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Reactions of dinuclear carboxylate ruthenium (I) complexes with alcohols. The unexpected oxidation of primary alcohols to carboxylic ligands

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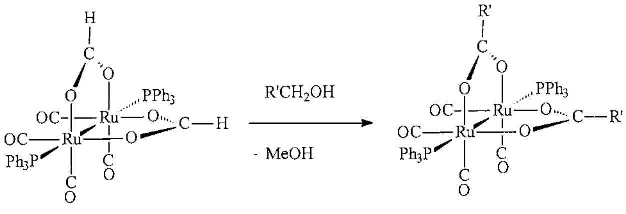
Abstract

The dinuclear ruthenium (I) complexes $[Ru_2(HCO_2)_2(CO)_4(PPh_3)_2]$ react with primary alcohols $R'CH_2OH$ in refluxing toluene, giving rise to $[Ru_2(R'CO_2)_2(CO)_4(PPh_3)_2]$ compounds. Other carboxylate bridging complexes react with alcohols $R''OH$ to give very unstable alkoxide compounds $[Ru_2(R''O)_2(CO)_4(PPh_3)_2]$.

Keywords: Ruthenium; Carboxylate; Formate; Alkoxide

Dinuclear carbonyl ruthenium (I) complexes bridged by heteroatom-containing anionic ligands are easy to prepare [1]. They have shown important catalytic activity in hydroformylation of olefins [2] and in the addition of carboxylic acids to alkynes [3]. In this family of compounds, the carboxylate bridges can easily be replaced by other three-electron anionic bridging ligands such as thiolates, diamides or other carboxylate ligands [4–6]. During our studies on the substitution of carboxylate ligands in complexes such as $[Ru_2(RCO_2)_2(CO)_4(PPh_3)_2]$ by other ligands we observed that they reacted slowly with alcohols in refluxing toluene. The reaction of the formate compound $[Ru_2(HCO_2)_2(CO)_4(PPh_3)_2]$ (**1**) with primary alcohols $R'CH_2OH$ gave rise to carboxylate-bridged complexes $[Ru_2(R'CO_2)_2(CO)_4(PPh_3)_2]$. The formation of carboxylate bridging ligands was the result of the oxidation of the alcohols by the formate groups. However, the reaction of dinuclear compounds containing alkyl or alkene carboxylate bridges $[Ru_2(RCO_2)_2(CO)_4(PPh_3)_2]$ ($R{=}CH_3$ (**4**) and $(CH_3)_2C{=}CH$ (**5**)) with phenol PhOH and alkyl alcohols $R''OH$ ($R''{=}CH_3CH_2CH_2CH_2$ and $(CH_3)_2CHCH_2CH_2$) produced very unstable compounds $[Ru_2(R''O)_2(CO)_4(PPh_3)_2]$ bridged by alkoxide groups.

The reaction of the formate complex $[Ru_2(HCO_2)_2(CO)_4(PPh_3)_2]$ (**1**) with an excess of *iso*-pentanol or *n*-butanol in refluxing toluene for 24 h led to pale-yellow carboxylate-bridged complexes $[Ru_2(R'CO_2)_2(CO)_4(PPh_3)_2]$ ($R'{=}(CH_3)_2CHCH_2$ (**2**) and



(1)

$R' = (CH_3)_2CHCH_2$ (**2**)
$R' = CH_3CH_2CH_2$ (**3**)

Scheme 1.

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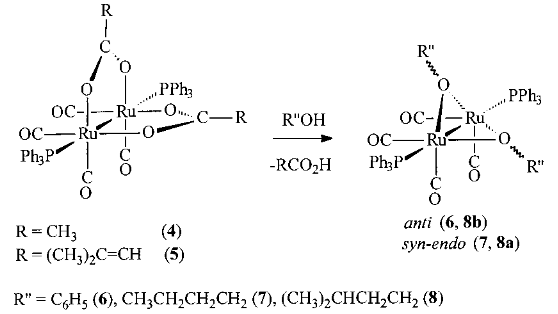
$CH_3CH_2CH_2$ (**3**)) (Scheme 1)[1]. The IR spectra of compounds **2** and **3** show three ν(C≡O) bands with the pattern expected for the $Ru_2(CO)_4$ fragment with a C_{2v} symmetry. The ν(OCO) bands are observed at 1565 and 1413–1415 cm^{-1} with $\Delta = \nu(OCO)_{asym} - \nu(OCO)_{sym} = 152$–$150$ cm^{-1}, which are normal values for η^2-carboxylate-bridging ligands [7]. The ^{1}H-NMR of complexes **2** and **3** display the expected signals of the hydrocarbon chain of the carboxylate ligand, and their $^{31}P\{^1H\}$-NMR spectra show a singlet at 14.8 and 12.5 ppm respectively, in accordance with two equivalent PPh_3 ligands bonded to ruthenium atoms in a *trans* arrangement [6]. A gas chromatography (GC) analysis of the crude of reaction revealed the formation of methanol, which is the product of the reduction of the formate group.

