From hydroxycetylammonium salts to their chiral counterparts. A library of efficient stabilizers of Rh(0) nanoparticles for catalytic hydrogenation in water.

Audrey Denicourt-Nowicki and Alain Roucoux

[a] Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, F-35708 Rennes cedex 7, France
[b] Université Européenne de Bretagne

Corresponding Author Email:

Audrey.Denicourt@ensc-rennes.fr
Alain.Roucoux@ensc-rennes.fr

Abstract

Nowadays, the nanometer-size and shape control of metallic species remains a strategic research area in material development due to their particular physical and chemical properties. Among their various applications, catalysis has emerged as one of the most pertinent due to its large range of potentialities. From now on, noble metal nanoparticles (NPs) are considered as an unavoidable family of catalysts, at the border between heterogeneous bulk materials and metal complexes. The design of stable noble metal nanoparticles in various solvents such as ionic liquids, fluorous or organic media has become a concern over the past few years. Nevertheless, for economic and ecological purposes, the development of green approaches remains an active research area, as well as the reusability of nanocatalysts. In this context, the stabilisation in colloidal suspension of nanoparticles providing a catalyst recycling thanks to a biphasic approach constitutes an efficient alternative to the heterogeneization of the nanocatalysts. Among the various water-soluble protective agents, easily modulated surfactants proved to be attractive candidates to efficiently stabilize catalytically active nanospecies in aqueous media. Here, we review our recent progresses in the hydrogenation of benzene derivatives by rhodium nanoparticles which were capped by an ammonium salts bearing an achiral or chiral polar head group.

Keywords: rhodium, nanoparticle, surfactant, ammonium, hydrogenation, water, biphasic catalysis, aqueous phase

I. Introduction

In a context of "environmental catalysis" and the development of sustainable processes, the use of efficient and cleanly reusable catalytic materials,[1-2] as well as more benign reaction media (e.g., water, fluorous and ionic liquids media, supercritical CO_2)[3], proved to be crucial parameters. Among a large variety of catalysts, metallic nanoparticles (MNPs), finely dispersed in water [4-7], have been considered with great interest, potentially offering relevant catalytic activities for various reactions, as well as interesting selectivities, owing to a great number of potential active sites and an original surface reactivity [8-10]. Moreover, water-soluble nanospecies have appeared as sustainable alternatives to usual molecular catalysts [11-13], potentially being easily reusable through a biphasic water/substrate approach [14-15].

Originally, rhodium(0) nanoparticles, prepared in neat water, have showed remarkable potential in arene hydrogenation reactions, presenting high catalytic activities and recyclabilities in mild conditions [16-17]. A crucial parameter in the MNPs synthesis remains their stabilization by protective agents, chosen according to the reaction media, to avoid their aggregation in bulk materials. In neat water, among the various water-soluble capping agents (polymers, cyclodextrins, dendrimers, etc.) [4], ammonium surfactants have been widely used as efficient protective agents thanks to their amphiphilic character, thus providing electrosteric stabilization of particles within the aqueous phase and producing size -controlled nanospecies with a good reproducibility.[18-20]

In a first part, we will mainly focus on the use of hydroxycetylammonium salts as pertinent capping agents of Rh^0 NPs for arene hydrogenation reactions in pure biphasic liquid-liquid conditions, namely when a liquid substrate constitutes the only organic phase (no solvent added). Secondly, the use of optically ammonium salts for the development of asymmetric hydrogenation reactions will be described as a challenging research area in nanocatalysis.

II. Hydroxycetylammonium salts: a toolbox for hydrogenation nanocatalysts

Quaternary ammonium salts [20] proved to be relevant capping agents for the efficient stabilization of transition metal nanospecies in various catalytic reactions under pure biphasic conditions.

In recent years, we have designed a library of *N*-(hydroxyalkyl)cetylammonium salts (HAA16X), bearing lipophilic chain of a 16 carbons, which could be easily modulated according to the polar head (mono- or poly-hydroxylated, with various lengths), as well as the counter-

ion thanks to anionic metathesis [21-23]. These ionic salts (Figure 1) could be readily synthesized by quaternarization of *N*,*N*-dimethylalcoholamine with the appropriate halogenoalkane for the HEA or HPA or HBA series [21, 24-26] or of hexadecylamine with chloroethanol for THEA16Cl [27]. In most cases, these ammonium compounds present a surfactant's behaviour and self-aggregate into cylindrical (rods) or spherical micelles above the critical micellar concentration (cmc) [21, 25].

