

*Journal of Organometallic Chemistry*, 121 (1976) C57—C60  
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

### Preliminary communication

## FORMATION OF CATIONIC AND NEUTRAL CARBAMATO AND RELATED RUTHENIUM(II) COMPLEXES FROM REACTION OF CO<sub>2</sub>, COS AND CS<sub>2</sub> WITH RUTHENIUM HYDRIDES IN ALCOHOL SOLUTION CONTAINING HNMe<sub>2</sub>. THE CRYSTAL STRUCTURE OF [Ru(O<sub>2</sub>CNMe<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>4</sub>]PF<sub>6</sub>

TERENCE V. ASHWORTH, MAGRIET NOLTE and ERIC SINGLETON\*

*National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0002 (Republic of South Africa)*

(Received September 8th, 1976)

### Summary

The salts [Ru(XYCR)(PMe<sub>2</sub>Ph)<sub>4</sub>]PF<sub>6</sub> (XY = OS, R = OEt; XY = S<sub>2</sub>, R = H), [Ru(XYCNMe<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>4</sub>]PF<sub>6</sub> (XY = O<sub>2</sub>, OS, S<sub>2</sub>) and the neutral product [RuH(O<sub>2</sub>CNMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>] are formed by interaction of CO<sub>2</sub>, COS or CS<sub>2</sub> with [RuH(PMe<sub>2</sub>Ph)<sub>5</sub>]PF<sub>6</sub> or [RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] in ethanol or ethanol/dimethylamine mixtures; the crystal structure of [Ru(O<sub>2</sub>CNMe<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>4</sub>]PF<sub>6</sub> has been determined.

A number of transition metal complexes have been reported [1] to catalyse the conversion of amines, CO<sub>2</sub> and H<sub>2</sub> into formamides at high pressures (54 atm) and high temperatures (100-125°C). No single mechanism was proposed for this reaction, although certain intermediates, in particular metal carbamato complexes were excluded, and a reaction scheme involving attack of HNMe<sub>2</sub> on a metal formato complex was said to be consistent with deuteration studies. However, we have now found that ruthenium formates, prepared from reactions either of formic acid or carbon dioxide with ruthenium hydrides give ruthenium carbamato complexes with HNMe<sub>2</sub>. Similar reactions with COS and CS<sub>2</sub> produce corresponding thio and dithiocarbamato compounds.

Refluxing ethanol solutions of [RuH(PMe<sub>2</sub>Ph)<sub>5</sub>]PF<sub>6</sub> (I) containing excess HNMe<sub>2</sub> reacted with CO<sub>2</sub>, COS and CS<sub>2</sub> to deposit [Ru(XYCNMe<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>4</sub>]PF<sub>6</sub> (II) (XY = O<sub>2</sub>, OS, S<sub>2</sub>) on cooling. Reaction of RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> with CO<sub>2</sub> gave the neutral product RuH(O<sub>2</sub>CNMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub> (III). In the absence of dimethylamine, (I) and COS or CS<sub>2</sub> produced the formato salts [Ru(XYCH)(PMe<sub>2</sub>Ph)<sub>4</sub>]PF<sub>6</sub> (IV) (XY = OS, S<sub>2</sub>) from cold ethanol solutions, whereas with CO<sub>2</sub> the

\*To whom correspondence should be addressed.

