Raney Ni–Al alloy-mediated reduction of alkylated phenols in water

Song-Liang Tan[a], Guo-Bin Liu[a]*, Xiang Gao[a] and Thies Thiemann[b]

[a]*Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, P.R. China.*

[b]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1, Kasuga-koh-en, Kasuga, Fukuoka 816-8580, Japan*

Raney Ni–Al alloy in a dilute aqueous alkaline solution has been shown to be a very powerful reducing agent in the hydrogenation of phenol and alkylated phenols to the corresponding cyclohexanol derivatives.

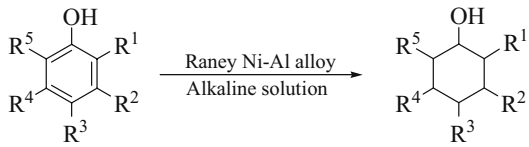
Keywords: Raney Ni–Al alloy, phenols, reduction, dilute alkaline solution, cyclohexanols

Much attention has been devoted to the development of new, cost-effective and eco-friendly procedures for the synthesis of cyclohexanol derivatives, which are important intermediates in the preparation of useful functional polymers[1] and of analgesics.[2] Recently, a strategy for the industrial production of cyclohexanol has been patented, which uses the hydrogenation of benzene to cyclohexene with subsequent hydration.[3] Nevertheless, the conversion of phenol to cyclohexanol is still the major industrial process for the production of cyclohexanol. It is thought to be the most important industrial process to-date that incorporates the hydrogenation of a monocyclic arene into the reaction sequence.[4,5] However the total or partial hydrogenation of the aromatic ring in phenols still presents industrial challenges. Typically catalytic transformations are carried out at high pressures and high reaction temperatures with homogeneous or heterogeneous Pd-, Pt-, Ni,- Co-, Rh or Ru catalysts.[6-18] More recently, the hydrogenation of arenes using Rh and Ru nanoparticles as catalysts or using aqueous colloidal suspensions of catalytically active iridium(0)-species under ultrasonic irradiation have been investigated extensively.[19-22] Furthermore, phenols can be hydrogenated using samarium diiodide (SmI_2) as reductant.[23] Several shortcomings have been noted for the literature methods that makes it more difficult to employ the procedures both at laboratory and industrial scale. These are the expense of some of the reductants, the fact that some of the procedures necessitate more severe conditions and special equipment such as autoclaves, and the lack of accessibility of the catalysts, especially of catalytic nanoparticles. Clearly, there is still need for the development of simple procedures for the transformation of phenols to cyclohexanols.

In the continuation of our work on the reduction of halogenated aromatic compounds,[24-27] we have found that Raney Ni–Al alloy in a dilute aqueous alkaline solution efficiently reduces phenols to cyclohexanols. We have reported that chlorinated or brominated phenols are reduced easily to cyclohexanols with Raney–Ni alloy,[28] and we have now found that non-halogenated, alkylated phenols undergo the reaction with ease.

The reductions were carried out by adding an aqueous alkaline solution dropwise to a suspension of a phenol and Raney Ni–Al alloy (350 mg/mmol of substrate) in water at 90 °C. The reactions are summarised in Table 1 and Scheme 1.

When a 1% aq. solution of KOH, CsOH, NaOH, LiOH, or $Ca(OH)_2$ was added to a mixture of *o*-cresol (**1a)** and Raney-Ni alloy in water, **1a** was reduced to 2-methylcyclohexanol (**2a**) selectively in yields of 90–95% with a ratio *syn/anti* of 1/4.5–4.6 (Table 1, runs 1–5). The reduction became sluggish, when alloy at less than 300 mg/mmol of substrate was employed. In those cases, unreacted **1a** (19.8%, according to GC measurement) was found to remain in the reaction mixture. At lower temperatures, the reduction was slow and the *cis/trans*-ratio was smaller than that found for the reactions carried out at 90 °C (runs 7 *vs* run 1). *m*-Cresol (**1b**) and *p*-cresol (**1c**) were reduced successfully to give the corresponding methylcyclohexanols **2b** and **2c** in 86.5% (*syn/anti* = 1/3.5) and 88.2% (*syn/anti* = 1/3.8) yield, respectively (runs 8 and 9).



