

### Preliminary communication

## Synthesis, isolation, and some reactions of hydroxycarbonyl- and alkoxy-carbonylruthenium complexes

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(Received February 5th, 1987)

### Abstract

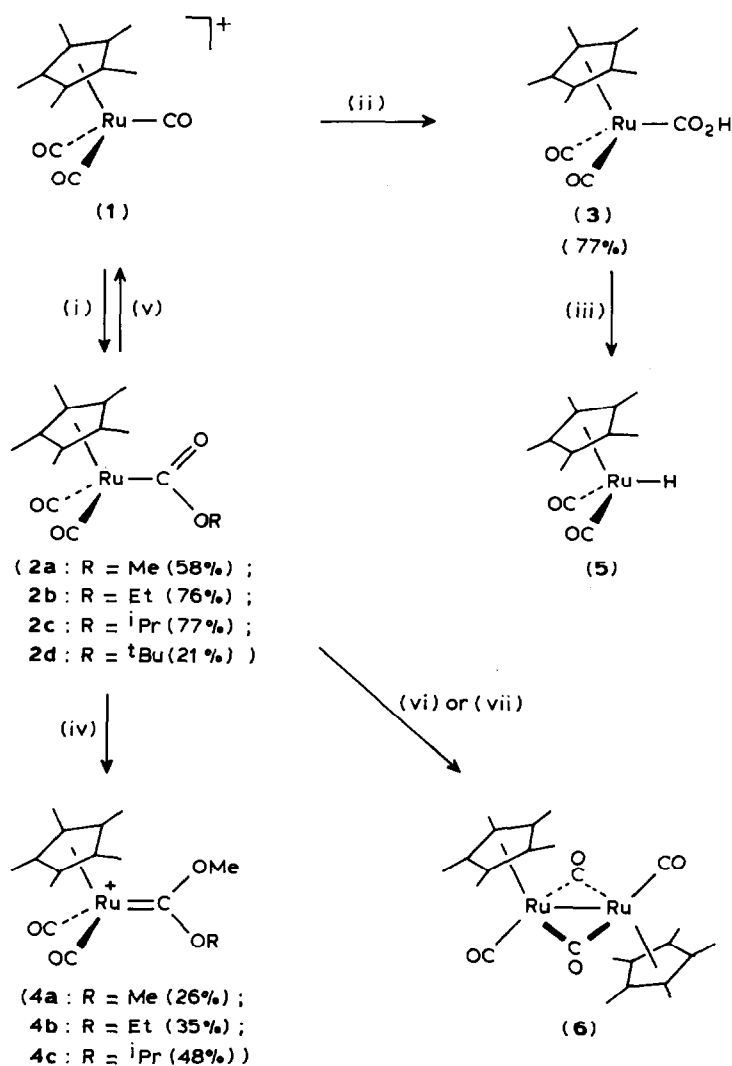
The reaction of  $[(C_5Me_5)Ru(CO)_3]BF_4$  with hydroxide and alkoxide anions in toluene results in the formation of hydroxycarbonyl- and alkoxy-carbonylruthenium(II) complexes,  $(C_5Me_5)Ru(CO_2R)(CO)_2$  (**2**: R = H, Me, Et, <sup>i</sup>Pr, <sup>t</sup>Bu). Treatment of **2** with  $CF_3SO_3CH_3$  yields the cationic dialkoxy-carbene complexes  $[(C_5Me_5)Ru=C(OMe)(OR)(CO)_2]CF_3SO_3$ . Both photolysis and reduction (with hydridic agents) of **2** leads to the dimeric complex,  $[(C_5Me_5)Ru(CO)_2]_2$ .

Hydroxycarbonyl and alkoxy-carbonyl complexes (i.e., metallocarboxylic acids and their esters) of transition metals are of interest because of the proposed intermediacy of such complexes in catalytic processes relating to carbon monoxide conversion, which are becoming increasingly well-known [1]. Here we report on the isolation and some reactions of hydroxycarbonyl- and alkoxy-carbonylruthenium(II) complexes.

Our results are summarized in Scheme 1, and the selected spectral data of the hydroxy- and alkoxy-carbonyl complexes are listed in Table 1.

Treatment of the tricarbonylruthenium cationic complex **1** [2] with sodium methoxide in toluene at ambient temperature gave a yellow slurry. Removal of the solvent in vacuo, extraction with n-pentane followed by cooling of the concentrated extract to  $-20^\circ C$  afforded the methoxycarbonylruthenium(II) complex **2a** in 58% yield as yellow prisms. Analogously the complexes **2b–2d** were synthesized by reaction of **1** with EtONa, <sup>i</sup>PrONa, or <sup>t</sup>BuOK, respectively.