TABLE I  
RELEVANT SPECTROSCOPIC DATA OF COMPOUNDS II AND III

Compound	M.p. (°C)	IR data <sup>d</sup> (cm <sup>-1</sup> )	<sup>1</sup> H NMR data <sup>b</sup> (τ values, J* in Hz)			
			<i>trans</i> -P(CH <sub>3</sub> ) <sub>2</sub> Ph	<i>cis</i> -P(CH <sub>3</sub> ) <sub>2</sub> Ph	N(CH <sub>3</sub> ) <sub>2</sub>	Other
[Ru(O <sub>2</sub> CNMe <sub>2</sub> )(PMe <sub>2</sub> Ph) <sub>4</sub> ]PF <sub>6</sub>	180--184	1565 vs, 1465 s, 1412 s, 1270 s	8.51 t, J* 6.5	8.25 pt, J* 8.5	7.53 s	
[Ru(OSCNMe <sub>2</sub> )(PMe <sub>2</sub> Ph) <sub>4</sub> ]PF <sub>6</sub>	160--162	1570 vs	8.70 t, J* 6.0 8.27 t, J* 6.0	8.20 d, J 8.0 7.95 d, J 8.0	7.69 s	
[Ru(S <sub>2</sub> CNMe <sub>2</sub> )(PMe <sub>2</sub> Ph) <sub>4</sub> ]PF <sub>6</sub>	145--148	1530 m, 1398 m	8.62 bs	8.10 bs	7.47 s	
[Ru(OSCH)(PMe <sub>2</sub> Ph) <sub>4</sub> ]PF <sub>6</sub>	97--101	1480 s, 1380 m	8.69 t, J* 6.0 8.33 t, J* 6.0	8.25 d, J 8.0 8.01 d, J 8.0		1.23 m OSCH
[Ru(OSCOMe)(PMe <sub>2</sub> Ph) <sub>4</sub> ]PF <sub>6</sub>	175--178	1532 vs, 1430 m, 1235 vs	8.72 t, J* 6.0 8.25 t, J* 6.0	8.17 d, J 8.0 7.93 d, J 8.0		7.83 s OCH <sub>3</sub>
[Ru(OSCOEt)(PMe <sub>2</sub> Ph) <sub>4</sub> ]PF <sub>6</sub>	163--167	1528 s, 1478 w, 1232 vs	8.72 t, J* 6.0 8.25 t, J* 6.0	8.17 d, J 8.0 7.93 d, J 8.0		9.36 t, 7.66 q J 7.0 OEt
[Ru(S <sub>2</sub> CH)(PMe <sub>2</sub> Ph) <sub>4</sub> ]PF <sub>6</sub> <sup>c</sup>	180	vibrations observed	8.5 bs	8.0 bs		Resonance of S <sub>2</sub> CH proton not observed
Ru(HO <sub>1</sub> CNMe <sub>2</sub> )(PPh <sub>3</sub> ) <sub>3</sub> <sup>d</sup>	122--125	1538 s, 1502 w, 1403 s, 1272 s				

<sup>c</sup> vs, very strong; s, strong; m, medium; w, weak; characteristic of the anionic ligand.

<sup>b</sup> Measured in CD<sub>2</sub>Cl<sub>2</sub> solution; t, triplet; pt, partial triplet; s, singlet; d, doublet; bs, broad singlet; m, multiplet; J\* separation of the outer two peaks.

<sup>c</sup> H NMR recorded at 0°C.

<sup>d</sup> [Ru-H] 1990 (m) cm<sup>-1</sup>; complex too insoluble to record an <sup>1</sup>H NMR spectrum.

monoalkylcarbonates  $[\text{Ru}(\text{OXCOEt})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  (V) ( $\text{X} = \text{O}$ ) are formed [2]. On prolonged boiling in ethanol I and COS gave V ( $\text{X} = \text{S}$ ) but IV ( $\text{XY} = \text{S}_2$ ) was the sole product from similar reactions with  $\text{CS}_2$ . The salts IV and V are readily converted into III on treatment with  $\text{NHMe}_2$ , while  $\text{RuH}(\text{O}_2\text{CH})(\text{PPh}_3)_3$  forms III.

The compounds II and III are stable in the solid but II slowly decomposes in solution in air. III is stable in solution only under an inert atmosphere. Their relevant spectroscopic data are listed in Table 1. To confirm our formulation of these products as carbamate complexes an X-ray diffraction study of  $[\text{Ru}(\text{O}_2\text{CNMe}_2)(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  was undertaken.

### Crystal data

$[\text{Ru}(\text{O}_2\text{CNMe}_2)(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  (mol. wt. 886.8) forms yellow monoclinic crystals, space group  $P2_1/c$ ,  $a$  14.94(2),  $b$  13.87(2),  $c$  19.43(2) Å,  $\beta$  91.0(2)°,  $D_m$  1.45,  $D_c$  1.46 g cm<sup>-3</sup>,  $Z$  = 4. Intensity data were collected on a Philips automatic four circle diffractometer with Mo- $K_\alpha$  radiation ( $\lambda$  0.7107 Å) and the structure was determined by Patterson and Fourier methods. Refinement by full-matrix least squares using isotropic temperature factors reduced  $R$  to 0.117 for the 2201 observed data and the refinement is continuing.

