Diphosphite ligands derived from carbohydrates as stabilizers for ruthenium nanoparticles: promising catalytic systems in arene hydrogenation†

Aitor Gual,[a] M. Rosa Axet,[b] Karine Philippot,*[b] Bruno Chaudret,[b] Audrey Denicourt-Nowicki,[c] Alain Roucoux,*[c] Sergio Castillon[d] and Carmen Claver*[a]

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Ruthenium nanoparticles (RuNPs) were prepared through the hydrogenation of [Ru(COD)(COT)] (COD = 1,5-cyclooctadiene, COT = 1,3,5-cyclooctatriene) in the presence of diphosphites derived from carbohydrates as stabilizing agents, and interestingly, structural modifications of the diphosphite backbone were found to influence nanoparticle size and dispersity, as well as their catalytic activity in arene hydrogenation.

Arene hydrogenation represents an important chemical process for the synthesis of fine chemicals,[1] with a wide range of applications from laboratory to industrial scale processes. The reaction is usually performed using heterogeneous catalysts, which are easily separated from the reaction products and recycled. Although rhodium catalysts have proved to be more active than other metals (such as Pd and Ni), less expensive ruthenium catalysts have also been successfully used in industrial processes.[2]

Homogeneous catalysts, for which the activity and the selectivity of the reactions are easily tunable by choosing suitable ligands, have also been reported for this process. However, when the nature of these homogeneous arene hydrogenation catalysts was later reinvestigated, it was shown that the active species were colloidal.[3]

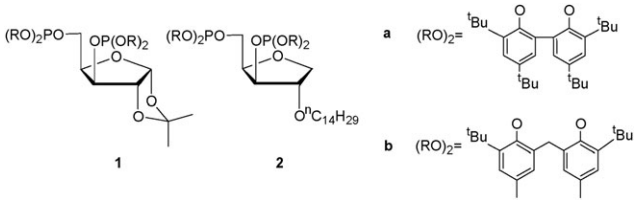
Nowadays, soluble metal nanocatalysts are considered as references in the hydrogenation of monocyclic arenes. Several different types of rhodium and ruthenium nanoparticles (NPs) have been reported as efficient catalysts under mild conditions.[4] The stabilizing agent used is chosen according to the "organic" or "aqueous" nature of reaction media, which generally depends on the metal precursor. Among the methods used to prepare metal NPs,[5] the decomposition of organometallic precursors in the presence of ligands as stabilizing agents provides a clean and efficient route for the synthesis of NPs under mild conditions.[6]

The use of chiral ligands as stabilizing agents for RuNPs offers the possibility of modulating the environment at the surface of the NPs through electronic or steric modifications. These variations can thus influence the catalytic properties of the NPs. For this purpose, we have used modified furanose ligands of *C*1-symmetry, such as **1** and its derivatives, in homogeneous asymmetric catalysis.[7] More recently, diphosphite **1a** was used as a stabilizing agent for PdNPs, and furthermore, these PdNPs were applied with success in asymmetric allylic alkylation.[8]

Here, we report the stabilization of new RuNPs by diphosphite ligands derived from carbohydrates **1** and **2**, and their preliminary use in the asymmetric hydrogenation of prochiral methylanisoles (Scheme 1). These ligands were selected because of their successful enantioselective discrimination in several catalytic processes and easy modification.[7,8] We also describe the influence of the ligand backbone structure on the size and dispersion of the RuNPs, as well as on their catalytic activity in hydrogenation of prochiral arenes, such as 3-methylanisole (**3**) and 2-methylanisole (**5**) (Scheme 2).

To the best of our knowledge, only a few papers have reported on this area, but no significant enantiomeric excesses were achieved.[6b,9]

The furanose derivative diphosphites **1** and **2** were used here to stabilize RuNPs. The synthesis of diphosphite **1a** has been previously reported,[7,8] and diphosphite **1b** was synthesized through similar procedures. Diphosphite **2b** can be easily prepared from 1,2-*O*-isopropylidene-D-xylose (see ESI†). Of particular interest, the selective reduction of the 1,2-*O*-isopropylidene acetal provides a hydroxyl function. A lipophilic chain was introduced by etherification of the hydroxyl function in a position away from the coordinating P atoms. Thus, the design of the diphosphite **2b**, containing a tetradecyl chain, was inspired by previous results, demonstrating the effect of such chains in non-coordinating stabilizers on the size and dispersion of the nanoparticles.[10]



Scheme 1 Diphosphite ligands derived from carbohydrates.

