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Preliminary Communications

A ruthenium dihydrogen complex as intermediate in the synthesis of $[RuH(CO)_2(MeCO_2)(P^nBu_3)_2]$ from $[Ru(H)2(CO)_2(P^nBu_3)_2]$

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Abstract

The acetatohydride, $[RuH(CO)_2(MeCO_2)(P^nBu_3)_2]$, a likely intermediate in the transformation of $[Ru(CO)_2(MeCO_2)_2(P^nBu_3)_2]$ into $[Ru(H)_2(CO)_2(P^nBu_3)_2]$ by reaction with dihydrogen, has been synthesized by reaction of $[Ru(H)_2(CO)_2(P^nBu_3)_2]$ with acetic acid, and then spectroscopically characterized. Evidence has been obtained of the involvement of the dihydrogen intermediate $[Ru(H_2)(CO)_2(P^nBu_3)_2]$.

The reactivity of some tributylphosphine-substituted ruthenium carbonyl carboxylato complexes, $[Ru(CO)_2(MeCO_2)_2(P^nBu_3)_2]$, **1**, $[Ru_2(CO)_4(MeCO_2)_2(P^nBu_3)_2]$, **2**, and $[Ru_4(CO)_8(MeCO_2)_4(P^nBu_3)_2]$, **3** with dihydrogen at different pressures and temperatures has been recently investigated by IR spectroscopy [1–3]. Dihydrogen promotes the loss of the acetato-ligand from the above complexes, leading to isolated and characterized hydrides of different complexities [1–3].

Even working with the simple mononuclear complex we were unable to detect an acetato hydride, which is likely to be an intermediate in the formation of the *cis*-dihydrido ruthenium complex $[Ru(H)_2(CO)_2(P^nBu_3)_2]$, **4** [1] (Scheme 1).

$$[Ru(CO)_2(MeCO_2)_2(P^nBu_3)_2] \underset{}{\overset{H_2 \quad MeCO_2H}{\rightleftharpoons}} [Ru(H)(CO)_2(MeCO_2)(P^nBu_3)_2] \quad (1)$$

1 **5a**

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$$[RuH(CO)_2(MeCO_2)(P^nBu_3)_2] \underset{}{\overset{H_2 \quad MeCO_2H}{\rightleftharpoons}} [Ru(H)_2(CO)_2(P^nBu_3)_2] \quad (2)$$

5a **4**

Scheme 1.

The difficulty in the detection of this intermediate may be due to its low concentration in solution, to the displacement of equilibrium (2) (Scheme 1) to the right by dihydrogen, or to the similarity of the spectrum of the intermediate and that of the final species.

We have then tried to synthesize the acetatohydride **5a** in order to determine if either of these propositions holds and to study its reactivity.

Acetic acid reacts [1] with the dihydrido-complex **4** to give **1** with evolution of dihydrogen (Scheme 1). This is a reversible reaction which, under dihydrogen at atmospheric pressure and room temperature, has an equilibrium only slightly displaced to the right.

In order to maximize the formation of the acetatomonohydride **5a**, we planned to allow the dihydrido-complex to react with acetic acid in 1:1 molar ratio in sealed NMR tubes, and follow the formation of the monohydride by ^{31}P-NMR and ^1H-NMR spectroscopies. Under these conditions, different volumes were available for the dihydrogen evolved, inevitably leading to the build up slightly different pressures.

In a standard experiment a solution of **4** (33 mmol) in C_6D_6 (2 cm^3), synthesized as reported in ref. [1], was placed in the NMR tube and then an equimolar amount of acetic acid was added, leaving 11 cm^3 of free volume. At room temperature, after 100 h, a high conversion of the dihydride into a new product (85%) and slight formation of the diacetato-derivative **1** (4%) were observed.

Under a dihydrogen pressure of 3 atm the same reaction gives only the new product, with 50% conversion.

The ^1H-, ^{31}P-, and ^{13}C-NMR spectra [4*], suggest the formula $[RuH(CO)_2(MeCOO)(P^nBu_3)_2]$ for the new product, an octahedral structure containing two *trans* phosphines and two *cis* carbonyl groups (Fig. 1, **5a**). This structure is in agreement with the two triplets found in the ^{13}C-NMR spectrum, attributable to two

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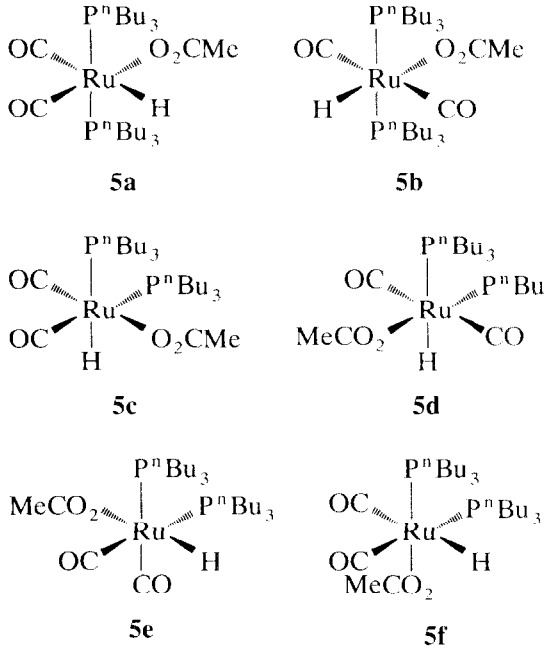
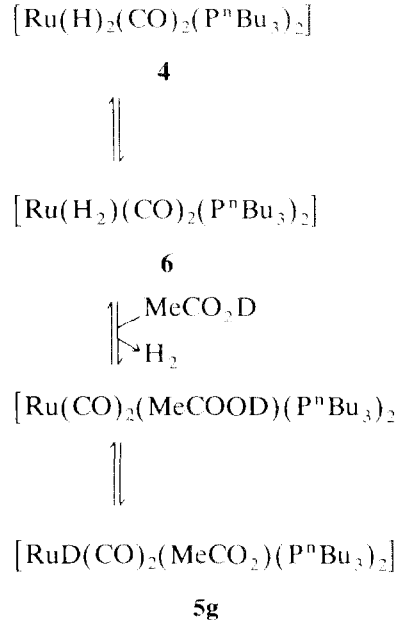


