Metallodendritic Catalysis for Redox and Carbon–Carbon Bond Formation Reactions: A Step towards Green Chemistry.

Didier Astruc,* Karine Heuzé, Sylvain Gatard, Denise Méry, Sylvain Nlate, Lauriane Plault

Nanosciences and Catalysis Group, LCOO, UMR CNRS N°5802, Université Bordeaux I, 33405 Talence Cedex, France
Fax: (+33)-540-00-69-94, e-mail: d.astruc@lcoo.u-bordeaux1.fr

Received: August 5, 2004; Accepted: November 19, 2004

This account article is dedicated to Professor Richard R. Schrock at the occasion of his 60th birthday.

Abstract: Metallodendritic catalysts combine the advantages of homogeneous and heterogeneous catalysts: they are soluble and perfectly well defined on the molecular level, and yet they can be recovered by precipitation, ultra-filtration or ultra-centrifugation (as biomolecules) and recycled several times. In this article, we summarize our recent work in this field with examples operating under ambient conditions in metathesis, Pd-catalyzed Sonogashira coupling, redox catalysis of nitrate and nitrite cathodic reduction to ammonia and various oxidation reactions by H_2O_2 catalyzed by polyoxometallates. The dendritic effects on the catalytic efficiencies are scrutinized, i.e., the comparison of the metallodentritic catalysts with their monomeric models and among the dendrimer generations. It is concluded that metallostars or low-generation metallodendrimers usually are optimized catalysts in terms of efficiency and recovery/re-use.

Keywords: catalysis; dendrimer; epoxidation; green chemistry; metathesis; redox; Sonogashira reaction

1 Introduction

Metal-alkyl,[1] metal-alkylidene[2] and metal-alkylidyne[3] complexes are the core of modern fundamental organometallic chemistry and, with the catalytic metathesis reactions of single,[4] double[5] and triple bonds,[6] their applications have spread over organic synthesis[7] and materials science.[8] This area of chemistry is an outstanding example showing that homogeneous catalysis provides the best defined catalysts at the molecular level leading to excellent mechanistic information and, consequently, optimized selectivity.[9] Thus, fixation of homogeneous catalysts in dendrimers recently appeared as a very promising solution to keep the molecular definition, mechanistic knowledge and catalytic efficiency together with providing the indispensable means of recovery and recycling.[10] Metallodendrimers are thus recyclable catalysts that function in a homogeneous, fully controllable way, and their recovery proceeds by precipitation, ultra-centrifugation or ultra-filtration using membranes because of their large size.

The constraints involving ecological and economical aspects are key parts of "green chemistry", and will increasingly become important in the forthcoming decades.[10] This area has been pioneered in industry by van Leeuwen in the early 1990 s[11] and in the academic world shortly afterwards by the groups of Brunner,[12] van Koten,[13] Ford[14] and DuBois.[15] The various possibilities of location of catalytic metal centers in dendrimers are represented schematically in Figure 1,[10a] and recovery and re-use of metallodendritic catalysts has recently been studied by several research groups. A few general reviews have appeared at the turn of the century,[10] and a special volume of *C. R. Chimie* entitled *"Dendrimers and Nanosciences"* that appeared in 2003 included a large section on metallodendritic catalysis.[16]

In this article, we will briefly review our recent own work on metallodendritic catalysis of various redox- and carbon-carbon bond forming reactions. This report

DOI: 10.1002/adsc.200404247

Didier Astruc has been a Full Professor of Chemistry at the University Bordeaux I since 1984, a Senior Member of the Institut Universitaire de France since 1995, the President of the Coordination Chemistry Division of the French Chemical Society since 2001 and a member of the National Committee of the CNRS since 2000. He did his Ph. D. in Rennes with R. Dabard, then his post-doc at MIT, Cambridge, with R. R. Schrock. He spent a sabbatical leave in Berkeley with K. P. C. Vollhardt in 1990–1991 where he wrote his first book on Electron Transfer and Radicals (ref.[32b]). His fields of interest now range from inorganic chemistry including catalysis and electron-transfer processes to molecular electronics, sensors and nanomaterials. He also is the author of a textbook on Organometallic Chemistry (ref.[21b]).

Karine Heuzé did her Ph. D. with Dr. P. Batail in Nantes and has been a CNRS fellow in Bordeaux since 2001 where she is presently working on dendrimer Pd catalysis.

Sylvain Nlate did his Ph. D. with Dr. V. Guerchais in Rennes, and has been a Maître de Conférence since 1998 in Bordeaux where he passed his Habilitation in 2003; his research deals with dendritic syntheses and catalysis.

Sylvain Gatard gained his Ph. D. in Prof. D. Astruc’s group in 2002 on dendritic ROMP and is presently a post-doctoral Fellow with Prof. Ronny Neumann in the Weizman Institute (Israël).

Lauriane Plault and *Denise Méry* did undergraduate studies in the University Bordeaux I and are presently preparing their Ph. D.s in Prof. D. Astruc’s group on metallodendritic catalysis for oxidation and C–C bond forming reactions, respectively.

