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Oligomerization and polymerization of alkynes catalyzed by rhodium(I) pyrazolate complexes

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Three new Rh(I) derivatives containing the dcmpz ligand (Hdcmpz: 3,5-dicarbomethoxypyrazole) have been prepared and employed as catalysts or catalyst precursors in the cyclotrimerization of terminal and internal alkynes and in the polymerization of ethyne to polyacetylene.

Keywords: Rhodium; Alkynes; Cyclotrimerization; Polymerization; Pyrazolate complexes

1. Introduction

Eighty-two years after the discovery by Berthelot in 1866 that acetylene thermally trimerizes to benzene in low yield at high temperature (>400 °C) [1], Reppe and Sweckendiek reported that this reaction is catalyzed in solution near room temperature by nickel complexes [2]. Since then, alkyne cyclotrimerization has become one of the most intensely studied synthetically useful transformations [3–7]. This reaction has long been known to be catalyzed by a wide range of organo-transition metal compounds both in heterogeneous and homogeneous phase [8–10]. Organo-cobalt and rhodium derivatives are among the most widely used catalysts and have contributed to the understanding of the reaction paths by permitting the isolation of some possible intermediates [11–13].

Several studies have been carried out in the last years in order to test the catalytic activity of some pyrazolate-bridged complexes in various reactions. These studies concerned the discovery of new catalytic systems as well as the elucidation of the function of the complexes during the catalytic cycle. In the catalytic mechanism involving group VIII metals, oxidative addition and reductive elimination have a predominant role. As they usually cause a dramatic distortion in the coordination geometry of the metallic center, we decided to use a particular ligand, 3,5-pyrazoledicarboxylic acid dimethyl ester (Hdcmpz), which, as demonstrated by earlier studies performed on pyrazolate copper(I) and copper(II) complexes [14], can coordinate to a metal with the ester carbonyl oxygen of COOMe substituents, thus affording an extra-stabilization of the complexes. In the present work, we describe the capability of the new pyrazolato rhodium(I)

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complexes $[Rh(dcmpz)(PPh_3)(C_2H_4)]_2$ and $[Rh(dcmpz)(PPh_3)_3]$ to act as catalyst precursors for the cyclotrimerization of terminal and internal alkynes.

2. Experimental

2.1. General procedures

All solvents used in the reactions were purified according to the standard procedures and were kept under nitrogen atmosphere. If not otherwise specified, all reactions were performed under an inert atmosphere of dry nitrogen. $[Rh(C_2H_4)_2Cl]_2$ and 3,5-dicarbomethoxypyrazole were prepared according to literature procedures [15,16]. The alkynes employed in catalytic reactions were taken from new bottles (Sigma–Aldrich) kept at −25 °C and their purity grade was confirmed by GC–MS analysis. Elemental analysis (C, H, N) were carried out at The Microanalytical Laboratory of the University of Milan. IR spectra were recorded on a Bio-Rad FTS 7, ^{1}H-NMR and ^{31}P-NMR were recorded on a Bruker 400 Avance. Quantitative analysis of products were performed on a Shimadzu GC-17A gas chromatograph fitted with a 30 m (0.25 mm) capillary column coupled with a Shimadzu MS QP5000 instrument. Naphtalene was employed as internal standard.

2.2. Synthesis of $[Rh(dcmpz)(C_2H_4)_2]_2$, **1**

To a suspension of $[RhCl(C_2H_4)_2]_2$ (0.500 g, 1.28 mmol) in 10 ml of degassed methanol, 0.590 g of Hdcmpz (3.21 mmol) and 0.200 ml of triethylamine were added. The suspension immediately turned red and was kept at room temperature for 1 h and then filtered off. The precipitate was washed with methanol and dried in vacuum (78% yield). Analysis: Found C 38.79, H 4.44, N 8.13%; Calculated for $C_{22}H_{30}N_4O_8Rh_2$ C 38.60, H 4.38, N 8.19%.

Crystals suitable for X-ray structural determination were obtained by slow diffusion of *n*-hexane through a toluene solution of the complex.

