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Intermolecular hydroamination *versus* stereoregular polymerization of phenylacetylene by rhodium catalysts based on N–O bidentate ligands

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ABSTRACT

N–O bidentate ligands, such as 8-quinolinol and aminoacids, in combination with the dinuclear precursor [{Rh(μ-OMe)(COD)}$_2$] are versatile catalytic systems. Thus, stereoregular polymerization of phenylacetylene (PA) is observed in the presence of secondary amines. Interestingly, the outcome of the catalysis changes drastically on addition of strong coordinating phosphines, giving the product of the intermolecular anti-Markovnikov hydroamination of phenylacetylene.

The large majority of rhodium catalyzed organic reactions use a variety of monodentate or bidentate phosphine ligands [1]. In contrast, rhodium complexes with mixed anionic N–O bidentate ligands have been scarcely used, in spite that some of them are readily available and relatively inexpensive, such as 8-quinolinol, one of the earliest analytical reagents, and α-aminoacids. Rhodium complexes with these ligands have been reported many years ago [2,3] but some decades elapsed until some applications in catalytic reactions were described. In particular, the interest on the investigation of the catalytic properties of rhodium aminoacidate complexes was driven by the chirality of these complexes, both on the ligand and the metal with the aim to achieve asymmetric catalytic transformations [4]. Concerning 8-quinolinolato rhodium complexes, only very recently some interesting catalytic reactions have been described [5,6]. In particular, Kakiuchi group has shown the capability of rhodium (I) quinolinolato complexes to promote several catalytic coupling reactions involving terminal alkynes [6]. Very recently our group has reported some phenylacetylene regioselective catalytic reactions promoted by rhodium (I) complexes with N-heterocyclic carbenes [7], as well as the stereoregular polymerization of phenylacetylene by rhodium (I) complexes with hemilabile phosphine ligands [8]. In this communication we report on the catalytic activity of rhodium (I) complexes with 8-quinolinolato and aminoacidate ligands in phenylacetylene transformations.

It has been reported that the bridging methoxo group of [{Rh(μ-OMe)(diolefin)}$_2$] starting complexes (diolefin = COD, NBD, TFB) is capable of taking a proton from any anionic acid bidentate ligand whose pK_a is stronger than that of methanol [9–11]. The resulting complexes can be isolated or simply used *in situ*. This is the case with the bidentate ligands used in this work. Thus, we have realized that the *in situ* reaction of [{Rh(μ-OMe)(COD)}$_2$] [9] (COD = 1,5-cyclooctadiene) with 8-quinolinol (HQ) afforded quantitatively the known complex [Rh(Q)(COD)] [2a,d] (1) upon release of methanol (NMR evidence, see Supporting Information). The yellow solutions obtained by following this protocol were utilized as such in the study of both the reactivity and catalytic performance of these species.

Interaction of 1 with phenylacetylene (PA) did not transform the alkyne in any observable way under regular conditions. However, when a secondary amine (such as piperidine) was present in the medium with catalytic amounts of solutions of 1, we observed the gradual consumption of PA at room temperature; however, we did not observe the presence of any organic compound by GC measurements. Work-up of the catalytic solutions by adding methanol afforded orange solids that were further characterized as stereoregular polyphenylacetylene (PPA) by using size-exclusion chromatography and NMR techniques. Given the unexpected nature of these catalytic reactions, we studied them in some detail. Table 1 shows the data obtained in the stereoregular polymerization of PA by using [{Rh(μ-OMe)(diolefin)}$_2$]/HQ/amine (diolefin = COD, NBD, TFB; NBD = 2,5-norbornadiene; TFB = tetrafluorobenzobarrelene) catalytic mixtures in toluene.

As it can be deduced from Table 1, the use of the methoxo- or the parent amido-bridged [12] COD-containing complexes as catalytic precursors does not have any significant effect in terms of catalytic performance (entries 1 and 3), since both afford polymers with comparable properties. In this line, the nature of the amine does not seem to