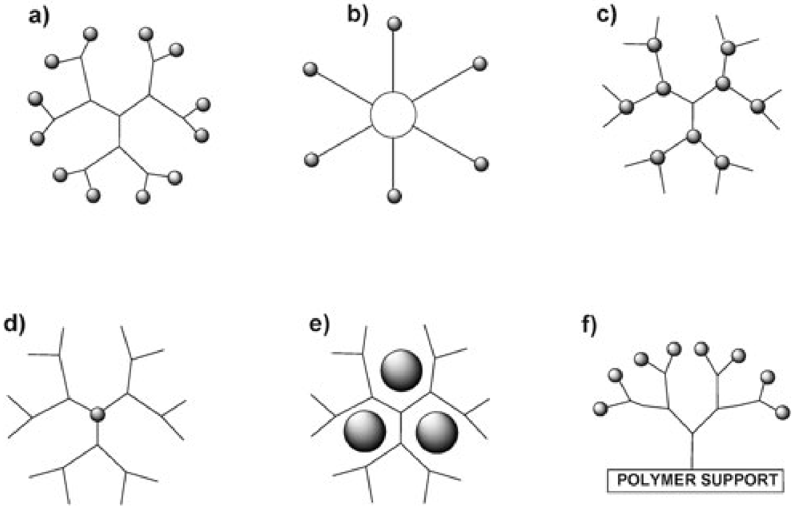
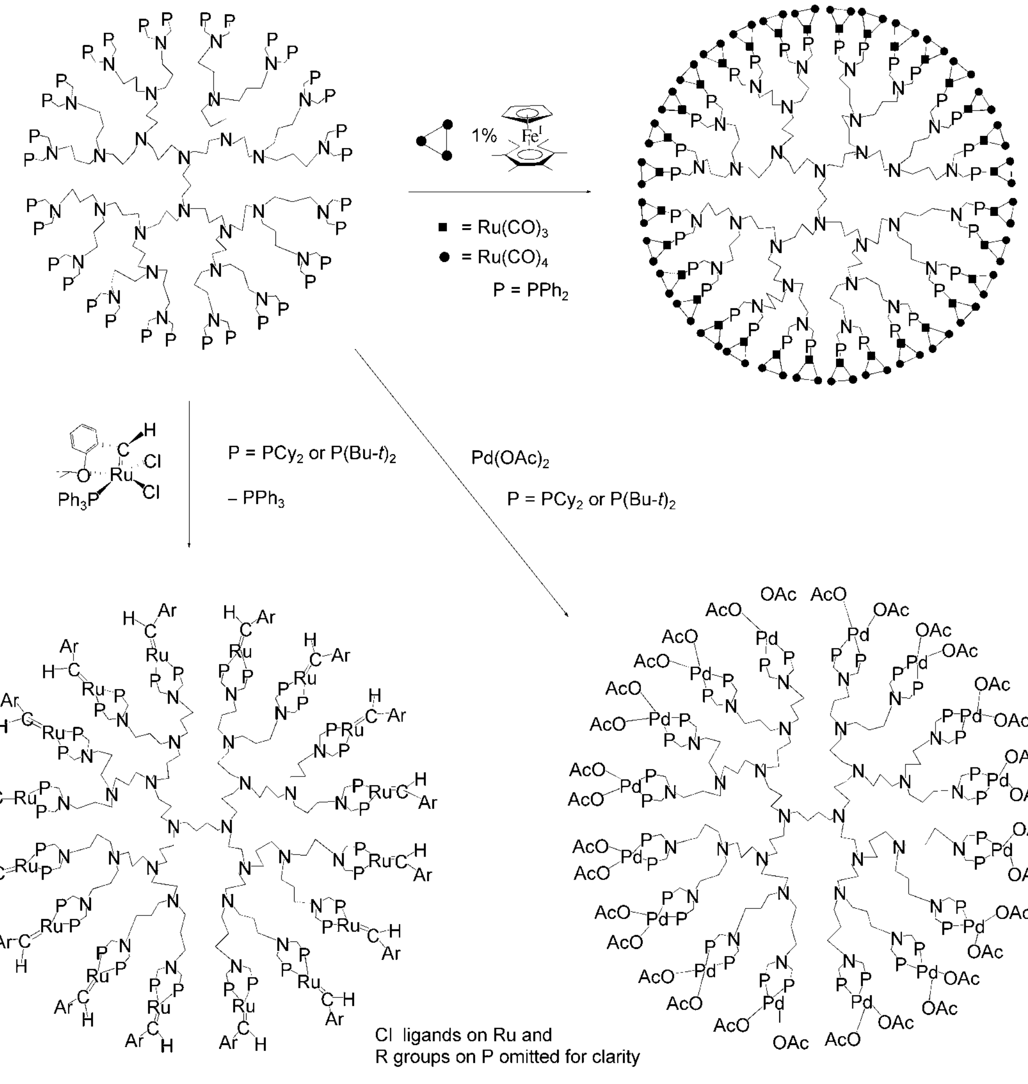


Figure 1. Various possibilities of location of catalysts in dendrimers (circles). For details, see ref.[10a]

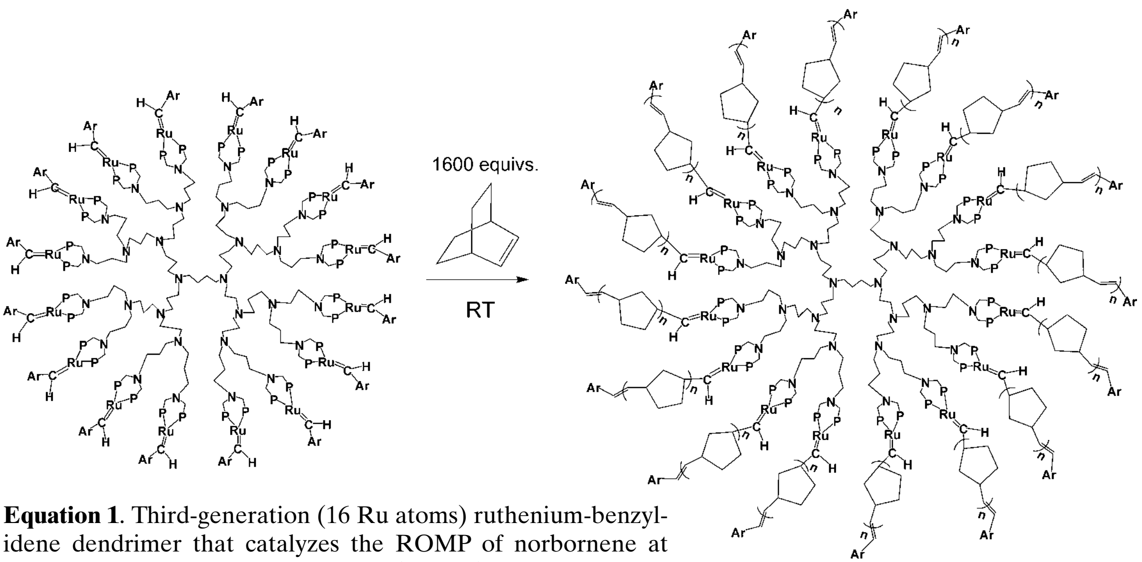
will illustrate some of the possibilities of metallodendritic catalysis including the originality of accessible polymeric materials, the selectivity and efficiency of metallodendritic catalysts, and eventually their recovery and reuse several times. We will also compare the metallodendritic catalysts with monometallic catalysts and discuss the dendritic effects. The reactions examined are the ROMP reaction of norbornene, the Sonogashira C–C coupling reaction, the redox-catalyzed cathodic reduction of nitrate and nitrate to ammonia in water and the polyoxophosphotungstate-catalyzed epoxidation of olefins in biphasic water-$CDCl_3$ medium.

