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SOME CATALYTIC PROPERTIES OF Rh(diphos)(η-BPh$_4$)

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Summary

The covalent complex Rh(diphos)(η-BPh$_4$) (I) reacts with CO in polar solvents to afford the cationic dicarbonyl *cis*-[Rh(diphos)(CO)$_2$](BPh$_4$). I is an effective catalyst for methylacetylene oligomerization and allene polymerization. In the presence of CO$_2$ and methylacetylene, I affords 4,6-dimethyl-2-pyrone.

Results and discussion

Recently [1], we reported the synthesis, structure and some chemical properties of the complex Rh(diphos)(η-BPh$_4$) (I). We now present further details of the chemistry of this complex.

In CH$_2$Cl$_2$ (or other polar solvents) I reacts with CO under controlled reaction conditions (both temperature and time) to afford *cis*-[Rh(diphos)(CO)$_2$]$^+$-(BPh$_4^-$). The stretching ν(CO) is found at 2100s and 2055s cm^{-1} in CH$_2$Cl$_2$. These values are in accord with those reported for analogous *cis*-dicarbonyl cationic Rh(I) complexes [2]. If I is exposed to 1 atm of CO for a long time (24 hours), the IR spectrum of the solution (CH$_2$Cl$_2$) shows the appearance of several other bands in the range 2010—1760 cm^{-1}, besides the bands at 2100 and 2055 cm^{-1} which eventually disappear. The products are under investigation. The cationic dicarbonyl complex is a 1 : 1 electrolyte in acetone (Λ_M = 110 S cm^2 mol^{-1}).

I reacts with allene in CH$_2$Cl$_2$ at low temperature to afford a yellow complex whose IR spectrum shows bands at 1820w, 1660s and 890vs cm^{-1} due to the coordinated allene [3]. Unfortunally this complex is not sufficiently stable to permit further spectroscopic characterization.

At higher temperature (50°C) I is an effective catalyst for allene polymerization. The density of the polymer obtained does not depend on the pressure used. The catalytic process is highly specific and 1,2,1,2-polyallene is always obtained (II). The IR spectrum of the polymer (film) shows bands at 1805mw, 1630vs. (C=C stretching) and 900vs cm^{-1} (δ CH_2) due to the vinylidene groups. No band at 1600 cm^{-1} and due to the 1,2,2,1-polyallene [4] is present. The latter polymer often contaminates the former in polymerization processes catalyzed by nickel [5] complexes. The formation of the 1,2,2,1-polymer has been shown to be promoted by Lewis bases such as pyridine or bromide ion [4]. The polymer obtained using the cationic Rh^I complex is insoluble in common organic solvents (aromatic, DMSO, chlorinated hydrocarbons, THF, DMF, ethyl ether, acetone) and in alkaline water solutions, but dissolves very readily in concentrated sulphuric acid to give a red solution. Unlike other polyallenes described in the literature [4,5], which melt in the range 60—130° C, II has a high melting point (>200° C). A more detailed characterization, including NMR spectra and X-ray structure, is in progress.

In contrast to 1,3-butadiene, which reacts with CO_2 in the presence of Pd complexes [6], allene does not react with CO_2 (60 atm) in the presence of Rh^I even at 120° C, 1,2,1,2-polyallene being formed preferentially.

I is a methylacetylene oligomerization catalyst. The products formed range from linear or branched dimers (A, B) to linear-(C, D) and cyclic-trimers (1.2.4, 1.3.5) (Fig. 1). This behaviour is similar to that reported for Ni^0 catalyzed sys-

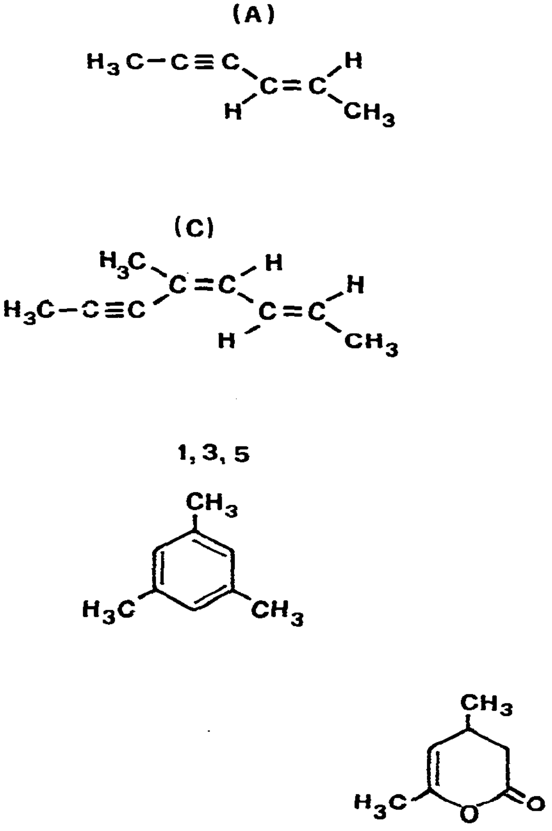
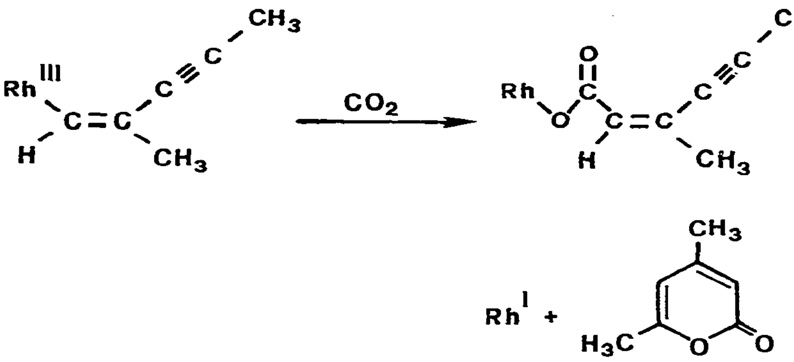


Fig. 1.

tems [7]. It is noteworthy that the Rh^I-allylaniline system [8] affords only dimers and cyclic trimers, while covalent Rh^I-phosphine systems [9] afford only linear or branched dimers.

