Journal of Organometallic Chemistry, 379 (1989) 171–175
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20332

Bis-insertion reactions of $Ru(CO)HCl(PPh_3)_3$ with methyl propiolate. The unexpected formation of (methoxycarbonylethenyl)triphenylphosphonium chloride

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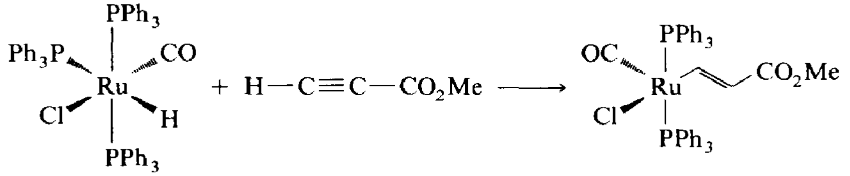
(Received July 24th, 1989)

Abstract

The reaction of $Ru(CO)HCl(PPh_3)_3$ with methyl propiolate gives two bis-insertion derivatives resulting from a head-to-head dimerization reaction. The eliminated triphenylphosphine ligand reacts with the alkyne to give an actylidephosphonium salt, which brings about substitution of the chloride ligand of $Ru(CO)Cl(CH{=}CHCOOMe)(PPh_3)_2$ by acetylide. The resulting phosphonium salt, methoxycarbonylethenyltriphenylphosphonium chloride has been characterized as the methanol adduct 2-methoxy-2-methoxycarbonylethyltriphenylphosphonium chloride.

Introduction

The reaction of $Ru(CO)HCl(PPh_3)_3$ with methyl propiolate in dichloromethane has been shown to give an alkenyl derivative **2** resulting from a *cis* insertion reaction and elimination of a phosphine ligand (eq. 1) [1]. Further reaction of this coordinatively unsaturated complex with excess of alkyne yields two bis-insertion derivatives **3** and **4**. The structure of **3** was established by an X-ray diffraction



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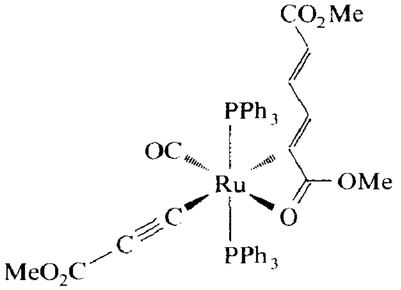
study, but the formulation of **4** as a coordinatively unsaturated (*E*,*E*)-1,2,4-trisubstituted butadienyl ruthenium complex was based only on its ^{1}H NMR spectrum [1]. We describe below the results of a more detailed study of the reaction of hydride **1** with methyl propiolate that has led to assignment of a different structure to the second product and to the observation of the involvement of two phosphonium salts in the reaction pathway.



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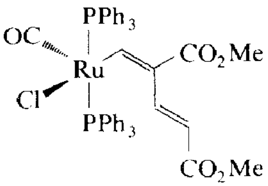

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Results and discussion

The reaction of alkenyl complex **2** with excess of methyl propiolate in dichloromethane gave a bis-insertion derivative exclusively in an almost quantitative yield. The same result was obtained when the reaction was performed in the presence of methanol as co-solvent. The ^{1}H NMR spectrum showed a pair of doublets at δ 4.87 (sharp) and 6.27 (broad) with a 15.6 Hz coupling assigned to an *E*-ethenyl sub-unit. A broadened signal at δ 5.76 corresponding to the second ethenyl unit showed a 1.1 Hz splitting that was previously interpreted arising from a $^3J(^1H-^{31}P)$ coupling [1]. However, irradiation at the 6.27 ppm doublet caused a collapse of the 5.76 ppm doublet to a singlet, slightly broadened because of long range ^{1}H–^{31}P coupling. More definitive proof of the structure of this bis-insertion derivative obtained by means of ^{1}H NMR nuclear Overhauser effect difference spectroscopy (^{1}H NOEDIFF), which unequivocally established the correct formulation was as the 1,1,4-trisubstituted butadienyl species **5** (Fig. 1). Particularly revealing is the enhancement observed for both H(3) and H(4) signals on irradiation at δ 5.76 (H(2)), suggesting a non-planar arrangement of the butadienyl ligand, which is in agreement with the rather low coupling between H(2) and H(3). The presence of a chelating ester carbonyl group was also supported by the presence of a ν(CO) band at 1655 cm^{-1}.

In an attempt to find the chemical relationship between **5** and **3** we tried to replace the chloride ligand of **3** by treatment with an excess of methyl propiolate, but unchanged **5** was recovered even when the reaction was carried out in the presence of hindered bases such as diisopropylethylamine or lithium diisopropylamide [2]. This rules out the intermediacy of **5** in the formation of acetylide **3**, and suggests that replacement of the chloride by acetylide may precede the insertion of the second alkyne molecule into the carbon–ruthenium bond. The unreactivity of **5** provides further support for the proposed coordinatively saturated structure.