Figure 1. near here

These *N*-(hydroxyalkyl)cetylammonium salts have been used as relevant capping agents of aqueous Rh^0 NPs suspensions. The nanospecies were easily obtained by chemical reduction of rhodium trichloride with sodium borohydride in dilute aqueous solution of quaternary ammonium salts (Figure 2). From optimization studies, a highly hydrophilic hydroxylated polar head, combined with a sufficiently lipophilic C16 chain, as well as a [Surfactant]/[Metal] molar ratio of 2 [28], offers effective electrosteric stabilization, avoiding NPs aggregation within the aqueous phase and achieving pertinent catalytic activities. The surfactant's nature has an influence on the particle morphology and size. Spherical geometries were largely observed with counter-ions such as halides or hydrogenocarbonate displaying a mean size in the range 2-3 nm and dentritic structures up to 6 nm in size with fluoride derivatives such as F^-, BF_4^- and $CF_3SO_3^-$ [21, 28]. Moreover, the presence of the cationic ammonium salt at the particle surface was demonstrated by positive potential zeta ζ values as well as its self-organization in bilayer structure (Figure 2) by thermogravimetric analyses [21]

Figure 2. near here

Ammonium-capped Rh^0 NPs, acting as micellar nanoreactors, are relevant catalysts for pure biphasic hydrogenation of various lipophilic arene derivatives [29], in mild conditions (atmospheric hydrogen pressure, room temperature) with high TurnOver Frequency (TOF) values. Rh^0 colloids capped with various protective agents are compared in benzene reduction (Table 1). For easy comparative comparison with the literature, the TurnOver Frequencies (TOFs) were determined considering an optimized reaction time for a total conversion of the substrate and the total introduced metal. Based on the fraction of active atoms located on the nanoparticle surface, these TOFs were clearly underestimated but were suitable from an economic point of view [30]. Nevertheless, even if the topology and the fraction of surface atoms could be modified during the catalytic process owing to the surface restructuration

[31], a corrected TurnOver Frequency was also calculated, in the case of spherical particles, according to the number of surface atoms to get a better estimation of the catalytic performances according to the particle size. Based on the literature data [30], considering that ca. 52 and 40% of Rh^0 atoms are present at the particle surface for an average diameter of 2.1 nm (HEA16Cl), and 3.0 nm (HPA16Cl, THEA16Cl), the corrected TOF values are respectively of 154 h^{-1} for HEA16Cl, 150 h^{-1} for HPA16Cl and 750 h^{-1} for THEA16Cl [25]. TOF values seem to be influenced by the nature of the protective agents, and thus by the morphologies obtained.

Table 1. near here

These ammonium-capped nanocatalysts presented also remarkable activities towards the reduction of various alkylated or functionalized aromatics. The reduction of disubstituted arenes, such as xylene isomers, affords predominantly the thermodynamically less stable *cis*-product, as usually observed with heterogeneous catalysts [32], through a "continuous" coordination of the substrate to the catalyst's surface during the reaction [33-34], thus favouring the addition of hydrogen atoms to only one face of the arene. According to recent works [25, 35] based on the use of the pertinent Rh^0@HEA16Cl system as reference's nanocatalyst, some results are given in Table 2

Table 2. near here

In all cases, the nanocatalysts dispersed in aqueous media could be easily recycled during several runs (up to 5 runs) by simple extraction of the product with an organic solvent, with reproducible TOFs and without metal leaching. These investigations have been previously described in the reduction of anisole, using Rh^0@HEA16Cl catalytic system [28].

To resume, quaternary *N*-(hydroxyalkyl)ammonium salts, used as capping agents of Rh^0 NPs, provide active and reusable micellar nanoreactors for pure biphasic arene hydrogenation under mild pressure and temperature conditions.

III. Towards asymmetric catalysis: Optically active ammonium counterparts

Although water soluble metal NPs proved to be relevant catalysts in many reactions owing to their unique surface reactivities [4], their use as effective catalytically active species in

asymmetric processes, through their stabilization by optically pure capping agents, still remains a challenge in nanocatalysis [36]. Few examples of metal nanospecies modified by chiral ligands in organic media were described in asymmetric allylic alkylations [37-38] or arene hydrogenations [39-40]. However, finely dispersed metal NPs in neat water, capped by water-soluble protective agents, still remain less explored.

Following the electrosteric approach for NPs stabilization, we have developed novel water-soluble and optically active hydroxylated ammonium salts [41-42] based on *N*-methylephedrine, *N*-methylprolinol or cinchona derivatives as polar heads, combined with various counter-ions, such as bromide, or (*S*)- or (*R*)-lactate (Figure 3).