Carboxylate dinuclear complexes $[Ru_2(RCO_2)_2(CO)_4(PPh_3)_2]$ (R=CH_3 (**4**) and $(CH_3)_2C$=CH (**5**)) reacted slowly with alcohols R″OH in refluxing toluene to give dark solutions that contained alkoxide dinuclear compounds $[Ru_2(R'O)_2(CO)_4(PPh_3)_2]$ (R′=C_6H_5 (**6**), $CH_3CH_2CH_2CH_2$ (**7**) and $(CH_3)_2CHCH_2CH_2$ (**8**)) (Scheme 2)[2]. These green products are very unstable and we have so far been unable to isolate them as pure solids. When the crude products of these reactions were chromatographed in columns containing florisil using a dichloromethane-ethylacetate mixture as eluant we obtained yellow solutions of alkoxide complexes **6**–**8**.The IR spectra of solutions containing complexes **6**–**8** showed three ν(C≡O) bands with different intensity patterns. The IR spectrum of **6** in the ν(C≡O) region suggested an *anti* configuration of alkoxide bridges, whereas the IR spectrum of (**7**) is consistent with a *syn* arrangement of alkoxide bridges. Complex **8** showed a ν(C ≡ O) pattern that suggested the presence of two stereoisomers with *syn* (**8a**) and *anti* (**8b**) configurations, respectively. The $^{31}P\{^1H\}$-NMR spectra of these complexes supported the IR data showing a singlet at 26.5 and 27.6 ppm for compounds **6** and **7** respectively and two singlets at 25.5 ppm for **8a** and 12.4 ppm for **8b**. Both *syn–endo* and *syn–exo* structures are possible for complexes **7** and **8a** but we assign *syn–endo* configurations for them because of the bulk of alkoxide substituents. These spectroscopic data are consistent with the formation of $[Ru_2(R''O)_2(CO)_4(PPh_3)_2]$ complexes and those found for the bis(methoxi)ruthenium compound $[Ru_2(MeO)_2(CO)_4(P^tBu)_2]$, which was prepared by reacting $[Ru(CO)_3(P^tBu_3)_2]$ with methanol [8]. On the other hand, the proposed geometries for alkoxides are concordant with those found for the thiolate bridged $[Ru_2(RS)_2(CO)_4(PPh_3)_2]$ compounds, which were previously reported by our group of research [5].



Scheme 2.

Acknowledgements

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[1] Analytical and spectroscopic data for **2** and **3**: (**2**) 40% yield. Anal. Calc. for $C_{50}H_{48}O_8P_2Ru_2$: C, 57.69; H, 4.65. Found: C, 56.87; H, 4.69%. IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 2022 s, 1978 m, 1949 s. IR (KBr, cm^{-1}): ν(OCO) 1565 m, 1413 m. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.6 (d, $J = 6.8$ Hz, 12 H), 1.5 (m, 2 H), 1.8 (d, $J = 6.8$ Hz, 4 H), 7.2–7.6 (m, 30 H) ppm. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 62 MHz): δ 22.3 (CH_3), 26.1 (CH), 46.5 (CH_2), 127.9, 133.7, 133.8, 133.9 (C_6H_5), 188.3 (CO_2), 205.4(CO) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$, 102 MHz): δ 14.8 ppm. (**3**) 30% yield. Anal. Calc. for $C_{48}H_{44}O_8P_2Ru_2$: C, 56.92; H, 4.38. Found: C, 56.87; H, 4.35%. IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 2022 s, 1979 m, 1959 s. IR (KBr, cm^{-1}): ν(OCO) 1565 m, 1415 m. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.5 (t, $J = 8.6$ Hz, 6 H), 1.1 (tq, $J_1 = 8.6$ Hz, $J_2 = 8.5$ Hz, 4 H), 1.9 (t, $J = 8.5$ Hz, 4 H), 7.1–7.6 (m, 30 H) ppm. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 62 MHz): δ 13.5 (CH_3), 19.0 (CH_2), 39.0 (CH_2CO_2), 128.1, 129.5, 133.8, 133.9 (C_6H_5), 188.3 (CO_2), 205.4 (CO) ppm $^{31}P\{^1H\}$-NMR ($CDCl_3$, 102 MHz): δ 12.5 ppm.

[2] Selected spectroscopic data for **6**, **7** and **8**: (**6**) 24% yield. IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 2056 s, 1995 s, 1954 m. $^{31}P\{^1H\}$-NMR ($CDCl_3$, 102 MHz): δ 26.5 ppm. (**7**) 20% yield. IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 2037 s, 1984 m, 1963 s. $^{31}P\{^1H\}$-NMR ($CDCl_3$, 102 MHz): δ 27.6 ppm. (**8** mixture of isomers): 25% yield. (**8a**) IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 2023 s, 1979 m, 1949 s. $^{31}P\{^1H\}$-NMR ($CDCl_3$, 102 MHz): δ 25.5 ppm. (**8b**) IR (CH_2Cl_2, cm^{-1}): ν(C≡O) 2036 s, 1986 s, 1964 m,. $^{31}P\{^1H\}$-NMR ($CDCl_3$, 102 MHz): δ 12.4 ppm.