An Acyl(hydroxo)ruthenium(II) Complex: En Route to Alcohol Homologation?

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The carbonylation of alcohols for the synthesis of carboxylic acids is an attractive alternative route to methods based on oxidation of hydrocarbon feedstocks [1]. Indeed, the rhodium-catalyzed carbonylation of methanol is now the preferred route for the manufacture of acetic acid [2]; synthesis of propionic acid by carbonylation of ethanol is an interesting alternative to manufacture via hydroformylation or hydroxycarbonylation of ethylene, especially if ethanol becomes cheaply available from methanol homologation, for example, eqn. (1):

$$CO + 2H_2 \longrightarrow CH_3OH \xrightarrow[-H_2O]{CO,\,2H_2} CH_3CH_2OH \xrightarrow{CO} CH_3CH_2CO_2H \quad (1)$$

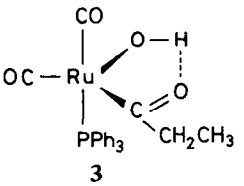
During studies on the reactivity of the hydridocarbonyl polymer $[RuH(CO)_3]_n$ [3] towards tertiary phosphines, we have isolated several products, and a lengthy work-up procedure involving finally ethanol has fortuitously yielded a hydroxo(propionyl)ruthenium(II) complex, the putative type of intermediate probably required for carbonylation of the ethanol.

Experimental

All operations were carried out under inert atmosphere conditions (N_2 or Ar) using Schlenk techniques. The dark, reddish brown $[RuH(CO)_3]_n$ polymer (**1**) was prepared as described previously [3] by treating aqueous solutions of $RuCl_3 \cdot 3H_2O$ (Johnson, Matthey Ltd., 39.91% Ru) with 1 atm CO at 85 °C. Complex **1** (1.63 g, 9 mmol Ru) and PPh_3 (4.62 g, 18.0 mmol) were refluxed in benzene (80 mL) with stirring under N_2 until the initially insoluble polymer had dissolved through reaction to give a red solution (2) (~5d). After removal of the benzene, the dark residue was treated with CH_2Cl_2 (25 mL), the mixture filtered and the filtrate evaporated to give a dark red solid; this was transferred to a silica gel column (3 × 45 cm, 60–200 mesh, Baker Analyzed Reagent 3405) that had been pretreated by initial passage of 1L of n-hexane. Elution of the red solid using n-hexane separated PPh_3, while use of n-hexane/CH_2Cl_2 (10:1 v/v) eluted a red band containing $Ru_3(CO)_9(PPh_3)_3$, a violet-red powder identified by elemental analysis, IR, and ^{31}P NMR, on comparison with an authentic sample prepared by a literature procedure [4]. The column was then eluted with CH_2Cl_2 to remove first a red band and then a yellow band (complexes isolated from these bands have not yet been identified). The remaining yellow fraction in the column was then eluted with absolute ethanol. Evaporation yielded an intense yellow glassy solid that was recrystallized from ethanol/CH_2Cl_2/hexane (5 mL of a 1:1:1 mixture) to give the yellow crystalline solid $Ru(OH)(COC_2H_5)(CO)_2(PPh_3)$, **3** (320 mg, 10% yield). *Anal.* Calcd for $C_{23}H_{21}O_4PRu$: C, 56.10; H, 4.09; P. 6.29. Found: C, 56.27; H, 3.94; P, 6.70. NMR [Bruker WP-80FT, C_6D_6, δ(ppm)]: $^{31}P\{H\}$ δ 26.13 s downfield from 85% H_3PO_4; ^1H downfield from TMS, δ 0.77 br (3H, CH_3–), 1.24 br (2H, $-CH_2-$), 4.30 s (1H, –OH), 7.2 br (15H, phenyl). IR (Nujol, cm^{-1}): 3365(m), 2050(s), 1992(s), 1976(m), 1965(sh), 1735(w), 1662(sh), 1656(m), 1625(s), 817(m), as well as bands attributable to coordinated PPh_3 (1100–1000, 750–690, 600–500 cm^{-1}).