1 **2**

a: R^1=Me, R^2=R^3=R^4=R^5=H; **b**: R^1=R^3=R^4=R^5=H, R^2=Me; **c**: R^1=R^2=R^4=R^5=H, R^3=Me;

d: R^1=MeO, R^2=R^3=R^4=R^5=H; **e**: R^2=MeO, R^1=R^3=R^4=R^5=H; **f**: R^1=R^2=R^4=R^5=H, R^3=MeO;

g:R^1=R^2=R^4=R^5=H, R^3=Et; **h**: R^1=R^3=R^4=R^5=H, R^1=*n*-Pr; **i**: R^1=R^2=R^4=R^5=H, R^3=*i*-Pr;

j: R^1=R^2=R^4=R^5=H, R^3=*n*-Bu; **k**: R^1=R^2=R^4=R^5=H, R^3=*t*-Bu; **l**: R^2=R^3=R^4=R^5=H, R^1=*t*-Bu;

m: R^1=R^3=R^4=R^5=H, R^2=*t*-Bu; **n**: R^1=R^2=R^4=R^5=H, R^3=*t*-Pent; **o**: R^1=R^2=Me, R^3=R^4=R^5=H;

p: R^2=R^3=Me, R^1=R^4=R^5=H; **q**:R^2=R^4=Me, R^1=R^3=R^5=H; **r**: R^1=R^4=Me, R^2=R^3=R^5=H;

s: R^1=*t*-Bu, R^2=R^4=R^5=H, R^3=Me; **t**: R^1=R^3=R^5=Me, R^2=R^4=H; **u**: R^1=R^2=R^4=Me, R^3=R^5=H;

v: R^1=R^2=R^3=R^4=R^5=H

Scheme 1

* Correspondent. E-mail: liuguobin@fudan.edu.cn

Table 1 Reduction of alkylated phenol (**1**)[a]

Run	Compd	Alkaline solution[b]/ml	Time/h	Temp./°C	Ratio/%[c,d]		
					1	**2**	*syn/anti*
1	**1a**	1%KOH (100) / H_2O (100)	10	90	0	**2a**:100 (95.2)[5d)]	1/4.6
2	**1a**	1% NaOH (100) / H_2O (100)	10	90	0	**2a**:100 (92.2)	1/4.5
3	**1a**	1% CsOH (100) / H_2O (100)	10	90	0	**2a**:100 (95.3)	1/4.5
4	**1a**	1% $Ca(OH)_2$ (100) / H_2O (100)	10	90	0	**2a**:100 (90.2)	1/4.5
5	**1a**	1%LiOH (100) / H_2O (100)	10	90	0	**2a**:100 (91.7)	1/4.6
6	**1a**	1%KOH (100) / H_2O (100)	10	70	**1a**:81.1	**2a**:81.9	1/4.4
7	**1a**	1%KOH (100) / H_2O (100)	10	50	**1a**:67.2	**2a**:32.8	1/2.8
8	**1b**	1%KOH (100) / H_2O (100)	12	90	0	**2b**:100 (91.5)[9)]	1/3.5
9	**1c**	1%KOH (100) / H_2O (100)	12	90	0	**2c**:100 (92.2)[9)]	1/3.8
10	**1d**	1%KOH (100) / H_2O (100)	16	90	0	**2v**:100 (90.8)[9)]	
11	**1e**	1%KOH (100) / H_2O (100)	16	90	0	**2v**:100(88.2)[9)]	
12	**1f**	1%KOH (100) / H_2O (100)	16	90	0	**2v**:100(89.8)[9)]	
13	**1g**	1%KOH (100) / H_2O (100)	20	90	0	**2g**: 100 (87)[5)]	1/4.2
14	**1h**	1%KOH (100) / H_2O (100)	12	90	0	**2h**: 100 (86)[5)]	1/4.9
15	**1i**	1%KOH (100) / H_2O (100)	12	90	0	**2i**:100 (87.5)[5)]	1/7.3
16	**1j**	1%KOH (100) / H_2O (100)	12	90	0	**2j**:100 (80.2)[28)]	1/19.0
17	**1k**	1%KOH (100) / H_2O (100)	12	90	0	**2k**:100 (82.7)[29-31)]	*anti* only
18	**1l**	1%KOH (100) / H_2O (100)	13	90	0	**2l**:100 (86.6)[30)]	*anti* only
19	**1m**	1%KOH (100) / H_2O (100)	14	90	0	**2m**:100 (85.8)[31)]	*anti* only
20	**1n**	1%KOH (100) / H_2O (100)	12	90	0	**2n**:100 (83.5)[33)]	*anti* only
21	**1o**	1%KOH (100) / H_2O (100)	18	90	0	**2o**:100 (82.8)[34)]	
22	**1p**	1%KOH (100) / H_2O (100)	18	90	0	**2p**:100 (82)[5)]	
23	**1q**	1%KOH (100) / H_2O (100)	18	90	0	**2q**:100 (88)[5)]	
24	**1r**	1%KOH (100) / H_2O (100)	19	90	0	**2r**:100 (90)[5)]	
25	**1s**	1%KOH (100) / H_2O (100)	18	90	0	**2s**:100 (92)[5)]	
26	**1t**	1%KOH (100) / H_2O (100)	20	90	0	**2t**:100 (89.5)[5)]	
27	**1u**	1%KOH (100) / H_2O (100)	20	90	0	**2u**:100 (91.2)[5)]	
28	**1v**	1%KOH (100) / H_2O (100)	3	90	0	**2v**:100 (93)[9)]	

