JOM 23172

Electronic and steric effects in the rhodium-complex catalysed co-cyclization of alkynes and nitriles to pyridine derivatives

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(Received June 2, 1992)

Abstract

A study of the properties exhibited by the catalyst precursors of formula $[Rh(\eta^5\text{-}C_5H_4R)(C_2H_4)_2]$ (R = NMe_2, ^tBu, Me, H, Cl, NO_2, CF_3, or COOMe) in the co-cyclization of a variety of 1-alkynes (R'CCH) and nitriles (R"CN) to pyridine derivatives is reported. Initial reaction rates as well as chemoselectivity and regioselectivity are markedly influenced by the electron donor–acceptor properties of the R groups on the cyclopentadienyl ring, as well as by the steric and electronic effects induced by the substituents (R' and R") attached to substrates.

1. Introduction

It has been known since 1973 that the co-cyclization of alkynes and nitriles to pyridine derivatives can occur in the presence of cobalt-based catalyst precursors [1]. As a consequence of the fundamental research carried out by Bönnemann and coworkers [2] and by Wakatsuki and Yamazaki [3], cobalt(I) complexes of the type $[CoYL_n]$ have attracted much interest, mainly with respect to the possibility of controlling their catalytic action by varying the effects caused by different Y which remain attached to cobalt throughout the catalytic cycle. In addition, the role played by the steric and electronic effects exerted by the substrate-attached groups in influencing the regioselectivity of the co-cyclization of 1-alkynes and nitriles has been the object of theoretical and experimental studies [4–6].

In 1983 we found that the co-cyclization of alkynes and nitriles to pyridines can also be carried out efficiently in the presence of half-sandwich rhodium(I) complexes of the type $[RhCp'L_n]$ [7]. Since the catalysis seems to occur on the "Cp'Rh" core generated by such complexes, the catalytic properties of the above rhodium catalyst precursors depend on the Cp' [8]. However, no systematic study of these interactions has yet been reported. Thus for the rhodium-catalysed reactions, it is not possible to evaluate the relative importance of steric and electronic effects of the cyclopentadienyl ligands. Some dramatic differences observed in the catalytic activity between "C_5H_5Rh" and "C_5Me_5Rh" systems were rationalized in terms of electronic effects, while the different regioselectivities exhibited by these systems were related to the markedly different steric demands of the two cyclopentadienyl ligands [8].

We find now that this last idea is substantially incorrect. The study we report here, of which preliminary results have already been communicated briefly [9], shows clearly that, as far as the Cp' is concerned, the electronic effects preponderate over the steric effects. Indeed, with substituents of different electron-releasing or electron-withdrawing properties on the cyclopentadienyl ring, it was possible to correlate the activity, the chemoselectivity, and the regioselectivity of a number of catalyst precursors of formula $[Rh(\eta^5\text{-}C_5H_4R)(C_2H_4)_2]$ (1) with the electron donor–acceptor properties of the cyclopentadienyl moiety. Moreover, comparison of these results with those obtained for catalysis by cyclopentadienyl cobalt(I) complexes [2], reveals a marked metal effect.

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0022-328X/93/$6.00

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2. Results and discussion

2.1. Choice and preparation of the catalyst precursors and general remarks on catalytic reactions

In order to minimize the steric demands of the Cp′ ligands, the monosubstituted cyclopentadienyl derivatives **1a–1h** were employed as catalyst precursors. At temperatures higher than 40°C [10], ligands η^5-C_5H_4R can easily assume the most favourable conformation by placing their substituents in the least sterically hindered molecular space. Hence the complexes **1a–1h** can be considered approximately identical as far as their steric influence on catalysis is concerned:

$[Rh(\eta^5\text{-}C_5H_4R)(\eta^2\text{-}C_2H_4)_2]$

1

1a, R = NMe_2; **1b**, R = ^{t}Bu; **1c**, R = Me;

1d, R = H; **1e**, R = Cl; **1f**, R = NO_2; **1g**, R = CF_3;

1h, R = COOMe

To the best of our knowledge **1a**, **1f**, and **1g** had not been reported. We report here what we believe are the first published preparations of these complexes which were performed according to a classic scheme based on the reaction of the appropriate Tl, Na, or Li cyclopentadienide with Cramer's salt. **1a** and **1f** were obtained in 16% and 3% yields respectively, and with some experimental difficulty. In particular, with **1a** the use of $CH_3SO_3NMe_2$ in the preparation of *N*,*N*-dimethyl-1,3-cyclopentadienylamine [11] may be dangerous as it decomposes explosively on standing at room temperature. Therefore, we used the more thermally stable *N*,*N*-dimethyl-*O*-(*p*-toluensulphonyl)hydroxylamine, *p*-$MeC_6H_4SO_3NMe_2$ [12].