Monitoring of the reaction of hydride **1** with methyl propiolate by ^{1}H NMR spectroscopy in deuterochloroform solution at 22 °C showed inmediate disap-

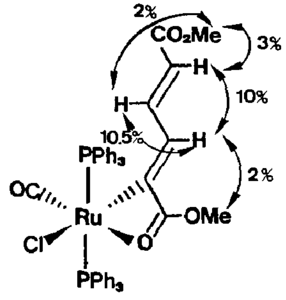

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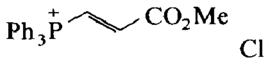
Fig. 1. Structure of bis-insertion complex **5** showing ^{1}H NOEDIFF enhancements.

pearance of **1**, and formation of alkenyl derivative **2**. Addition of a second equivalent of alkyne gave rise to two new sets of olefinic signals. The appearance of new multiplets at δ 8.47 (dd, $J = 19.8$, 16.9 Hz) and 6.8 (dd, $J = 20.5$, 16.8 Hz) indicated the formation of methoxycarbonyl-ethenyltriphenylphosphonium chloride (**6**), identical with the compound prepared by reaction of triphenylphosphine hydrochloride with methyl propiolate [3]. The second set of olefinic signals at δ 10.51 and 5.49 with a $^3J(^1H-^1H) = 16.3$ Hz were tentatively assigned to the acetylide complex $[Ru(CO)(CH{=}CHCO_2Me)(C{\equiv}CCO_2Me)(PPh_3)_2]$ (**7**). Unfortunately, all attempts to isolate **7** starting from either **1** or **2** gave mixtures of complexes **3** and **5**, and small amounts of other uncharacterized ruthenium complexes.



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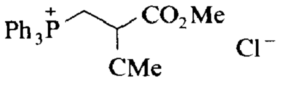

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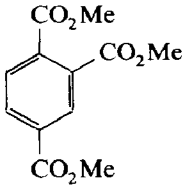
When the reaction of **1** with methyl propiolate was carried out in a dichloromethane/methanol mixture, complex **3** was obtained in 20% yield. The ^{1}H NMR spectrum of the crude reaction mixture revealed, however, the presence of another phosphonium salt **8**. Careful recrystallization afforded a pure sample of **8** as a hygroscopic yellow powder. Phosphonium salt **8** was also be made by treatment of **7** with methanol or, more conveniently, by performing a Michael-type addition of triphenylphosphine hydrochloride to methyl propiolate in a methanol/dichloromethane mixture [3]. Additionally, substantial quantities of poly(methyl propiolate) were formed in the bis-insertion reaction [4]. Small amounts (5–10%) of cyclotrimers **9** and **10** were also produced in a 2/1 molar ratio.



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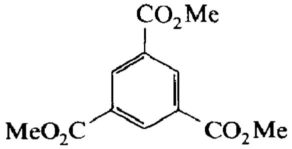

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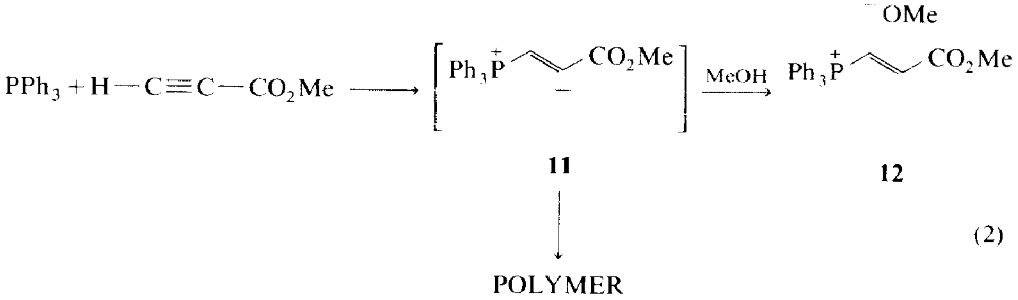
The formation of phosphonium salt **7** may provide the clue to the origin of complex **3**. Thus, reaction of free triphenylphosphine with methyl propiolate would form the unstable zwitterionic intermediate **11**, which could initiate the polymerization reaction or, alternatively, react with methanol to afford the phosphonium methoxide **12**, or the corresponding phosphorus ylide (eq. 2).



Removal of the acidic acetylene proton by **12** would generate the required acetylide anion, which undergoes substitution of chloride in unsaturated 16-electron ruthenium complex **2**. Accordingly, reaction of **2** and the alkyne performed in the presence of one equivalent of triphenylphosphine gave **3** and **5** in a 2/1 molar ratio.

In summary, the results reported herein provide insight into the mode of reaction of ruthenium hydride **1** with methyl propiolate. The bis-insertion derivatives **3** and **5** are produced with the same regiochemistry, and result from a head-to-head type dimerization reaction. Presumably, the second insertion of methyl propiolate is facilitated by prior coordination of the ester group to the ruthenium. The eliminated triphenylphosphine ligand plays an active role in the reaction sequence, providing a source of acetylide anion.