Figure 3. near here

These optically active surfactants were easily synthesized from commercially available precursors, following the same procedures as those reported for *N*-(hydroxyalkyl)cetyl ammonium salts. Moreover, the length of the lipophilic chain was modulated to provide efficient water-solubility, according to the polar head. These salts were used as efficient protective agents of spherical Rh^0 NPs [41-42], with mean sizes ranging from 0.8-2.5 nm according to the polar head group (Figure 4) and presenting a positive apparent charge in solution (+38 to 73 mV).

Figure 4. near here

III.**1. Enantioselective hydrogenation of ethylpyruvate**

In a first set of experiments, the chirally modified Rh^0 nanocatalysts were investigated in the asymmetric ethylpyruvate hydrogenation, as a model reaction, in neat water. Various parameters, such as the counter-ion in the *N*-methylephedrine series [41] and the polar head in the bromide series [42], were studied, as well as the use of cinchonidine, already known as a pertinent external chiral inducer in the presence of Pt^0 NPs capped with an achiral surfactant [43]. The results are gathered in Table 3, considering an optimum 40 bar H_2.

Table 3. near here

First, the steric hindrance of the optically active polar head seems to control the asymmetric induction, best results being achieved with the *N*-methylephedrinium salt while QCl, QCD and *N*MeProl derivatives gave poor results (*e.e.* < 5%). In the (-)-*N*MeEph12X series, the bromide and the (*S*)-lactate counter-ions are the most effective with *e.e.* values up to 13%

(Entries 1 and 4). The addition of (-)-cinchonidine as an external inducer did not significantly improve the enantiomeric excess (Entry 12). The lack of steric hindrance around the Rh^0 particles, as well as the dynamic behavior of the ammonium salt at the metal's surface, could explain the low asymmetric induction.

III.2. Stereoselective hydrogenation of arenes

Stereoselective hydrogenation of monocyclic polysubstituted arenes constitutes a smart synthetic method to optically active cyclohexyl compounds but remains one of the last challenging reactions in asymmetric catalysis owing to the lack of efficient catalysts [44-45]. In the drive towards ecologically-sound processes, heterogeneous catalytic asymmetric approaches are promising. First attempts have reported the use of either a chiral lipophilic amine or a chiral auxiliary covalently bound to the substrate, achieving only low asymmetric induction in the hydrogenation of 2-methylanisole [46-47].

Recently, the previously described Rh^0 NPs, capped with optically active ammonium salt [42], have been evaluated in the pure biphasic reduction of 3-methylanisole as model substrate, under 40 bar H_2 (Table 4).

Table 4. near here

These nanocatalysts present good catalytic activities towards the hydrogenation of 3-methylanisole, as well as high diastereoselectivity in favour of the *cis*-product, but without any asymmetric induction. This preferential *cis* selectivity, already described for heterogeneous catalysts, seems to depend on the chiral head groups, in the following order: (+)-QCD ≈ (+)-QCI > (−)-*N*MeEph ≈ (−)-*N*MeProl. The chiral counter-ion, (*S*)- or (*R*)-lactate$^-$ counter-ion, has no influence on the *cis*/*trans* ratio and on the no asymmetric induction (Entries 2-3).

We could assume that stabilization of metallic nanospecies thanks to optically active hydroxylated ammonium salts occurs through the adsorption of the anions at the particle surface, as already reported in colloid stabilization, and also through the steric stabilization and hindrance of the cationic lipophilic tail. However, compared to coordinating ligands, the enantiofacial control afforded by these ammonium salts remains too weak owing to their dynamic behavior at the metal surface, allowing the displacement of the capping agents by incoming substrates.

IV. Conclusion

To conclude, easily synthesized hydroxylcetylammonium salts have been widely used as capping agents of Rh^0 nanoparticles in neat water through efficient electrosteric stabilization. Moreover, easy modulation of the associated counter-ion or the polar head enables to tune the particle's size and morphology, as well as the stability of the aqueous suspensions, and the catalytic properties. Thus, relevant nanoreactors were achieved through the confinement of metallic nanospecies within the core of surfactant's micelles, possessing remarkable catalytic activities towards the reduction of arenes under mild reaction conditions and easy recyclability through biphasic (water/substrate) conditions. However, one of the last challenges in that field remains the development of chirally modified well-defined NPs as efficient asymmetric catalysts.