The ruthenium atom has a distorted octahedral geometry and the ligand arrangement is shown in Fig. 1. Some observed bond lengths are *trans*-Ru-P (mean) 2.41(1), *cis*-Ru-P (mean) 2.28(1), Ru-O (mean) 2.22(2), O-C ( $sp^2$ ) (mean) 1.28(2), N-C ( $sp^2$ ) 1.31(3) and N-C ( $sp^3$ ) (mean) 1.45(4) Å. The  $\text{O}_2\text{CNMe}_2$  moiety is planar and the bond lengths related to this ligand are similar to those found in two *N,N*-dimethylcarbamato complexes of early transition metals [3, 4]. The Ru-O bond lengths do not differ significantly from those observed [5] in other acetato- or formato-ruthenium(II) complexes. Distortions within the cation are similar to that found [6] in  $[\text{Ru}(\text{O}_2\text{CMe})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$  and can be ascribed to the *trans* influence of the phosphine ligands, steric repulsion between the phosphine ligands occupying adjacent facial sites and the small ORuO angle (ca. 58°) of the carbamate group.

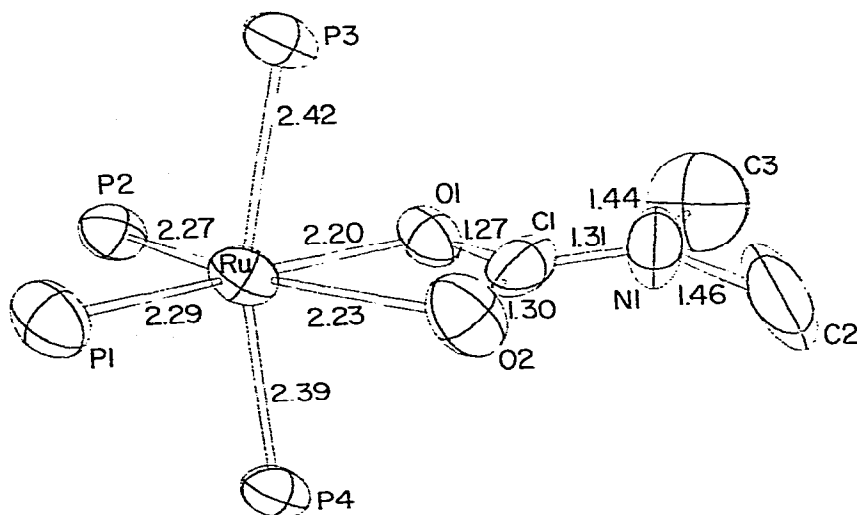
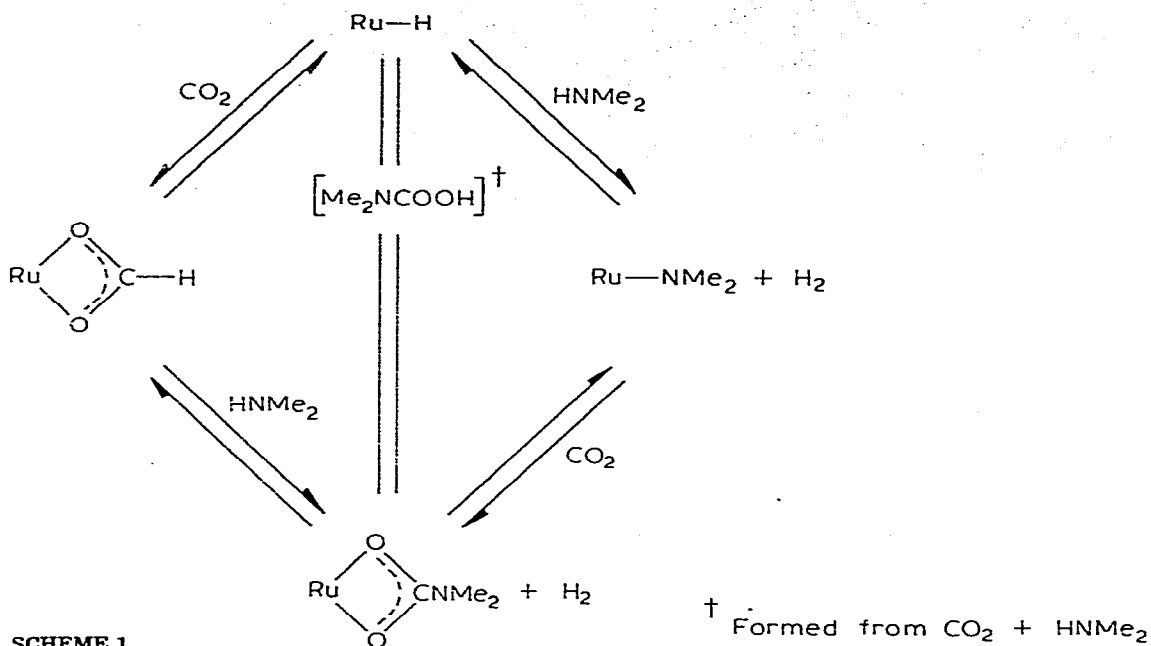


