DOI: 10.1002/adsc.200800075

Head-to-Head Homo-Coupling of Arylethynes Catalysed by (Dicarbonyl)ruthenium Chloride Metallacycles: Selective Synthesis of *(E)*-1,4-Diarylbut-1-en-3-ynes

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Received: February 4, 2008; Published online: June 2, 2008

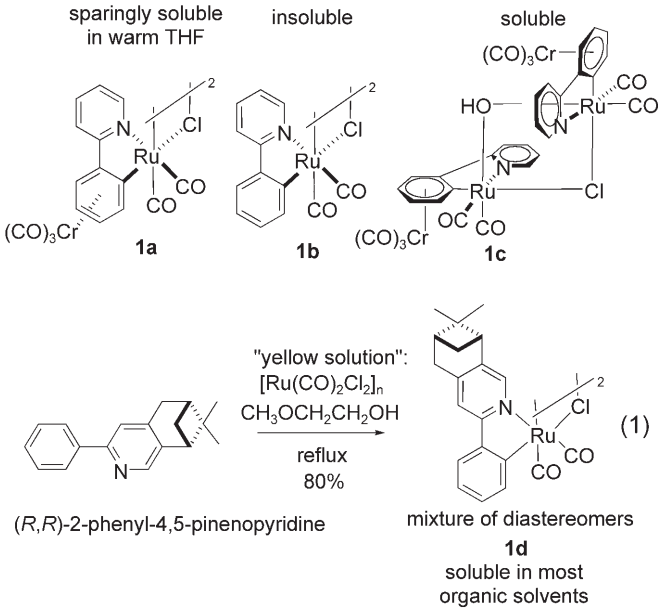
Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Exposure of various arylethynes to catalytic amounts of dimeric ruthenacycles containing the chloro(dicarbonyl)ruthenium [$Ru(CO)_2Cl$] motif efficiently and selectively leads to the formation of (*E)*-1,4-diaryl-but-1-en-3-ynes that result from head-to-head C–C coupling.

Keywords: alkyne dimerization; catalyst design; metallacycles; ruthenium

Conjugated 1,3-enynes constitute an important class of molecules which have been investigated for their antimicrobial activity[1] and more recently for their photo-physical properties.[2] The so-called metal-mediated "dimerisation" of terminal alkynes is one of the most direct ways to prepare such unsaturated compounds.[3] According to the extensive literature on the topic, four types of products can be expected in non-acidic media.[4] These are namely *Z* and *E* enynes resulting either from a head-to-head or a head-to-tail coupling, 1,2,3-butatrienes[5] and arenes, the latter resulting formally from a cyclotrimerisation.[6] We recently began a systematic investigation of the reactivity of (C,N) chelates of $Ru(CO)_2Cl$ and addressed the stereochemical issues related to the cycloruthenation of planar pro-chiral ligands by C–H bond activation.[7] Although the latter class of organometallic metallacycles has been known for more than 20 years,[8] only a few studies of their activity as catalysts in organic transformations have been reported to date.[9] In the present article, we deal with an unprecedented catalytic property of (C,N)$Ru(CO)_2Cl$ μ-chloro-bridged dimers that is the promotion of the stereoselective dimerisation of arylethynes into (*E*)-1,4-diarylbut-1-en-3-ynes.

The main difficulty in investigating the catalytic activity of $[(C,N)Ru(CO)_2\mu\text{-}Cl]_2$ compounds lies in their low solubility in organic solvents. Compound **1a**, which displays only moderate solubility in dimethylformamide, is only slightly soluble in warm tetrahydrofuran. *A contrario*, its $Cr(CO)_3$-free analogue **1b**[10] is insoluble in almost any solvent. Complex **1d**, which possesses a lipophilic terpene-derived appendage,[11] displays higher solubility in most conventional polar aprotic and protic solvents. According to ^1H NMR and ^{13}C NMR analyses, **1d** consists of a mixture of diastereomeric μ-chloro dimers (*cf.* Supporting Information). Introduction of the $Ru(CO)_2Cl$ fragment upon cyclometallation of this chiral ligand creates a new stereogenic centre at the ruthenium atom. Pro-