I.5. References

[1] I. P. Beletskaya, L.M. Kustov, Russ. Chem. Rev. 79 (2010) 441-461.
[2] N. Yan, C. Xiao, Y. Kou, Coord. Chem. Rev.254 (2010) 1179-1218.
[3] R.A. Sheldon, Chem. Commun. (2008) 3352-3365.
[4] A. Denicourt-Nowicki, A. Roucoux, Metallic Nanopartciles in Neat Water for Catalytic Applications in: P. Serp, K. Philippot, (Eds.), Nanomaterials in Catalysis, Wiley-VCH Verlag & Co, Weinheim, 2013, pp. 55-95.
[5] Y. Yuan, N. Yan, P.J. Dyson, ACS Catalysis 2 (2012) 1057-1069.
[6] M. Guerrero, N.T.T. Chau, S. Noel, A. Denicourt-Nowicki, F. Hapiot, A. Roucoux, E. Monflier, K. Philippot, Curr. Org. Chem. 17 (2013) 364-399.
[7] S. Noël, B. Léger, A. Ponchel, K. Philippot, A. Denicourt-Nowicki, A. Roucoux, E. Monflier, Catal. Today.
[8] J.P. Wilcoxon, B.L. Abrams, Chem. Soc. Rev. 35 (2006) 1162-1194.
[9] D. Astruc, Nanoparticles and Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008.
[10] A. Roucoux, A. Nowicki, K. Philippot, Rhodium and Ruthenium nanoparticles in catalysis., in: D. Astruc, (Ed.), Nanoparticles and Catalysis, Wiley-VCH, 2008, pp. 349-388.
[11] R. Narayanan, M. El-Sayed, Top. Catal. 47 (2008) 15-21.
[12] V. Polshettiwar, R.S. Varma, Green Chem. 112 (2010) 743-754.
[13] D. Astruc, F. Lu, J.R. Aranzaes, Angew. Chem. Int. Ed. 44 (2005) 7852-7872.
[14] C.J. Li, T.H. Chan, Comprehensive Organic Reaction in Aqueous Media, Wiley, New-York, 1997.
[15] B. Cornils, W.A. Hermann, Aqueous-Phase Organometallic Catalysis: Concepts and Applications, Second Edition, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005.
[16] A. Roucoux, Stabilized noble metal nanoparticles: An unavoidable family of catalysts for arene derivatives hydrogenation, in: C. Copéret, B. Chaudret, (Eds.), Topics in Organometallic Chemistry: Surface and Interfacial

