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Telomerisation of long-chain dienes with alcohols using Pd(IMes)(dvds) catalyst

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Several homogeneous palladium catalysts based on PPh$_3$ and nucleophilic carbene (NHC) ligands were screened in the telomerisation reaction of 1,3-pentadiene with methanol. A Pd(acac)$_2$-3PPh$_3$ system showed the highest activity; initially, poor activity was observed using the Pd(0)-NHC catalysts. However, when methanol solvent/nucleophile was replaced by longer chain alcohols 1-propanol and 1-butanol, improved activity and selectivity was observed. Similarly, 1,3-hexadiene was telomerised with 1-propanol and 1-butanol with good selectivity using Pd(IMes)(dvds) as the catalyst. Pd(II)-PPh$_3$ systems were ineffective as catalysts for the telomerisation of 1,3-hexadiene.

1. Introduction

The dimerisation of dienes with the incorporation of a nucleophile, known as telomerisation, is a well studied reaction of significant potential synthetic utility.[1-4] A wide range of nucleophiles have been shown to be active in this reaction, including alcohols,[5-8] amines and ammonia,[9-17] sugars[18-21] and polyols,[22-24] carbon dioxide,[25] *etc.*, suggesting a variety of novel applications. To date, the Kuraray telomerisation of butadiene with water, with subsequent double bond reduction to yield a linear 1-octanol,[26] is the only commercial realisation of a telomerisation process. However, recent advances in catalyst development, especially the introduction of highly active NHC-based catalysts, have improved the selectivity between telomerisation and diene dimerisation products,[5,27] and promised a more widespread application of the telomerisation reaction. Pilot scale telomerisation of butadiene using NHC-based catalysts has recently been reported,[28] promising potential new commercial processes exploiting this 100% atom efficient reaction.

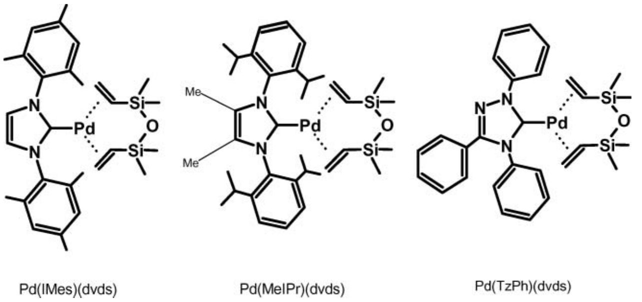
The diolefin most often studied for telomerisation with alcohols is 1,3-butadiene due to its low price and high reactivity;[6,27,29] isoprene (2-methyl-1,3-butadiene) has also been studied extensively due to the potential route to synthetic steroids.[10,11,16,30] Notably, there are no reports of successful telomerisation of dienes longer than a C$_4$ main chain. However, extending the telomerisation reaction to long-chain dienes would open up new opportunities for building high molecular weight and value-added functionalised molecules. An attractive potential source of long-chain dienes is fatty acids, obtained from renewable plant feedstocks.

In this paper, we report the telomerisation of 1,3-pentadiene and 1,3-hexadiene with primary alcohols using homogeneous palladium catalysts bearing PPh$_3$ or nucleophilic carbene (NHC) ligands.

2. Experimental

2.1 Catalyst preparation and characterization

The Pd(0) complexes Pd(IMes)(dvds) [(1,3-dimesitylimidazolin-2-ylidene)-Pd-η^2,η^2-1,1,3,3-tetramethyl-1,3-divinyl-disiloxane] and Pd(MeIPr)(dvds) [(1,3-bis-(2,6-diisopropylphenyl)-4,5-dimethylimidazolin-2-ylidene)-Pd-η^2,η^2-1,1,3,3-tetramethyl-1,3-divinyl-disiloxane] (Scheme 1) were synthesised by reacting stoichiometric amounts of the corresponding free carbene with an 8% Pd(0) in dvds solution in THF at −30 °C, with subsequent crystallization from n-hexane at −20 °C. The ^{1}H NMR spectrum of the products correspond to published data.[27]



Scheme 1 Molecular structures of the Pd(0)-carbene catalysts.

