Journal of Organometallic Chemistry, 384 (1990) C61–C64
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20671PC

Preliminary communication

Carbonylation of alkenyl-complexes of ruthenium. The formation of complexes containing, alkene or acyl ligands, and the reaction of the acyl complexes with methanol

M. Rosario Torres, Aurea Perales

Instituto de Quimica-Fisica "Rocasolano" C.S.I.C., Serrano 119, 28006-Madrid (Spain)

Hassane Loumrhari and Josep Ros *

Departament de Quimica, Universitat Autonoma de Barcelona, 08193-Bellaterra, Barcelona (Spain)

(Received December 18th, 1989)

Abstract

The unsaturated complexes $RuCl(CO)(RC{=}CHR')(PPh_3)_2$ react with CO to give the dicarbonyl complexes $RuCl(CO)_2(RC{=}CHR')(PPh_3)_2$ or the η^2-acyl complexes $RuCl(CO)(O{=}CC(R){=}CHR')(PPh_3)_2$, depending on the R and R′ groups. The $RuCl(CO)(O{=}CC(Me){=}CHMe)(PPh_3)_2$ complex reacts with methanol to give $RuCl(CO)(O_2CC(Me){=}CHMe)(PPh_3)_2$, which structure has been established by an X-ray diffraction study.

We recently reported the syntheses of unsaturated 16-electron alkenyl complexes of ruthenium(II) from the hydride complex $RuHCl(CO)(PPh_3)_3$ and alkynes [1,2,3]. The alkenyl complexes $RuCl(CO)(RC{=}CHR')(PPh_3)_2$ take up coordinating species such as dimethyl acetylenedicarboxylate [2], CS_2 [4], 3,5-dimethylpyrazole [5] and carboxylates [6], always to give saturated octahedral complexes. In continuation of our programme, we have examined their reactions with CO with the aim of comparing the results with those obtained by other groups. Thus Werner [7] and Mawby [8] reported the formation of dicarbonyl complexes $RuCl(CO)_2(RC{=}CHR)(PR_3)_2$ in related reactions, but no coupling alkenyl-CO was observed. Only with methyl derivatives of ruthenium was a coupling with CO and alkyl ligands observed [9]. A related system was investigated by Roper [10,11], and revealed the formation of an η^2-acyl ligand by arylation of $MHCl(CO)(PPh_3)_2$ (M = Ru and Os) complexes with HgR_2.

We find that the reaction of unsaturated complexes $RuCl(CO)(RC{=}CHR')(PPh_3)_2$ with CO when R = H and R′ = H, Ph, C_3H_7, $SiMe_3$, CMe_3, CO_2Me and CO_2Et; and R = R′ = CO_2Me give the dicarbonyl compounds $RuCl(CO)_2(HC{=}$

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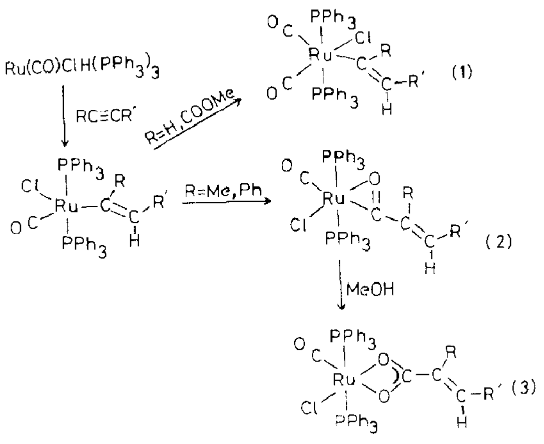

Scheme 1

CHR')$(PPh_3)_2$ (**1**) in very high yields (see Scheme 1). The products show two characteristic ν(CO) bands in their IR spectra, and their ^{1}H NMR spectra contain signals from η^1-alkenylic ligands *; in the monosubstituted alkenyl derivatives the *trans* disposition of the hydrogens is maintained [1,2]. When the addition of CO was performed with alkenyl compounds with R = R' = Me and Ph; and R = Ph and R' = Me, new products of the type **2** (see Scheme 1) were obtained in quantitative yields. The IR spectra of compounds **2** show only one ν(CO) band, at $\approx$ 1900 cm^{-1}, and a new absorption at $\approx$ 1535 cm^{-1} near to the position of the ν(C=O) bonds for η^2-acyl complexes reported by Roper. A peak at 271 ppm in the ^{13}C NMR of complex with R = R' = Me support the η^2-nature of the acyl ligand [14]. In summary, the presence of Me and Ph groups in the α position favours the formation of the η^2-acyl ligand, but that of H and CO_2Me groups in the same position induces formation of dicarbonyl complexes. This observation is different from that described by Roper, there is no equilibrium in solution between the two possible species, and we have isolated the pure products [10].

When the carbonylation was performed with the complexes RuI(CO)(HC=CHR')$(PPh_3)_2$ in CH_2Cl_2, a mixture of η^2-acyl and dicarbonyl derivatives was obtained as indicated by the IR spectra of the products in KBr discs. The IR spectrum of a solution of the mixture changes from solvent to solvent; in CH_2Cl_2 the dicarbonyl form predominates, but coexists with the acyl species, and in THF the acyl form is favoured. This allows to isolate nearly pure forms of the two types of complexes depending on the halide ligand and the solvent from which is precipitated. These observations are in accord with those previously reported [14], and indicate the importance of the steric and electronic effects in the formation of the η^2-acyl ligands, but in the case of the complex $RuCl(CO)_2(MeO_2CC{=}CHCO_2$-

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* For **1** (R' = CMe_3): IR (KBr) ν(CO) 2032, 1974 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.53 (s, 9H), 4.94 (d, *J* 17 Hz, 1H), 6.57 (d, *J* 17 Hz, 1H), 7.2–7.7 (Ph) ppm.