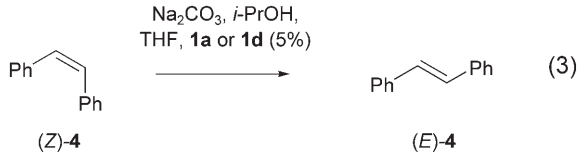
vided that the two CO ligands are likely located *cis* with respect to the carbanionic part of the chelating ligand,[7] two possible geometries of the $Ru(CO)_2Cl$ moiety relative to the dimethylmethylene bridge of the terpene-derived fragment can be expected: a *syn-facial* orientation with the CO ligand perpendicular to the chelate plane sharing the same face as the Me_2C bridge, and an *anti-facial* orientation in which these two moieties are on opposite faces of the chelate's plane. μ-Chloro bridges introduce yet another stereoisomerism, which further complicates the picture.[11]

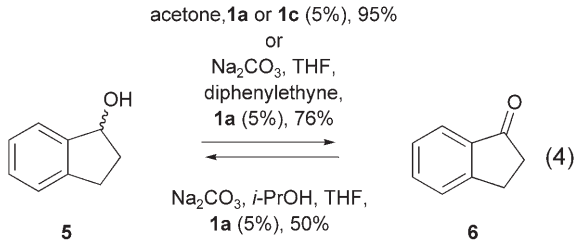
Nonetheless, treatment of **1d** with bistriphenylphosphoranilidene chloride ([PPN]Cl), which leads to the cleavage of the chloro bridge, led to two major chlororuthenate mononuclear anions in a *ca.* 1:1 ratio bearing putatively the *syn-facial* and *anti-facial* geometries as suggested by ^{1}H NMR characterisations.

Hence, we chose to probe the dimerisation of six non-volatile arylethynes, for example, **2a–f** [Table 1, Eq. (2)].

The structure of the products was ascertained on the basis of their ^{1}H NMR signature, which proved to be consistent with the data reported earlier by other authors for identical compounds. In all cases the products were found to result from a head-to-head coupling, and were identified as (*E*)-1,4-diarylbut-1-en-3-ynes. In the cases of **3b** and **c**, assignement of the *E* stereochemistry was based on the typical positions of the signals arising from the two ethylenic protons that were found to be consistent with those reported for (*E*)-**3a** and (*E*)-**3d–f**[12,13] in the literature. The yields in isolated enynes lie in the range between 54 and *ca.* 100% (Table 1). In cases where the reaction did not reach completion, ^{1}H NMR analyses of the raw mixtures indicated the presence of appreciable amounts of unreacted terminal alkyne.

Monitoring the dimerisation of **2a** by ^{1}H NMR indicated the predominance of (*E*)-**3a** with an *E*:*Z* ratio of *ca.* 60:1 at 2 h (conversion 5%) of reaction. Furthermore, it was found that the homo-coupling of **2a** catalysed by **1a** in refluxing dimethylformamide produced a 2.8:1 mixture of head-to-head enynes (*E*)- and (*Z*)-**3a**[14] in 58% yield. The low content in (*Z*)-enyne in the mixture of THF and *i*-PrOH was putatively ascribed to *Z*/*E* isomerisation promoted by **1a** and **1d**. This hypothesis was verified by submitting (*Z*)-stilbene, that is, (*Z*)-**4**, to the reaction conditions used for the dimerisation of arylacetylenes [Eq. (3)].

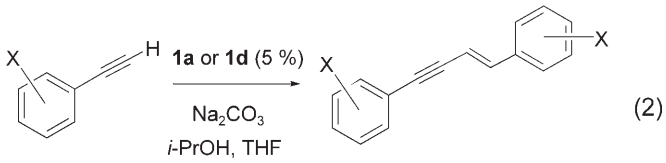




Complete conversion of (*Z*)-**4** into (*E*)-**4** isomer was reached after about 3 h of reaction using **1d** as a catalyst. Control experiments on the isomerisation of (*Z*)-**4** into (*E*)-**4** carried out without catalyst indicated almost no conversion, as well as those on the dimerisation of **2a** and **2d** without isopropyl alcohol in the presence of **1a** that indicated lower conversion (*cf.* Supporting Information).

