

New Water-Soluble Diamine Complexes as Catalysts for the Hydrogenation of Ketones Under Hydrogen Pressure

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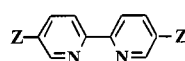
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New water-soluble rhodium and iridium complexes of 2,2'-bipyridines, functionalized with PO₃Na₂ groups, show very good catalytic activities in the reduction of various

substituted acetophenones under hydrogen pressure in basic aqueous media. No significant loss of catalyst activity is observed after one use.

Catalyst recovery and recycling is an important concern in relation to chemical processes that are homogeneously catalyzed by expensive transition metal complexes. For this reason, much effort has been directed towards the synthesis of new water-soluble catalytic species, the principal aim being to gain access to reusable catalytic systems that can be easily separated from the reaction products by simple extraction of the aqueous phase with an organic solvent. To the best of our knowledge, most of the attention has been focused on tertiary phosphanes,^[1] with TPPTS (triphenylphosphanetrissulfonate sodium salt) remaining the most widely used. A wide variety of polar functional substituents [e.g. SO₃Na, OSO₃Li, CO₂Na, OH, PMe₃⁺, NMe₃⁺, P(O)(ONa)₂, polyethers]^[2] have been incorporated in order to render the desired ligands water-soluble. Among these, the disodium phosphonate moiety is of particular interest since the reactivity of this group towards a wide range of metal salts, to yield metal phosphonates,^[3] also offers the possibility of heterogenizing catalytic complexes as phosphonate-based organic/inorganic hybrid solids, as first shown by our group in the (porphyrin)manganese(III) series.^[4]

The use of various N-containing ligands (based for example on 2,2'-bipyridines,^[5a–5c] phenanthrolines,^[5d] or C₂-symmetric diamines^[5e–5h]) as an alternative to phosphanes^[6] in the asymmetric hydrogenation of prochiral ketones is well documented in the literature, mainly in the context of transfer hydrogenation. To the best of our knowledge, however, there have been no reports of the preparation of water-soluble diamine complexes that might allow this reaction to be carried out under hydrogen pressure in water. In this context, we have recently reported in a preliminary communication^[7] the facile synthesis of 2,2'-bipyridine-based bis(phosphonic)acids. In the present paper, we wish to report the catalytic properties of such ligands and related compounds in the hydrogenation of aromatic ketones in aqueous media. The three diamines **1**, **2** and **3** (Scheme 1) were selected for this study.



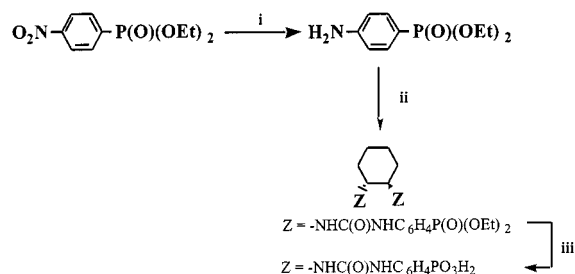
1 : Z = -C(O)NHC₃H₆PO₃H₂
2 : Z = -PO₃H₂



3 : Z = -NHC(O)NHC₆H₄PO₃H₂

Scheme 1. Hydrosoluble ligands tested for the reduction of ketones

Precursors **1** and **2** were prepared as we have described previously^[7] (for details, see Experimental Section). Compound **3** was synthesized by reaction of (1*R*,2*R*)-diaminocyclohexane with the functionalized isocyanate prepared in two steps (Scheme 2) from diethyl 4-nitrophenylphosphonate.^[8] The phosphonate groups were then converted into their acidic form under mild conditions using McKenna's method.^[9]



Scheme 2. Conditions: i) 5% Pd/C, HCO₂H, NEt₃ (82%); ii) (CCl₃O)₂CO, NEt₃, CH₂Cl₂, then (1*R*,2*R*)-diaminocyclohexane (75%); iii) Me₃SiBr, CH₂Cl₂, room temp., then MeOH, room temp., (quant.)