Experimental

IR spectra were recorded on a Perkin–Elmer 681 spectrophotometer. ^1H NMR spectra were recorded on a Varian XL 300 (300 MHz) or a Bruker AM-200 (200 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. ^{13}C NMR were obtained on a Bruker AM-200 (50 MHz) spectrometer with $CDCl_3$ as solvent and internal standard. ^{31}P NMR spectra were recorded on a Bruker WP-80 (32.4 MHz) with 85% H_3PO_4 as external standard.

Thin-layer chromatographic analyses (TLC) were performed on aluminum sheets precoated with silica gel 60F-254 (0.2 mm) (Merck). Flash column chromatography [5] was performed on silica gel 60 (Macherey Nagel 230–400 mesh). Dichloromethane was freshly distilled from calcium hydride. Methanol was dried over magnesium methoxide and stored over activated 4Å sieves under argon. Elemental analyses were performed by the Instituto de Química Orgánica (CSIC).

Reaction of Ru(CO)HCl(PPh$_3$)$_3$ (1) with methyl propiolate

A mixture of hydride **1** (363 mg, 0.38 mmol) and methyl propiolate (500 μl, 503 mg, 5.98 mmol) was stirred at 23°C for 22 h in a 2/1 methanol/dichloromethane (4.5 ml) mixture. The resulting suspension was then treated with diethyl ether (10 ml) and cooled to 0°C. The solid was filtered off and washed with diethyl ether to give poly(methylpropiolate) as a yellowish powder (116 mg, 23% yield based on methyl propiolate): IR(KBr, cm^{-1}) 2960, 1735, 1718, 1625, 1438, 1245, 1092, 998, 708 (identical with the literature spectrum [4]).

The filtrate was evaporated to yield an oil. The ^{1}H NMR spectrum showed this to be a mixture of phosphonium salt **8**, the bis-insertion derivative **3**, and the pair of cyclotrimers **9** and **10** in an approximate 10/3/1 ratio. Careful recrystallization from dichloromethane/ethyl ether afforded **8** as a pale yellow hygroscopic solid, characterized as the sesquihydrate (60–80 mg, 36–49%): IR(KBr, cm^{-1}) 3340br, 3060, 2950, 2870, 1730, 1625, 1585, 1485, 1440, 1295, 1245, 1165, 1120, 1030, 1000, 975, 865, 830, 800, 710, 700, 670, 640. ^{1}H NMR (300 MHz) δ 7.79 (m, 15 H), 4.79 (concentration dependent, usual range: 5.28–4.70, ddd, $J = 15.9$, 12.5, 4.4 Hz, 1H), 4.30 (4.43–4.25, ddd, $J = 13.0$, 8.5, 4.6 Hz, 1H), 3.95 (3.95–3.87, ddd, $J = 15.7$, 11.4, 8.6 Hz, 1H), 3.69 (s, 3H), 3.08 (s, 3H), 2.03 (H_2O). ^{13}C{^{1}H} NMR (50 MHz) δ 169.57 (d, $J = 12.8$ Hz), 134.68 (d, $J = 2.9$ Hz), 133.59 (d, $J = 10.4$ Hz), 129.96 (d, $J = 12.9$ Hz), 118.44 (d, $J = 87.8$ Hz), 74.06 (d, $J = 6.5$ Hz), 58.53 (s), 52.59 (s), 27.62 (d, $J = 5.5$ Hz), ^{31}P{^{1}H} NMR (32.4 MHz) δ 23.4. Anal. Found: C, 61.53; H, 6.00. $C_{23}H_{24}ClO_3P \cdot 1.5H_2O$ calc: C, 61.26; H, 6.26%.

Flash-column chromatography (4/1 hexane/EtOAc) of the filtrate gave a 2/1 mixture of esters **9** and **10** (5–10 mg, 5–10%). **9**: ^{1}H NMR (200 MHz) δ 8.43 (d, $J = 2.6$ Hz, 1H), 8.20 (dd, $J = 7.7$, 2.6 Hz, 1H), 7.76 (d, $J = 7.7$ Hz, 1H), 3.95 (s, 3H), 3.93 (s, 6H). **10**: ^{1}H NMR (200 MHz) δ 8.57 (s, 3H), 3.97 (s, 9H). Elution of the column with 2/1 hexane/EtOAc gave the bis-insertion derivative **3** as a yellow solid (68 mg, 20%) TLC (3/2 hexanes/EtOAc) R_f 0.28, identical (IR, ^{1}H NMR) with the complex prepared previously [1]. Under identical conditions complex **5** has a R_f 0.40.

When the reaction was carried out in $CDCl_3$ solution, phosphonium salt **6** was observed as an intermediate: ^{1}H NMR (300 MHz) δ 8.57 (dd, $J = 19.8$, 16.9 Hz, 1H), 7.91–7.60 (m, 18H), 6.56 (dd, $J = 20.5$, 16.8 Hz, 1H), 3.91 (s, 3H).

Acknowledgement

We thank the DGICYT (Grant PB 020102) for support of this work and Dr. Antionio Romero for the preparation of complex 2.

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