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Note

A simple and convenient synthesis of *cis/trans*-$RuH_2(Ph_2PCH_2PPh_2)_2$ and of *trans*-$RuHCl(Ph_2PCH_2PPh_2)_2$

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Abstract

Treatment of a suspension of *cis*-$RuCl_2(Ph_2PCH_2PPh_2)_2$ in ethanol or 2-propanol with a large excess of KOH leads, in a very clean reaction and in less than 2 min when ethanol is used, to the formation of *cis/trans*-$RuH_2(Ph_2PCH_2PPh_2)_2$ in yields of up to 90%. Similar treatment of the *cis*-dichloro complex with a small excess of KOH gives, over a longer period, *trans*-$RuHCl(Ph_2PCH_2PPh_2)_2$ in 64% yield and this complex can, in turn, be converted under similar conditions into the *cis/trans*-dihydride in moderate yields. *trans*-$RuCl_2(Ph_2PCH_2Ph_2)_2$ is unreactive under these conditions.

Keywords: Diphosphine complexes; Ruthenium complexes; Hydride complexes

1. Introduction

In earlier work, we have shown that treatment of salts of Ni(II) [1], Co(II) [2], Pd(II) [3], Pd(IV) [4,5] and Pt(II) or (IV) [5] with BH_4^- in the presence of bis(diphenylphosphino)methane (dppm) and CO leads to the direct formation of, usually, low-valent bi- or trinuclear M–CO complexes in which the framework of metal atoms is stabilized by bridging dppm. In marked contrast, such reactions carried out using longer-chain bis-phosphines such as bis(diphenylphosphino)ethane (diphos) result in the formation of complexes which almost always contain chelating phosphine ligands.

However, products of similar reactions using Fe(III), dppm, CO and $LiAlH_4$ contain primarily mononuclear Fe(II), hydride, chelating dppm and no CO [6]. One such product, *trans*-$Fe(H)_2(dppm)_2$, is readily protonated to form *trans*-dihydrogen complexes [6,7]. Since these Fe(III)-based reactions differ so strikingly from related reactions using Ni(II), Co(II) or Pd(II) with $NaBH_4$ as the reducing agent, and because synthetically useful dihydrogen complexes are so readily prepared from *trans*-$FeH_2(dppm)_2$, we commenced a parallel investigation of synthetic routes to and the reaction chemistry of carbonyl, hydridic and dihydrogen Ru(II)–dppm complexes bearing in mind that others have shown [8] that $RuCl_3 \cdot 3H_2O$/dppm/CO/$NaBH_4$ reactions are not good routes to Ru–CO–dppm complexes which are better prepared from Ru(III) acetate. While the main theme of this study is still under investigation, we have discovered in the preliminary work that *cis/trans*-$RuH_2(dppm)_2$ (the *trans* isomer of which has recently been shown [9] to exist in equilibrium with the corresponding dihydrogen complex in the presence of phenols and alcohols) and *trans*-$RuHCl(dppm)_2$ can be synthesized rapidly, conveniently and in high yield by an extremely simple route. In addition to being potential sources of dihydrogen complexes, these compounds may have catalytic activity of the type already observed [10] for the analogous $RuH_2(PPh_3)_4$ and related species. A brief report on these potentially useful and largely hazard-free syntheses is therefore given herein.

2. Experimental

2.1. Reagents and physical methods

$RuCl_3 \cdot xH_2O$ was obtained from Johnson Matthey while dppm was supplied by the Aldrich Chemical Company. The complexes *trans*-$RuCl_2(dppm)_2$ [11] and *cis*-$RuCl_2(dppm)_2$ [12] were prepared by literature methods. For the reactions reported herein, no precautions were taken to exclude oxygen or moisture. $^{31}P\{^1H\}$ NMR spectra were recorded using CH_2Cl_2 solutions on a Bruker AC-E 200 spectrometer at 81.015 MHz while FT-IR spectra (Nujol mulls)

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were obtained using a Bruker IFS-66 spectrophotometer. ^{31}P chemical shifts are reported as δ values with positive shifts downfield of the signal of external 85% H_3PO_4. Frequency lock was provided by a coaxial D_2O insert. X-ray powder diffraction was used to check that no significant amounts of KCl remained in the products of the synthetic reactions. This procedure, together with satisfactory C, H micronalyses and ^{31}P NMR evidence that no other phosphorus-containing species are present in the isolated products, was used to establish the purity of these known complexes.

2.2. *Syntheses*

2.2.1. *cis/trans-RuH$_2$(dppm)$_2$*

(a) To a stirred solution of KOH (4.98 g, 8.9×10^{-2} mol) in ethanol (30 ml) was added solid *cis*-$RuCl_2$(dppm)$_2$ (0.33 g, 3.5×10^{-4} mol). Stirring was continued for 2 min after which the suspension was filtered. The pale yellow solid product collected was washed with ethanol (2 × 10 ml), water (2 × 10 ml) to remove any remaining KCl, and then pentane (10 ml) after which it was dried by suction. Yield 80%. The $^{31}P\{^1H\}$ NMR and FT-IR parameters recorded for the product, which is free (^{31}P spectrum) of residual starting material, are virtually identical to the literature values reported for *cis*/*trans*-RuH_2(dppm)$_2$ [13,14]. Integration of the ^{31}P spectrum indicated a 3.5:1 *cis*:*trans* ratio.

(b) Using 2-propanol (35 ml) as the solvent, KOH (5.30 g, 9.5×10^{-2} mol), *cis*-$RuCl_2$(dppm)$_2$ (0.30 g, 3.2×10^{-4} mol) and a reaction time of 1.5 h, the above procedure gave a 90% yield of the mixed dihydrides in approximately the same ratio as that noted in (a) above.