Organometallic Chemistry and Catalysis, Springer GmbH, Heidelberg, 2005, pp. 261-279.
[17] A. Gual, C. Godard, S. Castillon, C. Claver, Dalton Trans. 39 (2010) 11499-11512.
[18] K.R. Januszkiewicz, H. Alper, Organometallics 2 (1983) 1055-1057.
[19] K. R. Januszkiewicz, H. Alper, Can. J. Chem. 62 (1984) 1031-1033.
[20] J. Schulz, A. Roucoux, H. Patin, Chem. Commun. (1999) 535-536.
[21] E. Guyonnet Bilé, R. Sassine, A. Denicourt-Nowicki, F. Launay, A. Roucoux, Dalton Trans. 40 (2011) 6524-6531.
[22] A. Roucoux, J. Schulz, H. Patin, Adv. Synth. Catal. 345 (2003) 222-229.
[23] V. Mevellec, B. Leger, M. Mauduit, A. Roucoux, Chem. Commun. (2005) 2838-2839.
[24] G. Cerichelli, L. Luchetti, G. Mancini, G. Savelli, Tetrahedron 51 (1995) 10281-10288.
[25] C.-H. Pélisson, C. Hubert, A. Denicourt-Nowicki, A. Roucoux, Top. Catal. 56 (2013) 1220-1227.
[26] M.G. Angelo da Silva, M.R. Meneghetti, A. Denicourt-Nowicki, A. Roucoux, RSC Adv. 3 (2013) 18292-18295.
[27] C. Hubert, A. Denicourt-Nowicki, J.P. Guegan, A. Roucoux, Dalton Trans. (2009) 7356-7358.
[28] J. Schulz, A. Roucoux, H. Patin, Chem. Eur. J. 6 (2000) 618-624.
[29] J. Schulz, S. Levigne, A. Roucoux, H. Patin, Adv. Synth. Catal. 344 (2002) 266-269.
[30] A.P. Umpierre, E. de Jesús, J. Dupont, ChemCatChem 3 (2011) 1413-1418.
[31] E. Redel, J. Krämer, R. Thomann, C. Janiak, J. Organomet. Chem. 694 (2009) 1069-1075.
[32] M. Boutros, F. Launay, A. Nowicki, T. Onfroy, V. Herledan-Semmer, A. Roucoux, A. Gédéon, J. Mol. Catal. A: Chem. 259 (2006) 91-98.
[33] T.Q. Hu, C.-L. Lee, B.R. James, S.J. Rettig, Can. J. Chem. 75 (1997) 1234-1239.
[34] C.M. Hagen, L. Vieille-Petit, G. Laurenczy, G. Suss-Fink, R.G. Finke, Organometallics 24 (2005) 1819-1831.
[35] C. Hubert, E. Guyonnet Bilé, A. Denicourt-Nowicki, A. Roucoux, Appl. Catal., A 394 (2011) 215-219.
[36] S. Roy, M.A. Pericas, Org. Biomol. Chem. 7 (2009) 2669-2677.
[37] S. Jansat, M. Gomez, K. Philippot, G. Muller, E. Guiu, C. Claver, S. Castillon, B. Chaudret, J. Am. Chem. Soc. 126 (2004) 1592-1593.
[38] S. Jansat, D. Picurelli, K. Pelzer, K. Philippot, M. Gomez, G. Muller, P. Lecante, B. Chaudret, New J. Chem. 30 (2006) 115-122.
[39] A. Gual, M.R. Axet, K. Philippot, B. Chaudret, A. Denicourt-Nowicki, A. Roucoux, S. Castillon, C. Claver, Chem. Commun. (2008) 2759-2761.
[40] A. Gual, C. Godard, K. Philippot, B. Chaudret, A. Denicourt-Nowicki, A. Roucoux, S. Castillón, C. Claver, ChemSusChem 2 (2009) 769-779.
[41] E. Guyonnet Bilé, A. Denicourt-Nowicki, R. Sassine, P. Beaunier, F. Launay, A. Roucoux, ChemSusChem 3 (2010) 1276-1279.
[42] E. Guyonnet Bilé, E. Cortelazzo-Polisini, A. Denicourt-Nowicki, R. Sassine, F. Launay, A. Roucoux, ChemSusChem 5 (2012) 91-101.
[43] V. Mévellec, C. Mattioda, J. Schulz, J.-P. Rolland, A. Roucoux, J. Catal. 225 (2004) 1-6.
[44] F. Glorius, Org. Biomol. Chem. 3 (2005) 4171-4175.

[45] Y.-G. Zhou, Acc. Chem. Res. 40 (2007) 1357-1366.
[46] K. Nasar, F. Fache, M. Lemaire, J.C. Beziat, M. Besson, P. Gallezot, J. Mol. Catal. 87 (1994) 107-115.
[47] F. Fache, S. Lehuede, M. Lemaire, Tetrahedron Lett. 36 (1995) 885-888.

Captions

Figure 1. *N*-(hydroxyalkyl)cetylammonium salts as efficient protective agents of Rh(0) NPs

Figure 2. *N*-(hydroxyalkyl)cetylammonium salts as efficient bilayer protective agents of size- and morphology-controlled Rh^0 NPs

Figure 3. Optically active hydroxylated ammonium salts as capping agents of Rh^0 NPs for asymmetric catalysis

Figure 4. TEM pictures and size histograms of chirally modified Rh^0 nanocatalysts with a) *N*-Methylephedrium, b) N-Methylprolinolium, c) Quicoridinium and d) Quicorinium bromide salts

Table 1. Total benzene hydrogenation using various ammonium-capped Rh^0 NPs in water. Influence of the surfactant counter-ion [a]

Table 2. Biphasic hydrogenation of arene derivatives with HEA16Cl-capped Rh^0 colloids [a]

Table 3. Asymmetric hydrogenation of ethylpyruvate with Rh^0 NPs capped with optically active ammonium salts in neat water[a]

Table 4. Asymmetric hydrogenation of 3-methylanisole with Rh^0 colloids capped with optically active ammonium salts in neat water[a]

Figure 1. *N*-(hydroxyalkyl)cetylammonium salts as efficient protective agents of Rh^0 NPs