2.3. Synthesis of $[Rh(dcmpz)(PPh_3)(C_2H_4)]_2$, **2**

0.450 g of **1** (0.658 mmol) were dissolved in 5 ml of degassed toluene. To the red solution, 0.517 g of PPh_3 (1.97 mmol) were added and gas evolution was noted. After 1 h stirring, the precipitate was filtered, washed with diethyl ether and dried in vacuum (89% yield). The compound was kept under nitrogen atmosphere at 0 °C. Analysis: Found C 56.69, H 4.80, N 4.41%; Calculated for $C_{54}H_{52}N_4O_8P_2Rh_2$ C 56.25, H 4.51, N 4.86%.

2.4. Synthesis of $[Rh(dcmpz)(PPh_3)_3]$, **3**

To a solution of 0.300 g (0.438 mmol) of $[Rh(dcmpz)(C_2H_4)_2]_2$, **1**, in 5 ml of toluene, 1.148 g of PPh_3 (4.38 mmol) were added, causing rapid evolution of gas. After 2 h stirring, the suspension was filtered off and the precipitate washed with diethyl ether and dried in vacuum. The compound was kept under nitrogen at 0 °C. (93% yield). Analysis: Found C 68.87, H 5.14, N 2.62%; Calculated for $C_{61}H_{52}N_2O_4P_3Rh$ C 68.28, H 4.85, N 2.61%.

2.5. Alkynes dimerization and cyclotrimerization

In a typical experiment, 10 mg of complex (**2** or **3**) were dissolved in 6 ml of degassed toluene obtaining a clear solution. The appropriate alkyne was then added under stirring in a unique step (Rh/alkyne, 1:100 molar ratio). The evolution of the reaction was monitored by GC–MS analysis.

2.6. Acetylene polymerization catalyzed by **2**

0.050 g of **2** (0.087 mmol Rh) were dissolved in 15 ml of acetonitrile under nitrogen. The solution was thermostated at 60 °C and then acetylene was bubbled through the solution at a constant rate (about one bubble every 2 s). After 5 h, the system was purged with dinitrogen and 0.046 g of PPh_3 (0.175 mmol) were added. The suspension was then filtered under nitrogen and the black solid washed with acetonitrile and dried under vacuum giving 2.7 g of *cis*/*trans*-polyacetylene mixture. The solid was kept at 0 °C under nitrogen atmosphere.

2.7. Cis/trans isomerization of polyacetylene

In a Schlenk tube, 1 g of the previously synthesized polymeric mixture was heated under nitrogen at 140 °C for 1 h by means of an oil-bath. The resulting

derivative was shown to be pure *trans*-polyacetylene (IR evidences, see text).

3. Results and discussion

3.1. Synthesis

When a suspension of the dinuclear $[RhCl(C_2H_4)_2]_2$ in methanol was treated with a small excess of Hdcmpz in the presence of triethylamine, a red precipitate was formed, which, on the basis of elemental analysis, IR and ^{1}H-NMR spectroscopy, was formulated as $[Rh(dcmpz)(C_2H_4)_2]_2$, **1** (Hdcmpz: 3,5-dicarbomethoxypyrazole), as later confirmed by a X-ray single crystal diffraction (Fig. 1) (Crystal data for **1**: $C_{22}H_{40}N_4O_8Rh_2$, fw = 684.32 g mol^{-1}, monoclinic, $P2_1/n$, a = 12.348(2), b = 18.297(4), c = 12.834(2) Å, β = 115.22(1); V = 2623.2(8) Å^3, Z = 4; ρ_c = 1.733 g cm^{-3}; μ = 1.31 mm^{-1}; $F(0\,0\,0)$ = 1376; 20256 reflections collected using graphite-monochromatized Mo Kα radiation on a SMART Bruker automated diffractometer; R1 and wR2: 0.038 and 0.056 for 4736 data (R_{int} = 0.024) collected in the $2 < \theta < 26^\circ$ range; GoF = 1.00. Further crystallographic data and final fractional atomic coordinates (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 192388. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Complex **1** belongs to a series of pyrazolato-bridged dirhodium complexes of general formula $[Rh(pz^*)L_2]$ (Hpz*: pyrazole, 3,5-dimethylpyrazole; L: π-acid ligands) originally prepared by Usón et al. [17]. The IR spectrum of **1** (nujol mull) shows two strong absorptions, respectively, at 1737 and 1706 cm^{-1}, due to the ν(CO) of the COOMe substituents on the pyrazole ring. In the ^{1}H-NMR spectrum (CD_2Cl_2, RT), a doublet centered at 3.21 ppm was assigned to olefinic protons, while signals at 3.82 and 6.79 ppm were associated to COOC***H***$_3$ and the C(4)–***H*** proton on 3,5-dicarbomethoxy pyrazole, respectively.