The catalytic activities of the three ligands **1–3** in the hydrogenation of various aromatic ketones in water under hydrogen pressure (40 atm H₂) were then studied. Solutions of the neutral tetrasodium forms of the ligands were first treated with [Ir(COD)Cl]₂ (ligand/Ir: 4-fold excess of the ligand to ensure the stability of the complex under H₂ pressure). The substrate was then added (neat if liquid or dissolved in ethyl acetate if solid) so as to give a 5% Ir/substrate molar ratio. At the end of the reaction, the products could easily be separated from the catalyst by simple extraction of the aqueous phase with ethyl acetate. In the case of ligand **1**, good catalytic activity was observed in the reduction of aromatic oxo esters and ketones (Table 1, entries 1, 3, 6), but the presence of electron-donating substituents

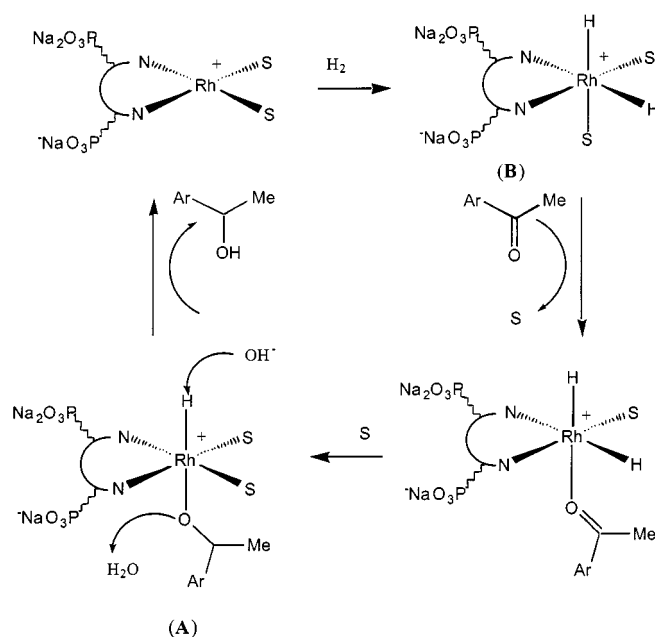
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in the *para* position (entries 7–9) or the use of a lower metal/substrate ratio (entry 4) led to a significant retardation of the reduction. It is worth noting that the aqueous catalytically active complex could be quantitatively recovered after carrying out the extraction in air with no particular precautions. Its stability is evidently quite good since the aqueous phase could be reused with only a slight loss of activity (entry 2). However, if rhodium was used instead of iridium, the catalytic activity was very low (entry 11). Moreover, in the case of iridium, ligand **2** exhibited a higher activity than **1** (entries 5, 10), in contrast to the chiral [(1*R*,2*R*)-diurea]iridium complex derived from (1*R*,2*R*)-diaminocyclohexane, which is not stable under the reaction conditions and precipitates black metal (entry 12). The higher efficiency of ligand **2** compared to **1** might stem from steric hindrance to good complexation of the iridium ion by the 2,2'-bipyridine core due to the CONHC₃H₆PO₃Na₂ chains. Another explanation invokes the higher electron density present on the nitrogen atoms in **2** compared to those in **1**, as established by semiempirical calculations (AM1 and PM3 methods).^[10] Finally, the water-soluble system gave better results than the related ligand (phosphonate ester form) in a homogeneous methanolic medium (entry 13), despite the better solubility of hydrogen in methanol compared to water. A possible explanation might be the presence of a cationic complex in water, with one phosphonate group in the PO₃Na[−] form acting as the counteranion to the iridium ion.^[11] In fact, some acceleration of reaction rates for cationic phosphane–metal complexes compared to the corresponding neutral species has previously been reported in the literature.^[12]

