Interplay of Phosphido and Phosphine Ligands in Dinuclear Ruthenium Complexes: Implication in the Catalytic Hydroformylation of Ethylene†

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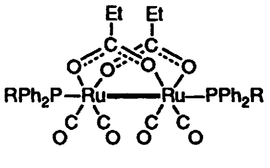
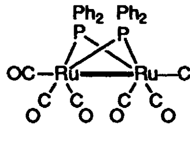
The conversion of the diphenylphosphine complex $[Ru_2(CO)_4(\mu\text{-}O_2CEt)_2(PPh_2H)_2]$ **1** into the diphenylphosphido complex $[Ru_2(CO)_6(\mu\text{-}PPh_2)_2]$ **2** under a pressure of CO and the conversion of **2** into the ethyldiphenylphosphine complex $[Ru_2(CO)_4(\mu\text{-}O_2CEt)_2(PPh_2Et)_2]$ **3** in the presence of ethylene and water have been studied; high-yield syntheses for the known complex **2** are also reported.

Dinuclear ruthenium complexes of the 'saw-horse' type $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2L_2]$, accessible from ruthenium carbonyl and carboxylic acids, are well known.[1–3] Some phosphine derivatives have been found to catalyse the hydroformylation of olefins.[4,5] Here we report the interconversion of the new phosphine complexes $[Ru_2(CO)_4(\mu\text{-}O_2CEt)_2(PPh_2R)_2]$ (R = H **1** or Et **3**) into the known phosphido complex $[Ru_2(CO)_6(\mu\text{-}PPh_2)_2]$ **2**, a process which seems to play a key role in the hydroformylation of ethylene.

The complexes **1** and **3** were prepared in quantitative yields by treating the polymer $[\{Ru(CO)_2(\mu\text{-}O_2CEt)\}_n]$[1] with the equivalent amounts of the phosphines PPh_2H and PPh_2Et, respectively.‡ Under a pressure of CO and at 160 °C the diphenylethylphosphine complex **1** is converted into the diphenylphosphido complex **2** with formation of propionic acid [equation (1)].§ Liberation of the carboxylic acid from complexes of this type has also been observed by Piacenti and coworkers[7,8] in a study on the thermal degradation of $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(PBu_3)_2]$ under carbon monoxide pressure to give mononuclear ruthenium complexes and the free acid. Complex **2**, in its turn, reacts at 160 °C under a pressure of 50 bar with ethylene and water to give the ethyldiphenylphosphine complex **3** (equation (2).¶ Below 150 °C no reaction takes place, and above 170 °C many decomposition products are observed.



1 R = H
3 R = Et



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$$[Ru_2(CO)_4(\mu\text{-}O_2CEt)_2(PPh_2H)_2] + 2\,CO \xrightarrow{\text{thf}} [Ru_2(CO)_6(\mu\text{-}PPh_2)_2] + 2\,EtCO_2H \quad (1)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad \mathbf{2}$$

$$[Ru_2(CO)_6(\mu\text{-}PPh_2)_2] + 4\,C_2H_4 + 2\,H_2O \xrightarrow{\text{thf}} [Ru_2(CO)_4(\mu\text{-}O_2CEt)_2(PPh_2Et)_2] \quad (2)$$
$$\mathbf{2} \qquad\qquad\qquad\qquad\qquad \mathbf{3}$$

The conversion of compound **2** into **3** involves the assembly of a μ-propionato ligand from a carbonyl ligand, ethylene and water; we established the feasibility of this process by ^{13}C and ^{18}O isotope labelling in the reaction of $[Ru_3(CO)_{12}]$ with

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† *Non-SI unit employed:* bar = 10^5 Pa.

‡ A slurry of $[\{Ru(CO)_2(\mu\text{-}O_2CEt)\}_n]$ (230 mg) with PPh_2H (186 mg, 1 mmol) or PPh_2Et (214 mg, 1 mmol) in tetrahydrofuran (thf) (30 cm^3) was stirred at room temperature for 2 h. Then the yellow solution was evaporated to dryness, the resulting oil was crystallized from pentane, filtered off and washed twice with small amounts of pentane. Yields: 417 mg (77%) **1**, 400 mg (69%) **3**. For both compounds satisfactory elemental analyses were obtained. Compound **1**: $\delta_H(CDCl_3$, 400 MHz, 298 K) 7.71–7.35 (20 H, m, C_6H_5), 6.31 [2 H, d, J(PH) 335.4, PH], 2.04 [4 H, q, ^3J(HH) 7.6, CH_2] and 0.77 [6 H, t, ^3J(HH), 7.6 Hz, CH_3]; $\delta_P(CDCl_3$, 162 MHz, 298 K, H_3PO_4) −2.51; ν_{max}(KBr) 2329w (PH), 2025s, 1976s, 1946vs(br), 1934(sh) (CO) and 1562s cm^{-1} (CO_2). Compound **3**: $\delta_H(CDCl_3$, 400 MHz, 298 K) 7.58–7.36 (20 H, m, C_6H_5), 2.48 [4 H, dq, ^2J(PH) 11.1, ^2J(HH) 7.45, PCH_2], 1.98 [4 H, q, ^3J(HH) 7.6, CH_2], 1.02 [6 H, dt, ^3J(PH) 17.0, ^2J(PH) 7.45, PCH_2CH_3] and 0.79 [6 H, ^3J(HH) 7.6 Hz, CH_3]; $\delta_P(CDCl_3$, 162 MHz, 298 K, H_3PO_4) 15.3; ν_{max}(KBr) 2026s, 1973s, 1949vs, 1914s (CO) and 1567 cm^{-1} (CO_2).