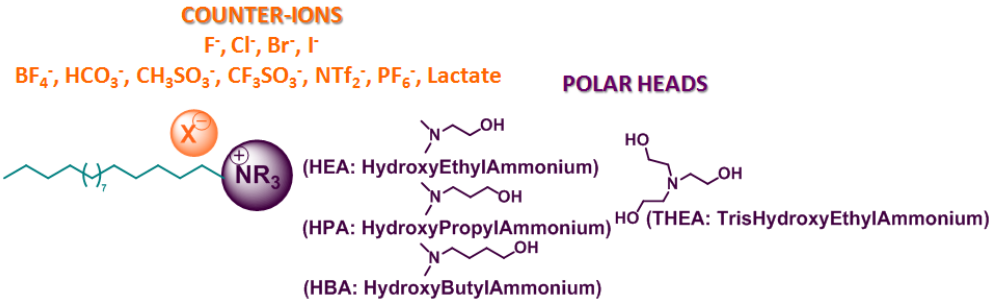


Figure 2. *N*-(hydroxyalkyl)cetylammonium salts as efficient protective agents of size-and morphology-controlled Rh^0 NPs

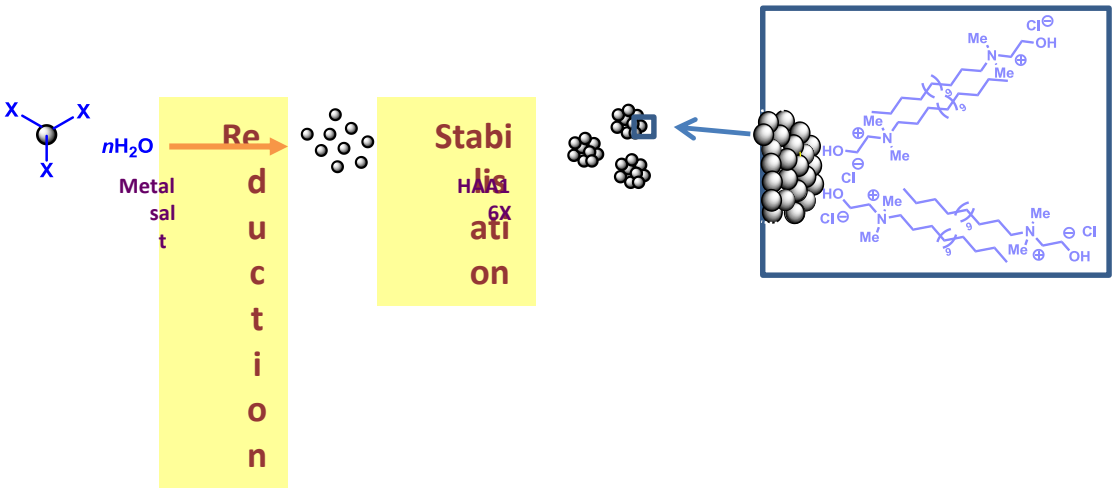


Table 1. Total benzene hydrogenation using various ammonium-capped Rh^0 NPs in water. Influence of the polar head and the surfactant counter-ion [a]

Entry	Surfactant	Ammonium group	Counter-ion	t (h)	TOF [b] (h^{-1})
2	HEA16Br	hydroxyethyl	Br	5.3	57
3	HEA16Cl	hydroxyethyl	Cl	3.6	83
4	HEA16F	hydroxyethyl	F	6	50
5	$HEA16BF_4$	hydroxyethyl	BF_4	3.7	81
6	$HEA16HCO_3$	hydroxyethyl	HCO_3	6	50
7	$HEA16CH_3SO_3$	hydroxyethyl	CH_3SO_3	3.7	81
8	$HEA16CF_3SO_3$	hydroxyethyl	CF_3SO_3	3	100
9	HPA16Cl	hydroxypropyl	Cl	5	60
10	THEA16Cl	*tris* hydroxyethyl	Cl	1	300

[a] Reaction conditions: Rh (3.8×10^{-5} mol), [Substrate]/[Metal]/[Surfactant]=100/1/2, H_2O, 1 bar H_2, 20 °C. [b] TurnOver Frequency determined by number of moles of consumed H_2 per mole of introduced Rh per hour.