Fig. 1. Ligand arrangement around the ruthenium atom in  $[\text{Ru}(\text{O}_2\text{CNMe}_2)(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ .



SCHEME 1

We are as yet uncertain as to the mode of formation of carbamato complexes but possible routes are given in Scheme 1. Recent studies [3, 4] have shown that  $\text{CO}_2$  rapidly inserts into metal-nitrogen bonds in metal amides to produce mono- and bi-dentate carbamato compounds, and the exchange of  $\text{CO}_2$  with  $\text{Nb}(\text{O}_2\text{CNMe}_2)_5$  is suggested [4] to occur via the intermediates  $\text{Nb}(\text{NMe}_2)_x(\text{O}_2\text{CNMe}_2)_{5-x}$ . The ready formation of II from the monoalkylcarbonates (V) may thus occur via the equilibrium  $\text{Ru}(\text{OXCOEt}) \rightleftharpoons \text{RuOEt} + \text{COX}$  ( $\text{X} = \text{O}, \text{S}$ ) in which ruthenium amide formation results from  $\text{HNMe}_2$ - $\text{RuOEt}$  interactions.

We have been unable to form  $\text{HCONMe}_2$  from reactions of either II or III ( $\text{XY} = \text{O}_2$ ) with  $\text{H}_2$  under a variety of conditions, and whereas carbamato complexes have been precluded as intermediates in the catalytic conversion of  $\text{CO}_2$ ,  $\text{HNMe}_2$  and  $\text{H}_2$  to  $\text{HCONMe}_2$  by deuteration studies, the suggested mechanism involving metal formato-amine reactions now seems improbable, as we expect carbamato intermediates to form by this route. Further studies on these systems are in progress, especially on the catalytic formation of  $\text{HCONMe}_2$ , where a more plausible route [7, 8] involving initial reduction of  $\text{CO}_2$  to  $\text{CO}$  is being investigated.

## References

- 1 P. Haynes, L.H. Slaugh and J.F. Kohnle, *Tetrahedron Lett.*, (1970) 365.
- 2 T.V. Ashworth and E. Singleton, *J. Chem. Soc. Chem. Commun.*, (1976) 204.
- 3 M.H. Chisholm and M. Extine, *J. Amer. Chem. Soc.*, (1974) 6214.
- 4 M.H. Chisholm and M. Extine, *J. Amer. Chem. Soc.*, (1975) 1623.
- 5 A.C. Skapski and F.A. Stephens, *J. Chem. Soc. Dalton*, (1974) 390; I.S. Kolomnikov, A.I. Gusev, G.G. Aleksandrov, T.S. Sobeeva, Yu.T. Struchkov and M.E. Vol'pin, *J. Organometal. Chem.*, (1973) 349.
- 6 T.V. Ashworth, M.J. Nolte and E. Singleton, *J. Chem. Soc. Dalton*, (1976) in press.
- 7 G.N. Schrauzer (Ed.), *Transition Metals in Homogeneous Catalysis*, Marcel Dekker, Inc. New York, 1971, p. 202.
- 8 H. Koinuma, Y. Yoshida and H. Hirai, *Chem. Lett.*, (1975) 1223.