Discussion

The isolation of the acyl(hydroxo)ruthenium(II) complex, **3**, was unexpected, but the IR and NMR data, coupled with the elemental analysis, are most readily interpreted in terms of a five-coordinate structure akin to that shown below. The IR in the 2000–1950 cm^{-1} region shows terminal CO groups, the



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pattern indicating a *cis*-disposition [5], while the major 1625 cm^{-1} band in the 1650–1600 cm^{-1} region shows the presence of the acyl carbonyl. In other ruthenium(II) acyls, in which the $\rangle C{=}O$ is *trans* to chloride [6] or carbonyl [7], the corresponding band is found at 1604 and ~1595 cm^{-1}, respectively. The methylene and methyl resonances in the ^1H NMR occur at appropriate shifts [6, 7], with the correct integrations relative to each other and the

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phenyl protons of the single PPh_3 ligand, although low solubility led to poor signal resolution and the multiplicities of the alkyl protons were not delineated. The position of the $^{31}P\{H\}$ signal of the PPh_3 group suggests that the phosphine is *trans* to a ligand of relatively high *trans* influence [8], and thus the PPh_3 is tentatively suggested to be situated as shown. Several other structural possibilities (distorted trigonal bipyramidal, distorted square pyramidal) could be written for **3**.

The intensity and position of the ν(OH) band at 3365 cm^{-1} strongly indicate a hydrogen-bonding situation [9], and we suggest interaction with the acyl carbonyl. Location of the hydroxide proton at δ 4.30 ppm seems plausible. Such metal hydroxide protons in platinum metal complexes have been detected generally anywhere in the region −5 to +5 ppm [8, 10–14]; shifts to lower fields occur with increasing covalency (decreased electron density) within the O–H bond, and such changes are reflected also in the IR [11]. This is exemplified generally within the following series of complexes (δ_{OH}, ppm: ν_{OH}, cm^{-1}): *cis*- or *trans*-$PtR(OH)(PPh_3)_2$, R = C_6F_5, Ph, $CH{=}CCl_2$, ~−2.1 ppm, ~3620 cm^{-1} [11, 13]; *trans*-$Rh(OH)(CO)(P^iPr_3)_2$, −0.96 ppm, 3644 cm^{-1} [14]; $RuH(OH)(PPh_3)_2(THF)$, 0.0 ppm, 3590 cm^{-1} [8]; *trans*-$Ir(OH)(CO)(PPh_3)_2$, +1.7 ppm, 3580 cm^{-1} [10]; *trans*-$Ir(OH)(NO)(PPh_3)_2$ + 3.33 ppm, 3454 cm^{-1} [10]. The observed δ + 4.30 ppm together with ν_{OH} at 3365 cm^{-1} for complex **3** are considered to fit well the suggested hydrogen-bonded structure. The three-bond coupling to phosphorus is not observed in the ^1H NMR; such coupling is usually small (~3 Hz [11]) and is not resolved here, although the singlet is somewhat broadened.

The distinctive, medium intensity, band found at 817 cm^{-1} is not present in the precursor polymer **1** or any of the other reaction products, and is attributed to the metal-oxygen stretch of the [Ru–O–H ⟷ Ru ⋯ O ⋯ H ⋯] moiety; the position of the band is intermediate between that of ν(M=O), 1000–900 cm^{-1} [15], and ν_{asym} (M–O–H), 750–500 cm^{-1} [10, 15].

Unfortunately, we have not succeeded yet in growing crystals satisfactory for X-ray analysis, and so the formulation of **3** remains somewhat tentative. The more common six-coordinate geometry for Ru(II) could be attained via an extra CO ligand but the elemental analysis required for the tricarbonyl (C, 55.38; H, 3.87; P, 5.95) tends to rule out such a formulation. There is no spectroscopic evidence for an orthometallated (o-$C_6H_4PPh_2$) group [16], coordinated hydride or water, or coordinated chloride (elemental analysis rules out the presence of halide, which in any case implies a Ru(III) complex and paramagnetism).