Table 2. Biphasic hydrogenation of arene derivatives with HEA16Cl-capped Rh^0 colloids [a]

Entry	Substrate	Product yield[b] (%)	t (h)	TOF [c] (h^{-1})
1	Toluene	Methylcyclohexane (100)	3.6	83
2	Anisole	Methoxycyclohexane (70)/ Cyclohexanone (30)	4	75
3	Ethylbenzoate	Ethylcyclohexanoate (100)	4.7	64
4	Aniline	Cyclohexylamine (100)	10	30
5	*o*-Xylene	1,2-dimethylcyclohexane (*cis*/*trans* : 91/9)	5.3	57
6	*m*-Xylene	1,3-dimethylcyclohexane (*cis*/*trans* : 80/20)	6.8	44
7	*p*-Xylene	1,4-dimethylcyclohexane (*cis*/*trans* : 65/35)	4.1	73
8	Chorobenzene	Cyclohexane (100)	1.7	-
9	2-Chloroanisole	Methoxycyclohexane (53)/ Cyclohexanone (47)	11	34

[a] Reaction conditions: Rh (3.8×10^{-5} mol), [Substrate]/[Metal]/[Surfactant]=100/1/2, H_2O, 1 bar H_2, 20°C. [b] Determined by Gas Chromatography. [c] TurnOver Frequency determined by number of moles of consumed H_2 per mole of introduced Rh per hour.

Figure 3. Optically active hydroxylated ammonium salts as capping agents of Rh^0 NPs for asymmetric catalysis

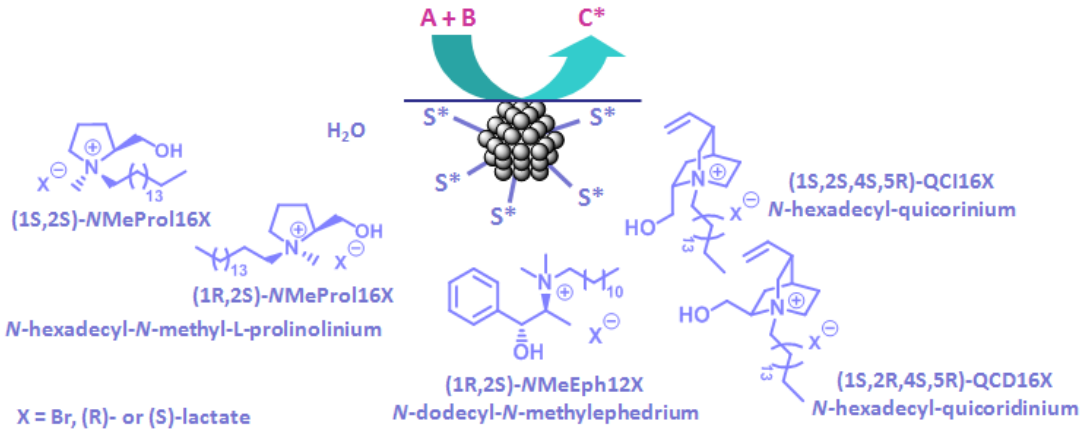
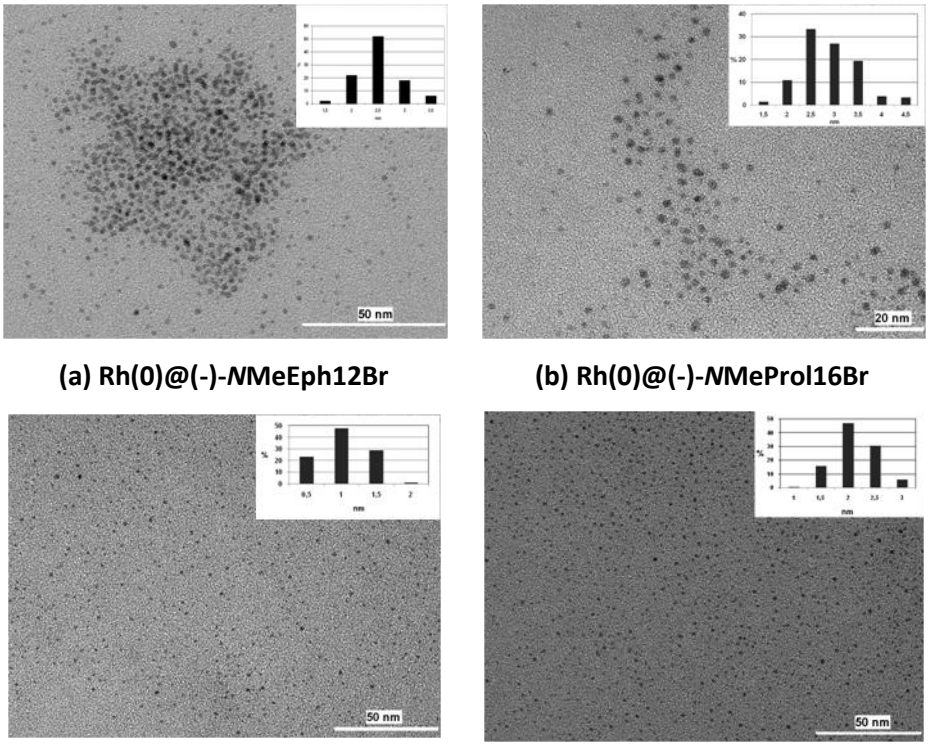