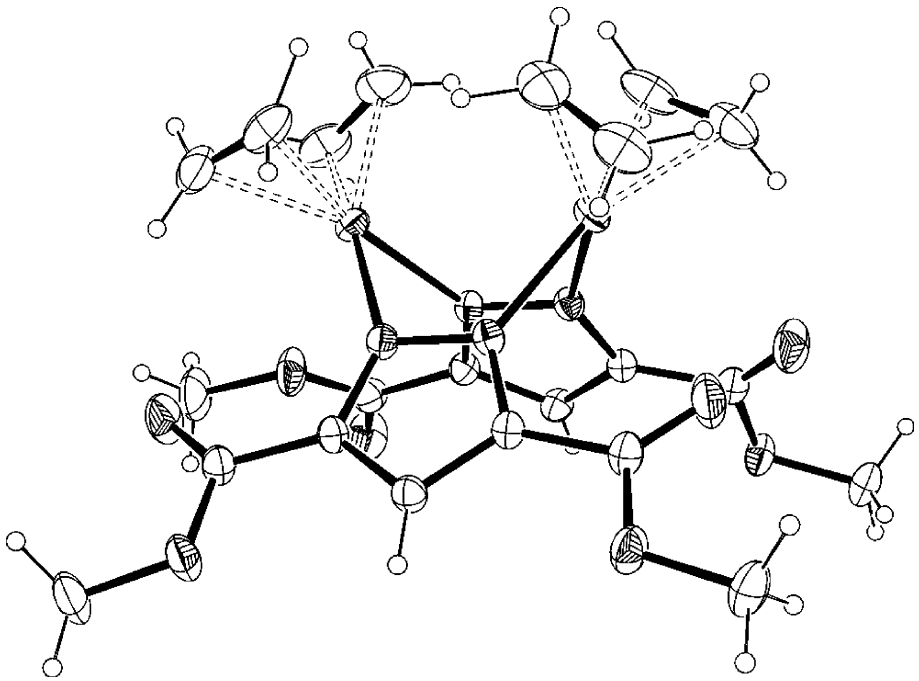
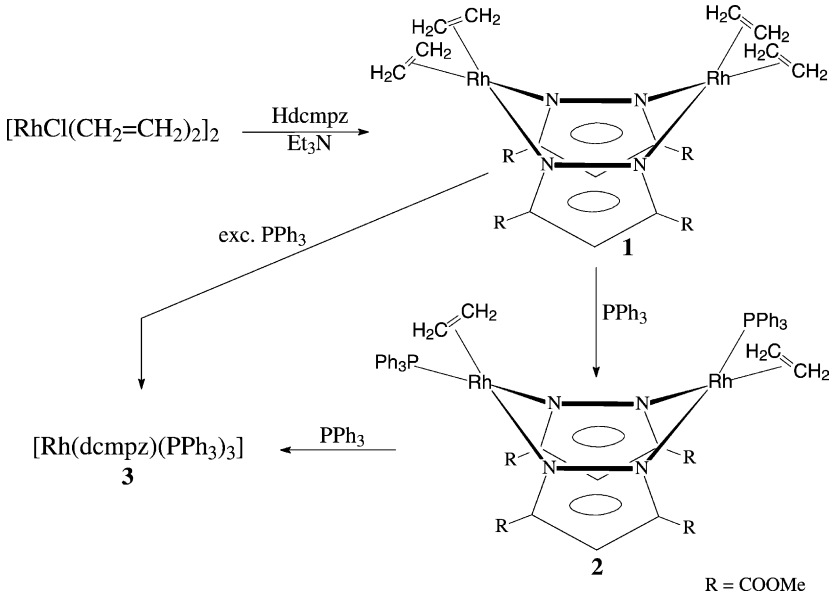