[a]**1** (10 mmol), 3.5 g Ni–Al alloy. [b]Added dropwise within 1.0 h. [c]GC ratio. [d]Isolated yields in parentheses. [e]*syn/ anti* ratio was determined by ^{1}H NMR.

Treatment of 2-, 3- and 4-methoxyphenols (**1d–f**) with Raney Ni–Al alloy did not give the desired methoxycyclohexanols and produced cyclohexanol (**2v**) in 88–90% yields (runs 10–12), via demethoxylation as reported previously.[28] In the case of 4-ethyl, 2-*n*-propyl, 4-*n*-propyl and 4-*n*-butylphenol (**1g–j**), the expected cyclohexanols (**2g–j**) were obtained in 80–87.5% yields.

As expected, phenols with bulky groups (**1k–n**) gave the *anti*-cyclohexanols (**2k–n)** exclusively in the yields of 82–86% (runs 17–20)**,** so that the bulky groups were not placed in an axial position. In the case of disubstituted phenols (**1o–u**), the desired cyclohexanols (**2o–u**) were obtained in high yields (runs 21–27), although the ratio of stereoisomers were not identified due to complicated ^{1}H NMR spectra. Under similar reaction conditions, treatment of phenol itself (**1v**) with Raney Ni–Al alloy gave the desired cyclohexanol (**2v**) in 93% yield.

A number of functional groups were reduced under these reaction conditions. Thus, 4-cyanophenol (**1w)** was transformed to 4-aminomethylphenol (**1y**)[35] in 89% yield. With trifluorophenol (**1x**) as starting material, *p*-cresol (**1c**) was obtained as the main product (68% yield), along with a small amount of 4-methylcyclohexanol (**2c**, 18% yield, *syn/ anti* = 1/3.8, ^{1}H NMR ratio) (Scheme 2).

In conclusion, we have developed a new efficient method for the reduction of alkylated phenols by using commercially available Raney Ni–Al alloy in a dilute alkaline aqueous solution. Cresols were reduced to give the corresponding methylcyclohexanols as a mixture of *syn/anti* isomers. In the case of bulky substituted phenols such as of *t*-butyl and *t*-pentylphenol, the desired *t*-butyl and *t*-pentylcyclohexanols were afforded exclusively as the *anti*-isomer. No organic solvents were used in the reactions. The advantages of the process lie in the ease of manipulation, the short reaction times necessary, and the mildness of the reaction conditions. Raney Ni–Al alloy is commercially readily available and is, of course, cheaper than the Raney-Ni catalyst made from it.