In the light of these results and taking into account the catalytic properties (for the hydrogenation of ketones) reported in the literature for (2,2'-bipyridine)rhodium complexes in basic methanolic media (no activity detected under neutral conditions),^[5a] the activity of the (1)rhodium complex in the reduction of acetophenone at pH = 9 (by addition of sodium hydroxide) was re-examined. Under these conditions, complete conversion was achieved (Table 2, entry 14) and the aqueous catalytic phase could be reused with only a slight loss of activity (entry 15). In addition, a strong activity enhancement of the water-soluble system based on ligand **1** was observed in basic media, since acetophenones substituted at the 4'-position by electron-donating groups (ethyl, methoxy) were easily reduced to the corresponding alcohols, using iridium as well as rhodium (entries 16, 17, 19, 20). As 4'-methoxyacetophenone is a solid substrate, it first had to be dissolved to carry out the catalytic test. The choice of solvent proved to be important; diethyl ether gave good results whereas ethyl acetate led only to low conversions (entry 18). Decreasing the ligand/Ir ratio to 2:1 had no significant effect on the degree of conversion (entry 22), but decreasing the Ir/substrate ratio slowed down the reaction and gave the alcohol with only 70% conversion (entry 23). However, when the aqueous phase from this latter experiment was reused and the catalytic test was run for a longer period (64 h; entry 24), the reduction was almost quantitative, again showing that the

catalyst can be recycled intact. As previously, ligand **2** performed better than bipyridine **1** under similar reaction conditions (entry 25). In order to assess to what extent the reaction time could be reduced, the degree of conversion was measured as a function of time in the experiments corresponding to entries 20 and 21 (Table 2, entries 20a and 21a). After 1 h, the conversion was very low (3–6%), but then sharply increased to over 90% after 8 h.

Based on the commonly accepted mechanism together with observations made in the literature,^[13] the main role of the added base might be to deprotonate the intermediate **A**, obtained by insertion of the ketone into one of the Rh–H bonds, while water could protonate the alkoxide ligand (Scheme 3).



Scheme 3. Proposed effect of NaOH in the catalytic site of Rh-catalyzed hydrogenation of ketones in water under hydrogen pressure; S = H₂O

This push-pull process would favor the reductive elimination of **A**, allowing the oxidative addition of hydrogen to regenerate **B**, thereby accelerating the reaction rate. The amount of base necessary to observe this reactivity enhancement (30 equiv. of OH[−] based on Ir or Rh in entries 14–25) was not optimized and might be reduced, since a 98% conversion was still obtained in entry 22 with only 5 equiv. of OH[−] added (based on Ir). Similarly, in the case of entry 25, 4'-methoxyacetophenone was converted in 95% yield with only 1.5 equiv. of OH[−] added (based on Ir), thus showing that the role of the promoter is probably catalytic.

In summary, we have synthesized new water-soluble 2,2'-bipyridine ligands. In the hydrogenation of various acetophenones in water under hydrogen pressure, the Rh and Ir complexes of these ligands show remarkable catalytic activities in basic media, in the absence of any phase-transfer agent. We are currently trying to extend these results to chiral diamines, known to be stable under hydrogen pressure, by functionalization of these ligands with PO₃Na₂ moieties. Moreover, the heterogenization of such systems as insoluble

metal phosphonates for supported catalysis is also being investigated.

Table 1. Hydrogenation of aryl ketones in the presence of water-soluble diamine-complexed transition metals (neutral pH)^[a]

Entry	Metal	Diamine ^[b]	Substrate	Conversion ^[c]
1	Ir	1	methyl phenylglyoxylate	> 99%
2	Ir	1 (after 1 use)	methyl phenylglyoxylate	96%
3	Ir	1	acetophenone	> 99%
4	Ir ^[d]	1	acetophenone	24%
5	Ir	2	acetophenone	> 99%
6	Ir	1	4'-nitroacetophenone ^[e]	> 99%
7	Ir	1	4'-chloroacetophenone	88%
8	Ir	1	4'-ethylacetophenone	38%
9 ^[f]	Ir	1	4'-ethylacetophenone	64%
10	Ir	2	4'-ethylacetophenone	95%
11	Rh	1	acetophenone	5%
12	Ir	3	acetophenone	unstable complex; metal precipitation ^[g]
13 ^[h]	Ir	1 (phosphonate ester form)	4'-ethylacetophenone	4%

^[a] Conditions: diamine/metal = 4:1; metal/substrate (neat) = 5%; 40 atm H₂; water; reaction time = 21 h. — ^[b] In its neutral sodium form. — ^[c] Yield in the corresponding alcohol = 100%. — ^[d] Metal/substrate = 1%. — ^[e] Dissolved in 0.5 mL of ethyl acetate. — ^[f] Reaction time = 66 h. — ^[g] Same result when rhodium used instead of iridium. — ^[h] Same conditions as for^[a], but with water replaced by methanol.