The new Pd(0) complex Pd(TzPh)(dvds) [(1,3,4-triphenyl-tri-1,2,4-azolin-5-ylidene)-Pd-η^2,η^2-1,1,3,3-tetramethyl-1,3-divinyl-disiloxane] was synthesised in a similar manner to the other complexes. The methanol adduct TzPh·MeOH (0.248 g, 0.75 mmol) was thermally decomposed at 90 °C overnight under vacuum,[31] and the resulting free TzPh carbene taken up in dry THF (10 mL) at −20 °C. A Pd(0)-dvds solution (1.00 mL, 8.5 wt%, 0.75 mmol) was added dropwise and the resulting solution

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stirred at room temperature for 1 h, then filtered under N_2 and the solvent removed *in vacuo*. The resulting solid was washed twice with dry pentane at −30 °C, yielding an off-white powder. ^{1}H NMR (400 MHz, C_6D_6, δ): 8.49 (d of m, 7.8 Hz, 2H, *Ph*); 7.34 (d of m, 7.4 Hz, 2H, *Ph*); 7.17 (t of m, 7.8 Hz, 2H, *Ph*); 7.01 (t of m, 7.6 Hz, 1H, *Ph*); 6.96–6.80 (m, 8H, *Ph*); 3.29 (br m, 2H, =C*H*); 2.93 (br m, 4H, =C*H₂*); 0.54 (s, 6H, Si–*Me*); –0.14 (s, 6H, Si–*Me*). ^{1}H NMR peaks labelled as: s - singlet; d - doublet; t - triplet; m - multiplet; br - broad.

2.2 Catalytic tests and materials

Palladium acetylacetonate (Pd(acac)$_2$), triphenylphosphine (PPh$_3$), 1,3-pentadiene, 1,3-hexadiene, methanol, ethanol, 1-propanol and 1-butanol were purchased from Fisher Chemicals and used without further purification. Reactions were carried out in Ace pressure tubes of 15 mL volume (Sigma Aldrich). These heavy-walled borosilicate glass tubes were rated to 11 bar and were equipped with a FETFE® O-ring which sat under the top rim of a PTFE bushing. A heater plate controlled by a Pt100 sensor was used to set the reaction temperature. In a typical experiment, the oil bath was pre-heated for 40 min before starting the reaction. Measured quantities of catalyst (8×10^{-6} moles), solvent, reactant and a magnetic stirrer bar were introduced inside the pressure tube and nitrogen was bubbled through the solution to remove oxygen. An initial sample was taken for analysis, then the tube was tightly closed, introduced into the oil bath and the reaction time set at $t = 0$. Samples during and at the end of the reaction were obtained by quenching the reaction in an ice bath to condense any vapour prior to removal of an aliquot for analysis.

Reaction products were analysed by gas chromatography using a Varian CP-3900 instrument equipped with a non-polar AT-5 capillary column (5% phenyl/95% methylpolysiloxane, 30 m × 0.32 mm) and a flame ionization detector (FID). GC-MS was used to discriminate between the telomerisation products and other reaction by-products. The material balance was closed in all reactions to within ±5%, and the accuracy of determination of concentrations by gas chromatography was calculated by five consecutive measurements of known concentrations of 1,3-pentadiene and 1,3-hexadiene, finding a standard deviation of ±5%. Conversion values were calculated relative to the disappearance of a reactant. The turnover frequency (TOF) was calculated per unit amount (mol) of palladium.

