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Reactions of Ruthenium Polyhydride Complexes with Thiols. Preparation of Hydrido Thio-alkyl and -aryl Complexes of Ruthenium(II)

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Although dinuclear alkyl- or arylthiolato bridged complexes are well known in the coordination chemistry of iron or rhodium [1], very little has been reported on such ruthenium complexes. So far the only dinuclear ruthenium(II) compounds described have been $(Ru(CO)(\mu\text{-}SR)(\eta^5\text{-}C_5H_5))_2$ [2, 3] and the triple bridged one $(L_3RuX_3L_3)^{+4}$ (X = SH, SMe, L = PMe_2Ph, $PMePh_2$ or $P(OMe)Ph_2$).

On the other hand, the reactions of $RuH_2(PPh_3)_4$ with weak acids are known to produce hydrido complexes of ruthenium [5]; with H_2O a hydrido hydroxo complex is obtained which can be easily dimerized to $(RuH(OH)(PPh_3)_2L)_2$ [6], (L = H_2O, Me_2CO, THF or ${}^tBuOH$).

We thus attempted the reactions of $RuH_2(PPh_3)_4$ or $RuH_4(PPh_3)_2$ with thiols or dimethyl disulfide.

$RuH_2(PPh_3)_4$ or $RuH_4(PPh_3)_3$ react rapidly with equivalent PhSH or $PhCH_2SH$ in diethyl ether. The colour of the suspension changes from yellow or white to purple. After 2 hours the suspension is filtered and the residue is recrystallised in a toluene/petrol mixture affording purple crystals of the complexes.

Similarly $RuH_2(PPh_3)_4$ reacts rapidly with half the equivalent MeSSMe in dichloromethane. The colour of the solution turns rapidly to deep purple and after half an hour the solution is evaporated to a small volume and addition of diethyl ether and cooling give purple crystals of the complex (yield *ca.* 60%).

These compounds are air sensitive and their aspect is similar to the one of $RuHCl(PPh_3)_3$ [7]. The infrared spectra of the complexes show, apart from the characteristic bands of PPh_3, the Ru–H stretch at 1985–1995 cm^{-1} together with very weak absorptions near 300 cm^{-1} which could be attributed to the Ru–S stretch.

The ^1H NMR spectrum (in C_6D_6) shows together with phenyl groups between τ 2.2 and τ 3.3, the methyl or methylene groups of SCH_3 and SCH_2Ph as singlets at τ 8.1 and 6.4 respectively and the high field hydride resonances as quartets towards τ 27 (J_{PH} ~ 25 Hz) (τ 28.1, J_{PH} = 26 Hz) for $RuHCl(PPh_3)_3$ [7] in (CH_2Cl_2).

TABLE I. Spectroscopic and Analytical Data.

Compound	[a]Yield %	IR	NMR			Found %					Expected %				
		νRu–H (cm^{-1})	τRu–H(J_{PH}Hz)	Other	$\delta^{31}P$[d]	C	H	Cl	P	S	C	H	Cl	P	S
$RuH(SMe)(PPh_3)_3\,CH_2Cl_2$	70	1995	27.7 (26)	8.1[b]		65.9	5.0	7.0	9.1	3.1	65.25	4.7	7.0	9.1	3.1
$RuH(SCH_2Ph)(PPh_3)_3$	60	1985	27.75(24)	6.4[c]	−55.57	71.4	5.2		8.8	3.2	72.4	5.2		9.2	3.1
$RuH(SPh)(PPh_3)_3$	45	1985	36.15(24)												

[a] After recrystallisation. [b] CH_3 of SMe. [c] CH_2 of SCH_2Ph. [d] At high field of external H_3PO_4.

The ^{31}P NMR spectrum of the complex $RuH(SCH_2Ph)(PPh_3)_3$ consists only in one broad singlet at δ −55.57 (at high field of external H_3PO_4) indicating three equivalent phosphorus atoms at room temperature like $RuHCl(PPh_3)_3$ [8].

Therefore we attribute to $RuH(SR)(PPh_3)_3$ the structure shown in Fig. 1 similar to that of $RuHCl(PPh_3)_3$.

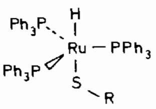

Fig. 1. Structure of $RuH(SR)(PPh_3)_3$.

When these compounds are heated or irradiated with a high pressure mercury vapour lamp in toluene, the colour of the solutions changes from purple to brown. This apparently does not produce a thiolato bridged dinuclear complex but rather sulphide compounds since we can observe by ^1H NMR spectroscopy the disappearance of the methyl signal of $RuH(SMe)(PPh_3)_3$. Finally the reactions of $RuH_2(PPh_3)_4$ with two or more equivalents of thiol, half an equivalent or one equivalent of dithiol, lead to brown powders which probably contain a mixture of sulphide complexes.

References

1 R. Poilblanc, *J. Organometal. Chem., 94,* 241 (1975).
2 G. R. Knox and A. Pryde, *J. Organometal. Chem., 74,* 105 (1974).
3 S. D. Killops and S. A. R. Knox, *J. Chem. Soc. Dalton,* 1260 (1978).
4 T. V. Ashworth, M. J. Nolte and E. Singleton, *Chem. Comm.,* 936 (1977).
5 D. J. Cole Hamilton and G. Wilkinson, *Nouv. J. Chim., 1,* 14 (1977).
6 B. N. Chaudret, D. J. Cole Hamilton, R. S. Nohr and G. Wilkinson, *J. Chem. Soc. Dalton,* 1546 (1977).
7 P. S. Hallmann, B. R. McGarvey and G. Wilkinson, *J. Chem. Soc. A,* 3143 (1968).
8 P. R. Hoffmann and K. G. Caulton, *J. Am. Chem. Soc., 97,* 4221 (1975).