Table 2. Hydrogenation of aryl ketones in the presence of water-soluble diamine-complexed transition metals (basic medium)^[a]

Entry	Metal	Diamine ^[b]	Substrate	Conversion ^[c]
14	Rh	1	acetophenone	> 99%
15	Rh	1 (after 1 use)	acetophenone	93%
16	Rh	1	4'-ethylacetophenone	> 99%
17	Ir	1	4'-ethylacetophenone	> 99%
18	Rh	1	4'-methoxyacetophenone ^[d]	7%
19	Rh	1	4'-methoxyacetophenone ^[e]	96%
20	Ir	1	4'-methoxyacetophenone ^[e]	> 99%
20a	conversion versus time for entry 20: 3% (1 h), 30% (3 h), 90% (8 h)			
21	Ir	2	4'-methoxyacetophenone ^[e]	> 99%
21a	conversion versus time for entry 21: 6% (1 h), 95% (8 h)			
22	Ir ^[f]	1	4'-methoxyacetophenone ^[e]	98%
23	Ir ^[g]	1	4'-methoxyacetophenone ^[e]	70%
24	Ir ^[g]	1 (after 1 use)	4'-methoxyacetophenone ^[e]	96% ^[h]
25	Ir ^[f,g]	2	4'-methoxyacetophenone ^[e]	93%

^[a] Conditions: diamine/metal = 4:1; metal/substrate (neat) = 5%; 40 atm H₂; water; reaction time = 21 h; NaOH/metal = 30:1. — ^[b] In its neutral sodium form. — ^[c] Yield in the corresponding alcohol = 100%. — ^[d] Dissolved in 0.5 mL of ethyl acetate. — ^[e] Dissolved in 0.5 mL of diethyl ether. — ^[f] Diamine/metal = 2:1. — ^[g] Metal/substrate = 1%. — ^[h] Reaction time = 64 h.

Experimental Section

General: ¹H- and ³¹P-NMR spectra were recorded with a Bruker AC-200 spectrometer with tetramethylsilane (¹H) and external 85% H₃PO₄ (³¹P) as references. High-resolution mass spectra were obtained with a Hewlett-Packard HP 5889A instrument. Gas chromatographic analyses were performed using a Hewlett-Packard HP 6890 gas-chromatograph with a J. & W. Scientific DB-1701 column (*l* = 30 m, *i.d.* = 0.25 mm). Melting points were determined with a Reichert-Kofler hotplate apparatus. Optical rotations were measured with a Perkin–Elmer 341 polarimeter. Energy Dispersive X-

ray Spectroscopy (EDXS) measurements were made on a Jeol JM-35C SEM with a Tracor TN5500 micro Z attachment.

General Procedure for Hydrogenation: In a 25-mL Schlenk tube, 0.12 mmol of ligand **1–3** and 0.48 mL of 1 M aq. sodium hydroxide solution were added to 5 mL of water under argon and the mixture was degassed. After complete dissolution of the ligand, 0.015 mmol of [M(COD)Cl]₂ (M = Ir, Rh) was added. After stirring for 24 h at room temperature, the deep-red (Ir) or yellow (Rh) solution was transferred to a 30-mL stainless steel glass-coated autoclave, and 0.6 mmol of substrate (neat when liquid or dissolved in 0.5 mL of solvent when solid; see Tables) was added. The autoclave was purged 3 times with argon, then 3 times with hydrogen, and the final H₂ pressure was adjusted to 40 atm. The mixture was stirred at room temperature for 21 h and then extracted with ethyl acetate. The aqueous phase was separated and reused, while the colorless organic layer was concentrated and analysed by gas chromatography and ¹H NMR to determine the conversions and reaction yields, using nonane (0.1 mmol) as an internal standard. No metal (Ir or Rh) could be detected on performing EDXS experiments on the residue from the organic phase. GC analyses of the aqueous phase confirmed that all the reaction products had been removed during the extraction process. The tests corresponding to entries 22 and 23 were run twice and the error limits were estimated as ±2%.

