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Selective formation of *cis*-PhCH=CH($SiEt_3$) by reaction of PhC≡CH with the stoichiometric amount of $HSiEt_3$, in the presence of ruthenium catalysts

Miguel A. Esteruelas *, Ana M. López, Luis A. Oro, José I. Tolosa

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain

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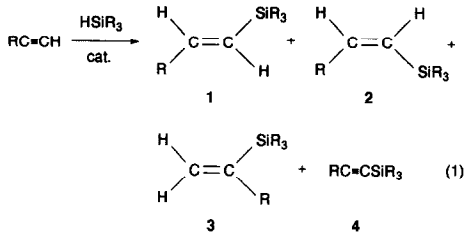
Abstract

The complexes $MH(\eta^2\text{-}H_2BH_2)(CO)(PPr^i_3)_2$, $M(C_2Ph)_2(CO)(PPr^i_3)_2$ and $M(\eta^2\text{-}C_2Ph_2)(CO)(PPr^i_3)_2$ (M = Ru, Os) are found to be very active and highly selective catalysts for the reaction of PhC≡CH with the stoichiometric amount of $HSiEt_3$; in the presence of the ruthenium catalysts, the reactions lead to *cis*-PhCH=CH($SiEt_3$) with selectivities of about 95%.

Keywords: Hydrosilylation; Ruthenium

1. Introduction

The addition of silanes to alkynes to give vinylsilanes is a reaction of considerable interest in connection with important industrial processes [1]. Furthermore, the hydrosilylation of alkynes catalyzed by transition metal complexes has synthetic value because the vinylsilane products have shown to be versatile intermediates in organic synthesis [2]. With alk-1-ynes the formation of four products (Eq. 1) is possible [3], and much effort has been expended in developing highly selective catalysts [4].



(1)

Following our previous work on the hydrosilylation of phenylacetylene with $HSiEt_3$ [5], we now report the catalytic activity of complexes **5–10**. The results are of interest not only because the catalysts are highly selective for the reaction of

* Corresponding author.

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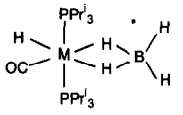
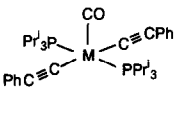
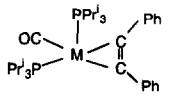
PhC≡CH with the stoichiometric amount of $HSiEt_3$, but also because the main product of the reaction is the thermodynamically less stable *cis*-isomer **2**.



M = Ru 5, Os 8



M = Ru 6, Os 9



M = Ru 7, Os 10

2. Experimental

Catalytic experiments were carried out under argon in a 50 ml two-neck flask with a condenser and containing a magnetic stirring bar. The second neck was capped with a Suba-seal to allow samples to be removed by syringe. In a typical procedure, the catalyst (0.019 mmol) was dissolved in a 1,2-dichloroethane solution (8 ml) containing $HSiEt_3$ (1.92 mmol), PhC≡CH (1.92 mmol) and C_6H_{12} (0.96 mmol). The flask was then immersed in a bath at 60°C, and the reaction mixture was magnetically stirred. The reaction was followed by measuring the silane consumption as a function of time using C_6H_{12} as the internal standard with a 15% β,β'-oxodipropionitrile on Chromosorb W-HP 80/100-mesh column at 40°C on a Perkin Elmer 8500 gas chromatograph with a flame ionization detector. The analysis of the reaction products was carried out by using a FFAP on Chromosorb GHP 80/100-mesh column at 175°C.

3. Results and discussion

The reactions were performed in 1,2-dichloroethane at 60°C, with concentrations 0.24 M of $HSiEt_3$ and PhC≡CH, and 2.4×10^{-3} M of catalyst. Results from experiments are summarized in Table 1.

The major product is in all cases *cis*-PhCH=CH($SiEt_3$), resulting from the *anti*-addition of the silane to the alkyne. In the presence of the ruthenium catalysts this product is obtained with selectivities of about 95%. The osmium catalysts are less active and the reactions also are less selective (about 65%). *Anti*-addition of silanes to alkynes has previously been observed. However, similar selectivities to those reported for the ruthenium complexes in Table 1, have only been seen in a few cases, when some reactions are carried out in the presence of an excess of alkyne [3b] or silane [4j].

The mechanisms previously proposed for the formation of the *anti*-addition product involve the initial insertion of the alkyne into a M–Si bond to

Table 1
Hydrosilylation of phenylacetylene

Catalyst [a]	t/h	Yield (%) [b]				Selectivity (%) [c]
		cis-PhCH=CH($SiEt_3$)	*trans*-PhCH=CH($SiEt_3$)	Ph($SiEt_3$)C=CH_2	PhC≡C$SiEt_3$	
RuH(η^2-H_2BH_2)(CO)(PPr^i_3)$_2$ **5**	3.0	87	3	2	3	91
Ru(C_2Ph)$_2$(CO)(PPr^i_3)$_2$ **6**	2.5	91	1	1	2	96
Ru(η^2-C_2Ph_2)(CO)(PPr^i_3)$_2$ **7**	1.2	91	2	1	3	94
OsH(η^2-H_2BH_2)(CO)(PPr^i_3)$_2$ **8**	7.5	32	15	1	3	62
Os(C_2Ph)$_2$(CO)(PPr^i_3)$_2$ **9**	8.9	55	19	2	4	69
Os(η^2-C_2Ph_2)(CO)(PPr^i_3)$_2$ **10**	2.2	21	6	1	2	70