[a] *Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel.lí Domingo, s/n 43007 Tarragona, Spain. E-mail: carmen.claver@urv.net; Fax: +34 977 559563; Tel: +34 977 559575*
[b] *Laboratoire de Chimie de Coordination, UPR CNRS 8241, route de Narbonne, 31077 Toulouse, France*
[c] *Equipe Chimie Organique et Supramoléculaire, UMR CNRS 6226 «Sciences Chimiques de Rennes», Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc, 35700 Rennes, France*
[d] *Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Marcel.lí Domingo, s/n 43007 Tarragona, Spain*
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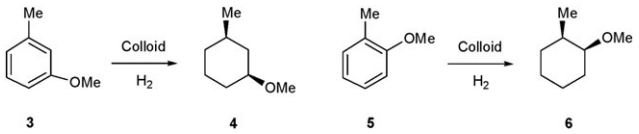
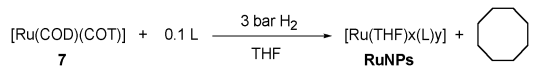


Scheme 2 Hydrogenation of prochiral methylanisoles catalyzed by RuNPs.



Scheme 3 Synthesis of RuNPs by the decomposition of Ru(COD)(COT) in the presence of ligand (**L**).

The RuNPs reported here were synthesised according to previously reported procedures.[10b,11] [Ru(COD)(COT)] (**7**) was decomposed in THF at room temperature in the presence of the appropriate ligand (**1** or **2**; Ru/L = 10 : 1) under 3 bar of H_2 (Scheme 3). The RuNPs were isolated as black powders after pentane precipitation.

Transmission electron microscopy (TEM) revealed the presence of small particles of 1 to 4 nm in size, as seen in Fig. 1, with a hexagonal compact (hcp) structure for the ruthenium bulk (WAXS). The mean size of the nanoparticles (d_{mean}) is clearly influenced by the diphosphite structure, being smaller for **Ru/2b** (d_{mean} = 1.8 ± 1.0 nm) than for **Ru/1b** (d_{mean} = 2.9 ± 1.5 nm) and **Ru/1a** (d_{mean} = 4.0 ± 2.0 nm). Thus, the use of diphosphite moiety **b** (**Ru/1a** *vs.* **Ru/1b**), and the introduction of a lipophilic chain in the diphosphite backbone (**Ru/1b** *vs.* **Ru/2b**) enables RuNPs of smaller size and good dispersity to be achieved.

These RuNPs were tested in the hydrogenation of **3** and **5** at room temperature, with a substrate/Ru ratio of 100 : 1, for 15 h. The conversion and the selectivity were determined by chiral gas chromatography (GC) analysis. The influence of the ligand, and parameters such as solvent and pressure, on the hydrogenation of prochiral **3** is presented in Table 1.

No conversion was observed when the reaction was carried out in THF or CH_3CN (runs 1 and 2, Table 1), but an efficient activity was measured in pentane (run 3, Table 1). This difference may be explained by competitive adsorption between the substrate and the solvent (THF and CH_3CN) at the NP surface that prevents the reaction. The influence of the ligand structure was thus explored in pentane. The **Ru/1b** system displayed a higher catalytic activity than the **Ru/1a** system (runs 3 and 4, Table 1). This result indicates that small changes in the diol moiety influence the activity of the colloid. Furthermore, and more significantly, the **Ru/2b** system displays a higher catalytic activity than **Ru/1b** (runs 5 and 6, Table 1). This result could be explained by a more highly active surface due to the smaller size of the NPs with diphosphite **2b**, and by a better dispersion of the particles in solution, which would lead to easier access to the active sites. Finally, a decrease in H_2 pressure from 10 to 2 bar with the most promising system, **Ru/2b**, resulted in a decrease in activity. However, under these conditions, the conversion is still significant (runs 3 and 7, Table 1). In all cases, formation of the *cis*-product was favoured. In contrast with previously reported related RuNPs stabilized by oxazoline, the diphosphite-stabilized RuNPs reported here show the opposite selectivity and higher activity.[11]

