

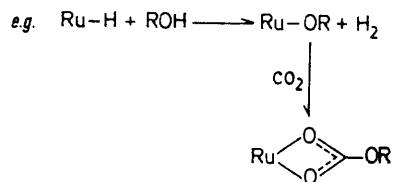
Stable Cationic Monoalkylcarbonate Complexes of Ruthenium(II) from the Reactions of CO₂ with Alcohol Solutions of Ruthenium Hydrides

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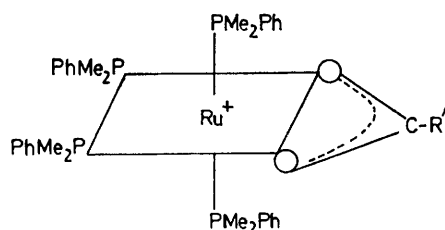
Summary The salt $[\text{Ru}(\text{O}_2\text{COR})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ (R=Me, Et), containing a bidentate monoalkylcarbonate ester, is produced from the reaction of $[\text{RuH}(\text{PMe}_2\text{Ph})_5]\text{PF}_6$ and CO₂ in methanol or ethanol or by recrystallising the formate complex $[\text{Ru}(\text{O}_2\text{CH})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ from acetone-ROH (R=Me, Et).

bidentate carbonate esters from a metal hydride, CO₂ and alcohols appears unusual, their stereochemistry and formulation were assigned from the following evidence.



SCHEME

THOUGH reactions of metal compounds with carbon dioxide are quite numerous those involving insertion into a metal-hydride bond are relatively few.¹ These insertions, usually performed in aromatic solvents, produce metal formate complexes which can also be synthesised from the metal hydride and formic acid. During our studies on the formation and reactivity of cationic ruthenium(II) systems² we



for (II), R' = OR; (R = Me, Et)
(III); R' = R; (R = Me, Et, Ph)

FIGURE

found that the new,³ highly reactive salt $[\text{RuH}(\text{PMe}_2\text{Ph})_5]\text{PF}_6$ (I) formed very stable monoalkyl carbonate complexes with carbon dioxide in ethanol or methanol solution. The complexes were characterised† as $[\text{Ru}(\text{O}_2\text{COR})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ (R = Me, Et) (II) and, although the formation of

(i) The pattern of the methyl hydrogen atoms of the phosphine ligands in the ¹H n.m.r. spectra of (II; R = Me, Et) is almost identical with that in the spectra of the carboxylate complexes³ $[\text{Ru}(\text{O}_2\text{CR})(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ (R = Me, Ph, Et) (III) one of which (R = Me) has been characterised structurally⁴ and shown to have the stereochemistry given in the Figure. (ii) The ¹H n.m.r. spectrum of (II; R = Me) contains a singlet at τ 6.96 which is significantly shifted upfield from methanol methyl protons (τ 6.58) and which is assigned to the methoxy protons of the carbonic ester. Similarly a quartet at τ 6.79 (τ 6.35 for ethanol) and a triplet at τ 9.02 (τ 8.82) are assigned to the ethoxy protons of (II; R = Et). (iii) No OH or formate C-H stretching frequencies were observed in the i.r. spectra of (II), and the $\nu(\text{OCO})_{\text{sym}}$ and $\nu(\text{OCO})_{\text{asym}}$ modes (Table) differ by at least 20 cm⁻¹, indicating non-identical complexes. (iv) Strong $\nu(\text{CO})$ bands for the C-O-C linkages are observed in the region 1085–1100 cm⁻¹ and were characterised from a comparison of the i.r. spectra of (II; R = Me, Et) with (III; R = Me, Et). (v) The melting points of the two complexes differ by 10 °C.

† Satisfactory microanalyses were obtained for all complexes reported.

TABLE

Complex	m.p./°C	$\nu(\text{CO})^a$ in			$\nu(\text{CH-})^a$ in HCO_2^-
		O—C—O	C—O—C		
$\text{Ru}(\text{O}_2\text{CH})(\text{PMe}_2\text{Ph})_4^+$	79—80	1535(m), 1353(s), 1295(s)		2820(w)	
$\text{Ru}(\text{O}_2\text{COMe})(\text{PMe}_2\text{Ph})_4^+$	139—140	1564(m), 1475(vs), 1375(vs)	1085(s)		
$\text{Ru}(\text{O}_2\text{COEt})(\text{PMe}_2\text{Ph})_4^+$	130—131	1545(m), 1430(vs), 1340(vs)	1090(s)		
$\text{RuH}(\text{O}_2\text{CH})(\text{PPh}_3)_3^b$	75—78	1565(s), 1420(m), 1340(m)		2910(m), 2820(m)	
$\text{RuH}(\text{O}_2\text{COMe})(\text{PPh}_3)_3$	96—97	1575(m), 1465(s), 1360(vs)	1087 ^c		
$\text{RuH}(\text{O}_2\text{COEt})(\text{PPh}_3)_3$	101	1565(m), 1425(s), 1338(vs)	1085 ^c		

^a KBr discs, cm^{-1} ; ^b data quoted from ref. 7; ^c observed as a shoulder on a triphenylphosphine vibration.

Though the formate complex (III; R = H) [the product of the reaction of (I) with formic acid] gave (II; R = Me, Et) on recrystallisation from acetone-ROH (R = Me, Et) respectively, we think that a mechanism involving alcohol attack on the formate carbon atom is unlikely. To date the only reported⁵ formation (but not isolation) of a metal alkylcarbonate species involved the ready insertion of carbon dioxide into the copper-oxygen bond in cupric dimethoxide, and thus, we think that a more likely route to (II) involves the insertion of carbon dioxide into a ruthenium alkoxide intermediate generated from initial reactions of the ruthenium hydride with the alcohol (*e.g.* Scheme). Our attempts to characterise Ru-OR intermediates by treating (I) with alcohols or phenols under anaerobic conditions have so far led to intractable products. In the presence of air (I) and alcohols produce the carboxylate complexes (III).

The formation of (II) from the formate compound (III);

R = H) can be explained by the equilibrium $[(\text{PMe}_2\text{Ph})_4\text{Ru}(\text{O}_2\text{CH})] \rightleftharpoons [(\text{PMe}_2\text{Ph})_4\text{Ru}(\text{H})(\text{CO}_2)]$ readily occurring in solution and support for this equilibrium was obtained from the broad hydride resonance at τ 17.4 observed in the ¹H n.m.r. spectrum of (III; R = H) in CD_2Cl_2 at 30 °C.

We are at present investigating the generality of carbonate ester formation in other transition-metal systems and also their possible intermediacy in recently reported catalytic processes^{1,6} involving CO_2 insertions in alcohol solvents. We now find that the reaction of CO_2 with $[\text{RuH}_2(\text{PPh}_3)_4]$, which gives the formate complex $[\text{Ru}(\text{H})(\text{O}_2\text{CH})(\text{PPh}_3)_3]$ (IV) in benzene,⁷ produces $[\text{Ru}(\text{H})(\text{O}_2\text{COR})(\text{PPh}_3)_3]$ (V; R = Me, Et) from alcohol solution. Compound (V) is also obtained from (IV) on warming the complex in methanol or ethanol.

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