These results suggest that the isomerisation process could rely on the formation of a ruthenium hydride species.[15] This assumption was strengthened by further experimental evidence that indicated that catalysts **1a** and **1d** could promote both the *Oppenauer*-type dehydrogenation of indanol[16] and *Merwein–Pondorf–Verley*-type hydrogenation of indanone [Eq. (4)] (*cf.* Supporting Information). Worthy of note here, the hydroxo-bridged dimer **1c**,[7,17] a soluble by-product in the cyclometallation reaction leading to **1a**, displayed a better catalytic activity than **1a** in the *Oppenauer* dehydrogenation of indanol,[18] providing in-

Table 1. Homo-coupling of arylethynes: catalyst (5% mol), Na_2CO_3 (excess), THF/*i*-PrOH 2:1, 15–18 h, 80 °C (reflux). Yields were determined after chromatographic purification.



2a – f (*E*)-**3a – f**

X	Substrate	Catalyst	Product	Yield [%]
H	**2a**	**1a**	(*E*)-**3a**[a]	98
		1d	(*E*)-**3a**[a]	100
4-*n*-C_5H_{11}	**2b**	**1a**	(*E*)-**3b**[b]	67
		1d	(*E*)-**3b**[b]	54
3-CH_3	**2c**	**1a**	(*E*)-**3c**[b]	70
		1d	(*E*)-**3c**[b]	76
4-CH_3	**2d**	**1a**	(*E*)-**3d**[c]	100
		1d	(*E*)-**3d**[c]	92
OMe	**2e**	**1a**	(*E*)-**3e**[a]	83
		1d	(*E*)-**3e**[a]	85
F	**2f**	**1a**	(*E*)-**3f**[c]	74
		1d	(*E*)-**3f**[c]	100

[a] See ref.[12]
[b] *Cf.* Supporting Information.
[c] See ref.[13]

danone in 96% yield when using acetone as the hydrogen atom acceptor.

The rationalisation of the formation of enynes may assume a mechanism similar to the one proposed by Verpoort et al.[19] which involves a ruthenium(II) vinylidene acetylide[20] and a ruthenium-enynyl[21] as key intermediates. Worthy of note, compound **1a** did not show any propensity to undergo alkyne insertion into the C_{Ar}–Ru bond, a reaction reported earlier for a μ-iodo-bridged dimer analogous to **1b**.[22]

The ability of (C,N) chelates containing the $Ru(CO)_2Cl$ motif to promote C–C coupling reactions and hydrogen atom transfer reactions is unprecedented to the best of our knowledge. The results disclosed herein give valuable information on the potential of such complexes in homogenous catalysis. Our current efforts are dedicated to the investigation of the mechanism of the above-mentioned transformations and to further studies of the catalytic activity of hydroxo-bridged ruthenacycles[7b] similar to **1c**. Further results will be disclosed in due time.

Experimental Section

Synthesis of 1d

2-Phenyl-4,5-pynenopyridine (1.6 g, 6.4 mmol) was dissolved in a solution of $[Ru(CO)_2Cl_2]_n$ in 2-methoxyethanol (30 mL) prepared from $RuCl_3 \cdot 3H_2O$ (2 g, 6.4 mmol).[10] The resulting solution was refluxed overnight and subsequently concentrated and filtered (yield: 2.26 g, 80%). The resulting solid was recrystallised from warm methanol to afford pure **1d** as an off-white solid.

General Procedure for the Dimerisation of Phenylethynes

A mixture of arylethyne, Na_2CO_3 and either **1a** or **1d** (molar ratio: 5%) in a mixture of THF/*i*-PrOH (2:1) was refluxed for *ca.* 15 h. After cooling, the solvents were removed and the crude product was purified by silica gel column chromatography, using a mixture of *n*-pentane and acetone (8:1) as eluent. The structure of the products was ascertained by comparison of their ^1H NMR spectra with those of identical standards.

Supporting Information

Details of experimental procedures, NMR spectra, high-resolution mass spectra. Crystallographic data (excluding structure factors) for the structure of **1d** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 683648. Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: (internat.) +44-1223-336-033, e-mail: deposit@ccdc.com.uk].

Acknowledgements

The authors are grateful to the National Research Agency (ANR Project JCJC-0086–01) and the CNRS for financial support. The authors thank Drs Louis Ricard and Xavier-Frédéric Le Goff (Ecole Polytechnique, Palaiseau) for supplying the crystallographic data of compound ***1d****.*

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