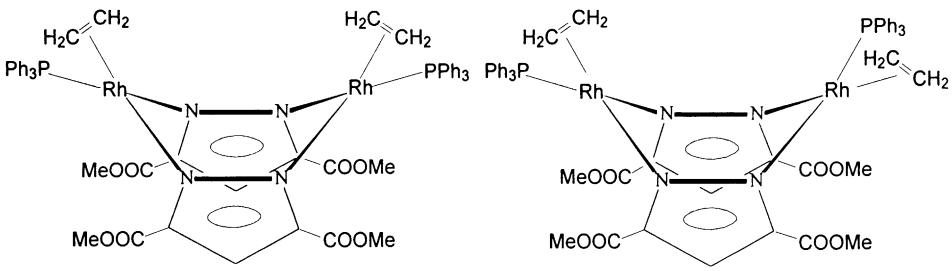
Fig. 1. ORTEP drawing of the $[Rh(dcmpz)(C_2H_4)_2]_2$, **1**, molecule. Thermal ellipsoids are drawn at the 30% probability level, hydrogen atoms of arbitrary size. Dashed bonds connect Rh–C atoms.



Scheme 1.

3.2. Reactions of $[Rh(dcmpz)(C_2H_4)_2]_2$ with PPh_3

A toluene solution of complex **1** treated with PPh_3 afforded two different species, depending on the Rh/PPh_3 ratio (Scheme 1). When a 1:1.5 Rh/PPh_3 ratio was used, an orange precipitate, formulated, on the basis of elemental analysis and spectroscopic data, as $[Rh(dcmpz)(PPh_3)(C_2H_4)]_2$, **2**, was formed. The IR spectrum of **2** (nujol mull) shows, besides the expected absorptions related to the presence of phenyl groups (900–600 cm^{-1}), two carbonyl stretching at 1723 and 1705 cm^{-1}, assigned to the COOMe substituents. The ^{31}P-NMR registered in $CDCl_3$ at room temperature shows a doublet centered at 45.10 ppm indicating two equivalent PPh_3 ligands coupled with the metal centers [^1J (^{103}Rh-^{31}P) = 172 Hz]. As ^{31}P-NMR does not permit to discriminate between the two possible *cis/trans* (related to the binuclear core) isomers of complex **2**, we tentatively assign to **2** the *trans* geometry, in analogy with the geometry of similar derivatives reported in the literature [18], and taking into account the lesser steric demand of the *trans* derivative with respect the *cis* one, rendering the former the thermodynamically favorite species.



When the reaction was carried out in the presence of a larger excess of PPh_3, namely a Rh/PPh_3 ratio of 1:5, the complete substitution of the ethylene ligands takes place and the formation of the mononuclear $[Rh(dcmpz)(PPh_3)_3]$, **3**, species occurs. The IR spec-

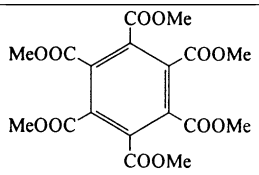
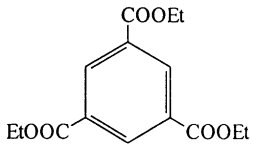
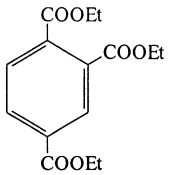
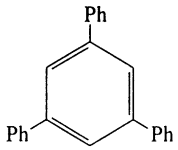
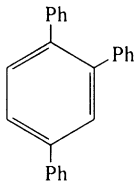
trum of **3** presents the COOMe carbonyl adsorptions at 1730 and 1707 cm^{-1} (nujol mull). Complex **3** can also be easily obtained by reacting **2** with excess PPh_3 (see Scheme 1).