Fig. 1. Possible structures of $[RuH(CO)_2(MeCO_2)(P^nBu_3)_2]$, 5.

non-equivalent carbonyl groups (one *trans* to the acetato-group and the other *trans* to the hydrido-hydrogen) coupling with two equivalent phosphine molecules *cis* to the carbonyl groups. Moreover, the presence in the ^{1}H-NMR spectrum of a triplet in the hydridic hydrogen region, and the value of the coupling constant with the phosphines, are in keeping with the presence of a hydrogen *cis* to two equivalent phosphines [5,6]. Such an arrangement is analogous to that found in the dihydrido-complex used as starting material [1].

The other possible structures **5b–5f** (Fig. 1) are excluded by the spectral data: i) structure **5b** has two equivalent carbonyl groups which would produce only one triplet in the ^{13}C-NMR spectrum; ii) structures **5c**, **5d** and **5f** have inequivalent phosphine molecules and, moreover, in the ^{1}H-NMR spectrum there is no coupling constant J(P–H) = 70 – 80 Hz, characteristic [5,6] of a phosphorus atom *trans* to a hydridic hydrogen; iii) structure **5e** because it has two equivalent carbonyl groups which, coupling with two chemically equivalent phosphine molecules, *trans* and *cis*, should cause a doublet of doublets in the ^{13}C-NMR spectrum.

To understand the equilibrium (2) (Scheme 1) better, **4** was allowed to react with $MeCO_2D$ in a sealed NMR tube as previously and NMR spectra were recorded every 5 min. At 15% conversion of **4**, the isotopomer $[RuD(CO)_2(MeCO_2)(P^nBu_3)_2]$, **5g**, and an approximately equivalent amount of dihydrogen in solution were detected. These data suggest that the acetatohydride, **5a**, is formed from **4** according to Scheme 2: the dihydrogen intermediate $[Ru(H_2)(CO)_2(P^nBu_3)_2]$, **6**, is formed through hydrogen rearrangement (reductive elimination) in **4**. $MeCO_2D$ then displaces the weakly coordinated dihydrogen and gives rise to the isotopomer **5g** by oxidative addition.



Scheme 2.

Several dihydrogen metal complexes have been reported recently [7–17]. Their unusual reactivity and catalytic activity have been ascribed to the ease of displacement of the dihydrogen.

The IR spectrum of **5a** in the 2200–1500 cm^{-1} region has been obtained from that of the solution of the crude material, by subtracting the contributions due to the dihydrido-complex **4**, and the diacetato-derivative **1**. In the ν(CO) and ν(RuH) regions, a band of **5a** at 2034 cm^{-1} may be obscured in a mixture by a band at 2040 cm^{-1} due to the diacetato-complex **1** and the band at 1950 cm^{-1} obscured by that at 1958 cm^{-1} due to the dihydrido complex **4**. This explains why we could not detect **5a** by IR spectroscopy.

Although in the carboxylato-stretching region, the spectra of the acetatohydride **5a** and of the diacetato-complex **1** are sufficiently different to allow detection, when compound **2** is also present this becomes impossible. This last material is present in the mixture obtained from **1** and H_2 at 120°C [1].

* Reference number with asterisk indicates a note in the list of references.

Acknowledgements

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4 The spectral data for compound **5a** are: IR spectrum, 2034(vs), 1950(vs) and 1575(w) cm^{-1}; ^{1}H-NMR spectrum, −5.02 (t, 1H, *H*Ru, J(H–P) = 20.6 Hz), 0.91 (t, 18 H, J(H–H) = 7.2 Hz, *Me*$CH_2CH_2CH_2P$), 1.37 (m, 12H, Me$CH_2CH_2CH_2P$), 1.56 (m, 12H, Me$CH_2CH_2CH_2P$) 1.76 (m, 12H, Me$(CH_2)_2CH_2P$) and, 2.19 (s, *Me*COO), ppm; ^{13}C{^{1}H}-NMR spectrum, 13.9 (s, *Me*CH_2), 20.9 (s, *Me*COO), 24.7 (t, J(C–P) = 6.4 Hz, *C*$H_2CH_2CH_2P$), 26.0 (s, *C*H_2CH_2P), 26.8 (t, J(C–P) = 13.2 Hz, *C*H_2P), 175.9 (s, Me*C*OO), 198.3 (t, J(C–P) = 7.5 Hz, *C*O) and 203.2 (t, J(C–P) = 12.4 Hz, *C*O) ppm; ^{31}P{^{1}H}-NMR spectrum, a singlet at 27.3 ppm.
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