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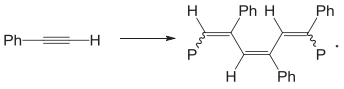
influence on the polymer properties (entry 2, pyrrolidine used as amine). The addition of bulky phosphines (PCy_3, $P(o\text{-}OMeC_6H_4)_3$) to the *in situ* preformed [(Q)Rh(COD)] complex also rendered polymeric PPA under the same conditions (entries 4 and 5, respectively), although in less yields than those obtained with the phosphine-free ternary catalytic systems. Changing of the diene in the methoxo starting dinuclear complexes $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ from COD to other known diolefins with higher π-acidity such as NBD or TFB did have a pronounced effect on the outcome of the catalytic reactions. As a matter of fact the polymerization reactions proceeded much faster with the NBD and TFB-containing complexes than those with the system containing COD, as confirmed by direct comparison of the kinetic experiments performed with these precursors by monitoring PA consumption (see Figure S1). These observations, in line with some reports from Masuda and coworkers on some related cationic rhodium complexes [13,14], indirectly point out that the diene ligand should be present in the active catalytic rhodium species, since it affects both the efficiency of the catalytic process and the nature of the PPAs obtained (M_w and M_n). More precisely, the NBD- and TFB-containing catalytic systems increase the efficiency indexes of the reactions (I_{eff}; entries 6 and 7, respectively), which in general are modest and comparable to those obtained with other reported rhodium catalytic systems based on chelate ligands [15]. Interestingly, the polydispersity ratios observed do not seem to depend on the nature of the diene, and were found to be in general quite good (1.3–2.0). The analysis of the orange polymers by NMR spectroscopy showed them to be stereoregular (see Figure S2); in all cases they showed a significant sharp singlet at 5.84 ppm in their ^1H NMR spectra and peaks at 131.9 and 139.2 ppm in the $^{13}C\{^1H\}$ NMR spectra corresponding to the "CH═C" functional groups.

Table 1
Catalytic data in stereoregular in Rh-catalyzed polymerization of PA



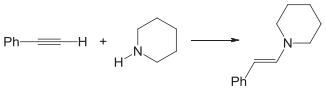
Entry	Catalytic system	M_n	M_w	M_w/M_n	Conv. (%)	I_{eff}[a]
1	$[\{Rh(OMe)(COD)\}_2]$/HQ	79,600	123,000	1.55	81	1.02
2	$[\{Rh(OMe)(COD)\}_2]$/HQ	96,800	170,000	1.76	90[b]	0.93
3	$[\{Rh(NH_2)(COD)\}_2]$/HQ	84,150	147,800	1.76	88	1.05
4	$[\{Rh(OMe)(COD)\}_2]$/HQ	15,250	38,960	2.55	39[c]	6.56
5	$[\{Rh(OMe)(COD)\}_2]$/HQ	26,900	71,100	2.64	86[d]	3.72
6	$[\{Rh(OMe)(NBD)\}_2]$/HQ	79,600	167,000	2.10	100[e]	1.26
7	$[\{Rh(OMe)(TFB)\}_2]$/HQ	64,000	83,120	1.30	100[f]	1.56

Conditions: RT, in toluene, 24 h, 10% mol [Rh], piperidine (3 mmol), except in entry 2, where pyrrolidine was used.
[a] Initiation efficiency, $I_{eff} = M_{theor} / M_n \times 100$; where $M_{theor} = [PA]_0 / [Rh] \times MW_{phenylacetylene} \times$ polymer yield [18].
[b] Pyrrolidine.
[c] Two molar-equiv. of PCy_3 added.
[d] Two molar-equiv. of $P(o\text{-}OMeC_6H_4)_3$ added.
[e] Reaction time 3.5 h.
[f] Reaction time 0.5 h.

As mentioned earlier, the addition of steric-demanding phosphines to the ternary catalytic mixture composed of $[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/amine did not have apparently any effect on the polymer structures. The yields of these polymerization reactions were however relatively low, particularly in the case of the sterically demanding $P(o\text{-}OMeC_6H_4)_3$ phosphine, in which the *o*-methoxo substituent precludes an easy coordination to the metal center. The situation changes drastically when strong-coordinating phosphines such as the ubiquitous PPh_3 or $P(p\text{-}OMeC_6H_4)_3$ are present in the formation of the catalytic precursors: under given conditions, piperidine adds to PA affording the corresponding enamine through an intermolecular hydroamination catalytic process and no polymerization was observed. In this line, recent reports by Kakiuchi and coworkers showed that the isolated $[Rh(Q)(PR_3)_2]$ mononuclear complexes were active species in catalytic transformations of terminal alkynes such as hydroalkoxylation [6a], hydroamination [6b], cycloaddition [6c] and dimerization [6d] that showed an unexpected activity of these quinolato rhodium complexes.