The very low yields obtained in the synthesis of **1f** may be due to the poor nucleophilicity of the nitrocyclopentadienyl anion as a result of a high charge delocalization due to the nitro group [13]. Very little chloride displacement from Cramer's salt results under our experimental conditions (reaction medium diethyl ether + pentane, or diethyl ether, or tetrahydrofuran; reaction time 6–16 h; reaction temperature −78 to 25°C). Finally, **1g** was obtained in *ca.* 50% yield by reaction of (trifluoromethyl)cyclopentadienylthallium [14] with Cramer's salt in THF.

The complexes were isolated and purified by column chromatography on alumina (silica-gel, in the case of **1f**) and were analysed by ^{1}H NMR spectroscopy. **1a**, **1f**, and **1g** were also characterized by elemental analysis.

All catalytic runs were carried out under dinitrogen, employing an alkyne-to-nitrile ratio of 1/5.4 and a catalyst precursor-to-alkyne ratio of 1/100 [8]. The pairs of substrates we used were 1-hexyne and propionitrile, *t*-butylacetylene and propionitrile, phenylacetylene and propionitrile, trimethylsilylacetylene and propionitrile, and 1-hexyne and *t*-butyl cyanide.

In all cases different amounts of arenes (1,2,4- and 1,3,5-trisubstituted regio-isomers) were obtained in addition to pyridine derivatives, these being mixtures of 2,4,6- and 2,3,6-trisubstituted regioisomers, **2** and **3** respectively (Scheme 1).

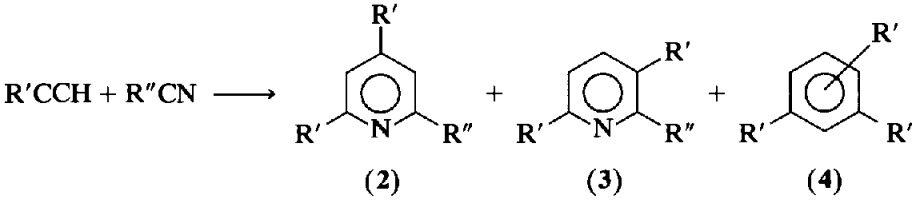
2.2. Activity of the catalyst precursors 1a–1h

Between 80 and 150°C, **1a–1h** are active in the co-cyclization of 1-alkynes and nitriles and lead to very variable amounts of pyridine and benzene derivatives, depending on the cyclopentadienyl ligand.

In the co-cyclization of 1-hexyne with propionitrile, the lowest pyridine yields were obtained using the catalyst precursor **1f** (R = NO_2) (see Table 1 and Fig. 1). Due to this and to the difficulty of preparing this compound, its catalytic properties were not investigated further.

The unique behaviour of **1a** (R = NMe_2) is evident: it is the only precursor which furnishes some pyridine at temperatures lower than 80°C and it exhibits its highest activity at 80°C, while the other catalyst precursors give the highest pyridine yields at temperatures around 130°C. **1a** is the only rhodium-based catalyst precursor known to exhibit some activity in pyridine synthesis at temperatures below 80°C [8]. Above this temperature, its activity decreases slowly. In contrast, at temperatures between 80 and 130°C, the pyridine yields obtained employing **1b**, **1c**, **1d**, **1e**, **1g**, and **1h** increase to more than 60%, with the exception of **1e** (R = Cl) (maximum yield 32%). Finally, between 130 and 150°C, all catalysts show a decrease in activity.

At 80°C, the catalyst precursors with electron-donating R substituents on Cp′, *i.e.* **1a** (R = NMe_2), **1b** (R = ^{t}Bu), and **1c** (R = Me), are better in terms of



Scheme 1.

TABLE 1. Influence of reaction temperatures on pyridine and benzene derivative yields in the co-cyclization of 1-hexyne and propionitrile catalysed by the complexes **1a–1h**

Catalyst precursor	Temperature (°C)					
	60	70	80	100	130	150
1a	6.0	18.3	30.5	26.3	21.3	17.6
	(8.5)	(23.9)	(39.5)	(41.1)	(34.5)	(31.8)
1b	–	–	3.5	28.3	67.8	60.0
	(–)	(–)	(2.7)	(10.6)	(17.3)	(18.2)
1c	–	–	1.2	18.4	62.3	56.0
	(–)	(–)	(2.8)	(7.6)	(19.6)	(20.6)
1d	–	–	0.3	6.6	64.5	61.0
	(–)	(–)	(0.4)	(3.3)	(18.7)	(20.0)
1e	–	–	0.7	8.3	32.2	29.1
	(–)	(–)	(0.8)	(7.3)	(20.0)	(18.8)
1f	–	–	–	2.6	8.0	–
	(–)	(–)	(–)	(17.6)	(14.5)	(–)
1g	–	–	0.2	9.0	65.7	65.0
	(–)	(–)	(2.2)	(9.2)	(15.5)	(18.0)
1h	–	–	0.5	10.8	67.7	67.9
	(–)	(–)	(2.3)	(5.6)	(19.4)	(17.8)

Yields are based on starting alkyne; benzene derivative yields are given in parentheses; reaction conditions are 1-hexyne 8.74 mmol; [1-hexyne]/[propionitrile] 1/5.4; [1-hexyne]/[Rh] 100; reaction time 3 h.

pyridine yield than those carrying electron-withdrawing R groups or H. At 100°C, considerable differences are still observed, a sharp boundary lying between **1a**, **1b**, and **1c**, on the one hand, and **1d** (R = H), **1e** (R = Cl), **1g** ($R = CF_3$), and **1h** (R = COOMe), on the other. At 130°C, these differences become smaller and **1b**, **1c**, **1d**, **1g**, and **1h** give pyridine yields ranging from 62% to 68%.