Proton NMR studies on the red solution **2** gave no evidence for a metal-hydride, while $^{31}P\{H\}$ showed equally intense resonances at 55.12 ppm (identical to that of a prepared sample of $Ru(CO)_3(PPh_3)_2$ [17]) and −5.81 ppm (due to PPh_3); a less intense (×1/6) peak at 36.64 ppm is due to $Ru_3(CO)_9(PPh_3)_3$, while minor resonances were seen also at 24.05 ppm ($OPPh_3$) and 38.53 and 15.83 ppm (unidentified). There was no evidence for the presence of **3** even after adding ethanol to the solution. If the red solution was allowed to stand overnight at room temperature, pale yellow crystals of $Ru(CO)_3(PPh_3)_2$ were formed and these could be isolated in *ca.* 30% yield (based on $RuH(CO)_3$) after recrystallization from CH_2Cl_2/n-hexane (1:1 v/v); the remaining red filtrate on chromatography with the hexane-pretreated silica gel gave a separation of red and yellow bands, and again elution of the final yellow residue with ethanol gave the acyl(hydroxo) complex **3**.

Attempts to synthesize **3** directly from $Ru(CO)_3(PPh)_2$ or $Ru_3(CO)_9(PPh_3)_3$ by reaction with ethanol in the absence or presence of silica gel have been unsuccessful, and thus one of the further unidentified species present in the red solution appears to be the required precursor. The net stoichiometry of complex **3** results theoretically from just oxidative addition of ethanol to a $Ru(CO)_3(PPh_3)$ moiety (albeit *via* an unprecedented C–O bond cleavage) with subsequent insertion of one of the CO ligands into the Ru–C_2H_5 bond. Catalysis via trace halide ($C_2H_5OH + X^- \rightleftharpoons C_2H_5X + OH^-$) oxidative addition via C_2H_5–X seems the likely pathway, with final replacement of X^- at the Ru by OH^- to give the hydrogen bonded-stabilized five-membered ring product. The carbonylation of methanol is correspondingly catalyzed by I^-, although here, following CO insertion, reductive elimination of CH_3COI occurs and then hydrolysis of this to the acid [2].

The fate of the hydrogen of the $[RuH(CO)_3]_n$ polymer has not been substantiated but slow removal as H_2 seems probable, eqn. (2):

$$2RuH(CO)_3 \rightleftharpoons 2'Ru(CO)_3' + H_2 \quad (2)$$

We are aware of the unusual reaction of ethanol with ruthenium complexes, eqn. (3), noted by Roper *et al.* [18], in which the alcohol is oxidized

$$Ru(O_2)(CO)(CNR)(PPh_3)_2 + CH_3CH_2OH \longrightarrow Ru(CO)(CHNR)(O_2CCH_3)(PPh_3)_2 + H_2O \quad (3)$$

$$Ru(O_2)(CO)_2(PPh_3)_2 + CH_3CH_2OH \longrightarrow Ru(OH)(CO)_2(O_2CCH_3)(PPh_3) + H_2 + PPh_3 \quad (4)$$

using coordinated dioxygen to acetate that binds in a bidentate fashion. Trace O_2 coordinated to a Ru(0) centre in our work could have initiated a corresponding reaction, with hydrogen being transferred to an oxygen rather than isocyanide, for example, eqn. (4); and it should be noted that the suggested precursor dioxygen complex is known [19]. However, the

spectroscopy rules out the presence of acetate. The isolated complex is highly reactive, consistent with unsaturated character, and activity towards H_2, H_2O, O_2 and CO is being studied.†

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†Note added in proof. A recent paper [20] has reported on a related propionyl complex $RuCl(COC_2H_5)(CO)(PPh_3)_2$ that is also coordinatively unsaturated; the theoretically favoured square-pyramidal structure for five-coordinate d^6 complexes was preferred for this species. The reported spectral data are quite compatible with those presented for complex 3.