*3.3. Catalysis: cyclotrimerization of alkynes catalyzed by **2** and **3***

Species **2** promoted alkyne cyclotrimerization in very mild conditions (toluene, RT) with high yields and selectivity. For example, the reaction with dimethylacetylene dicarboxylate (DMAD) showed a turnover frequency of about 8000 h^{-1}, to be compared with those reported in literature for other Rh(I) complexes, such as [(triphos)Rh(Cl)(C_2H_4)] [12] and [(COD)Rh(X)($Ph_2PC_6H_4$-3-SO_3Na)] [13].

Species **2** was active both with internal (DMAD) and with terminal alkynes (ethyl propiolate). A particular trend was noted with phenylacetylene as substrate; apart from the expected 1,2,4- and 1,3,5-triphenyl benzenes, the formation of head-to-head and head-to-tail dimers took place, the latter being predominant versus cyclotrimerization products. The presumed mechanism for this dimerization, different from that proposed for alkyne trimerization, probably involves the formation of a vinylidene species which subsequently undergoes acetylene insertion and reductive elimination. A similar mechanism can

Table 1
Catalytic activity of species **2** and **3**

Alkyne	Products	Selectivity (%)	
		2	**3**
MeOOC–C≡C–COOMe		100	100
H–C≡C–COOEt		72	71
		28	29
H–C≡C–Ph		14	traces
		3	traces
	Ph–C≡C–CH=CH(Ph)	52	82
	Ph–C≡C–C(Ph)=CH_2	31	17

be proposed for the polymerization of acetylene, HC≡CH, to give poly-acetylene, also catalyzed by $[Rh(dcmpz)(PPh_3)(C_2H_4)]_2$ (vide infra).

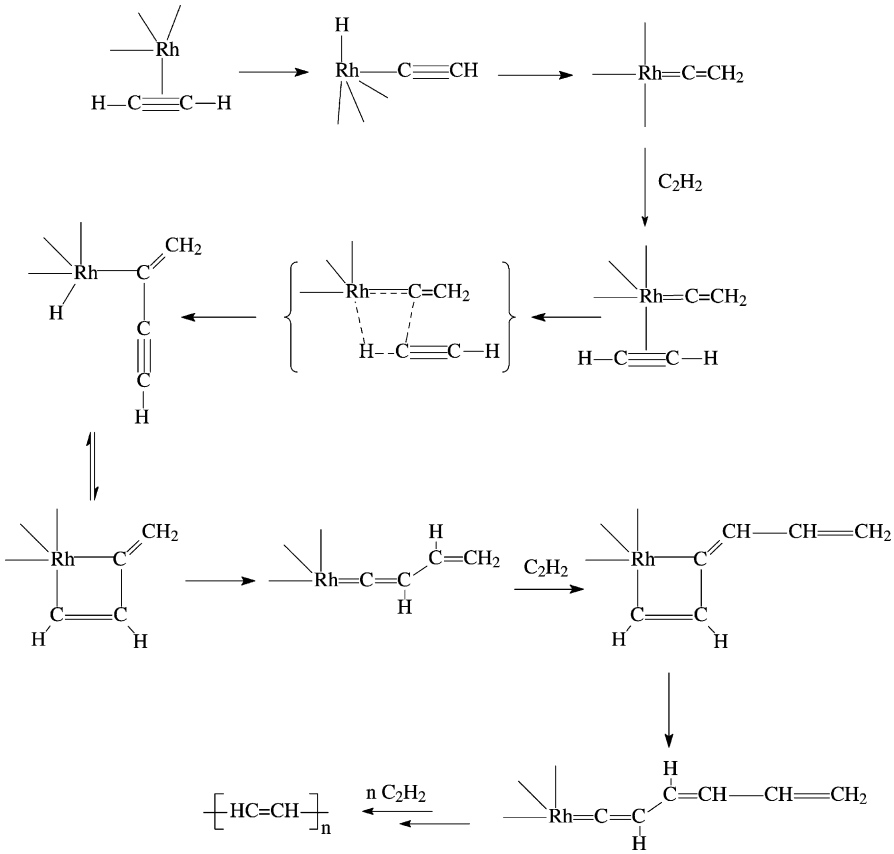
As previously cited, even species **3** was active in alkynes cyclotrimerization and oligomerization. A comparison of the catalytic activity of species **2** and **3** is reported in Table 1. Products distribution in phenylacetylene oligomerization was rather different using the two catalysts. The dinuclear $[Rh(dcmpz)(PPh_3)(C_2H_4)]_2$, **2**, afforded 17% of trisubstituted benzenes, dimers being the major products, but with the mononuclear $[Rh(dcmpz)(PPh_3)_3]$, **3**, the dimerization was even further favored, and benzene derivatives were detected only in traces. Similar results were reached with species **2** as catalyst in the presence of a small amount of free PPh_3 in the reaction mixture.