§ Compound **1** (150 mg, 0.18 mmol) was dissolved in thf (10 cm^3) and stirred for 18 h under CO pressure (50 bar) at 160 °C in a stainless-steel autoclave. After cooling and venting, the solution was evaporated to dryness, the residue was dissolved in CH_2Cl_2 (5 cm^3) and separated on TLC plates (Alox) using CH_2Cl_2–hexane (1:4) as eluent. Compound **2** was obtained from the first colourless band as white crystals, m.p. 175 °C (decomp.), yield 80 mg (60%); IR and NMR spectra are in accordance with published data.[6]

¶ Compound **2** (150 mg, 0.2 mmol) was dissolved in thf (10 cm^3) and water (5 cm^3) added. The mixture was pressurized with 50 bar ethylene in an autoclave and heated at 160 °C for 18 h with stirring. After cooling and venting, the yellow solution was evaporated to dryness. The remaining oil was dissolved in CH_2Cl_2 (5 cm^3) and separated by TLC [alox, CH_2Cl_2–hexane (2:3)]; after crystallization from pentane the yellow band yielded 30 mg (15%) of compound **3**.

ethylene and water to give $[\{Ru(CO)_2(\mu\text{-}O_2CEt)\}_n]$.[3] We believe the conversion of **2** into **3** to proceed through the intermediacy of **1**, which is supposed to take up further ethylene to give **3**. While we could not detect **1** in the reaction mixture, we were able to show that **1** is in fact converted into **3** under a pressure of ethylene (50 bar, 160 °C).

The phosphine complexes $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2L_2]$ [R = Me, Ph, CMe_3 or CF_3; L = PPh_3, PBu_3, $P(OMe)_3$ or $P(OPh)_3$] have been reported to be active catalyst precursors for the hydroformylation of olefins in the presence of water.[4,5] In accordance with these findings, the new ethyldiphenylphosphine complex **3** is also active for the hydroformylation of ethylene in the presence of water to give propionaldehyde, propanol and diethyl ketone; **3** can be recovered unchanged after the catalytic run.* The interplay of phosphine and phosphido ligands and the assembly of propionato ligands from carbonyl ligands, ethylene and water [equations (1) and (2)] are assumed to be key steps of the catalytic cycle. Under hydroformylation conditions, however, propionaldehyde and its reduction products propanol and diethyl ketone are formed in place of propionic acid.

The diphenylphosphido complex **2**, which we found upon pressurizing of **1** with CO, has been known since 1972;[9] it is observed in many reactions, but only low yields (traces up to 25%) have been reported so far.[6,10–16] The carbonylation of **1** according to equation (1) gives 60% of **2**, but we also found that **2** can be prepared either from $[Ru_3(CO)_{12}]$ and PPh_2H (44% yield) or from $[Ru_3(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}H)_2]$ and carbon monoxide (90% yield).†

Recently[18] another route (yield 46%) has been reported.

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* A stainless-steel autoclave (100 cm^3) containing thf (10 cm^3), water (5 cm^3) and compound **3** (200 mg, 0.225 mmol) was pressurized with 15 bar C_2H_4, 15 bar CO and 10 bar H_2. After 18 h at 160 °C the autoclave was cooled and vented, the organic phase was distilled [4 Torr (*ca.* 532 Pa), 30 °C] and analysed by GC (column SPB®-1, 60 m × 0.25 mm). Molar ratio propionaldehyde:propanol:diethyl ketone 14:62:24; catalytic turnover 111.

† (*a*) A solution of $[Ru_3(CO)_{12}]$ (320 mg, 0.5 mmol) and PPh_2H (0.186 cm^3, 1 mmol) in thf (20 cm^3) was heated in a pressure Schlenk tube for 2 h at 100 °C. After cooling the tube was vented and the mixture placed in a stainless-steel autoclave, pressurized with 80 bar of CO, and stirred at 160 °C for 24 h. After cooling and venting the solution was evaporated to dryness in the dark and the $[Ru(CO)_5]$ formed was pumped away for 1 h *in vacuo*. The residue was dissolved in CH_2Cl_2 (5 cm^3) and separated by TLC [Alox, CH_2Cl_2–hexane (1:4)]; the first colourless band yielded 163 mg (44%) of compound **2**.

(*b*) A solution of $Na[Ru_3(CO)_9(\mu\text{-}PPh_2)_2(\mu\text{-}H)]$[17] (460 mg, 0.5 mmol) in thf (20 cm^3) was treated with an excess of H_3PO_4 (85%, 0.75 cm^3) at room temperature for 1 h. The resulting yellow-orange solution was evaporated to dryness, and the residue extracted three times with CH_2Cl_2 (20 cm^3) and filtered through silica gel; the filtrate was reduced to 5 cm^3 and separated on TLC plates [silica gel, CH_2Cl_2–hexane (1:4)]. The compound $[Ru_3(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}H)_2]$ was extracted from the yellow band in almost quantitative yield. It (0.5 mmol) was dissolved in thf (10 cm^3), pressurized with 80 bar CO and stirred at 160 °C over 24 h. After work-up by TLC [Alox, CH_2Cl_2–hexane (1:4)], 333 mg (90%) of compound **2** was isolated.