Compound 1: This ligand was prepared from the 5,5'-dimethyl-2,2'-bipyridine derivative (easily obtained according to Lemaire et al. by coupling of 2-bromo-5-methylpyridine).^[14] The methyl substituents were oxidized to carboxylic acid groups (CrO₃/H₂SO₄, 70%), then converted into acyl chlorides (SOCl₂, quantitative). To a solution of diethyl 3-aminopropylphosphonate (2.84 g, 14 mmol) in freshly distilled dichloromethane (200 mL) and triethylamine (2.05 mL, 14 mmol), a solution of 5,5'-bis(chlorocarbonyl)-2,2'-bipyridine (1.02 g, 3.6 mmol) in 300 mL of dichloromethane was added dropwise. The reaction mixture was stirred at room temperature for 18 h. After hydrolysis (water) and extraction (dichloromethane), the solvent was evaporated from the combined organic solutions to give a yellow oil, which was purified by column chromatography (SiO₂; 10% EtOH/CH₂Cl₂). The desired compound was obtained as a colorless oil in 75% yield. — ¹H NMR (200 MHz, CDCl₃): δ = 1.32 (t, 12 H, ³J = 7 Hz, CH₃ ethyl), 1.9 (m, 8 H, CH₂CH₂P), 3.6 (q, 4 H, ³J = 6 Hz, NHCH₂), 4.1 (quint, 8 H, ³J_{HH} = ³J_{HP} = 7 Hz, CH₂ ethyl), 7.9 (t, 2 H, ³J = 6 Hz, CONH), 8.3 (dd, 2 H, ³J = 8 Hz, ⁴J = 2.3 Hz, bipyridine), 8.5 (dd, 2 H, ³J = 8 Hz, ⁵J = 0.8 Hz, bipyridine), 9.2 (dd, 2 H, ⁴J = 2.3 Hz, ⁵J = 0.8 Hz, bipyridine). — ³¹P NMR (81 MHz, CDCl₃): δ = 31.6. — MS (EI); *m/z* (%): 598 (1) [M⁺], 377 (100). — The tetraethyl ester form of ligand **1** thus obtained was converted into the corresponding bis(phosphonic acid) using bromotrimethylsilane, as described in the synthesis of compound **3** (see below). — ¹H NMR (200 MHz, DMSO): δ = 1.7 (m, 8 H, CH₂CH₂P), 3.3 (q, 4 H, ³J = 6 Hz, NHCH₂), 8.4 (dd, 2 H, ³J = 8 Hz, ⁴J = 2 Hz, bipyridine), 8.5 (d, 2 H, ³J = 8 Hz, bipyridine), 8.9 (t, 2 H, ³J = 6 Hz, CONH), 9.1 (d, 2 H, ⁴J = 2 Hz, bipyridine). — ³¹P NMR (81 MHz, DMSO): δ = 26.5.

Diethyl 4-Aminophenylphosphonate: 5.23 mL of formic acid (136 mmol) was added dropwise to a stirred mixture of 10.7 g (41.3 mmol) of diethyl 4-nitrophenylphosphonate,^[8] 23.5 mL (181 mmol) of triethylamine, and 100 mg of 5% Pd/C. The mixture was refluxed for 1 h, then poured into water and extracted with dichloromethane. The combined organic layers were washed with brine, dried (MgSO₄), and concentrated. The desired compound was crystallized from toluene (pale-yellow crystals; 82% yield). — M.p. 131 °C. — ¹H NMR (200 MHz, CDCl₃): δ = 1.3 (t, 6 H, ³J = 7 Hz, CH₃ ethyl), 4.05 (m, 6 H, CH₂ ethyl and NH₂), 6.7 (dd, 2 H,

$^3J = 8$ Hz, $^4J_{\text{HP}} = 3.5$ Hz, phenyl), 7.6 (dd, 2 H, $^3J = 8$ Hz, $^3J_{\text{HP}} = 13$ Hz, phenyl). – ^{31}P NMR (81 MHz, CDCl_3): $\delta = 20.5$. – MS (EI); m/z (%): 229 (63) [M^+], 173 (49), 156 (39), 93 (100).