Experimental

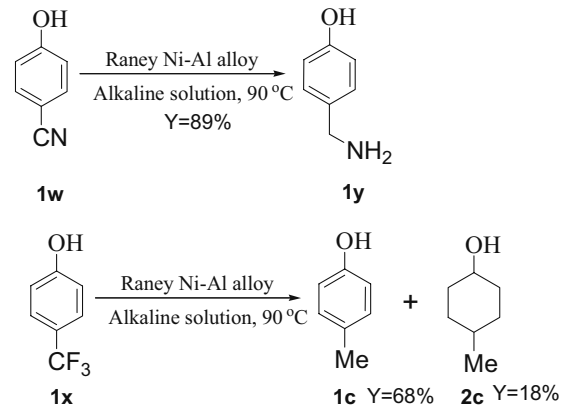
General

IR spectra were measured with Nicolet FT-IR 360, JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^{1}H at 270 MHz and ^{13}C at 67.8 MHz) and a Bruker DMX-500. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer [electron impact mode (EI), 70 eV or fast atom bombardment (FAB)] and with a GC-MS 6890[GC]/HP MS5973 combination.

The Raney-Ni alloy was acquired commercially from Jinzhou Catalyst Company (16, Wenshengli, Linhe, Jinzhou 12100, P.R. China).

General procedure

To a suspension of **1a** (10 mmol, 1.08 g), and Raney Ni–Al alloy (3.5 g) in water (100 ml) was added dropwise a 1$^w/_v$% aq. KOH solution (100 ml) within 1.0 h and at 90 °C. After being heated for 10 h at 90 °C, the mixture was cooled to room temperature and filtered through Celite. The residue was washed with ethyl acetate.



Scheme 2

The filtrate was neutralised with aq. hydrochloric acid, and the ensuing mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$. After removal of the solvent, 2-methylcyclohexanol (**2a**) (1.09 g, 95.2%) was obtained as a colourless oil (Table, run 1).

2-Methylcyclohexanol (**2a,** *a mixture of syn and anti-isomers*):[22] ν_{max} (neat/cm^{-1}) 3370 (bs, OH), 2920, 2880, 1450, 1062, 1045, 1030, 978, 917, 840; δ_H (400 MHz, $CDCl_3$) 1.02–1.88 (12H, m), 2.02 (1H, s, OH), 3.14 (0.82 H, dt, J = 4.2 and 9.4 Hz, C**H**OH*, anti*-isomer), 3.80 (0.18 H, quintet, J = 2.6 Hz, C**H**OH*, syn*-isomer); δ_C (67.8 MHz, $CDCl_3$) for *syn*-isomer: 20.6, 24.5, 28.8, 30.9, 32.5, 35.8, 71.1; for *anti*-isomer: 18.5, 25.2, 25.7, 33.6, 35.5, 40.2, 76.5; MS (EI, 70 eV) *m/z* (%) 114 (M^+) (38), 96 (100), 81 (88), 68 (64), 58 (58).

3-Methylcyclohexanol (**2b,** *a mixture of syn and anti-isomers*):[22] ν_{max} (neat/cm^{-1}) 3380 (bs, OH), 2940, 2880, 1452, 1105, 1045, 1030, 1000, 945, 935; δ_H (400 MHz, $CDCl_3$) 0.98–1.80 (12H, m), 2.00 (1H, s, OH), 3.24 (0.78H, m, C**H**OH*, anti*-isomer), 3.72 (0.22H, m, C**H**OH*, syn*-isomer); δ_C (67.8 MHz, $CDCl_3$) for *syn*-isomer: 20.0, 22.0, 26.5, 33.1, 34.2, 41.5, 66.9; for *anti*-isomer: 22.3, 24.2, 31.4, 34.1, 35.4, 44.7, 70.8; MS (EI, 70 eV) *m/z* (%) 114 (M^+) (3.7), 96 (100), 81 (62), 71 (62).

4-Methylcyclohexanol (**2c,** *a mixture of syn and anti-isomers*):[22] ν_{max} (neat/cm^{-1}) 3370 (bs, OH), 2920, 1450, 1358, 1185, 1047, 980; δ_H (400 MHz, $CDCl_3$) 0.86–1.78 (12H, m), 2.00 (1H, s, OH), 3.40 (0.79H, m, C**H**OH*, anti*-isomer), 3.80–3.84 (0.21H, m, C**H**OH*, syn*-isomer); δ_C (67.8 MHz, $CDCl_3$) for *syn*-isomer: 21.6, 29.0 (2C), 31.1, 32.2 (2C), 66.9; for *anti*-isomer: 21.6, 31.4 33.0 (2C), 35.3 (2C), 70.6; MS (EI, 70 eV) *m/z* (%) 114 (M^+) (5.5), 96 (100), 81 (95), 70 (38), 57 (55).