(c) To a stirred solution of KOH (2.34 g, 4.2×10^{-2} mol) in ethanol (35 ml) was added *trans*-RuHCl(dppm)$_2$ (0.13 g, 1.4×10^{-4} mol, prepared as outlined in Section 2.2.2 below) and the mixture was stirred for 2 h. The resulting suspended solid was collected by filtration, washed as outlined in (a) above and dried to give 0.084 g of product. ^{31}P NMR (CH_2Cl_2 solution) examination of this product showed it to be a mixture of the two dihydrides *cis*/*trans*-RuH_2(dppm)$_2$ and unreacted starting material which constituted (integration) about 25% of the mixture. The mass of the product mixture obtained, together with the ^{31}P NMR integration, indicated a yield of about 43% for the mixed dihydride component. Several similar experiments showed that the optimum reaction time is 2 h and that the reaction cannot be taken to completion under these conditions.

2.2.2. *trans-RuHCl(dppm)$_2$*

To a stirred solution of KOH (0.047 g, 8.4×10^{-4} mol) in ethanol (35 ml) was added solid *cis*-$RuCl_2$(dppm)$_2$ (0.308 g, 3.27×10^{-4} mol) and stirring was continued for 30 min. The suspended product was isolated by filtration and the solid was washed in sequence with 20 ml each of ethanol, water and pentane after which it was dried by suction. Yield 64%. ^{31}P NMR (CH_2Cl_2, D_2O lock): δ – 1.4(s). This value, compensating for the difference in frequency lock, is virtually identical to that (δ –2.2) previously reported [13] for CD_2Cl_2 solutions. ^1H NMR parameters for this complex are in agreement with those previously published [13].

3. Results and discussion

In connection with our aforementioned studies of synthetic routes to (and the chemistry of) CO and hydridic Ru(II)–dppm complexes, we had occasion to treat ethanolic suspensions of both *cis*- and *trans*-$RuCl_2$(dppm)$_2$ with a large excess of KOH in the manner outlined in Section 2. With the *cis* isomer, no apparent significant dissolution occurred but a small change in the colour of the suspended material (from lemon yellow to very pale yellow) took place very rapidly and both $^{31}P\{^1H\}$ NMR and FT-IR examination of the washed and dried product, obtained as a fine powder, showed it to be a mixture (3.5:1) of *cis*- and *trans*-RuH_2(dppm)$_2$. No unreacted starting material remained despite the apparently heterogeneous nature of the reaction. These spectroscopic characteristics and isomer ratios are virtually identical to those recorded in the literature [13,14] for these complexes obtained by other, less convenient, routes. The reaction is complete within 2 min of KOH addition in ethanol and yields of up to 80% of the pure material are routinely obtained by this method. A similar, but much slower (approximately 1.5 h), reaction occurs in 2-propanol to give yields of up to 90% of the mixed hydrides. No reaction occurs in tert-butanol and *trans*-$RuCl_2$(dppm)$_2$ is unreactive in all three alcohols.

If only a small excess of KOH is used in the reaction with *cis*-$RuCl_2$(dppm)$_2$, the product is pure *trans*-RuHCl(dppm)$_2$ (30 min, 64% yield) which can, in turn, be converted, by ethanolic KOH, into a mixture of *cis*- and *trans*-dihydrides in moderate yield (43%) with the same isomer ratio as that noted above but with the product contaminated with starting material.

It seems likely, therefore, that the very rapid conversion of *cis*-$RuCl_2$(dppm)$_2$ into a mixture of *cis*- and *trans*-RuH_2(dppm)$_2$ proceeds via stepwise replacement of the two chlorides by hydride ligands with some ligand reorganization occurring during these replacements. While no mechanistic study has been undertaken, it is probable that dissociation of a chloride ion from *cis*-$RuCl_2$(dppm)$_2$ (high *trans* influence) occurs followed by its replacement by an alkoxide ion (present in low concentration in the KOH/alcohol system) and intramolecular hydride transfer. A similar sequence of events could, in the presence of an excess of alkoxide ion, also occur for the initial product *trans*-RuHCl(dppm)$_2$. The five-coordinate intermediates involved would allow for the ligand reorganization required for the production of the *cis*/*trans* mixture of RuH_2(dppm)$_2$ obtained.

The reaction pathway suggested above would be a solution process and, although no dissolution of the starting materials is obvious during the reactions, some very rapid starting material dissolution/product precipitation must occur during the 2 min required for completion of the fastest of these reactions.

Solubility, therefore, is probably a factor in determining rates since reactions are much slower in 2-propanol (although yields are slightly higher). Other factors which are likely to play some part in determining reaction rates are alkoxide ion concentration (determined by the amount of KOH present) and the ease of hydride transfer (greater for ethoxy than for 2-propoxy). Hydride transfer would not be possible for *tert*-butanol in which the system is unreactive.

Whatever the mechanism, these syntheses are more convenient, of comparable or higher yield, and generally less hazardous than those previously published. Thus, *cis*/*trans*-RuH$_2$(dppm)$_2$ has been prepared by treatment of Ru(cod)(cot) with dppm under H$_2$ (16 h reaction time, 80% yield) [13] or by the reaction of *trans*-Ru(O$_2$CEt)$_2$(dppm)$_2$ with NaBH$_4$ in ethanol/benzene (2.5 h reflux, 69% yield) [14]. *trans*-RuHCl(dppm)$_2$ can be obtained [13] from the *cis*/*trans*-dihydride by stirring in CHCl$_3$ (1 h, 80% yield) or by treatment of *cis*-RuCl$_2$(dppm)$_2$ with LiAlH$_4$ in THF (5 min reflux, 75% yield) [15].

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