The influence of reaction time upon the yields of pyridine derivatives is illustrated by the data in Fig. 2. There is a marked difference between **1a** ($R = NMe_2$) and **1e** (R = Cl) on the one hand, and **1b**, **1c**, **1d**, **1g**, and **1h**, on the other hand, these last showing similar yields with time. Electron-releasing substituents on Cp′ produce slightly higher initial reaction rates.

The pyridine yields under constant experimental

TABLE 2. Influence of substrate structure on pyridine and benzene derivative yields in the co-cyclization of alkynes and nitriles catalysed by the complexes **1a–1h**

Catalyst precursor	Substrate couple					
	BuCCH EtCN	^{t}BuCCH EtCN	PhCCH EtCN	$MeOCH_2CCH$ EtCN	Me_3SiCCH EtCN	^{n}BuCCH ^{t}BuCN
1a	21.3	4.7	7.4	40.2	17.0	10.4
	(34.5)	(24.2)	(26.7)	(41.0)	(60.0)	(4.5)
1b	67.8	4.8	16.0	58.0	8.8	16.4
	(21.6)	(19.5)	(22.8)	(20.9)	(34.6)	(28.4)
1c	62.3	7.9	19.8	60.0	6.9	23.4
	(19.6)	(10.5)	(53.8)	(22.2)	(38.0)	(39.4)
1d	64.5	4.7	36.3	41.9	4.8	16.3
	(18.7)	(14.0)	(45.0)	(11.0)	(24.9)	(26.5)
1e	32.2	4.8	14.0	11.2	10.1	5.4
	(20.0)	(17.3)	(49.0)	(14.3)	(24.5)	(17.3)
1f	8.0	–	–	–	–	–
	(14.5)	(–)	(–)	(–)	(–)	(–)
1g	65.7	9.1	32.1	72.6	24.6	15.4
	(15.5)	(12.0)	(46.1)	(19.4)	(11.1)	(23.1)
1h	67.7	8.5	29.9	67.1	31.7	13.5
	(19.4)	(14.3)	(52.3)	(12.3)	(31.5)	(29.4)

Yields are based on starting alkyne; benzene derivative yields are given in parentheses; reaction conditions are alkyne 8.74 mmol; [alkyne]/[nitrile] 1/5.4; [alkyne]/[Rh] 100; reaction temperature 130°C; reaction time 3 h.

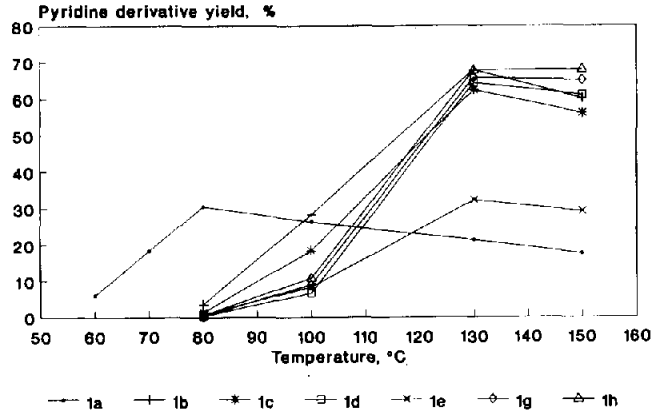


Fig. 1. Pyridine derivative yield as a function of reaction temperature. Catalyst precursors **1a, 1b, 1c, 1d, 1e, 1g, 1h**; [1-hexyne]/[Rh] 100; [1-hexyne]/propionitrile] 1/5.4; reaction time 3 h; yields are based upon the starting alkyne (8.74 mmol).

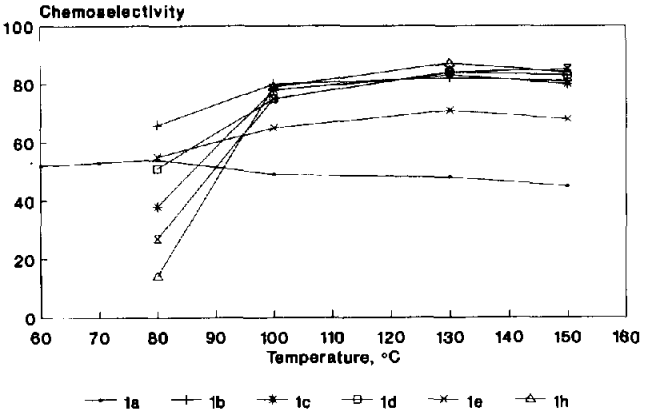


Fig. 3. Chemoselectivity, given as [mol of pyridine derivatives/(mol of pyridine derivatives + mol of benzene derivatives)] × 100, as a function of reaction temperature. Catalyst precursors **1a, 1b, 1c, 1d, 1e, 1g, 1h**; [1-hexyne]/[Rh] 100; [1-hexyne]/[propionitrile] 1/5.4; reaction time 3 h.