2 Dendritic Ruthenium-Benzylidene Catalysts that form Dendrimer-Cored Stars with Norbornene by ROMP

A few metal-carbene metallodendritic catalysts with four branches were known and metathesis activity had been recorded,[17] but good recyclability is still a challenge. The difficulty resides in the need to sustain both metathesis activity and stability of the metallodendrimer. Thus, we selected the ruthenium family of catalysts, and designed metallodendrimers containing ruthenium-benzylidene fragments located at the dendrimer periphery and chelating phosphine ligands on the branch termini. The choice of chelating phosphines may seem counter-intuitive, because the activity of Grubbs' catalysts involves the decoordination of a phosphine from these *trans*-bis-phosphine complexes.[18] Studies by the groups of Hofmann, Fog and Leitner, however, have shown the metathesis activity of *cis*-bis-phosphine-ruthenium-benzylidene catalysts.[19] We therefore used Reetz's bis-phosphines derived from the commercial polyamine DAB dendrimers.[20] These dendritic bis-phosphines are useful and versatile in metallodendritic catalysis and provided the first recyclable metallodendritic catalysts.[20] They also very cleanly yielded, with two phenyl groups on each phosphorus atom, the



Scheme 1. Synthesis of third-generation metallodendrimers from various dendritic bis-phosphines.

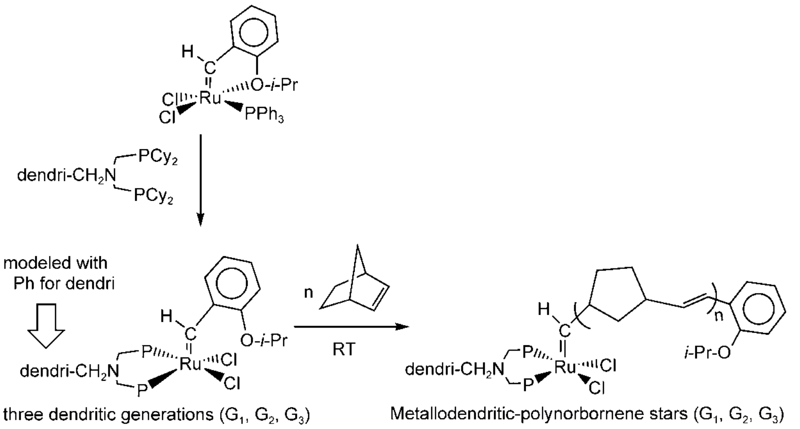


(1)

Equation 1. Third-generation (16 Ru atoms) ruthenium-benzylidene dendrimer that catalyzes the ROMP of norbornene at 25 °C to form dendrimer-cored stars (n = 100).

first dendrimers decorated with clusters at the periphery by an efficient electron-transfer chain reaction with $[Ru_3(CO)_{12})]$ catalyzed by $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$ leading to the substitution of a carbonyl by a dendritic phosphine on each tether.[21] Related dendritic bis-phosphines with two cyclohexyl groups on each phosphorus were decorated with ruthenium-benzylidene metathesis using Hoveyda's ruthenium-benzylidene metathesis catalyst[22] as a starting point. These reactions provided the four generations of new, stable metallodendrimers containing ruthenium-benzylidene fragments at the periphery (Scheme 1).[23] The fourth-generation metallodendrimer containing 32 ruthenium-benzylidene fragments, however, was found to have a rather low solubility in common organic solvents, unlike the three first-generation complexes that respectively contained 4, 8 and 16 ruthenium-benzylidene moieties. This weak solubility of the 32-Ru dendrimer is presumably due to steric congestion at its periphery. The X-ray crystal structure of the model mononuclear complex in which the dendritic branch was replaced by a benzyl group showed the distorted square pyramidal geometry and the classic geometric features of an Ru=C double bond (Scheme 2). The oxygen atom of the isopropyl aryl ether group is not coordinated unlike the situation in Hoveyda's complex. The fundamental organometallic chemistry of this monomeric model complex was also original and was reported elsewhere.[24]

The three first generations of metallodendrimers and the model complex were efficient catalysts for the ROMP of norbornene under ambient conditions, giving dendrimer-cored stars (Scheme 2).[23] Analysis of the molecular weights by SEC gave data that were close to the theoretical ones, which indicated that all the branches were efficiently polymerized. Dendritic-cored stars with an average of about 100 norbornene units on each dendritic branch were synthesized with the three first generations of ruthenium-carbene dendrimers containing respectively 4, 8 and 16 Ru=C bonds.



Scheme 2. Strategy for the ROMP of norbornene by Ru-benzylidene dendrimers to form dendrimer-cored stars.

Two kinds of dendritic effect were found upon analysis of the kinetic data:[23,24]

1) The dendrimers were more efficient catalysts than the monomeric model complex. This could possibly be due to labilization of metal-phosphine bonds that is facilitated in dendrimers as compared to the monomer for entropic reasons. Indeed, DFT calculations showed that the catalytic process must involve decoordination of a phosphorus atom, since the interaction of the olefin with the diphosphine complex is non-bonding.[24] The dendritic ruthenium-benzylidene dendrimers are air-sensitive in contrast to the monomer model complex, consistent with the more rapid dissociation of the alkylphosphine in the dendrimers than in the monomer.
2) The efficiency of catalysis decreased upon increasing the dendrimer generation. This second dendritic effect is thus a negative one, and it is probably related to the more difficult access to the metal center due to the increasing steric effect at the dendrimer periphery when the generation increases.

The analogous ruthenium-benzylidene dendrimers were very recently synthesized with two *tert*-butyl groups on each phosphorus, and they were slightly more reactive ROMP catalysts for the polymerization of norbornene than those involving the cyclohexyl substituents.[25] These new dendritic ligands proved very efficient in palladium catalysis.

