

## Selective Linear Codimerization of Acetylenes and Buta-1,3-diene Catalysed by Dihydridotetrakis(trialkylphosphine)ruthenium Complexes

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**Summary** Selective linear codimerization of terminal acetylenes and buta-1,3-diene catalysed by the first example of a dihydridotetrakis(trialkylphosphine)-ruthenium complex is reported.

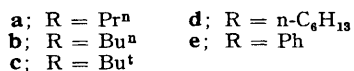
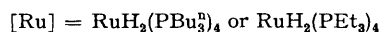
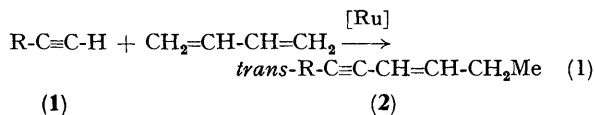
RECENTLY, the characteristic ability of ruthenium complexes for catalysing carbon-carbon bond formation has been demonstrated.<sup>1-3</sup> We now report the first example of

linear codimerization of terminal acetylenes with buta-1,3-diene catalysed by a dihydridotetrakis(trialkylphosphine)-ruthenium complex.

$\text{RuH}_2(\text{PBU}_3)_4$ † (0.1—0.2 mmol), benzene (5 cm<sup>3</sup>), buta-1,3-diene (20 mmol) and the aliphatic terminal acetylenes (**1a—d**) (10 mmol) were placed in an ampoule which had been flushed with argon and the mixture was heated at 60—80 °C for several hours. The products were isolated by

† Although various  $\text{RuH}_2(\text{PR}_3)_4$  complexes, where R is aromatic or an alkoxide group, are well known (see e.g. J. Chatt and J. M. Davison, *J. Chem. Soc.*, 1965, 843; T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, 1970, **92**, 3011; J. J. Leuison and S. D. Robinson, *J. Chem. Soc. A*, 1970, 2947; D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1972, **94**, 4545; R. O. Harris, N. K. Hota, S. Sararoy, and J. M. C. Yuen, *J. Organomet. Chem.*, 1973, **54**, 259), no trialkylphosphine complex has been reported.  $\text{RuH}_2(\text{PBU}_3)_4$  was prepared by adding a solution of  $\text{NaBH}_4$  (25 mmol) in ethanol to a mixture of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (5 mmol) and  $\text{PBU}_3$  (30 mmol) in ethanol at 70 °C (yield, 42%).  $\text{RuH}_2(\text{PET}_3)_4$  was prepared in a similar manner (yield, 44%). Both complexes gave satisfactory analytical and spectral data.

careful vacuum distillation. Analytical, spectral, and g.l.c. data of the products showed that (2a—d)‡ were formed in excellent yields [see equation (1) and Table]. The reaction



was highly selective and only the *trans*-isomer was formed. Phenylacetylene also gave the corresponding product (2e), but in low yield, the main product being a homodimer of phenylacetylene (yield, 64%). RuH<sub>2</sub>(PEt<sub>3</sub>)<sub>4</sub> was also an

TABLE. Linear codimerization of acetylenes and buta-1,3-diene.<sup>a</sup>

Acetylene	Catalyst <sup>b</sup> (mmol)	Temp./°C	Time/h	Product	Yield/% <sup>c</sup>
(1a)	A (0.1)	60	2	(2a) <sup>d</sup>	96 (67)
(1b)	A (0.2)	60	4	(2b)	100
(1c)	A (0.2)	60	4	(2c)	100
(1d)	A (0.1)	60	4	(2d)	92
(1d)	A (0.1)	80	2	(2d)	99 (88)
(1d)	B (0.2)	80	2	(2d)	83
(1e)	A (0.2)	80	4	(2e) <sup>e</sup>	31

<sup>a</sup> Acetylene: 10 mmol; buta-1,3-diene: 20 mmol. <sup>b</sup> A = RuH<sub>2</sub>(PBu<sub>3</sub>)<sub>4</sub>; B = RuH<sub>2</sub>(PEt<sub>3</sub>)<sub>4</sub>. <sup>c</sup> Determined by g.l.c. based on the amount of acetylene. Isolated yields are given in parentheses. <sup>d</sup> See text. <sup>e</sup> Homodimers of phenylacetylene, *trans*- and *cis*-1,4-diphenylbut-1-en-3-yne, were formed in 64% yield (*trans*: *cis* = 62:38).

‡ To our knowledge, (2a), (2b), (2d), and (2e) have not been reported before. These products gave satisfactory elemental analyses and spectral data. The formation of (2c) has been reported briefly (H. Kleijn, J. Westmijze, K. Kruithof, and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 27).

§ When RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> is used as a catalyst, only a trace of (2) was formed, and instead RC≡C-CH=CH-CH=CH<sub>2</sub> was obtained in ca. 10% yield; details will be reported in a full paper.

<sup>1</sup> E.g. T. Mitsudo, K. Kokuryo, and Y. Takegami, *J. Chem. Soc., Chem. Commun.*, 1976, 772; T. Mitsudo, K. Kokuryo, T. Shinsugi, Y. Nakagawa, Y. Watanabe, and Y. Takegami, *J. Org. Chem.*, 1979, **44**, 4492.

<sup>2</sup> H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1976, 841.

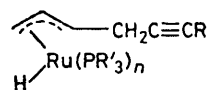
<sup>3</sup> G. Braca, G. Sbrana, G. Valentini, G. Andrich, and G. Gregorio, *J. Am. Chem. Soc.*, 1978, **100**, 6239; B. D. Dombek, *ibid.*, 1980, **102**, 6855.

<sup>4</sup> D. Wittenberg, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 153.

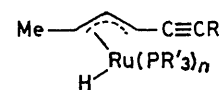
<sup>5</sup> P. Heimback, 'Aspects of Homogeneous Catalysis,' vol. 2, ed. R. Ugo, Reidel, Boston, 1974, p. 144.

effective catalyst (Table).§ These results showed that the selective linear codimerization of terminal acetylenes and buta-1,3-diene accompanied by a 1,3-hydrogen shift occurred catalytically under mild conditions.

This reaction may be rationalized by assuming that a zerovalent ruthenium-olefin or -acetylene complex is formed by the reaction of RuH<sub>2</sub>(PR'<sub>3</sub>)<sub>4</sub> with the olefin or acetylene and subsequent oxidative addition of an acetylene molecule may then give an alkynylhydridobutadiene-ruthenium(II) complex. Insertion of the butadiene into the Ru-alkynyl bond would give (3) which may isomerize to (4) followed by the reductive elimination induced by the co-ordination of the olefin or acetylene to give the product (2) and the zerovalent species again.



(3)



(4)

Although several examples of linear<sup>4</sup> or cyclic<sup>5</sup> co-oligomerizations of acetylenes and buta-1,3-diene are well known this reaction is, to our knowledge, the first example of the linear codimerization.

We thank Professor Y. Takegami for support.

(Received, 9th February 1981; Com. 143.)