Compound 3: 125 mg of triphosgene (0.42 mmol) was dissolved in 2.3 mL of dichloromethane under argon. To this, a solution of diethyl 4-aminophenylphosphonate (265 mg, 1.15 mmol, in 4 mL of dichloromethane and 0.17 mL of triethylamine) was slowly added by means of a syringe pump (4 mL/h). The reaction mixture was stirred for 30 min and then a solution of (1*R*,2*R*)-diaminocyclohexane (66 mg, 0.57 mmol, in 6 mL of dichloromethane and 0.17 mL of triethylamine) was rapidly added. The resulting mixture was stirred for a further 1 h and then concentrated under reduced pressure. The crude residue obtained was redissolved in chloroform, the resulting solution was washed with water, and the organic layer was dried and concentrated to give a white solid, which was rinsed with acetone and collected by filtration (75% yield). – M.p. 255°C. – $[\alpha]_{\text{D}}^{20} = +61$ ($c = 1$, CHCl_3). – ^1H NMR (200 MHz, DMSO): $\delta = 1.2$ (t, 12 H, $^3J = 7$ Hz, CH_3 ethyl), 1.3 (m, 4 H, $\text{NCHCH}_2\text{CH}_2$ cyclohexyl), 1.65 (m, 2 H, NCHCH_2 cyclohexyl), 1.95 (m, 2 H, NCHCH_2 cyclohexyl), 3.45 (m, 2 H, NCH cyclohexyl), 3.95 (quint, 8 H, $^3J_{\text{HH}} = ^3J_{\text{HP}} = 7$ Hz, CH_2 ethyl), 6.2 (d, 2 H, $^3J = 7$ Hz, CHNHCO), 7.5 (m, 8 H, phenyl), 8.85 (s, 2 H, CONHC_6H_4). – ^{31}P NMR (81 MHz, DMSO): $\delta = 18.7$. – MS (EI); m/z (%): 395 (38) [M^+], 229 (66), 199 (100). – The tetraethyl ester form of compound 3 (210 mg, 0.33 mmol) was suspended in 5.5 mL of dichloromethane and bromotrimethylsilane (0.35 mL, 2.6 mmol) was added. The resulting clear yellow solution was stirred for 24 h at room temperature under argon. After evaporation of the solvent, 20 mL of methanol was added and the resulting solution was stirred for 18 h, whereupon a white precipitate was gradually deposited. This white solid was isolated by filtration, washed with dichloromethane, and dried in vacuo to afford a quantitative yield of ligand 3. – ^1H NMR (200 MHz, DMSO): $\delta = 1.2$ (m, 4 H, $\text{NCHCH}_2\text{CH}_2$ cyclohexyl), 1.65 (m, 2 H, NCHCH_2 cyclohexyl), 1.95 (m, 2 H, NCHCH_2 cyclohexyl), 3.4 (m, 2 H, NCH cyclohexyl), 6.15 (d, 2 H, $^3J = 6$ Hz, CHNHCO), 7.45 (m, 8 H, phenyl), 8.7 (s, 2 H, CONHC_6H_4). – ^{31}P NMR (81 MHz, DMSO): $\delta = 13.8$.

[1] [1a] E. G. Kunz, *Chemtech* **1987**, 570–575. – [1b] For a review, see W. A. Herrmann, C. W. Kohlpainter, *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1524–1544. – [1c] See also: *Aqueous Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1998**.