3 Copper-Free, Recoverable Dendritic Catalysts for the Sonogashira Reaction

The Sonogashira reaction, Equation (2), couples aryl or vinyl halides to terminal alkynes.[26] It is very widespread, because it is efficient without requiring the preparation of an organometallic intermediate. A possible drawback in terms of “green chemistry” and metallodendritic catalysis, however, is the usual requirement of both palladium and copper catalysts. Indeed, very few copper-free catalysts are known.[27]

(2)

X= I, Br, Cl

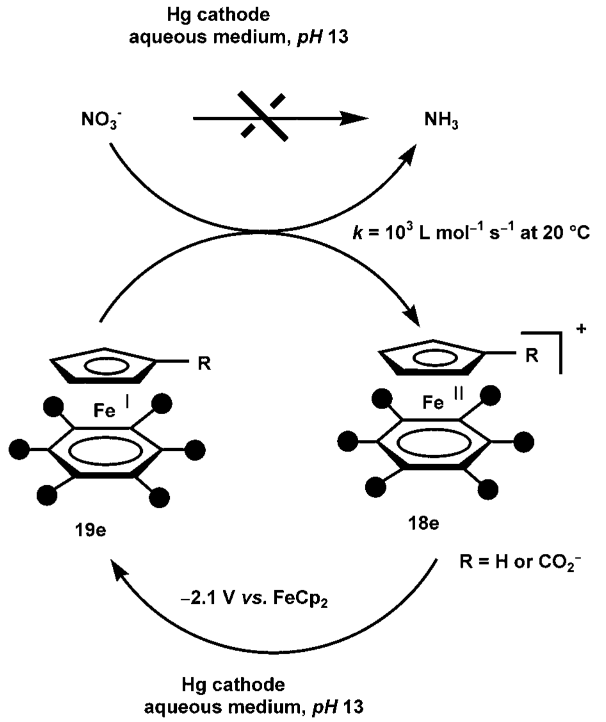
R= Aryl, Vinyl

We first investigated the catalytic efficiency of the palladium acetate catalyst using both bis-phosphines $PhCH_2N(CH_2PR_2)_2$ (R = Cy or *t*-Bu) already used as models in the Ru-catalyzed ROMP reactions described above. Both catalysts $[Pd(OAc)_2\{PhCH_2N(CH_2PR_2)_2\}]$ were efficient copper-free catalysts for the Sonogashira coupling of iodo- and bromobenzene with phenylacetylene [Equation (2), R = R′ = Ph] in NEt_3. The *t*-Bu catalyst was much more efficient than the Cy catalyst, and coupling with iodobenzene could proceed even at −40 °C using the former; at room temperature, inactivated bromoarenes were found to couple quantitatively in one hour, and activated chloroarenes gave low yields of hetero-coupling products.[28] The metallodendrimers of generations 1–3 were synthesized in both the Cy and *t*-Bu series, and were also found to be efficient copper-free catalysts for the Sonogashira coupling reaction. The *t*-Bu dendrimer series again catalyzed the Sonogashira reaction of iodoarenes with phenylacetylene at room temperature, although longer reaction times than with monomeric catalysts were required, and the Cy catalysts were active at 80 °C. The Cy series of catalysts proved easier to recover than the *t*-Bu ones for solubility reasons, however, and kept the same catalytic efficiency after five recycling operations.[29,30]

These dendritic palladium catalysts showed a negative dendritic effect, i.e., not only are the metallodendritic catalysts slower than the monomer model, but also the efficiency decreased as the dendrimer generation increased from 1 to 3. The two first generations containing respectively 4 and 8 catalytic palladium centers had about the same activity (the decrease was very weak from the first to the second generation), but the conversion yields dropped by half from the first to the third generation.

4 Water-Soluble Star-Shaped Organometallic Redox Catalyst for the Cathodic Reduction of Nitrate and Nitrite to Ammonia in Water

The catalytic reduction of nitrate has been known for a long time,[31] but the use of the redox catalyst $[Fe^{II}(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-}C_6Me_6)][PF_6]$ was the first example of an organometallic catalyst for this reaction. Electrosyntheses catalyzed by $[Fe^{I}(\eta^5\text{-}C_5H_4R)(\eta^6\text{-}C_6Me_6)]$ under these conditions showed that NH_3 was produced in 63% chemical yield and 57% electrical yield with R = CO_2^-. Nitrite, hydroxylamine, hydrazine and dinitrogen (minute amounts) were intermediates towards the formation of ammonia. The cathodic reduction stopped at the level of hydroxylamine when the experiment was carried out at pH 7 instead of 13. Kinetic studies in homogeneous basic aqueous solution using a polarographic method were carried out with $[Fe^{II}(\eta^5\text{-}C_5H_4R)(\eta^6\text{-arene})]$, R = CO_2^-, or when only the cationic Fe^{II} form was soluble in the medium (R = H; arene = benzene, *m*-xylene, hexamethylbenzene).



Scheme 3. Redox catalysis mechanism for the cathodic reduction of nitrate (and nitrite) to NH_3 catalyzed by the water-soluble Fe^{II} organometallic sandwich complex.

These studies led to the conclusion that the rate of redox catalysis (Scheme 3) was independent of the nature of the catalyst within this series.[32] This conclusion has recently been reconsidered, however, with the series of complexes $[Fe^{II}(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-arene})][PF_6]$, arene $= C_6Me_{6\text{-}n}$, n = 0 to 6. Polarographic, cyclic voltammetry and chrono-amperometry techniques were used to investigate the kinetics of the redox catalysis. The three techniques provided similar results.[33,34]

Thus, the rate constant of the redox catalysis can be calculated from the enhancement of the intensity of the cyclovoltammogram wave observed upon addition of the nitrate or nitrite salt into the electrochemical cell (Figure 2). A Marcus-type linear relationship was found between the logarithms of the rate constants and the standard redox potentials of the catalysts, indicating that the electron transfer in solution between the 19-electron Fe^I complex and nitrate or nitrite ion is rate limiting.[33,34]

In order to investigate the reaction mechanism, i.e., whether its proceeds by inner-sphere or outer-sphere electron transfer, other catalysts of the type $[Fe^{II}(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-arene})][PF_6]$ were synthesized with bulky arenes such as 1,3,5-tris-*t*-butylbenzene and $C_6(CH_2CH_2\text{-}p\text{-}C_6H_4OH)_6$. In these catalysts, the redox-active group is at the center of a star or dendritic core framework. The rate constants were found to be one to two orders of magnitude lower than what would be expected for the same driving force if the steric effect was not interfering, by comparison with the above series of catalysts with polymethylbenzene ligands. This showed a significant inner-sphere component to the electron-transfer process, although the kinetic drop would have been even more dramatic with a fully inner-sphere electron-transfer mechanism. It is likely that nitrate and nitrite ions coordinate to the 17-electron form of the Fe^I catalysts and that electron transfer proceeds in such intermediates rather than by outer sphere. However, the bond between an oxygen atom of nitrate or nitrite to such a low oxidation-state center must be very loose and long because π-back bonding is impossible with these ligands.[34]

We also synthesized water-soluble hexametallic redox catalysts of this type using the $CpFe^+$ induced hexa-allylation of hexamethylbenzene (Scheme 4).[33]

