
Calcd.	72.2	5.5	3.2

[a] KBr disk. [b] In CD_2Cl_2 at room temperature (100 MHz). [c] Solvated toluene is contained.

Complex **1** was characterized by IR and NMR spectra as well as by elemental analysis (Table I). In the ^1H NMR spectrum resonances of both mercapto hydrogen and hydrido ligand are split into a quartet due to $^{31}P{-}^1H$ coupling with three phosphorus atoms at 35 °C. $^{31}P\{^1H\}$ NMR spectrum at 35 °C shows only one broad signal as in $RuHCl(PPh_3)_3$ [12] and $RuH(SCH_2Ph)(PPh_3)_3$ [9]. However, quite different $^{31}P\{^1H\}$ NMR spectra from those of $RuHCl(PPh_3)_3$ were observed at lower temperatures, as shown in Fig. 1. It indicates the exchange of only two PPh_3 ligands (P_B and P'_B in Fig. 1) of **1** below −40 °C, whereas in $RuHCl(PPh_3)_3$ interchange of all three PPh_3 ligands is prevented at the same temperature [12]. This NMR behavior of **1** is interpreted by transformation of coordination sites of P_B and P'_B in square pyramidal structure, as shown in Scheme 1.



Scheme 1. A possible scheme for the ligand exchange of the complex **1** at −40 ~ −80 °C. P_B and P'_B may be reversed.

Intermolecular hydrogen exchange of the mercapto ligand and protic media such as methanol

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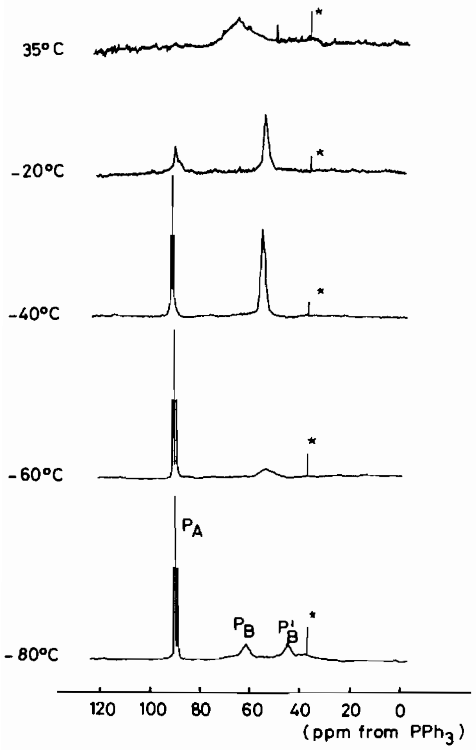

Fig. 1. Temperature dependence of $^{31}P\{^1H\}$ NMR of **1** (40 MHz, CD_2Cl_2). The resonance with asterisk is due to $OPPh_3$ formed during preparation of the sample for NMR. Peak area of P_A, P_B and P'_B is 1:1:1.

was confirmed by means of ^1H NMR spectroscopy. The time course of the decrease in peak areas of the SH, RuH and C_6H_5 (in PPh_3) signals of ^1H NMR in CD_2Cl_2 containing 4% of CD_3OD is shown in Fig. 2. Besides the decrease of the peak area of the mercapto hydrogen, those of hydrido ligand and phenyl hydrogen of PPh_3 ligands also diminish. These facts may be interpreted by the three simultaneous hydrogen exchange processes: (i) intermolecular exchange of hydrogen between mercapto ligand and methanol, (ii) intramolecular hydrogen exchange of hydrido and mercapto hydrogen, as is observed in $PtH(SH)(PPh_3)_2$ [6], and (iii), reversible orthometalation [13]. Direct intermolecular hydrogen exchange between hydrido or hydrogen of PPh_3 ligands and deuterium of CD_3OD seems improbable because similar hydrido complexes $RuHCl(PPh_3)_3$ and $RuH(SPh)(PPh_3)_3$ show no H–D change, as shown by their ^1H NMR spectra in a CD_2Cl_2–CD_3OD mixture (even after 4 days).

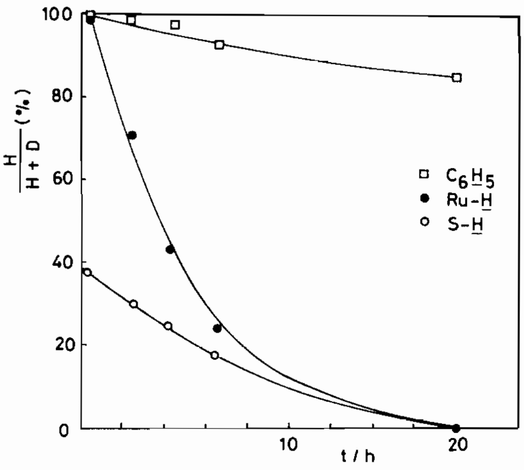

Fig. 2. H–D Exchange of **1** in CD_3OD–CD_2Cl_2 at 20 °C.

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