Therefore we carried out our own study focused on assessing the catalytic performance of the *in situ* ternary systems composed of $[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/$PR_3$ (ratio 1:2:4) in this catalytic transformation that accounts for an 100% atom economy and affords enamines, which are themselves a valuable source to be used for further transformation to other N-containing compounds. NMR experiments showed that replacement of the diene takes place fast and renders the bis(phosphine) complexes of the type $[Rh(Q)(PR_3)_2]$ quantitatively (see Supporting Information). Table 2 shows the available catalytic data obtained from the testing of HQ and 5-chloro-8-hydroxyquinoline (5-Cl-HQ) derivatives as bidentate ligands for the rhodium-catalyzed hydroamination of PA with piperidine.

Table 2
Catalytic data in intermolecular hydroamination of PA with piperidine.[a]



Entry	Catalytic system	T (°C)	Time (h)	Conv. (%)	TOF (h^{-1}) (%)[b]
1	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/$PR_3$	RT	24	100	1.3 (51%)
2	$[\{Rh(\mu\text{-}NH_2)(COD)\}_2]$/HQ/$PR_3$	RT	24	100	1.2 (47%)
3	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/$PR_3$	RT	24	92[c]	1.3 (52%)
4	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/$PR_3$	40	24	100	4.4 (44%)
5	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/$PR_3$	RT	24	33[d]	0.1 (33%)
6	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/$PR_3$	RT	24	63[e]	0.4 (46%)
7	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/$PR_3$	RT	48	43[f]	0.2 (41%)
8	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/HQ/$PR_3$	RT	48	28[g]	0.3 (28%)
9	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/5-Cl-HQ/$PR_3$	RT	24	100	2.3 (35%)
10	$[\{Rh(\mu\text{-}OMe)(COD)\}_2]$/5-Cl-HQ/$PR_3$	40	8	100	9 (45%)

[a] Conditions: 0.05 mmol (10 mol%) [Rh], 0.1 mmol HQ (or 5-Cl-HQ), 1 mmol PA, 3 mmol piperidine, 0.2 mmol $P(p\text{-}OMeC_6H_4)_3$, toluene (2 mL), mesitylene (1.8 mmol) as internal standard.
[b] TOF = Mol PA/mol Rh/h, calculated at the indicated PA consumption (%).
[c] 1 mmol Cs_2CO_3 added.
[d] 0.2 mmol PPh_3.
[e] 0.2 mmol $P(p\text{-}FC_6H_4)_3$.
[f] THF used as solvent.
[g] 2% mol [Rh].

The reactions proceeded at room temperature and in all cases they were regioselective rendering the *E*-enamine showed above, the product of an anti-Markovnikov amine addition. Several trends were established upon changing key catalytic parameters in the model reaction. The need of using a loading of 10% [Rh] of catalyst became evident from the first screening experiments in order to achieve quantitative conversions to the enamine (compare entries 1 and 8). On the other hand, the use of PPh_3 or $P(p\text{-}FC_6H_4)_3$ as external ligands in these reactions gave only moderate yields of the enamine after 24 h at room temperature (entries 5 and 6, respectively). The catalytic performance was found to be substantially increased by shifting to the more basic $P(p\text{-}OMeC_6H_4)_3$, which was then chosen as the added phosphine in the catalyses. Again, the use of the amido precursor $[\{Rh(\mu\text{-}NH_2)(COD)\}_2]$ or the methoxo-bridged analog in combination with HQ/$P(p\text{-}OMeC_6H_4)_3$ in these catalytic processes did not change the activity of the resulting catalytic species in terms of yields of enamine (entries 1 and 2), which indirectly proves that the bridging ligands (NH_2 and OMe) are the key for deprotonating the HQ derivatives and subsequently coordinating them to rhodium. On the other hand, the use of an external weak base (such as Cs_2CO_3) does not really affect the catalytic performance, although slight less yields of the enamine are obtained (entry 3). In this line the shifting to more polar THF as solvent in the catalytic reactions was not beneficial in terms of yield, since a drop to 43% was achieved (compare entries 1 and 7). A subtle change in the HQ skeleton does have a noticeable positive effect in catalysis; more specifically, the shifting from HQ to 5-Cl-HQ provides quantitative conversions to the

E-enamine (see entries 9 and 10), as does the HQ-containing system; however an increase in the TOF (measured at approximately 50% conversion of PA) is observed (compare entries 1 and 9). Another parameter that has an impact in the TOF values is the temperature; in this way, when the catalytic reactions are carried out at 40 °C, the TOF increases from 1.3 to 4.4 h^{-1} (HQ-based system, entries 3 and 4) and from 2.3 to 9 h^{-1} (5-Cl-HQ-based system, entries 9 and 10), without the loss of the regio- and chemoselectivity.