Thus, one could then compare the kinetics of an $[FeCp(arene)]^+$-centered star or dendritic core to that of a star bearing $[FeCp(arene)]^+$ catalysts at the periphery (Scheme 4). Remarkably, the kinetics of catalysts bearing the $[FeCp(arene)]^+$ moiety at the center of a

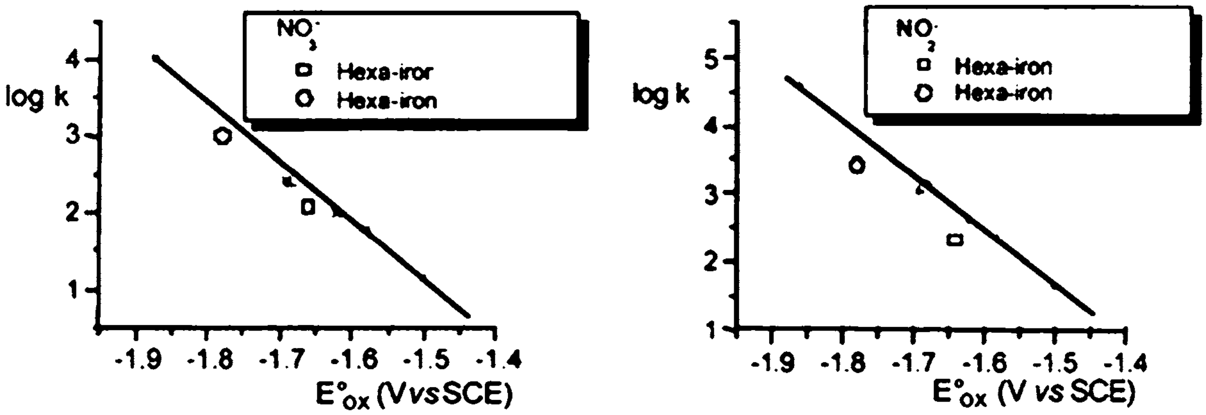
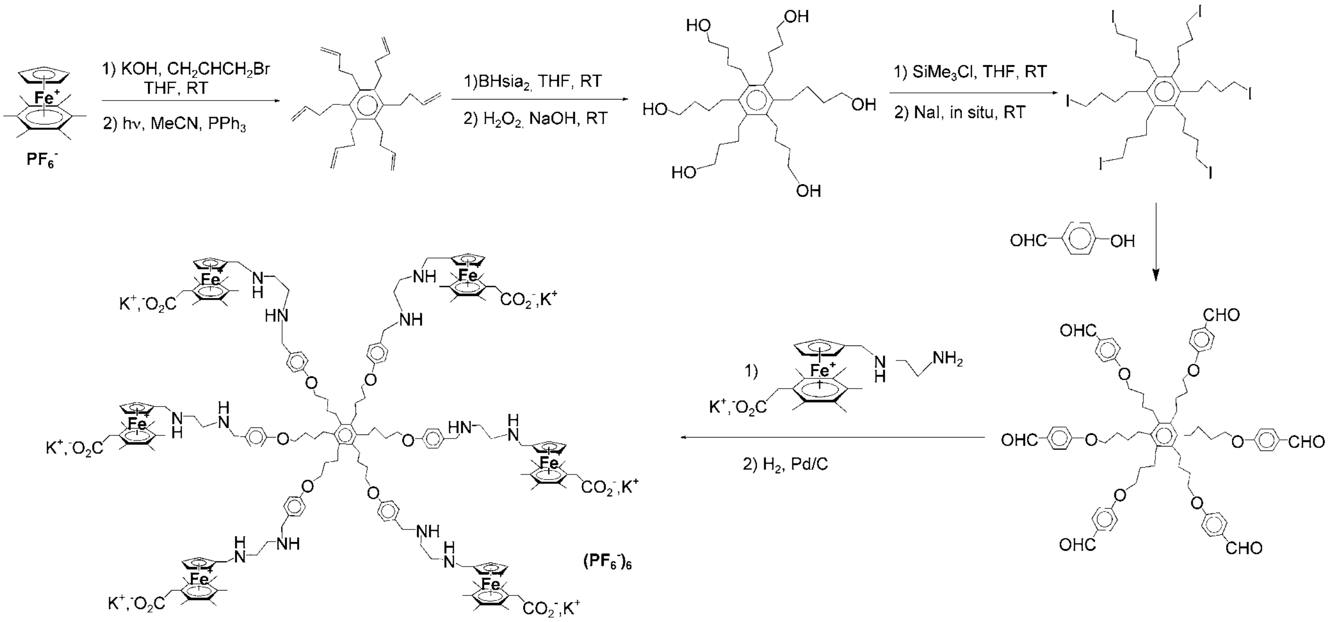


Figure 2. Marcus-type relationship between the kinetics (log k) and thermodynamics (E°_{ox}) for the redox-catalyzed reduction of nitrate indicating that the primary electron transfer (mainly outer sphere) is rate limiting. The crosses on the lines correspond to mono-iron complexes with different driving forces and two-star hexanuclear complexes are shown for comparison.



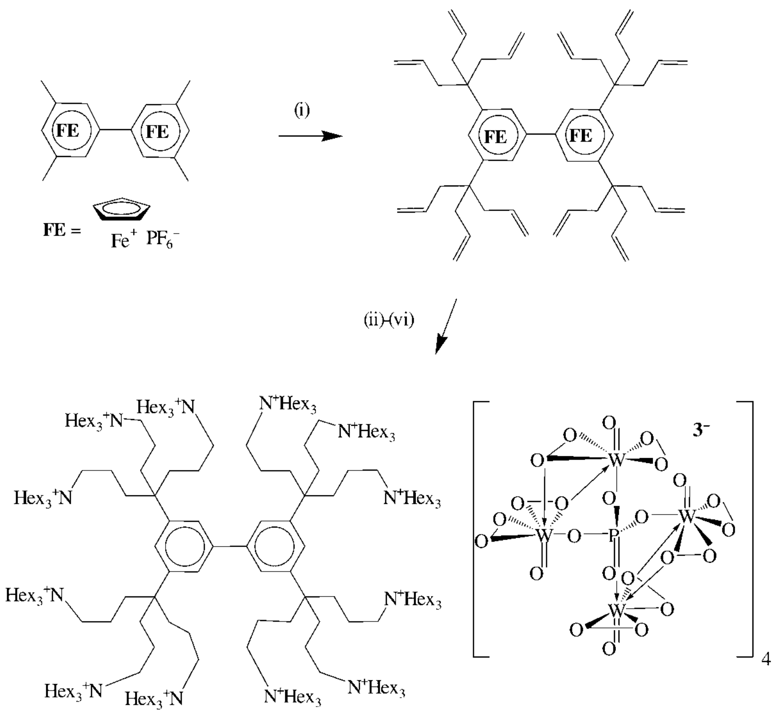
Scheme 4. CpFe$^+$-induced hexa-allylation of C_6Me_6 and subsequent hexafunctionalization of the aromatic stars with the heterodifunctional, water-soluble organometallic redox catalysts (bottom) for the cathodic reduction of nitrates and nitrites to ammonia in water.