In the IR spectrum, complexes **2** exhibit two characteristic absorption bands for terminal CO stretching vibration, at  $2010–2022\text{ cm}^{-1}$  and  $1961–1976\text{ cm}^{-1}$ . The absorptions for acyl-CO appear in the region  $1634–1641\text{ cm}^{-1}$  and are well within the usual range for  $\eta^1$ -acyls of metallocarboxylates [1]. The <sup>13</sup>C NMR shifts of the carbonyl carbons are also consistent with the presence of COOR groups. The resonances around  $\delta$  202 ppm are tentatively assigned to terminal carbonyl carbons



Scheme 1. (i)  $\text{RO}^-$ ,  $\text{C}_6\text{H}_5\text{CH}_3$ ; (ii)  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_5\text{CH}_3$ ; (iii)  $\text{CH}_3\text{NO}_2$  or  $\text{Et}_2\text{O}$ ; (iv)  $\text{CF}_3\text{SO}_3\text{CH}_3$ ,  $\text{CH}_2\text{Cl}_2$ ; (v)  $\text{HBF}_4$ ,  $\text{Et}_3\text{OBF}_4$ , or  $\text{CF}_3\text{SO}_3\text{SiMe}_3$ ,  $\text{CH}_2\text{Cl}_2$ ; (vi)  $\text{LiBEt}_3\text{H}$  or  $\text{BH}_3$ , THF; (vii)  $h\nu$ ,  $\text{C}_6\text{H}_6$ .

because the intensity of the signals is stronger than that observed at  $\delta$  191 ppm, by a factor of ca. 2. The signal at  $\delta$  191 ppm disappears after the reaction with  $\text{CF}_3\text{SO}_3\text{CH}_3$  which leads to the carbene complexes 4. The complexes were further characterized by  $^1\text{H}$  NMR spectroscopy and elemental analyses.

Reaction of tricarbonyl 1 with water in toluene in the presence of  $\text{Na}_2\text{CO}_3$  yielded a hydroxycarbonyl complex 3 as colorless needles. The OH stretching band observed at  $2701\text{ cm}^{-1}$  is indicative for the dimeric or oligomeric structure of 3 via hydrogen bonds. The hydroxycarbonyl complex 3 decomposes smoothly to monohydride 5 at ambient temperature in diethyl ether or nitromethane; however, the stoichiometry of the decomposition could not be clarified.

Table 1  
Selected spectral data for  $(C_5Me_5)Ru(CO)_2(COOR)$

	R	IR <sup>a</sup> (cm <sup>-1</sup> )		<sup>1</sup> H NMR <sup>b</sup> (ppm, <i>J</i> in Hz)		<sup>13</sup> C NMR <sup>b</sup> (ppm)	
		$\nu(CO)_t$ <sup>c</sup>	$\nu(CO)_a$ <sup>d</sup>	$\delta(C_5Me_5)$	$\delta(R)$	$\delta(CO)_t$ <sup>c</sup>	$\delta(CO)_a$ <sup>d</sup>
<b>2a</b>	Me	2022 1961	1641	1.61	3.58	202.1	192.0
<b>2b</b>	Et	2015 1976	1641	1.63	4.26 (q, <i>J</i> 7.1) 1.15 (t, <i>J</i> 7.1)	202.2	191.5
<b>2c</b>	<sup>i</sup> Pr	2014 1963	1634	1.63	5.33 (sept, <i>J</i> 6.4) 1.21 (d, <i>J</i> 6.4)	202.3	191.0
<b>2d</b>	<sup>t</sup> Bu	2010 1968	1637	1.65	1.53	202.4	191.3
<b>3</b>	H	2014 1963	1602	1.97 <sup>e</sup>	7.98 <sup>e</sup>	<i>f</i>	<i>f</i>

<sup>a</sup> Measured in KBr. <sup>b</sup> Measured in C<sub>6</sub>D<sub>6</sub>. <sup>c</sup> Terminal CO. <sup>d</sup> Acyl CO. <sup>e</sup> Measured in CD<sub>2</sub>Cl<sub>2</sub>. <sup>f</sup> Spectrum could not be obtained because of the instability of **3** in solution.

The alkoxycarbonyl complexes **2** react with a variety of substrates under mild conditions. The low frequency of the acyl-CO stretching of **2** which suggests that the bonding in alkoxycarbonyl complexes involves a contribution from a carbene-like resonance hybrid  $(C_5Me_5)Ru=C(OMe)(O^-)$ , which is quenched by reaction with electrophiles. Treatment of **2** with methyl trifluoromethanesulfonate in dichloromethane at ambient temperature gave the cationic dialkoxycarbene complexes **4a–4c**, tricarbonyl complex **1**, and ROME. The carbene complexes **4** are formed via electrophilic attack of Me<sup>+</sup> on the acyl oxygen atom of **2**. In contrast, Cutler et al. reported that an iron analogue of **2**, CpFe(CO<sub>2</sub>Me)(CO)<sub>2</sub>, could not be converted to a carbene complex [CpFe=C(OMe)<sub>2</sub>(CO)<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub> by treatment with CF<sub>3</sub>SO<sub>3</sub>Me [3].