[a] Catalysts were prepared by published methods [8–10].
[b] Yields were measured by GC with C_6H_{12} (0.12 M) as internal standard.
[c] Selectivity of the reaction for *cis*-PhCH=CH($SiEt_3$) relative to the total moles of obtained product.

give a (*Z*)-silylvinyl intermediate, which isomerizes to the less sterically congested *E*-isomer, via a zwitterionic carbene complex. In addition, β-elimination of the *endo*-hydrogen atom of the (*E*)-silylvinyl group could lead to the dehydrogenative silylation product $PhC{\equiv}CSiEt_3$ [4e,3b]. The results collected in Table 1 can be rationalized according to this proposals. However, the participation of alkynyl intermediates should not be completely rejected. A recent study on the addition of triethylsilane to phenylacetylene catalyzed by $[Ir(COD)(\eta^2\text{-}Pr^i_2PCH_2CH_2OMe)]BF_4$ has revealed that under the catalytic conditions both hydrido-alkynyl and hydrido-silyl intermediates are formed. Hydrido-alkynyl species are the key intermediates for the formation of $PhC{\equiv}CSiEt_3$, while, hydrido-silyl species are the key intermediates for the formation of *cis*-$PhCH{=}CHSiEt_3$ [6]. In this context, it should be noted that complexes **6** and **9** are bis-alkynyl compounds, and complexes **5**, **7**, **8** and **10** react with terminal alkynes to give alkynyl derivatives [7,8].

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References

[1] F.A. Noels and A.J. Hubert in A. Mortreux and F. Petit (Eds.), Industrial Applications of Homogeneous Catalysis, D. Reidel, Boston, 1988, Chap. 3.1.3.

[2] (a) T.H. Chan, Acc. Chem. Res., 10 (1977) 442; (b) P.F. Hudrlik, in D. Seyferth (Ed.), New Applications of Organometallic Reagents in Organic Synthesis, Elsevier, Amsterdam, 1976, p. 127; (c) F. Cook, R. Moerck, J. Schwindeman and P. Magnus, J. Org. Chem., 45 (1980) 1406; (d) I. Fleming, J. Dunogues and R.H. Smithers, Org. React., 37 (1989) 57.

[3] (a) M.J. Fernández, L.A. Oro and B.R. Manzano, J. Mol. Catal., 45 (1988) 7; (b) C.H. Jun and R.H. Crabtree, J. Organomet. Chem., 447 (1993) 177.

[4] (a) I. Ojima, M. Kumagai and Y. Nagai, J. Organomet. Chem., 66 (1974) C14; (b) H. Watanabe, M. Asami and Y. Nagai, J. Organomet. Chem., 195 (1980) 363; (c) K.A. Brady and A.T. Nile, J. Organomet. Chem., 206 (1981) 299; (d) K.H. Pannell, J.M. Rozell, J. Lii and S.Y. Tien-Mayr, Organometallics, 7 (1988) 2524; (e) I. Ojima, N. Clos, R.J. Donovan, P. Ingallina, Organometallics, 9 (1990) 3127; (f) R.S. Tanke and R.H. Crabtree, J. Chem. Soc., Chem. Commun., (1990) 1056; (g) L.N. Lewis, K.G. Sy, G.L. Bryant, Jr. and P.E. Donahue, Organometallics, 10 (1991) 3750; (h) M.P. Doyle, K.G. High, C.L. Nelsoney, T.W. Clayton, Jr. and J. Lin, Organometallics, 10 (1991) 1225; (i) V. Gevorgyan, L. Borisora, J. Popelis, E. Lukevics and Z. Foltynowicz, J. Gulinski and B. Marciniec, J. Organomet. Chem., 424 (1992) 15; (j) R. Takenchi and N. Tanouchi, J. Chem. Soc., Chem. Commun., (1993) 1319; (k) B. Marciniec and J. Gulinski, J. Organomet. Chem., 446 (1993) 15.

[5] M.A. Esteruelas, L.A. Oro and C. Valero, Organometallics, 10 (1991) 462; (b) M.A. Esteruelas, J. Herrero and L.A. Oro, Organometallics, 12 (1993) 2377; (c) M.A. Esteruelas, O. Nürnberg, M. Oliván, L.A. Oro and H. Werner, Organometallics, 12 (1993) 3264.

[6] M.A. Esteruelas, M. Oliván, L.A. Oro and J.I. Tolosa, J. Organomet. Chem., in press.

[7] J. Espuelas, M.A. Esteruelas, F.J. Lahoz, L.A. Oro and C. Valero, Organometallics, 12 (1993) 663.

[8] H. Werner, U. Meyer, M.A. Esteruelas, E. Sola and L.A. Oro, J. Organomet. Chem., 366 (1989) 187.

[9] H. Werner, M.A. Esteruelas, U. Meyer and B. Wrackmeyer, Chem. Ber., 120 (1987) 11.

[10] J. Espuelas, M.A. Esteruelas, F.J. Lahoz, A.M. López, L.A. Oro and C. Valero, J. Organomet. Chem., 468 (1994) 223.