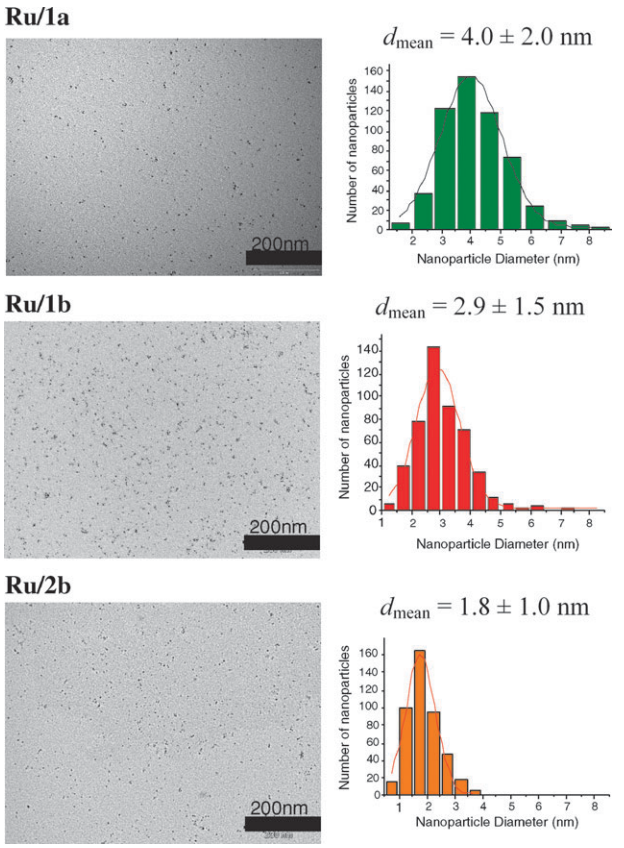


Fig. 1 TEM micrographs and the corresponding size histograms of nanoparticles **Ru/1a**, **Ru/1b** and **Ru/2b**.

The influence of the ligand structure on the hydrogenation of **5** was then investigated, and the results are reported in Table 2. A similar trend to that shown in Table 1 was observed. Interestingly, the **Ru/2b** system showed the most promising performances in terms of catalytic activity when compared to **Ru/1b** and **Ru/1a** nanocatalysts (runs 1, 2 and 3 *vs.* 4 and 5, Table 2). Moreover, the sole product exhibited a *cis*-conformation, indicating 100% diastereoselectivity.

Table 1 Hydrogenation of **3** with RuNPs[a]

Run	RuNPs/ Solvent	P_{H_2}/ bar	Conversion (%)[b]	Selectivity (%)[b,c]	TON[d]
1	**Ru/1a**/THF	40	0	—	—
2	**Ru/1a**/CH_3CN	40	0	—	—
3	**Ru/1a**/Pentane	40	39	78	46
4	**Ru/1b**/Pentane	40	100	79	98
5	**Ru/1b**/Pentane	10	13	81	13
6	**Ru/2b**/Pentane	10	100	79	87
7	**Ru/2b**/Pentane	2	48	73	42

[a] Substrate/Ru = 100 : 1, **3** = 1.24 mmol, 10 mL solvent, T = 20 °C. [b] Substrate conversion and selectivity determined by GC using a chiral column: Chirasil-Dex CB. [c] *cis*-Product **4**. [d] TON = mol of hydrogenated product/mol of Ru metal in the NPs based on elemental analysis.

Table 2 Hydrogenation of **5** with RuNPs[a]

Run	RuNPs/ Solvent	P_{H_2}/ bar	Conversion (%)[b]	Selectivity (%)[b,c]	TON[d]
1	**Ru/1a**/Pentane	40	14	100	17
2	**Ru/1b**/Pentane	40	100	100	98
3	**Ru/1b**/Pentane	10	65	100	64
4	**Ru/2b**/Pentane	10	77	100	67
5	**Ru/2b**/Pentane	2	39	100	34

[a] Substrate/Ru = 100 : 1, **5** = 1.24 mmol, 10 mL solvent, T = 20 °C. [b] Substrate conversion and selectivity determined by GC using a chiral column: Chirasil-Dex CB. [c] *cis*-Product **6**. [d] TON = mol of hydrogenated product/mol of Ru metal in the NPs based on elemental analysis.

In conclusion, we have demonstrated that by using appropriate diphosphites, it is possible to control the size and dispersity of RuNPs. Thus, the modification of the diol moiety, and even more significantly the introduction of a long lipophilic chain, stabilizes smaller and better dispersed NPs that are more soluble in organic media. Moreover, the **Ru/2b** nanocatalyst provides good results in terms of activity and diastereoselectivity (*cis*/*trans* ratio). Nevertheless, no significant enantioselectivity was observed. Further investigations are ongoing to design new carbohydrate ligands and improve the properties of such colloidal catalytic systems.

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