3. Results and discussion

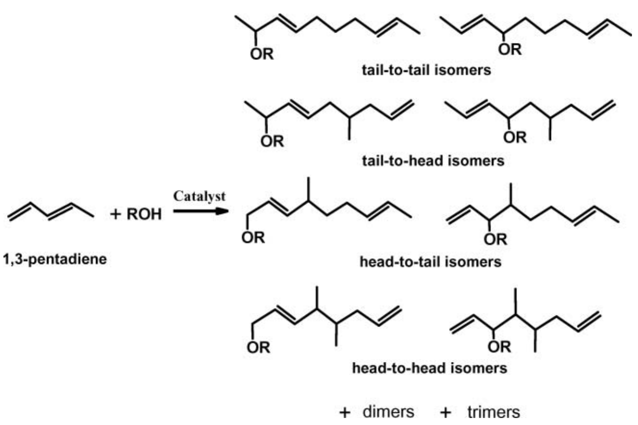
3.1 Telomerisation of 1,3-pentadiene

The telomerisation of asymmetric molecules, such as 1,3-pentadiene and 1,3-hexadiene, with alcohols leads to the potential product distribution shown in Scheme 2. The different telomer products are determined by the orientation of the 'head' (diene moiety) and 'tail' (methyl or ethyl group) during coupling, and the terminal or internal addition of the nucleophile. The side-products are normally dimers and trimers of the diene;[28] Diels–Alder addition products can also form, especially at higher temperatures.[27] Selectivity to telomerisation products *vs.* dimerisation products was calculated for all isomers, but the telomer isomer distribution was not determined since at this stage we are only concerned with determining the feasibility of telomerising long-chain dienes.

Table 1 The telomerisation of 1,3-pentadiene with methanol and different catalysts

Catalyst	T/°C	TON	Conversion @ 7 h (%)	Selectivity @ 7 h (%)
Pd(OAc)$_2$ + 3 equiv. PPh$_3$	70	46	2.4	100
Pd(acac)$_2$ + 3 equiv. PPh$_3$	70	457	24.4	100
Pd(MeIPr)(dvds)	70	25	1.3	100
Pd(TzPh)(dvds)	70	91	4.8	91.8
Pd(IMes)(dvds)	70	157	8.4	97.9

Reaction conditions: 1.5 mL 1,3-pentadiene (2 M), solvent: 5 mL dry 1% NaOMe in MeOH, 1 mL decane as internal standard. Time: 7 h. Catalyst: 8×10^{-6} mol of Pd.



Scheme 2 A scheme of potential telomer products from 1,3-pentadiene and 1,3-hexadiene telomerisation, exemplified with 1,3-pentadiene.

Several *in situ*-formed Pd-PPh$_3$ and pre-formed Pd(0)-carbene catalysts were screened for the telomerisation of 1,3-pentadiene with methanol (Table 1). Appreciable conversion values were obtained only when using the Pd(acac)$_2$-PPh$_3$ combination; with the Pd(IMes)(dvds) and Pd(TzPh)(dvds) complexes producing lower amounts of telomer products. The alternative Pd(OAc)$_2$-PPh$_3$ combination and Pd(MeIPr)(dvds) showed negligible conversion. High to very high selectivity values towards telomerisation products were obtained for all the catalysts tested.

3.1.1. The influence of the alcohol. Primary alcohols of increasing chain length (methanol, ethanol, 1-propanol and 1-butanol) were used as nucleophiles for the telomerisation of 1,3-pentadiene using Pd(IMes)(dvds) and Pd(acac)$_2$-3PPh$_3$ as catalysts (Table 2). No conversion using either catalyst system was observed when the secondary alcohol isopropanol was used as the nucleophile.

In the case of the Pd(acac)$_2$-PPh$_3$ catalyst, increasing the chain length of the alcohol resulted in a decrease in telomerisation conversion, corresponding with the previously observed activity trends in the telomerisation of 1,3-butadiene.[29] The low overall conversions meant that it was difficult to study the influence of the nucleophile on selectivity in these reactions.

In contrast, the carbene catalyst Pd(IMes)(dvds) showed greater conversions as the chain length of the alcohol nucleophile increased (see Fig. 2). Although the observed trend is not perfect, the conversion with ethanol as a nucleophile being unusually

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Table 2 The influence of the alcohol on the telomerisation of 1,3-pentadiene

Catalyst	Nucleophile	$T/°C$	TON	Conversion @ 7 h (%)	Selectivity @ 7 h (%)
Pd(IMes)(dvds)	MeOH	70	157	8.4	98.2
Pd(IMes)(dvds)	EtOH	70	409	21.8	100
Pd(IMes)(dvds)	1-Propanol	70	314	16.7	100
Pd(IMes)(dvds)	1-Butanol	70	451	24.1	100
$Pd(acac)_2$ + 3 equiv. PPh_3	MeOH	70	457	24.4	100
$Pd(acac)_2$ + 3 equiv. PPh_3	EtOH	70	15	0.8	100
$Pd(acac)_2$ + 3 equiv. PPh_3	1-Propanol	70	—	—	—

Reaction conditions: 1.5 mL 1,3-pentadiene (2 M), solvent: 5 mL 1% NaOMe in the alcohol, 1 mL decane as internal standard. Catalyst: 8×10^{-6} mol of Pd.

high in this correlation plot, the overall trend seems to be clear. Observation of the reaction solutions after completion of the catalytic runs showed extensive deposition of Pd black only in the presence of methanol, with the higher alcohols producing gradually less turbid and coloured solutions as the nucleophile chain length was increased (Fig. 1).