In the presence of CO_2, besides the oligomerization products (A, B, C, D, 1.2.4, 1.3.5), 4,6-dimethyl-2-pyrone is formed. The formation of such a lactone can be interpreted as a CO_2 insertion into the Rh—C σ-bond of the intermediate, which generates B as in Scheme 1. Such a reaction is similar to that reported by Inohue [10] for the Ni^0 catalyzed 1-hexyne-carbon dioxide reaction.

SCHEME 1



Experimental

Allene and methylacetylene (Matheson, 99.5%) and carbon dioxide (Matheson 99.999%) were used without further purification. I was prepared as described elsewhere [1]. The VPC analyses were performed using a Hewlett-Packard 5750 gas chromatograph. IR spectra were recorded on a Perkin-Elmer 577 spectrometer. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected.

Preparation of cis-[Rh(diphos)(CO)$_2$] [BPh$_4$]

A solution of Rh(diphos)(η-BPh_4) (0.500 g, 0.6 mmol) in CH_2Cl_2 (50 cm^3) was kept under CO (1 atm) at 20° C and the IR spectrum registered at intervals of time (ca. 1 hour). After 5 hours, the IR spectrum of the solution showed two intense bands at 2100 and 2055 cm^{-1} and a weak band at 1955 cm^{-1}. The solution was pumped in vacuo and concentrated to 10 cm^3 and nitrogen was admitted to the flask. Pentane was added and the mixture cooled to —20° C to give a yellow precipitated, which was filtered off, washed with pentane, and dried in vacuo. Anal. Found: C, 71.2; H, 5.1; P, 7.09%. $C_{52}H_{44}BO_2P_2Rh$ Calcd.: C, 71.24; H, 5.06; P, 7.07%.

Preparation of 1,2,1,2-polyallene

a) In a 250 cm^3 rocking autoclave immersed in a thermostated oil bath was placed a glass container filled with 10 cm^3 of a 10^{-2} *M* solution of Rh(diphos)-

(η-BPh_4) in CH_2Cl_2. 4 g of allene were condensed in at —50° C with rigorous exclusion of air. The system was heated at 50° C for 12 hours. The starting pressure in the autoclave was approximately 8 atm. The polymer yield was 65%.

b) The run was performed as reported in a) except that N_2 (60 atm) or CO_2 (65 atm) was introduced into the autoclave. The polymer yield was about 75% with respect to the starting monomer.

The polymer samples obtained at low and high pressure had the same spectroscopic properties.

Methylacetylene oligomerization

The catalytic runs were carried out as described above at 60° C for 12 hours. 4 g of methylacethylene were condensed into the reaction vessel which contained 15 cm^3 of a 5×10^{-2} *M* solution of I in CH_2Cl_2. The conversion of the alkyne was 50—60%. The products formed were determined using a 3 m Silicone-Chromosorb column or a 3 m Apiezon L column. The product distribution was: dimers 50% (A/B = 3), linear trimers 8%, and cyclic trimers 42% (1.2.4/1.3.5 = 2.5).

When the reaction was carried at 120°C in CH_3CN in the presence of CO_2 (60 atm), along with the above oligomers (linear dimers 2%, linear trimers 4%, cyclic trimers 89%), 4,6-dimethyl-2-pyrone (3%) was also formed.

Acknowledgements

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References

1 P. Albano, M. Aresta and M. Manassero, Inorg. Chem., 1979 in press.

2 R. Uson, P. Lahuerta, D. Carmona, L.A. Oro and K. Hildebrand, J. Organometal. Chem., 157 (1978) 63.

3 F.L Bowden and R. Giles, Coord. Chem. Rev., 20 (1976) 81.

4 J.G. Van Ommen, H.J. Van der Ploeg, P.C.J.M. Van Berkel and P. Mars, J. Molec. Cat., 2 (1977) 409.

5 S. Otsuka, K. Mori and F. Imaizumi, J. Amer. Chem. Soc., 87 (1965) 3018.

6 (a) Y. Sasaki, Y. Inohue, H. Nashimoto, J. Chem. Soc. Chem. Commun., (1976) 605. (b) A. Musco, C. Perego and V. Tartiari, Inorg. Chim. Acta, 28 (1978) L147.

7 I.S. Meriwether, M.F. Leto, E.C. Colthup and G.W. Kennerly, J. Org. Chem., 27 (1962) 3730.

8 M. Aresta and M. De Fazio, J. Organometal. Chem., 186 (1980) 109.

9 S. Yoshikawa, J. Kiji, and J. Furukawa, Makromol. Chem., 178 (1977) 1077.

10 Y. Inohue, I. Itoh and H. Hashimoto, Chem. Lett., (1977) 855.