These different selectivities could probably derive from the different steric hindrance around the rhodium atoms in the two complexes. The bulky phosphine ligands in species **3** are likely to prevent the formation of the metallacycle involved in alkyne cyclotrimerization mechanism, thus favoring the dimerization reaction through a less hindered vinylidene species.

3.4. Acetylene polymerization catalyzed by $[Rh(dcmpz)(PPh_3)(C_2H_4)]_2$

Since Ziegler's studies on aluminium-alkyls [19], acetylene polymerization has always represented an important purpose in organo-metallic chemistry [20]. The interest is related to the possibility to generate semi-conducting species, i.e. *trans*-polyacetylene, later susceptible of chemical doping with formation of conducting solids of metallic lustre.

When gaseous acetylene was bubbled through an acetonitrile suspension of $[Rh(dcmpz)(PPh_3)(C_2H_4)]_2$, **2**, a dark precipitate formed, in a temperature-depen-



Scheme 2. Proposed mechanism for acetylene polymerization.

dent rate, which increased with increasing temperature. Consequently, all polymerization tests were performed at 60 °C. The black precipitate was not easily recovered. The addition of triphenylphosphine (PPh_3/Rh, 1:1 molar ratio) to the reaction medium generates an amorphous (XRPD evidences), but easily filterable, species. This was recognized (IR evidences) as a mixture of *cis* and *trans* isomers of polyacetylene. Indeed, in the region of the C–H out of plane bending, two strong absorptions (740 and 1010 cm^{-1}) are present, attributable to *cis*- and *trans*-polyacetylene isomers, respectively. According to an empirical equation reported in literature [21] from the area of the absorption bands, is possible to obtain the *cis/trans* ratio in the mixture, namely 3:1 in our experiments. Heating the solid to 140 °C under nitrogen turned the mixture completely into the *trans* form, thermodynamically more stable, as confirmed by the presence in the IR spectrum of heated samples of a single C–H adsorption at 1010 cm^{-1}.

The mechanism of polymerization (Scheme 2) is probably similar to that proposed for acetylene polymerization by titanium(I) compounds [22], the first step being the coordination of HC≡CH to the rhodium center, followed by oxidative addition to form an acetylide–hydride species. ^{1}H-NMR evidences confirmed the presence of hydridic species in the quenched polymerization reaction. Subsequently, a vinylidene species is formed, which undergoes the continuous insertion of acetylene molecules generating the polymeric chain. In the absence of triphenylphosphine, this highly conjugated polymer can probably act as a ligand for rhodium centers, giving place to a kind of *supported catalyst*. The presence of PPh_3 hampers the formation of the anchored species, freeing the polymer as an easily recoverable species. Since addition of PPh_3 can indifferently occur at the beginning (under acetylene flow) or at the end of the polymerization reaction (under nitrogen), we can safely exclude participation of the free phosphine into the reaction mechanism.