conditions vary widely with the nitrile–alkyne couple, with **1a** ($R = NMe_2$) or **1e** ($R = Cl$) rather low pyridine yields are obtained, whatever substrates are used (Table 2). However, the catalyst precursors **1a–1h** give their highest pyridine yields when 1-hexyne–propionitrile or methylpropargyl ether–propionitrile couples are used. Sterically hindered alkynes lead to yields which never exceed 10%. The yields obtained in the case of ^{t}BuCCH–EtCN co-cyclization catalysed by **1g** ($R = CF_3$) or **1h** ($R = COOMe$) (9.1% and 8.5% respectively) are nevertheless the best figures ever observed for such substrates [8]. Finally, both the co-cyclizations of phenylacetylene or trimethylsilylacetylene with propionitrile give rather low yields in pyridine derivatives with all catalyst precursors **1a–1h**.

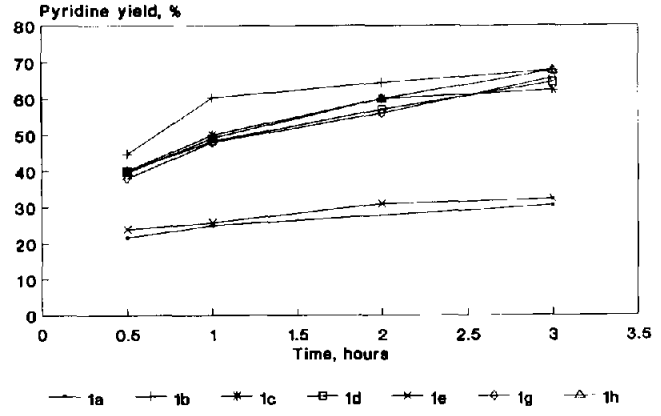


Fig. 2. Pyridine derivative yield as a function of reaction time. Catalyst precursors **1a, 1b, 1c, 1d, 1e, 1g, 1h**; [1-hexyne]/[Rh] 100; [1-hexyne]/[propionitrile] 1/5.4; reaction temperature 130°C; yields are based upon the starting alkyne (8.74 mmol).

2.3. Chemoselectivity of the catalyst precursors 1a–1h

The catalytic synthesis of pyridines by co-cyclization of alkynes and nitriles is accompanied by the formation of different amounts of arene arising from alkyne self-cyclotrimerization, whatever the catalyst precursor [1,2,8]. In particular, it has already been found that the chemoselectivity (defined as the number of moles of pyridine derivatives divided by the number of moles of pyridine plus benzene derivatives, all multiplied by 100) of the rhodium-catalysed reactions increases on increasing the nitrile-to-alkyne ratio, being highest when this is greater than five [8].

We now find that the chemoselectivity observed in the reaction catalysed by **1a–1h** depends on the nature of the Cp′ and the reaction temperature. No significant dependence upon the reaction time was observed. A further peculiarity of **1a** ($R = NMe_2$) that its chemoselectivity is almost uninfluenced by temperature (Fig. 3), whereas in the case of the other catalyst precursors a sharp increase in selectivity is observed when the reaction temperature increases from 80 to 100°C. However, the chemoselectivities known by **1a** were never higher than 54%, while the highest chemoselectivities for the other catalyst precursors range from 80% to 87%, with the exception of **1e** ($R = Cl$) (maximum chemoselectivity 71% at 130°C).

Whatever the substrates, the chemoselectivity increases slightly with the electron-withdrawing power of the substituents on the Cp′ ring (Fig. 4). However, sterically hindered alkynes or nitriles, as well as trimethylsilyl- or phenyl-substituted acetylenes, invariably lead to chemoselectivities rather lower than those obtained in the co-cyclizations of 1-hexyne or methylpropargyl ether with propionitrile.

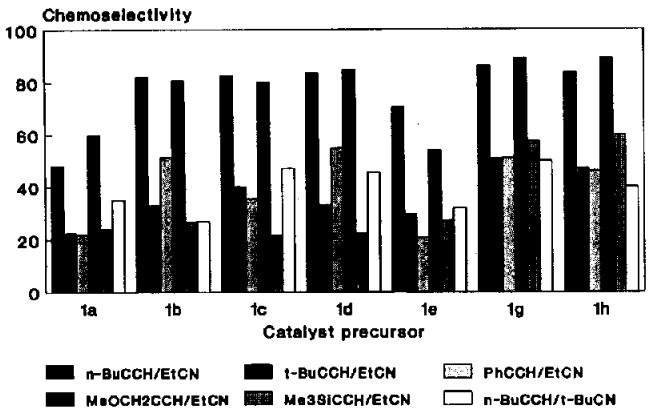


Fig. 4. Chemoselectivity, given as [mol of pyridine derivatives/(mol of pyridine derivatives + mol of benzene derivatives)] × 100, as a function of the structure of reactive substrates. Catalyst precursors **1a**, **1b**, **1c**, **1d**, **1e**, **1g**, **1h**; [1-alkyne]/[Rh] 100; [1-alkyne]/[nitrile] 1/5.4; reaction time 3 h; reaction temperature 130°C.