star or dendritic core is one order of magnitude lower than that of such a star bearing the catalyst at the periphery. We know that, as in cytochromes, electron transfer between an electrode and a redox center located at the center of a dendrimer is slow. On the other hand, the kinetics of the hexanuclear star in which the redox moieties are located at the star periphery is about the same as those of mononuclear redox catalysts of the same type and driving force. This category of electron transfer between an electrode and redox centers located at a dendritic periphery is fast due to the fast rotation of the dendrimer as compared to the electrochemical time scale. Note that we have first chosen a star topography rather than a dendritic one in order to avoid the problem of bulk encountered in dendrimers in which the catalytic groups located at the periphery are marred by steric inhibition preventing the substrate to approach the metal coordination sphere. This redox catalysis technique could be very useful in order to investigate this problem in dendrimers.

5 Highly Efficient Recoverable Dendritic Polyoxometallate Catalysts for the Epoxidation of Olefins with H_2O_2 in Biphasic Medium under Ambient Conditions

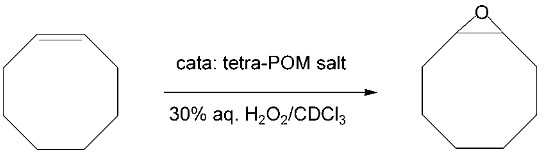
Polyoxometallates (POMs) are the source of fascinating architectures and very rich redox chemistry[35] that provides the basis for their catalytic activity in oxidation reactions.[36] Among the POMs, we have selected the Keggin-type complex $\{PO_4[WO(O_2)_2]_4\}^{3-}$ that is known for its catalytic properties in olefin epoxidation and alcohol oxidation.[37] In order to build the supramolecular assembly of the dendritic oxidation catalyst in which each POM trianion is connected to a trication, we have designed tricationic tripods consisting of tris-ammonium groups.[37] For this purpose, our synthetic strategy has consisted in using polymethylarenes in which each methyl group can be functionalized by three allyl groups using the temporary complexation/activation by the 12-electron fragment CpFe$^+$.[38] The BF_4^- ammonium salts were transformed into the desired polyammonium salts of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ by reaction with an aqueous solution of the commercial heteropolyacid $H_3PW_{12}O_{40}$ and H_2O_2. Mono-, bis-, tris- and tetra-POMs (Scheme 5) were synthesized in this way.

Epoxidation of cyclooctene by 35% aqueous H_2O_2 in a biphasic water/$CDCl_3$ system was carried out at room temperature, and was catalyzed by 0.3 equivalents of POM embedded in the ionic dendrimer, Equation (3). Under these conditions, monitoring the kinetics of the reaction by plotting the ratio between the intensity of the disappearing ^{1}H NMR signal of cyclooctene at 5.6 ppm *vs.* TMS and that of the rising peak of the epoxide at 2.9 ppm *vs.* TMS showed that the reaction was complete after 6 hours. Comparison between the mono-, bis-, tris-, and tetra-POM epoxidation catalysts indicated that there was no measurable dendritic effect on the reaction kinetics within this series. The key dendritic effect, however, was noted in the recovery of the catalysts. The latter are precipitated from the organic



Scheme 5. Example of synthetic scheme for $CDCl_3$-soluble poly POM epoxidation catalyst. Synthesis of the tetra-POM dodecahexylammonium salt starting from a bis-iron complex.[40] The counter cation for each POM^{3-} unit is a tris-ammonium tripod: (i) allyl bromide, KOH, THF, RT, (ii) disiamylborane, THF, RT, then 30% aqueous H_2O_2, 0.1 M aqueous NaOH; (iii) Me_3SiI, NaI, THF, RT; (iv) $NHex_3$, 80 °C; (v) $AgBF_4$, EtOH; (vi) $H_3PW_{12}O_{40}$, 30% aqueous H_2O_2.

phase by addition of pentane leaving a clear solution in the case of the tris-POM and tetra-POM catalysts, unlike the cases of the mono- and bis-POM catalysts, thus the yield of catalyst recovery was higher for the tris- and tetra-POM catalysts than those obtained for the mono- and bis-POM catalysts.



(3)

Out of a catalytic amount as low as 20 mg, the recovery of 3-POM by precipitation and filtration was between 70 and 85% after each catalytic cycle, and the efficiency of the catalyst was reproducible. After catalysis, the ^{31}P NMR spectrum of the dendritic POM catalyst was checked, and was shown to be unchanged.

Other catalytic oxidations reactions by H_2O_2 in the biphasic water/$CDCl_3$ system could also be carried out using the dendritic-POM complexes as catalysts. For instance, selective oxidation of dialkyl sulfide to dialkyl sulfone was catalyzed by 1% tris-POM and was quantitative at room temperature after 2 hours. This reaction was carried out using aqueous H_2O_2 in a biphasic water/$CDCl_3$ system. The tris-POM catalyst could be recovered analogously in both cases as in the epoxidation experiments, and it was checked by ^{31}P NMR that it was unchanged after recovery.[38]

6 Concluding Remarks and Outlook

Many metallodendritic catalysts synthesized during this work proved to be remarkably recoverable and were reused several times without lost of activity. The homogeneous catalytic systems of various kinds allowed us to carry out kinetics showing very noteworthy dendritic effects that varied with the studied systems. A general trend, however, is that reaction kinetics becomes weaker as the metallodendrimer generation increases. We believe that this is due to increasing bulk around the catalytic metal centers at the dendrimer periphery when the generation increases. Thus, it is necessary to find a compromise between molecular size for recovery and steric inhibition.

We found, through these studies, that stars may be more appropriate than dendrimers, because they do not suffer from bulk problems at the periphery. This was shown here in particular in the kinetic studies of the redox catalysis of hexa-iron stars whose efficiency is about the same as that of monomers with equivalent driving forces. Small dendrimers can be highly efficient as well if the tethers are long enough to avoid steric congestion, but the best generations are usually probably around the second generation containing, for instance, 8 catalytic centers. Recovery proceeds quite well with such dendrimers (but not systematically).