The <sup>1</sup>H and <sup>13</sup>C NMR parameters of the carbene ligands of **4a–4c** characterize their structural types. The resonances of methoxy protons of **4** are shifted downfield considerably,  $\delta$  4.28 ppm for **4a**,  $\delta$  4.28 ppm for **4b**, and  $\delta$  4.25 ppm for **4c**, compared with that of the methoxycarbonyl complex **2a**,  $\delta$  3.58 ppm. In the <sup>13</sup>C NMR spectrum of **4b**, the carbene-carbon resonance appears at 239.8 ppm which is comparable with the values for [CpFe=C(OMe)<sub>2</sub>(CO)<sub>2</sub>]PF<sub>6</sub> ( $\delta$  251.9 ppm) [4], for [CpFe=C(OMe)<sub>2</sub>(CO)<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub> [5] ( $\delta$  251.8 ppm), and for [CpFe=C(OMe)(OEt)(CO)<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub> [5] ( $\delta$  250.4 ppm).

Addition of other electrophiles such as HBF<sub>4</sub>, Et<sub>3</sub>OBF<sub>4</sub>, or CF<sub>3</sub>SO<sub>3</sub>SiMe<sub>3</sub> to ester **2** in dichloromethane gave the cationic tricarbonyl complex **1** quantitatively by electrophilic attack on the alkoxy oxygen.

Reaction of **2** with excess LiBEt<sub>3</sub>H or BH<sub>3</sub>(THF) in tetrahydrofuran gave [(C<sub>5</sub>Me<sub>5</sub>)Ru(CO)<sub>2</sub>]<sub>2</sub> [6] via the monohydride **5** as an intermediate, which was confirmed by monitoring the reaction by <sup>1</sup>H NMR. The dimeric complex **6** was also obtained as sole non-volatile product in the photolysis reaction of **2a** in benzene.

## References

- (a) A.C. Harkness and J. Halpern, *J. Am. Chem. Soc.*, 83 (1961) 1258; (b) S. Nakamura and J. Halpern, *ibid.*, 83 (1961) 4102; (c) J.E. Bercaw, L.Y. Goh, and J. Halpern, *ibid.*, 94 (1972) 6534; (d) R.

- Pettit, C. Maudlin, T. Cole, and H. Kang, *Ann. N.Y. Acad. Sci.*, 295 (1977) 151; (e) P.C. Ford, *Acc. Chem. Res.*, 14 (1981) 31; (f) T. Kruck and M. Noack, *Chem. Ber.*, 97 (1964) 1693; (g) A.J. Deeming and B.L. Shaw, *J. Chem. Soc. A*, (1969), 443; (h) T.G. Appleton and M.A. Bennet, *J. Organomet. Chem.*, 55 (1973) C88; (i) E.G. Bryan, A.L. Burrows, B.F.G. Johnson, J. Lewis, and G.M. Schiavon, *ibid.*, 129 (1977) C19; (j) C.P. Casey, M.A. Andrews, and J.E. Rinz, *J. Am. Chem. Soc.*, 101 (1979) 741; (k) N. Grice, S.C. Kao, and R. Pettit, *ibid.*, 101 (1979) 1627; (l) M. Catellani and J. Halpern, *Inorg. Chem.*, 19 (1980) 566; (m) D.H. Gibson, W.-L. Hsu, and F.U. Ahmed, *J. Organomet. Chem.*, 215 (1981) 379; (n) P. Eilbracht and E. Henkes, *Chem. Ber.*, 114 (1981) 1559; (o) J.R. Sweet and W.A.G. Graham, *Organometallics*, 1 (1982) 982; (p) W. Tam, G.-Y. Lin, W.K. Wong, W.A. Kiel, V.K. Wong, and J.A. Gladysz, *J. Am. Chem. Soc.*, 104 (1982) 141; (q) J.G. Alton and L.A.P. Kane-Maguire, *J. Organomet. Chem.*, 246 (1983) C23; (r) C.F. Barrientos-Penna, A.B. Gilchrist, and D. Sutton, *Organometallics*, 2 (1983) 1265; (s) M.A. Bennet and A. Rocicki, *J. Organomet. Chem.*, 244 (1983) C31; (t) D.H. Gibson, K. Owens, and T.-S. Ong, *J. Am. Chem. Soc.*, 106 (1984) 1125; (u) D.H. Gibson, T.-S. Ong, *Organometallics*, 3 (1984) 1911; (v) P.L. Burk, D.V. Engen, and K.S. Campo, *ibid.*, 3 (1984) 493; (w) M.A. Bennet and A. Rocicki, *ibid.*, 4 (1985) 180; (x) M.A. Lilga and J.A. Ibers, *ibid.*, 4 (1985) 590.
- 2 (a) G.O. Nelson, *Organometallics*, 2 (1983) 1474; (b) G.O. Nelson and C.E. Sumner, *ibid.*, 5 (1986) 1983.
- 3 T. Forschner, K. Menard, and A. Cutler, *J. Chem. Soc., Chem. Commun.*, (1984) 121.
- 4 M.H. Quick and R.J. Angelici, *J. Organomet. Chem.*, 160 (1978) 231.
- 5 F.B. McCormick and R.J. Angelici, *Inorg. Chem.*, 20 (1981) 1111.
- 6 R.B. King, M.Z. Iqbal, and A.D. King, Jr., *J. Organomet. Chem.*, 171 (1979) 53.