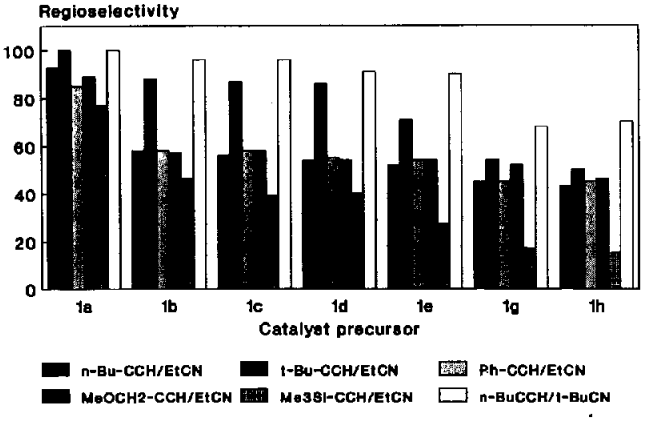


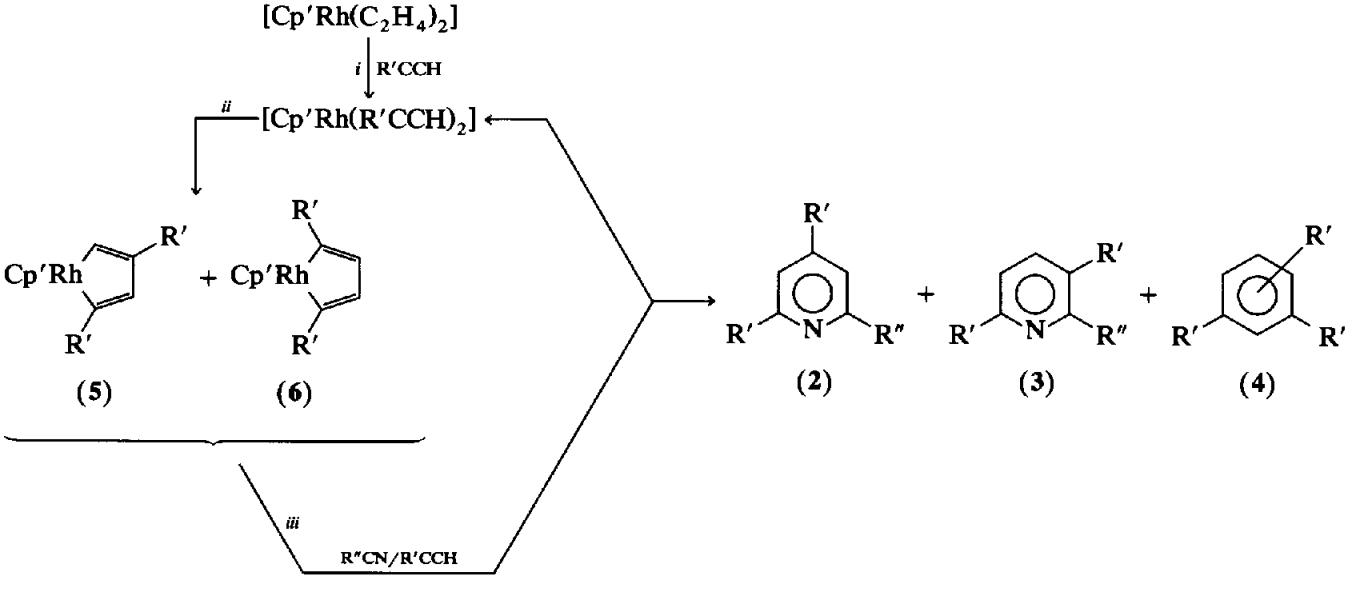
Fig. 5. Regioselectivity, given as [mol of pyridine isomer **2**/(mol of pyridine isomer **2** + mol of pyridine isomer **3**)] × 100, as a function of the structure of reactive substrates. Catalyst precursors **1a**, **1b**, **1c**, **1d**, **1e**, **1g**, **1h**; [1-alkyne]/[Rh] 100; [1-alkyne]/[nitrile] 1/5.4; reaction time 3 h; reaction temperature 130°C.

2.4. Regioselectivity of the catalyst precursors **1a–1h**

In addition, the regioselectivity, (defined as the number of moles of isomer **2** divided by the number of moles of isomers **2** and **3**, all multiplied by 100) while little affected by reaction temperature or time, varies markedly with the electronic properties of the Cp′. Indeed, catalyst precursors carrying electron-releasing groups on Cp′, such as **1a** ($R = NMe_2$), **1b** ($R = {}^tBu$), and **1c** (R = Me), cause the 2,4,6-trisubstituted isomer **2** to be more abundant than the 2,3,6-trisubstituted isomer **3** (Fig. 5). In particular, **1a** leads to the nearly exclusive formation of isomer **2**, typical regioselectivity figures being around 90% or higher.