From these studies, we have learnt that metallostars and metallodendritic catalysts are perfectly defined, highly efficient and fulfill "green chemistry" conditions. Dendritic effects in catalysis are sensitive, which allows their optimization, in contrast to the black box often encountered in supported catalysis. Interestingly, dendritic effects are negative upon increasing generation, whereas the opposite was found in molecular recognition.[41] That small metallostars and metallodendrimers are optimal for catalysis fits to their easy access and commercialization. Metallodendritic catalysts will obviously occupy a place of choice in to-morrow's catalysis.

Acknowledgements

We are grateful to the colleagues and students cited in the references who have contributed to the idea and efforts that have provided aspects of this chemistry, in particular Drs. Jean-Claude Blais (Paris, MALDI TOF mass spectroscopy), Marie-Hélène Delville and Stephane Rigaut (redox catalysis), Jaime Ruiz (dendrimer syntheses) and Prof. Jean-Yves Saillard (Rennes, theoretical studies). Financial support from the Institut Universitaire de France (DA, IUF), the Centre National de la Recherche Scientifique (CNRS), the Ministère de la Recherche and the University Bordeaux I is gratefully acknowledged.

References and Notes

[1] R. R. Schrock, G. W. Parshall, *Chem. Rev.* **1976**, *76*, 243.

[2] R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796; R. R. Schrock, *Acc. Chem. Res.* **1979**, *12*, 98; R. R. Schrock, *Science* **1983**, *219*, 13; J. Feldman, R. R. Schrock, *Prog. Inorg. Chem.* **1991**, *39*, 1; R. R. Schrock, *Pure Appl. Chem.* **1994**, *66*, 1447; R. R. Schrock, in: *Handbook of Metathesis*, (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, Vol. 1, Chap. 1.3, p. 8.

[3] a) L. J. Guggenberger, R. R. Schrock, *J. Am. Chem. Soc.* **1975**, *97*, 2935; b) R. R. Schrock, *Chem. Rev.* **2002**, 102, 145; c) R. R. Schrock, in: *Handbook of Metathesis*, (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, Vol. 1, Chap. 1.11, p. 173.

[4] The formation of Schrock's first alkylidene complex[2] and other α-H elimination reactions can be viewed as early examples of σ-bond metathesis.

[5] First evidence of metal-alkylidene catalysts of metathesis and of molecular delineation of the Chauvin mechanism with Ta: R. R. Schrock, S. M. Rocklage, J. H. Wengrovius, G. Rupprecht, J. Feldman, *J. Mol. Cat.* **1980**, *8*, 73; with W: J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, W. J. Young, *J. Am. Chem. Soc.* **1980**, *102*, 4515; R. R. Schrock, in: *Handbook of Metathesis*, (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, Vol. 1, Chap. 1.3, p. 8.

[6] J. H. Wengrovius, J. Sancho, R. R. Schrock, *J. Am. Chem. Soc.* **1981**, *103*, 3932; J. Sancho, R. R. Schrock, *J. Mol. Cat.* **1982**, *15*, 75; R. R. Schrock, *Acc. Chem. Res.* **1986**, *19*, 342.

[7] *Handbook of Metathesis*, (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, Vol. 2: *Applications in Organic Synthesis.*

[8] *Handbook of Metathesis*, (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, Vol. 3: *Applications in Polymer Synthesis.*

[9] D. Evans, J. A. Osborn, F. H. Jardine, G. Wilkinson, *Nature* 1965, **208**, 1203; *Applied Homogeneous Catalysis with Organometallic Compounds*, (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1996**.

[10] a) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991; b) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem. Intern. Ed. Engl.* **2001**, *40*, 1828; c) R. Kreiter, A. W. Kleij, R. J. M. Klein Gebbink, G. van Koten, in: *Dendrimers IV: Metal Coordination, Self Assembly, Catalysis*, (Eds.: F. Vögtle, C. A. Schalley), *Top. Curr. Chem.* Springer-Verlag, Berlin, **2001**, Vol. 217, p. 163; d) R. van Heerbeeck, P. C. J. Kamer, P. W. N. M. van Leuwen, J. N. H. Reek, *Chem. Rev.* **2002**, *102*, 3717.

[11] R. A. Kleij, P. W. N. M. van Leeuwen, A. W. van der Made, *EP* 0456317, **1991**; *Chem. Abstr.* **1992**, *116*, 129870. For a review of van Leeuwen's work in the area, see ref.[10b]

[12] a) H. Brunner, J. Fürst, J. Ziegler, *J. Organomet. Chem.* **1993**, *454*, 87; b) H. Brunner, J. Fürst, *Tetrahedron* **1994**, *50*, 4303; c) H. Brunner, J. Fürst, U. Nagel, A. Z. Fischer, *Naturforsch. B* **1994**, *49*, 1305; d) H. Brunner, P. Bublak, *Synthesis* **1995**, 36; e) H. Brunner, G. Net, *Synthesis*, **1995**, 423; for a review of Brunner's pioneering work in the area, see: H. Brunner, *J. Organomet. Chem.* **1995**, *500*, 39.

[13] J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659.

[14] J.-J. Lee, W. T. Ford, J. A. Moore, Y. Li, *Macromolecules* **1994**, *27*, 4632; J. J. Lee, W. T. Ford, *J. Am. Chem. Soc.* **1994**, *116*, 3753.

[15] A. Miedaner, C. J. Curtis, R. M. Barkley, D. L. DuBois, *Inorg. Chem.* **1994**, *33*, 5482; A. Miedaner, D. L. DuBois, *Polym. Mater. Sci. Eng.* **1995**, 279.

[16] *Dendrimers and Nanosciences*, (Ed.: D. Astruc), *C. R. Chimie*, Elsevier, Paris, **2003**, *6*, Vols. 8–10; see the chapters on metallodendritic catalysis therein by Y. Niu, R. M. Crooks (p. 1049), J. N. H. Reek, D. de Groot, G. E. Oosterom, P. C. J. Kramer, P. W. N. M. van Leeuwen (p. 161), G. P. M. van Klink, H. P. Dijkstra, G. van Koten (p. 1079), Y. Ribourdouille, G. D. Engel, L. Gade (p. 1087), K. Soai, I. Sato (p. 197), C.-M. Che, J.-S. Huang, J.-L. Zhang (p. 1105), and D. Astruc, J.-C. Blais, M.-C. Daniel, S. Gatard, S. Nlate, J. Ruiz, (p. 1117).