For **2** (R = R' = Me): IR (KBr) ν(CO) 1900, ν(C=O) 1538 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.04 (s, 3H), 4.25 (d, *J* 6 Hz, 3H), 5.78 (q, *J* 6 Hz, 1H), 7.2–7.7 (Ph) ppm; ^{13}C NMR ($CDCl_3$): 271 (O=C), 151 (CO) ppm.

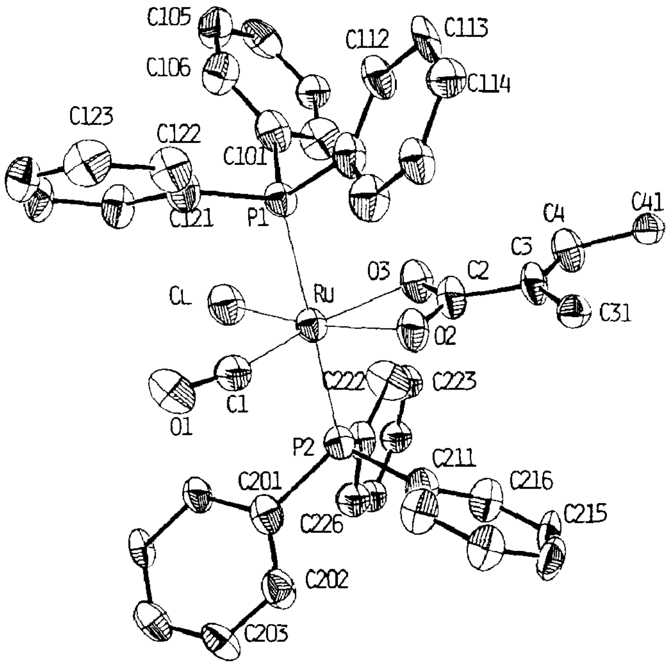

Fig. 1. ORTEP view of compound 3 showing the atomic numbering scheme. Selected bond distances (Å): Ru–P1 2.381(1), Ru–P2 2.383(1), Ru–Cl 2.390(2), Ru–Cl 2.958(1), Ru–O2 2.114(4), Ru–O3 2.205(4), C1–O1 1.173(1), C2–O2 1.272(8), C2–O3 1.270(8), C2–C3 1.482(11), C3–C4 1.343(12), C3–C31 1.489(13), C4–C41 1.491(23). Selected angles (deg): P1–Ru–P2 117.17(5), O2–Ru–O3 60.43(16), Cl–Ru–O2 164.35(13), Cl–Ru–O3 161.44(12), O2–C2–O3 117.6(6).

Me)$(PPh_3)_2$, containing strong electron-drawing substituents, the observations are in conflict with the phase of some tungsten complexes since a decrease in the electron density at the metal centre favours formation of the η^2-acyl species [15].

The complex $RuCl(CO)(O{=}C(Me)C{=}CHMe)(PPh_3)_2$ underwent an interesting transformation in methanol. After three days in methanol in the absence of air a new product crystallized out (3, 15% yield). The IR spectrum of 3 shows only one band in the ν(CO) region, at 1943 cm^{-1}, and no acyl band. The exact nature of the product was established by an X-ray diffraction study *, which revealed that an η^2-alkenecarboxylate ligand has been formed, probably by nucleophilic attack of the methanol on the acylic carbon. The molecular structure of 3 with some relevant distances and angles, is shown in Fig. 1. The octahedral ruthenium atom is bonded to two phosphines in a disposition, and the Cl and the carbonyl ligands are *trans* to oxygens of the carboxylate ligand in the equatorial plane. The alkenecarboxylate ligand is planar and contains two methyls in a *cis* disposition. The C3–C4 distance

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* *Crystal data*: $C_{42}H_{37}ClO_3P_2Ru$; M_m 750.9; monoclinic; a 17.7552(6), b 17.3151(8), c 12.2581(4) Å; β 96.152(2)°; V 3746.8(2) Å^3; $Z = 4$; four circle diffractometer PW 1100 Philips; Bisecting geometry; Graphite oriented monochromator: Cu-K_α (μ 52.4 cm^{-1}); space group $P2_1/n$; D_{calc} 1.33 g cm^{-3}. Data collection and processing. Scanning range for θ: $2 < \theta < 65$°; Number of reflections: 6623 measured and 5151 observed ($3\sigma(I)$ criterion); absorption correction applied. The structure was solved by direct methods (Multan 80 and Dirdif). Refinement: All atoms anisotropic except C1 and O1; H atoms were placed in calculated positions. Final R and R_w; 6.1, 6.4%. Anomalous dispersion correction applied for Ru, O, Cl, and P.

corresponds to a double bond (1.34(1) Å), and the C2–O2 and C2–O3 distances are similar to one another (1.272(8) and 1.270(8) Å). The small O2–C2–Os angle of 60.4(2)° is reflected in an increase in the remaining equatorial angles. The P1–Ru–P2 angle is 177.17(5)°, and the distances Ru–Cl (2.39(2) Å), Ru–C1 (1.958(4) Å), Ru–P1 (2.281(1) Å) and Ru–P2 (2.283(1) Å) are comparable with those in related complexes [2,3].

The metal-catalysed reaction of acetylenes with CO and alcohols to form acrylic esters is a well known [16], but to our knowledge possible mechanisms involving η^2-acyl and η^2-alkene-carboxylate intermediates have not been postulated.

Acknowledgements. We are grateful to CICYT of Spain for financial support and to the Ministère de l'Education Nationale du Maroc for a Fellowship (to H.L.).

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