4-Ethylcyclohexanol (**2g,** *a mixture of syn and anti-isomers*):[5] ν_{max} (neat/cm^{-1}) 3380 (bs, OH), 2925, 2865, 1450, 1083, 1052; δ_H (400 MHz, $CDCl_3$) 0.83–1.74 (14H, m), 2.02 (1H, s, OH), 3.44 (0.81H, m, C**H**OH*, anti*-isomer), 3.74–3.80 (0.19H, m, C**H**OH*, syn*-isomer).

2-n-Propylcyclohexanol (**2h,** *a mixture of syn and anti-isomers*):[5] δ_H (400 MHz, $CDCl_3$) 0.90–1.78 (16H, m), 2.00 (1H, s, OH), 3.10 (0.83H, dt, J = 4.0 and 9.2 Hz, C**H**OH*, anti*-isomer), 3.68 (0.17H, quintet, J = 2.4 Hz, C**H**OH*, syn*-isomer).

4-i-Propylcyclohexanol (**2i,** *a mixture of syn and anti-isomers*):[5] δ_H (400 MHz, $CDCl_3$) 0.86–1.72 (16H, m), 1.98 (1H, s, OH), 3.40 (0.88H, m, C**H**OH*, anti*-isomer), 3.70–3.76 (0.12H, m, C**H**OH, *syn*-isomer).

4-n-Butylcyclohexanol (**2j,** *anti-isomer*):[29-31] δ_H (400 MHz, $CDCl_3$) 0.86–1.72 (18H, m), 1.96 (1H, s, OH), 3.42 (0.95H, m, C**H**OH*, anti*-isomer), 3.68–3.70 (0.05H, m, C**H**OH, *syn*-isomer).

4-t-Butylcyclohexanol (**2k,** *anti-isomer*):[29-31] ν_{max} (neat/cm^{-1}) 3345, 2985, 2880, 1452, 1370, 1068; δ_H (400 MHz, $CDCl_3$) 0.90–0.96 (2H, m), 1.02 (9H, s, Bu^t), 1.20–1.22 (2H, m), 1.60–1.82 (5H, m), 2.02 (1H, s, OH), 3.44 (1H, m, C**H**OH).

2-t-Butylcyclohexanol (**2l,** *anti-isomer*):[30] ν_{max} (neat/cm^{-1}) 3490 (bs, OH), 2935, 1477, 1450, 1385, 1371, 1205, 973; δ_H (400 MHz, $CDCl_3$) 0.88–0.92 (2H, m), 1.00 (9H, s, Bu^t), 1.18–1.21 (2H, m), 1.64–1.80 (5H, m), 2.00 (1H, s, OH), 3.14 (1H, dt, J = 4.0 and 9.4 Hz, C**H**OH).

3-t-Butylcyclohexanol (**2m,** *anti-isomer*):[31] δ_H (400 MHz, $CDCl_3$) 0.86–0.90 (2H, m), 1.00 (9H, s, Bu^t), 1.16–1.20 (2H, m), 1.62–1.80 (5H, m), 2.00 (1H, s, OH), 3.22 (1H, m, C**H**OH).

4-t-Pentylcyclohexanol (**2n,** *anti-isomer*):[33] δ_H (400 MHz, $CDCl_3$) 0.70–0.76 (3H, t, J = 9.8 Hz), 0.80–0.84(4H, m), 0.88 (6H, s), 1.22–1.34 (3H, m), 1.50–1.80 (4H, m), 2.00 (1H, s, OH), 3.50 (1H, m, C**H**OH).

2,3-Dimethylcyclohexanol (**2o**):[34] ν_{max} (neat/cm^{-1}) 3375 (bs, OH), 2925, 1450, 1101, 1050, 1015; δ_H (400 MHz, $CDCl_3$) 0.83–1.74 (14H, m), 2.00 (1H, s, OH), 3.42–3.68 (1H, m, C**H**OH). The isomeric ratio was not determined due to the complexity of the NMR spectrum.