Following our interest on the catalytic activity of transition metal complexes with aminoacidato ligands [4a,16], we screened some natural-occurring aminoacids as N–O scaffolds for active rhodium species under the conditions optimized as described above for intermolecular hydroamination (Table 2). In all cases, the pre-formation of the catalytic system was achieved *in situ* by mixing complex [{Rh(μ-OMe)(COD)}$_2$] and the corresponding aminoacid and the phosphine P(*p*-OMeC$_6$H$_4$)$_3$, which resulted to be better ligand for hydroamination than PPh_3 in terms of catalytic activity. During the course of this work, we realized however that the influence of both the temperature and the nature of the aminoacidate ligand were crucial for the outcome of the catalytic reactions. Exploratory studies by using the aminoacid *L*-proline as bidentate ligand in the Rh-catalyzed hydroamination of PA with piperidine (chosen as the model catalytic reaction throughout this report) allowed us to realize that both polymerization and intermolecular hydroamination were competitive processes within a given range of temperatures and conditions. This is true for all the α-aminoacid tested, although this competition was observed at different rates for each specific aminoacid. Several tuning experiments led us to detect, however, that the increasing of the temperature inhibited polymer formation favoring in turn alkyne hydroamination (see figure S3).

We performed several catalytic experiments to find out that in general, working at 100 °C suppresses completely the polymerization mechanism allowing the intermolecular hydroamination to be the only operative process, maintaining under these conditions the *anti*-Markovnikov regioselectivity observed at RT in the Q-based systems (in comparison, working at less temperatures led to polymer formation). In this way, the aminoacids *L*-phenyl glycine and *L*-phenyl alanine are the less suitable ligands for hydroamination, since under optimum conditions (100 °C and a [PA]/[piperdine] = 1/3) polymer formation cannot be inhibited (12% and 44% polymer obtained, respectively). However, the choice of these conditions with *L*-threonine, *L*-alanine, *L*-leucine, *L*-proline and *L*-histidine as N–O ligands gave excellent catalytic performance in the addition reaction and no polymer was formed. The reactions were fast and regioselective, affording in all cases the corresponding *anti*-Markovnikov *E*-enamine in quantitative yields. The calculation of the TOF values at this temperature proved to be very difficult to achieve because of the high activity and reaction rates showed by the catalysts. We were able, however, to calculate the TOF value for the *L*-histidine aminoacid, which was found to be very high (510 h^{-1} at 85% of PA conversion). This value is around 40 times superior to that observed with the 5-Cl-HQ systems (TOF = 9 h^{-1} at 40 °C), which is indicative of a more productive catalytic behavior.

The [{Rh(OMe)(COD)}$_2$]/aminoacid systems in the presence of amines and the absence of phosphines act only as polymerization catalysts, similarly to the behavior observed for the [{Rh(OMe)(COD)}$_2$]/HQ systems. Some experimental evidences indicate that the diene is present on the catalyst during polymerization. These facts allow us to speculate about the mechanism operative in this process. Under the catalytic conditions used, π-coordination of PA to rhodium is a plausible process to occur, and in this situation the deprotonation of the terminal alkyne hydrogen atom by the external amine would render most probably Rh–alkynyl species that are known for its ability of acting as powerful precursors for alkyne polymerization [17,18]. On the other hand, we lack information enough to propose a viable mechanism for the hydroamination reactions. At this point, we assume that the formation of bis(phosphine) square-planar species of the type [(N–O)Rh(PR$_3$)$_2$] is responsible for the hydroamination activity (since the diolefin is lost in the process). These unsaturated and electronic rich species may be in principle able to bind PA by π-coordination, resembling one of the proposed first steps in the polymerization. However in the bis(phosphine) metallic fragment, a possible nucleophilic attack of the amine to this intermediate (or rather to its vinylidene-rhodium isomer) cannot be excluded.

In summary, we have shown in this piece of work the activity of N–O rhodium-based systems for catalytic processes of different nature. We were able to tailor the reaction conditions in order to favor one or the other catalytic outcome. In this way, polymerization is operative in the presence of an amine and the absence of phosphines at room temperature. Thus, the use of these P-donor ligands at 100 °C, on the other hand, inhibits polymerization giving place to the hydroamination product in a regioselective way. Further work designed to assess the scope of this addition reactions is currently under study.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.11.034.

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