[2] [2a] R. G. Nuzzo, S. L. Haynie, M. E. Wilson, G. M. Whitesides, *J. Org. Chem.* **1981**, 46, 2861–2867. – [2b] D. Sinou, *Bull. Soc.*

- Chim. Fr.* **1987**, 3, 480–486. – [2c] Y. Amrani, L. Lecomte, D. Sinou, J. Bakos, I. Toth, B. Heil, *Organometallics* **1989**, 8, 542–547. – [2d] I. Toth, B. E. Hanson, M. E. Davis, *Tetrahedron: Asymmetry* **1990**, 1, 913–930. – [2e] S. Ganguly, J. T. Mague, D. M. Roundhill, *Inorg. Chem.* **1992**, 31, 3500–3501. – [2f] T. L. Schull, J. C. Fetting, D. A. Knight, *Inorg. Chem.* **1996**, 35, 6717–6723. – [2g] H. Gulyas, P. Arva, J. Bakos, *J. Chem. Soc., Chem. Commun.* **1997**, 2385–2386. – [2h] F. Joo, J. Kovacs, A. C. Benyei, A. Katho, *Angew. Chem. Int. Ed.* **1998**, 37, 969–970 and references therein.
- [3] A. Clearfield in *Progress in Inorganic Chemistry* (Ed.: K. D. Karlin), John Wiley & Sons, Inc., New York, **1998**, vol. 47, p. 371–510.
- [4] D. Deniaud, B. Schöllhorn, D. Mansuy, J. Rouxel, P. Battioni, B. Bujoli, *Chem. Mater.* **1995**, 7, 995–1000. – [4b] D. Deniaud, G. A. Spyroulias, J. Bartoli, P. Battioni, D. Mansuy, C. Pinel, B. Bujoli, *New J. Chem.* **1998**, 22, 901–905. – [4c] See also, D. Villemain, P. A. Jaffres, B. Nechab, F. Courivaud, *Tetrahedron Lett.* **1997**, 38, 6581–6584.
- [5] See, for example: [5a] G. Mestroni, G. Zassinovich, A. Camus, *J. Organomet. Chem.* **1977**, 140, 63–72. – [5b] C. Botteghi, G. Chelucci, G. Chessa, G. Delogu, S. Gladiali, F. Socolini, *J. Organomet. Chem.* **1986**, 304, 217–225. – [5c] K. Töllner, R. Popovitz-Biro, M. Lahav, D. Milstein, *Science* **1997**, 278, 2100–2102. – [5d] S. Gladiali, L. Pinna, G. Delogu, S. De Martin, G. Zassinovich, G. Mestroni, *Tetrahedron: Asymmetry* **1990**, 1, 635–648. – [5e] P. Gamez, F. Fache, M. Lemaire, *Tetrahedron: Asymmetry* **1995**, 6, 705–718. – [5f] P. Gamez, B. Dunjic, M. Lemaire, *J. Org. Chem.* **1996**, 61, 5196–5197. – [5g] R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, 30, 97–102, and references therein. – [5h] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed.* **1998**, 37, 1703–1707.
- [6] For a recent review, see: V. Fehring, R. Selke, *Angew. Chem. Int. Ed.* **1998**, 37, 1827–1830.
- [7] V. Penicaud, F. Odobel, B. Bujoli, *Tetrahedron Lett.* **1998**, 39, 3689–3692.
- [8] T. Hirao, T. Masunaga, O. Yoshiro, T. Agawa, *Synthesis* **1981**, 56–57.
- [9] C. E. McKenna, M. T. Higa, N. H. Cheung, M. C. McKenna, *Tetrahedron Lett.* **1977**, 155–158.
- [10] All calculations were performed with a Silicon Graphics Indy workstation using the program package Spartan 4.0 wave function, Inc., 18401 von Karman, #210, Irvine, CA, USA.
- [11] Such features have been reported in the case of diphosphane functionalized with sulfate SO_4Li or sulfonate SO_3Na groups. See ref. [2g] and C. Lensink, J. G. de Vries, *Tetrahedron: Asymmetry* **1992**, 3, 235–238.
- [12] P. A. Wender, H. Takahashi, B. Witulski, *J. Am. Chem. Soc.* **1995**, 117, 4720–4721.
- [13] Q. Jiang, Y. Jiang, D. Xiao, P. Cao, X. Zhang, *Angew. Chem. Int. Ed.* **1998**, 37, 1100–1103.
- [14] V. Penalva, J. Hassan, L. Lavenot, C. Gozzi, M. Lemaire, *Tetrahedron Lett.* **1998**, 39, 2559–2560.

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