3,4-Dimethylcyclohexanol (**2p**):[5] ν_{max} (neat/cm^{-1}) 3380 (bs, OH), 2920, 2870, 1452, 1365, 1102, 1037; δ_H (400 MHz, $CDCl_3$) 0.80–1.72 (14H, m), 2.02 (1H, s, OH), 3.40–3.64 (1H, m, C**H**OH). The isomeric ratio was not determined due to the complexity of the NMR spectrum.

3,5-Dimethylcyclohexanol (**2q**):[5] ν_{max} (neat/cm^{-1}) 3370 (bs, OH), 2910, 1455, 1345, 1027, 900, 848; δ_H (400 MHz, $CDCl_3$) 0.84–1.78 (14H, m), 1.98 (1H, s, OH), 3.44–3.68 (1H, m, C**H**OH). The isomeric ratio was not determined due to the complexity of the NMR spectrum.

2,5-Dimethylcyclohexanol (**2r**):[5] ν_{max} (neat/cm^{-1}) 3385 (bs, OH), 2915, 1453, 1129; δ_H (400 MHz, $CDCl_3$) 0.82–1.74 (14H, m), 2.00 (1H, s, OH), 3.40–3.62 (1H, m, C**H**OH). The isomeric ratio was not determined due to the complexity of the NMR spectrum.

4-Methyl-2-t-butylcyclohexanol (**2s**):[5] δ_H (400 MHz, $CDCl_3$) 0.78–1.70 (18H, m), 1.98 (1H, s, OH), 3.36–3.58 (1H, m, C**H**OH). The isomeric ratio was not determined due to the complexity of the NMR spectrum.

2,4,6-Trimethylcyclohexanol (**2t**):[5] δ_H (400 MHz, $CDCl_3$) 0.82–1.70 (16H, m), 2.00 (1H, s, OH), 3.44–3.62 (1H, m, C**H**OH). The isomeric ratio was not determined due to the complexity of the NMR spectrum.

2,3,5-Trimethylcyclohexanol (**2u**):[5] δ_H (400 MHz, $CDCl_3$) 0.78–1.72 (16H, m), 2.00 (1H, s, OH), 3.40–3.60 (1H, m, C**H**OH). The isomeric ratio was not determined due to the complexity of the NMR spectrum.

4-Hydroxybenzylamine (**1y**):[35] Colourless solid, m.p. 117 °C; δ_H (270 MHz, CD_3OD) 3.70 (2H, s), 6.74 (2H, m), 7.16 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 46.4 (CH_2), 116.8 (2C, CH), 130.0 (2C, CH), 134.2 (C_{quat}), 158.2 (C_{quat}).

For a final identification, the compounds were separated by column chromatography on silica gel, when mixtures of structures were obtained from the reactions. All of the compounds were compared with authentic samples and/or their structures were assigned on the basis of ^{1}H NMR, IR and GC-MS spectroscopic data.

Received 26 September 2008; accepted 10 November 2008
Paper 08/0188 doi: 10.3184/030823409X393637
Published online: 16 January 2009