The co-cyclization of trimethylsilylacetylene and propionitrile deviates from such a trend. However, even in this case isomer **2** is formed preferentially to **3** (77% *vs.* 23%) if **1a** is used as catalyst precursor.

Electron-withdrawing substituents on Cp′ cause an inversion of the above trend: in particular, in the co-cyclizations catalysed by **1g** ($R = CF_3$) and **1h** (R = COOMe), the percentage of **3** exceeds that of isomer **2** unless sterically hindered alkynes or nitriles are used. As expected, this tendency is amplified in the case of the co-cyclization of trimethylsilylacetylene with propionitrile, the isomer **3** now predominating (Fig. 5).



Scheme 2.

The trend is now qualitatively similar to that found for the cobalt-catalysed pryidine synthesis [2], *i.e.* the percentages of the isomers **2** and **3** vary with the electron density on cobalt caused by the electronic properties of Cp'. However, percentages of isomer **2** higher than 85% had never been observed in the absence of strong steric restrictions introduced by the reactive substrates, with either cobalt- or rhodium-based catalysts. Moreover, it is now possibly to direct the co-cyclization of 1-alkynes and nitriles towards isomers of type **3**, by changing the structure of the catalyst precursor.

3. Conclusions

This study shows that even small changes of the structure of half-sandwich rhodium(I)-based catalyst precursors may cause marked effects in the co-cyclization of alkynes and nitriles to pyridine derivatives. Moreover, on the basis of this work it is clear that, as far as the Cp' is concerned, the electronic effects overcome the steric effects. Even though the data reported in this study were not obtained under isoconversion conditions of one of the two reactants (alkyne and nitrile), the observed trends clearly indicate that an increase in the electron-withdrawing power of the substituents on Cp' rings gives lower activity at low temperatures, with a somewhat higher chemoselectivity and a lower percentage of 2,4,6-isomer.

A persuasive rationalization of some of these trends can be based on the commonly accepted mechanism [2,5,6,8] (Scheme 2).

In the case of the cobalt-catalysed pyridine synthesis, it has been shown that the substitution of the ancillary L ligands by two alkyne molecules is of primary importance in controlling the activity of catalyst precursors of the type $[CoCp'L_2]$ [2,3], such a reaction being kinetically favoured by the presence of electron-withdrawing substituents on the Cp' ring [3,12,15].

As far as the catalyst precursors **1a–1h** are concerned, this study shows that electron-releasing substituents on the Cp' ring make the corresponding complexes more active, at least at temperatures between 60 and 100°C, the most remarkable effects having been observed in the case of **1a** ($R = NMe_2$). While ruling out the substitution of ethylene by alkyne molecules as a rate-determining step in rhodium catalysis, these results may implicate the oxidative cyclization reaction (scheme 2, step ii) as a kinetically important step. Since the electronic effects of the substituents on the Cp' ring should be transmitted to the central atom [12], such an oxidative process should be facilitated by electron-releasing groups. Moreover, a more electron-rich, less acidic rhodium(III) centre should be less efficient in discriminating between σ-donating species (nitriles) and π-acceptor species (alkynes), leading to a lower pyridine-to-benzene ratio.

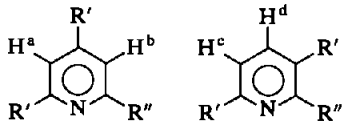
The observed dependence of regioselectivity on the structure of the catalyst precursor employed cannot be explained easily. Because the 2,4,6-trisubstituted isomer is derived from the metallacycle **5** and the 2,3,6-trisubstituted one from the metallacycle **6** (scheme 2), one obvious conclusion is that the regiochemistry of the oxidative cyclization step is influenced not only by the electronic [4] and steric [5,6,8] effects of the reactive substrates, but also by the electron density on the rhodium atom, which is influenced by the Cp' ligands. Thus, **1g** ($R = CF_3$) and **1h** (R = COOMe), which both give principally the 2,3,5-trisubstituted isomer, should favour the formation of the metallacycle **6** (scheme 2). This metallacycle should not be favoured on the basis of purely electronic factors associated with 1-alkynes [4].

The knowledge as a whole we now have of the effects of the Cp' ligands not only offers the opportunity of tuning the cobalt or rhodium half-sandwich catalyst for the synthesis of a given pyridine derivative, but may also illuminate the possible role of Cp' ligands in controlling other reactions catalysed by cyclopentadienyl derivatives of transition metals.