Figure 4. TEM pictures and size histograms of chirally modified Rh^0 nanocatalysts with a) *N*-Methylephedrium, b) N-Methylprolinolium, c) Quicoridinium and d) Quicorinium bromide salts



(a) Rh(0)@(-)-*N*MeEph12Br **(b) Rh(0)@(-)-*N*MeProl16Br**

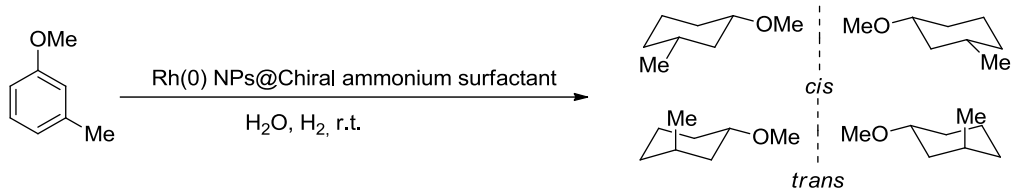
(c) Rh(0)@(+)-QCD16Br **(d) Rh(0)@(+)-QCl16Br**

Table 3. Asymmetric hydrogenation of ethylpyruvate with Rh^0 NPs capped with optically active ammonium salts in neat water[a]

Entry	Surfactant	t (h)	Conversion[b] (%)	*e.e.*[b] (%)
1	(1*R*,2*S*)-(-)-*N*MeEph12Br	1	100	12 (*R*)
2	(1*S*,2*R*)-(+)-*N*MeEph12Br	1	100	15 (*S*)
3	(1*R*,2*S*)-(-)-*N*MeEph12(*R*)-Lactate	1	100	9 (*R*)
4	(1*R*,2*S*)-(-)-*N*MeEph12(*S*)-Lactate	1	100	13 (*R*)
5	(2*S*)-(-)-*N*MeProl16Br	0.5	100	1
6	(1*S*,2*S*)-(-)-*N*MeProl16Br	1	100	3
7	(1*R*,2*S*)-(+)-*N*MeProl16Br	1	100	5
8	(1*S*,2*S*,4*S*,5*R*)-(+)-QCl16Br	2[c]	100	1
9	(1*S*,2*R*,4*S*,5*R*)-(+)-QCD16Br	2	60	0
10	(1*R*,2*S*)-(-)-*N*MeEph12Br[d]	1	100	15 (*S*)
11	(1*R*,2*S*)-(-)-*N*MeEph12(*S*)-Lactate[d]	1	100	18 (*S*)

[a] Reaction conditions: Rh (3.8×10^{-5} mol), [Substrate]/[Metal]/[Surfactant]=100/1/2, H_2O (10mL), 40 bar H_2, 20 °C. [b] Determined by Gas Chromatography analysis using a chiral column (Chiralsil-Dex CB). [c] Non-optimized. [d] Addition of (-)-cinchonidine

Table 4. Asymmetric hydrogenation of 3-methylanisole with Rh^0 colloids capped with optically active ammonium salts in neat water[a]



Entry	Surfactant	t (h)	Conv.[b] (%)	Yield *cis*/*trans* (*e.e.*) (%)[b]
1	(1*R*,2*S*)-(-)-*N*MeEph12Br	3	100	62 (0)/ 38 (0)
2	(1*R*,2*S*)-(-)-*N*MeEph12(*R*)-Lactate	3	100	65 (1)/ 35 (0)
3	(1*R*,2*S*)-(-)-*N*MeEph12(*S*)-Lactate	3	100	66 (0)/ 34 (0)
4	(2*S*)-(-)-*N*MeProl16Br	16[c]	100	60 (1)/ 40 (1)
5	(1*S*,2*S*,4*S*,5*R*)-(+)-QCl16Br	1	82	70 (1)/ 30 (2)
6	(1*S*,2*R*,4*S*,5*R*)-(+)-QCD16Br	1	55	70 (1)/ 30 (2)

[a] Reaction conditions: Rh (3.8×10^{-5} mol), [Substrate]/[Metal]/[Surfactant]=100/1/2, H_2O (10mL), 40 bar H_2, 20 °C. [b] Determined by Gas Chromatography analysis using a chiral column (Chiralsil-Dex CB). [c] Non-optimized.