[17] P. Wijkens, J. T. B. H. Jastrzebski, P. A. van der Schaaf, R. Kolly, A. Hafner, G. van Koten, *Org. Letters* **2000**, *2*, 1621; S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H.

Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168; H. Beerens, F. Verpoort, L. Verdonck, *J. Mol. Cat.* **2000**, *151*, 279; **2000**, *159*, 197.

[18] M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 749; T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18.

[19] S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisenträger, P. Hofmann, *Angew. Chem. Int. Ed.* **1999**, *38*, 1273; S. Hansen, F. Rominger, M. Metz, P. Hofmann, *Chem. Eur. J.* **1999**, *5*, 557; C. Adlhart, M. A. O. Volland, P. Hofmann, P. Chen, *Helv. Chim. Acta* **2000**, *83*, 3306; D. Amoroso, D. E. Fogg, *Macromolecules* **2000**, *33*, 2815; C. Six, K. Beck, A. Wegner, W. Leitner, *Organometallics* **2000**, *19*, 4639.

[20] M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1526.

[21] a) E. Alonso, D. Astruc, *J. Am. Chem. Soc.* **2000**, *122*, 3222; b) D. Astruc, *Chimie Organométallique*, EDP Science, Les Ullis, **2000**, p. 133; *Quimica Organometallica*, Reverte, Barcelona, **2003**, p. 132.

[22] J. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791.

[23] S. Gatard, S. Nlate, E. Cloutet, G. Bravic, J.-C. Blais, D. Astruc, *Angew. Chem. Int. Ed.* **2003**, *42*, 452.

[24] S. Gatard, S. Kahlal, D. Méry, S. Nlate, E. Cloutet, J.-Y. Saillard, D. Astruc, *Organometallics* **2004**, *23*, 1313.

[25] D. Méry, D. Astruc, *J. Mol. Catal.* **2004**, *227*, 1.

[26] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467; K. Sonogashira, *Comprehensive Organic Synthesis*, (Eds.: B. M. Trost, M. Fleming), Pergamon Press, Oxford, **1991**, Vol. 3, p. 521; R. Rossi, A. Carpita, F. Bellina, *Org. Prep. Proc. Int.* **1995**, *27*, 129; J. S. Moore, *Acc. Chem. Res.* **1997**, *30*, 402; *Modern Arene Chemistry*, (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2002**.

[27] L. Casar, *J. Organomet. Chem.* **1975**, *93*, 253; H. A. Dieck, F. R. Heck, *J. Organomet. Chem.* **1975**, *93*, 259; J.-P. Genêt, E. Blart, M. Savignac, *Synlett* **1992**, 715; M. Alami, F. Ferri, G. Linstrumelle, *Tetrahedron Lett.* **1993**, *34*, 6403; V. P. Böhm, W. A. Hermann, *Eur. J. Org. Chem.* **2000**, 3679; M. Pal, K. Parasuraman, X. Fu, S. Zhang, J. Yin, D. Schumacher, *Tetrahedron Lett.* **2002**, *43*, 6673; S. Gupta, K. R. Yeleswarapu, *Synlett* **2002**, *12*, 1976; D. Gelman, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2003**, *42*, 5993; D. A. Alonso, C. Najera, M. C. Pacheco, *Tetrahedron Lett.* **2002**, *43*, 9365; L. Djakovitch, P. Rollet, *Tetrahedron Lett.* **2004**, *45*, 1367.

[28] D. Méry, K. Heuzé, D. Astruc, *Chem. Commun.* **2003**, 1934.

[29] K. Heuzé, D. Méry, D. Astruc, *Chem. Commun.* **2003**, 2274.

[30] K. Heuzé, D. Méry, D. Gauss, J.-C. Blais, D. Astruc, *Chem. Eur. J.* **2004**, *10*, 3936.

[31] M. Tokuaka, *Collect. Czech. Chem. Commun.* **1932**, *4*, 444; **1934**, *6*, 339.

[32] a) A. Buet, A. Darchen, C. Moinet, *J. Chem. Soc. Chem. Commun.* **1979**, 447; b) D. Astruc, *Electron Transfer and Radical Processes in Transition Metal Chemistry*, VCH, New York, **1995**, p. 522.

[33] S. Rigaut, M.-H. Delville, D. Astruc, *J. Am. Chem. Soc.* **1997**, *119*, 1132.

[34] S. Rigaut, M.-H. Delville, J. Losada, D. Astruc, *Inorg. Chim. Acta*, **2002**, *334*, 225 (issue dedicated to Andrew Wojicki).

[35] a) M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34; b) E. Dimitris, C. Katsoulis, *Chem. Rev.* **1998**, *98*, 359; issue dedicated to POMs: *Chem. Rev.* **1998**, *98*.

[36] a) I. V. Kozhevnikov, *Catalysis by Polyoxometalates*, John Wiley & Sons, Chichester, **2002**; b) I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171–198; c) N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199.

[37] C. Venturello, R. D'aloisio, *J. Org. Chem.* **1988**, *53*, 1553; C. Venturello, R. D'aloisio, J. C. J. Bart, M. Ricci, *J. Mol. Catal.* **1985**, *32*, 107; Y. Ishii, M. Ogawa, *Reviews on Heteroatom Chemistry*, (Eds.: A. Ohno, N. Furukawa), MYU, Tokyo, **1990**, Vol. 3, p. 121; Y. Ishii, Y. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 3587.

[38] a) L. Plault, A. Hauseler, S. Nlate, D. Astruc, J. Ruiz, S. Gatard, R. Neumann, *Angew. Chem. Int. Ed.* **2004**, *43*, 2984; b) S. Nlate, D. Astruc, R. Neumann, *Adv. Syn. Catal.* **2004**, *346*, 1445.

[39] D. Astruc, *Acc. Chem. Res.* **2001**, *33*, 287; D. Astruc, S. Nlate, J. Ruiz, in: *Modern Arene Chemistry*, (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2002**, Chap. 12, p. 400.

[40] V. Martinez, J.-C. Blais, D. Astruc, *Org. Letters* **2002**, *4*, 651; V. Martinez, J.-C. Blais, G. Bravic, D. Astruc, *Organometallics* **2004**, *23*, 861.

[41] D. Astruc, *Pure Appl. Chem.* **2003**, *75*, 461.