4. Experimental details

^1H NMR spectra were run at 200 MHz on a Varian Gemini 200 instrument using Me_4Si as internal standard. Mass spectra were obtained with a VG 70-70E instrument. GLC analyses were performed on a Perkin–Elmer Sigma 3B instrument equipped with FID, using 6 foot × 1/8 inch stainless steel columns packed with 10% Carbowax 20M + 2% KOH on Supelcoport (Supelchem) and with 3% silicon gum rubber SE 30 on Supelcoport (Supelchem). All manipulations of organometallic compounds were routinely carried out using standard Schlenk techniques under dinitrogen. Diethyl ether, tetrahydrofuran, benzene, and pentane were first refluxed and distilled from potassium in the presence of benzophenone and then from lithium aluminium hydride under dinitrogen. *N,N*-Dimethylformamide was distilled from calcium dihydride under dinitrogen. Di-μ-chlorotetrakis(η^2-ethylene)dirhodium(I) [16], (η^5-cyclopentadienyl)bis(η^2-ethylene)rhodium(I) [17], (η^5-*t*-butylcyclopentadienyl)bis(η^2-ethylene)rhodium(I) [10], bis(η^2-ethylene)(η^5-methylcyclopentadienyl)rhodium(I) [10], (η^5-chlorocyclopentadienyl)bis(η^2-ethylene)rhodium(I) [18], (η^5-carboxymethylcyclopentadienyl)bis(η^2-ethylene)rhodium(I) [10], nitrocyclopentadienylsodium [13], trifluoromethylcyclopentadienylthallium [14], and *N,N*-dimethyl-

TABLE 3. ^{1}H NMR and MS data for pyridine derivatives



Pyridine derivative	$M^+(m/e)$	^{1}H NMR
$R' = C(CH_3^g)_3$	219	7.5, d (J = 8.4), H^d; 7.0, d (J = 8.4), H^c; 7.1, d (J = 1.7), H^a;
$R'' = CH_2^fCH_3^g$		6.9, d (J = 1.7), H^b; 2.7–3.0, m, H^f; 1.2–1.5, m, H^g and H^e
$R' = Si(CH_3^e)_3$	251	7.6, d (J = 7.4), H^c; 7.3, d (J = 7.4), H^d; 7.3, d (J = 40), H^a and H^b;
$R'' = CH_2^fCH_3^g$		2.8–3.0, m, H^f; 1.3–1.4, m, H^g; 0.3, m, H^e
$R' = C_6H_5^e$	259	8.2–7.3, m, H^a–H^e; 3.0–2.8, m, H^f; 1.5–1.2, m, H^g
$R'' = CH_2^fCH_3^g$		

[a] Measured on mixtures of the two pyridinic isomers in $CDCl_3$ using Me_4Si as internal standard, and given as chemical shifts (δ), multiplicity, coupling constants in hertz: d doublet, m multiplet.

aminocyclopentadienyllithium [12] were prepared as described. 1-Hexyne (Aldrich), phenylacetylene (Aldrich), methylpropargyl ether (Aldrich) and trimethylsilylacetylene (Aldrich) were distilled under dinitrogen before use. Propionitrile (Aldrich) and *t*-butylcyanide (Aldrich) were distilled from P_4O_{10} and stored under dry dinitrogen.

4.1. Bis(η^2-ethylene)(η^5-N,N-dimethylaminocyclopentadienyl)rhodium(I) 1a

A reaction mixture containing *N,N*-dimethylaminocyclopentadienyllithium (180 mg, 1.5 mmol) and $[Rh_2Cl_2(C_2H_4)_4]$ (300 mg, 0.75 mmol) in THF (30 ml) was prepared at −30°C and kept at this temperature for 2.5 h. The mixture, on evaporation to dryness under vacuum at −30°, left a brown solid residue that was extracted with pentane (40 ml) at room temperature. The pentane extract was concentrated to 2 ml and chromatographed on an alumina column (Merck, activity grade II–III, 70–230 mesh, length 12 cm, diameter 1 cm) using pentane as the eluant. The first yellow band gave the title compound (65 mg, 16% yield) as a yellow microcrystalline solid (16% yield). ^{1}H NMR (C_6D_6): δ 4.7 (m, 2H), 4.55 (m, 2H), 2.6–3.2 (m, 4H), 2.2 (s, 6H), 0.9–1.5 (m, 4H) ppm. Anal. calcd. $C_{11}H_{18}NRh$: C, 49.45; H, 6.79; N, 5.24%. Found: C, 49.40; H, 6.70; N, 5.19%.

4.2. Bis(η^2-ethylene)(η^5-nitrocyclopentadienyl)rhodium(I) 1f

A reaction mixture containing nitrocyclopentadienylsodium (468 mg, 4 mmol) and $[Rh_2Cl_2(C_2H_4)_4]$ (300 mg, 0.75 mmol) in THF (40 ml) was kept at room temperature for 8 h. The mixture, on evaporation to dryness under vacuum, furnished a dark brown residue that was extracted with pentane (40 ml). The pentane extract was concentrated to 2 ml and chromatographed on a silica gel column (Merck, 70–230 mesh, length 8 cm, diameter 1 cm) using a pentane + diethyl ether mixture (1/1, v/v) as the eluant. The title compound was obtained as a yellow–orange microcrystalline compound by evaporation to dryness of the first orange band. None of many preparations that were carried out furnished yields exceeding 3%. ^{1}H NMR (C_6D_6): δ 5.2 (m, 2H), 4.5 (m, 2H), 0.6–1.5 (m, 8H) ppm. Anal. calcd. $C_9H_{12}NO_2Rh$: C, 40.16; H, 4.49; N, 5.20%. Found: C, 40.11; H, 4.41; N, 5.15%.