References

1 D.J. Sikkema, P. Hoogland, J. Bik and P.T. Lam, *Polymer*, 1986, **27**, 1441.
2 D. Lednicer, P.F. VonVoigtlander and D.E. Emmert, *J. Med. Chem.*, 1981, **24**, 404.
3 W. Peschel, T. Adrian, H. Rust, A. Boettcher, T. Hill, U. Mueller and R. Papp, (BASF AG), 2003, *PCT Int. Appl. WO2003074453*; *Chem. Abstr.*, 2003, **139**, 232194.
4 K. Weissermel and H.J. Arpe, *Industrial organic chemistry*, VCH, New York, 2nd edn, 1993, pp. 343-346.
5 H.E. Ungnade and A. Ludutsky, *J. Org. Chem.*, 1945, **10**, 520.
6 A. Roucoux, J. Schulz and H. Patin, *Chem. Rev.*, 2002, **102**, 3757.
7 P.J. Dyson, *J. Chem. Soc. Dalton Trans.*, 2003, 2964.
8 J.A. Widegren and R.G. Finke, *J. Mol. Catal. A: Chem.*, 2003, **198**, 317.
9 J.A. Widegren and R.G. Finke, *Inorg. Chem.*, 2002, **41**, 1558.
10 F. Sabra, J. Bassus and R. Lamartine, *Mol. Cryst Liq. Cryst.*, 1990, **186**, 69.
11 L.W. Covert, R. Connor and H. Adkins, *J. Am. Chem. Soc*., 1932, **54**, 1651.
12 H. Adkins and H.R. Billica, *J. Am. Chem. Soc*., 1948, **70**, 695.
13 J. English, Jr and G.W. Barber, *J. Am. Chem. Soc*., 1949, **71**, 3310.
14 V.I. Bogdan and V.V. Lunin, *Neftekhimiya*, 1988, **28**, 379; *Chem. Abstr.*, 1989, **110**, 114392.
15 K. Tatsuta, *Jpn. Kokai Tokkyo Koho* **2003**, *JP 2003313150*; *Chem. Abstr.*, 2003, **139**, 351944.
16 H.E. Ungnade and A.D. McLaren, *J. Am. Chem. Soc*., 1944, **66**, 118.
17 R.L. Frank, R.E. Berry and O.L. Shotwell, *J. Am. Chem. Soc*., 1949, **71**, 3889.
18 H.E. Ungnade and A. Ludutsky, *J. Org. Chem.*, 1945, **10**, 520.
19 K. Pelzer, O. Vidoni, K. Philippot, B. Chaudret and V. Colliere, *Adv. Funct. Mater.*, 2003, **13**, 118.
20 M. Ohde, H. Ohde and C.M. Wai, *J. Chem. Soc. Chem. Commun.*, **2002**, 2388.
21 J.-L. Pellegatta, C. Blandy, V. Colliere, R. Choukroun, B. Chaudret, P. Cheng and K. Philippot, *J. Mol. Catal. A: Chem.*, 2002, **178**, 55.
22 V. Mevellec, A. Roucoux, E. Ramirez, K. Philippot and B. Chaudret, *Adv. Synth. Catal*., 2004, **346**, 72.
23 Y. Kamochi and T. Kudo, *Tetrahedron Lett.*, 1994, **35**, 4169.
24 H. Tsuzuki, H. Iyama, T. Tsukinoki, M. Mukumoto, T. Yonemitsu, Y. Nagano, T. Thiemann, S. Mataka and M. Tashiro, *J. Chem. Res. (S)*, 1994, 302.
25 H. Tsuzuki, H. Iyama, T. Tsukinoki, M. Mukumoto, T. Yonemitsu, Y. Nagano, T. Thiemann, S. Mataka and M. Tashiro, *J. Chem. Res.* (*M*), 1994, 1701.
26 T. Tsukinoki, T. Kakinami, Y. Iida, M. Ueno, Y. Ueno, T. Mashimo, H. Tsuzuki and M. Tashiro, *J. Chem. Soc. Chem. Commun.*, 1995, 209.
27 G.-B. Liu, T. Tsukinoki, T. Kanda, Y. Mitoma and M. Tashiro, *Tetrahedron Lett.* 1998, **39**, 5991.
28 G.-B. Liu, L. Dai, X. Gao, M.-K. Li and T. Thiemann, *Green Chem.*, 2006, **8**, 781.
29 J.-X. Chen, J.F. Daeuble, D.M. Brestensky and J.M. Stryker, *Tetrahedron*, 2000, **56**, 2153.
30 P.B. Bahia, M.A. Jones and J.S. Snaith, *J. Org. Chem.*, 2004, **69**, 9289.
31 E.L. Elliel and F.J. Biros, *J. Am. Chem. Soc*., 1966, **88**, 3334.
32 Y. Kobayashi, E. Takahashi, M. Nakano and K. Watatani, *Tetrahedron*, 1997, **53**, 1627.
33 A. Farooq and J.R. Hanson, *J. Chem. Res. (S)*, **1996**, 104.
34 C.H. Collins and G.S. Hammond, *J. Org. Chem.*, 1960, **25**, 911.
35 G.V.S. Reddy, G.V. Rao, R.V.K. Subramanyam and D.S. Iyengar, *Synth. Commun.*, 2000, **30**, 2233.