4. Conclusions

A new rhodium(I) pyrazolate complex, [Rh(dcmpz)$(C_2H_4)_2]_2$, **1**, was synthesized and fully characterized by standard spectroscopic techniques and single crystal X-ray diffraction. Starting from **1**, by reaction with triphenylphosphine, other two new rhodium(I) pyrazolate complexes, [Rh(dcmpz)$(PPh_3)(C_2H_4)]_2$, **2** and [Rh(dcmpz)$(PPh_3)_3$], **3**, were synthesized and characterized. Complexes **2** and **3** showed high activity in catalytic oligomerization and cyclotrimerization of both terminal and internal alkynes. In particular, with monosubstituted alkynes, products distribution deeply differentiates from that based on purely statistical calculations.[1] Interesting results occurred with phenylacetylene and acetylene itself, which underwent oligomerization or polymerization, respectively. As the nature of ancillary ligands probably plays an important role on the catalytic activity of these species, a systematic study about electronic and steric influence of aryl- and alkyl-phosphines, different from PPh_3, will be conducted.

Acknowledgements

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References

[1] M. Berthelot, Ann. Chim. 9 (1866) 431.
[2] W. Reppe, W.J. Sweckendiek, Ann. Chim. 560 (1948) 104.
[3] N.E. Schore, Chem. Rev. 88 (1988) 1081.
[4] A.J. Fletcher, S.D.R. Christie, J. Chem. Soc., Perkin Trans. (2000) 1657.
[5] N.E. Shore, in: B.M. Trost, I. Fleming, L.A. Paquette (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991, p. 1037, 1129.
[6] S. Saito, Y. Yamamoto, Chem. Rev. 100 (2000) 2901.
[7] D.B. Grotjahn, in: F.W. Abel, F.G.A. Stone, G. Wilkinson, L.S. Hegedus (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Elsevier, New York, 1995, p. 741.
[8] N. Mori, S. Ikeda, Y. Sato, J. Am. Chem. Soc. 121 (1999) 2722.
[9] A. Takeda, A. Ohno, I. Kadota, V. Gevorgyan, Y. Yamamoto, J. Am. Chem. Soc. 119 (1997) 4547.

[1] For asymmetric alkynes, depending on the head-to-head, head-to-tail or tai-to-tail coupling, a total of $2^3 = 8$ statistical configurations can be envisaged, which result in two isomers in 6:2 (asym/sym) ratio.

[10] R.J. Baxter, G.R. Knox, J.H. Moir, P.L. Pauson, M.D. Spicer, Organometallics 18 (1999) 206.
[11] G.A. Ardizzoia, S. Brenna, G. LaMonica, N. Masciocchi, A. Maspero, J. Organomet. Chem. 649 (2002) 173.
[12] C. Bianchini, D. Masi, A. Meli, M. Peruzzini, A. Vacca, Organometallics 10 (1991) 636.
[13] W. Baidossi, N. Goren, J. Blum, H. Schumann, H. Hemling, J. Mol. Catal. 85 (1993) 153.
[14] M. Angaroni, G.A. Ardizzoia, G. LaMonica, E.M. Beccalli, N. Masciocchi, M. Moret, J. Chem. Soc. Dalton Trans. (1992) 2714.
[15] R. Cramer, Inorg. Synth. 15 (1975) 14.
[16] R.V. Rothenburg, Chem. Ber. 27 (1894) 1098.
[17] R. Usón, L.A. Oro, M.A. Ciriano, M.T. Pinillos, A. Tiripicchio, M. Tiripicchio-Camellini, J. Organomet. Chem. 205 (1981) 247.
[18] H. Schumann, H. Hemling, V. Ravindar, Y. Badrieh, J. Blum, J. Organomet. Chem. 469 (1994) 213.
[19] K. Ziegler, Angew. Chem. 67 (1955) 541.
[20] Encyclopedia of Polymer Science and Engineering, vol. 1, 1985, p. 87.
[21] T. Ito, H. Shirakawa, S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. 12 (1974) 11.
[22] A. Ohff, V.V. Burlakov, U. Rosenthal, J. Mol. Catal. 108 (1996) 119.