4.3. Bis(η^2-ethylene)(η^5-trifluoromethylcyclopentadienyl)rhodium(I) 1g

$[Rh_2Cl_2(C_2H_4)_4]$ (600 mg, 1.5 mmol) and THF (30 ml) were added to trifluoromethylcyclopentadienylthallium (1.01 g, 3 mmol), at −78°C. While stirring, the mixture was allowed to warm up to room temperature, then kept for 1 h at this temperature, and finally was worked up exactly as described above for the preparation of **1a**. The title compound was obtained as an orange–yellow oil (432 mg, 47% yield). ^{1}H NMR (C_6D_6): δ 4.86 (m, 2H), 4.65 (m, 2H), 2.4–3.4 (m, 4H), 0.6–1.7 (m, 4H) ppm. Anal. calcd. $C_{10}H_{12}F_3Rh$: C, 41.12; H, 4.14%. Found: C, 40.65; H, 4.12%.

4.4. General procedure for catalytic reactions

A Pyrex Carius tube (25 ml capacity) fitted with a Corning Rotaflo Teflon tap (DISA, Milan) was charged under dinitrogen with the appropriate amount of catalyst precursor and with nitrile and acetylenic compound, at room temperature. The Teflon tap was closed and the Carius tube was immersed into a thermostatted (±0.2°C) oil bath and kept at the desired temperature for the appropriate reaction time. After cooling, the reaction mixture was worked up and analysed as already described [8]. Table 3 reports the ^{1}H NMR and MS data for the pyridinic isomers which are not given in refs. 8 or 6.

Acknowledgments

This work was supported by a grant from the C.N.R. (Rome) programme 'Chimica Fine'. The authors thank the 'Centro del C.N.R. per lo studio delle macromolecole stereordinate ed otticamente attive' (Pisa, Italy) for the use of the NMR and MS facilities.

References

1 Y. Wakatsuki and H. Yamazaki, *Tetrahedron Lett.*, (1973) 3383.
2 (a) H. Bönnemann, W. Brijoux, R. Brinkmann, W. Meurers and R. Mynott, *J. Organomet. Chem., 272* (1984) 231; (b) H. Bönnemann and W. Brijoux, in R. Ugo (ed.), *Aspects of Homogeneous Catalysis*, Vol. 5, Reidel, Dordrecht, 1984, p. 77; (c) H. Bönnemann, *Angew. Chem., Int. Ed. Engl., 24* (1985) 248.
3 Y. Wakatsuki and H. Yamazaki, *Bull. Chem. Soc. Jpn., 58* (1985) 2715.
4 A. Stockis and R. Hoffmann, *J. Am. Chem. Soc., 102* (1980) 2952.
5 Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma and H. Yamazaki, *J. Am. Chem. Soc., 105* (1983) 1907.
6 P. Diversi, G. Ingrosso, A. Lucherini and D. Vanacore, *J. Mol. Catal., 41* (1987) 261.
7 G. Ingrosso, P. Ronca and P. Cioni, *Italian Patent 1164249*, May 27, 1983.
8 P. Cioni, P. Diversi, G. Ingrosso, A. Lucherini and P. Ronca, *J. Mol. Catal., 40* (1987) 337.
9 P. Diversi, L. Ermini, G. Ingrosso and A. Lucherini, *Congresso Interdivisionale della Società Chimica Italiana, CISCI 90, San Benedetto del Tronto, 30 September – 5 October 1990*, Abstracts, p. 596.
10 M. Arthurs, S. M. Nelson and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, (1977) 779.
11 (a) G. Boche, N. Mayer, M. Bernheim and K. Wagner, *Angew. Chem., Int. Ed. Engl., 17* (1978) 687; (b) M. Bernheim and G. Boche, *Angew. Chem., Int. Ed. Engl., 19* (1980) 1910.
12 M. Cheong and F. Basolo, *Organometallics, 7* (1985) 2041.
13 A. Davison and P. E. Rakita, *Inorg. Chem., 9* (1970) 289.
14 P. G. Gassman and C. H. Winter, *J. Am. Chem. Soc., 108* (1986) 4228.
15 M. E. Rerek and F. Basolo, *J. Am. Chem. Soc., 106* (1984) 5908.
16 R. Cramer, *Inorg. Chem., 1* (1962) 722.
17 R. B. King, *Inorg. Chem., 2* (1963) 528.
18 M. Arthurs, H. K. Al-Daffaee, J. Haslop, G. Kubal, M. D. Pearson, P. Thatcher and E. Curzon, *J. Chem. Soc., Dalton Trans.*, (1987) 2615.