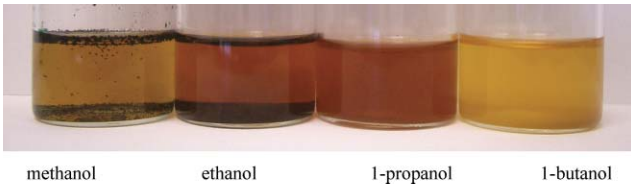

Fig. 1 Visual assessment of the decomposition of Pd(IMes)(dvds) catalyst in the telomerisation of 1,3-pentadiene using different alcohol nucleophiles.

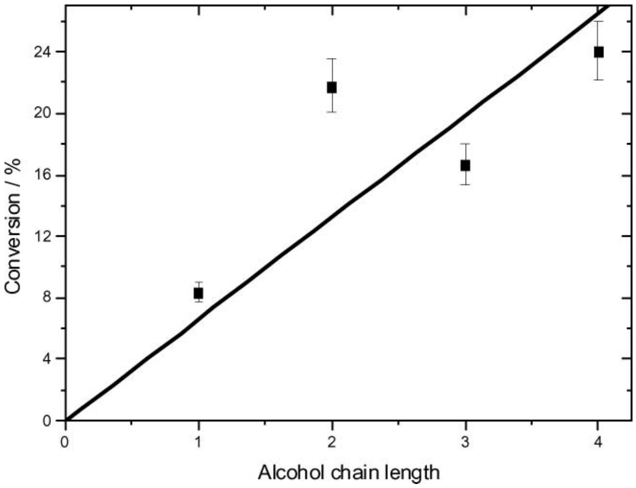

Fig. 2 1,3-Pentadiene conversion in the telomerisation reaction catalysed by Pd(Imes)(dvds) as a function of the alcohol nucleophile chain length.

The contrasting yields resulting from the telomerisation of 1,3-pentadiene with primary alcohol homologues using either the Pd(IMes)(dvds) or $Pd(acac)_2$-$3PPh_3$ catalyst systems suggests that the stability of the active catalyst derived from the Pd-carbene complex improved in the longer chain alcohols. This corresponds with the observed absence of Pd black deposition in Pd(IMes)(dvds) catalysed reaction runs in the higher alcohols. Conversely, the catalyst derived from the $Pd(acac)_2$-$3PPh_3$ system was destabilised as the alcohol chain length increased, forming Pd black. The impact of factors not related to the nature of the catalytic species, such as improved reactant solubility in the longer chain alcohols, were discounted by the extremely poor activity of the $Pd(acac)_2$-$3PPh_3$ system in any alcohol other than methanol.

The observed low reactivity in the presence of a secondary alcohol (such as isopropanol) is in agreement with a recent report on the telomerisation of glycerol,[32] in which no products with a secondary glycerol hydroxy group were observed. Furthermore, the reaction did not proceed in the absence of low molecular weight PEG. The influence of PEG was assigned to the solubilisation of the glycerol reactant. Similarly, in a more systematic study of the influence of the structure of poly-ol nucleophiles on telomerisation activity,[33] telomerisation was found to be more active with primary alcohols and with an increased chain length of the alcohol. The explanations given were based on the increased solubility of both the ligand and the reactant diene in longer chain alcohols and the increased hydrophobicity of longer chain alcohols. The low reactivity of secondary alcohols in telomerisation is not entirely understood, but appears to be a general trend for both carbene and phosphine ligand catalysts.

3.2 Telomerisation of 1,3-hexadiene

The telomerisation of 1,3-hexadiene with methanol was unsuccessful using any of the Pd catalysts previously tested on 1,3-pentadiene, despite the use of elevated temperatures and longer reaction times. Noting the activity improvements gained using longer chain alcohols in the telomerisation of 1,3-pentadiene, a similar study was carried out with 1,3-hexadiene using Pd(IMes)(dvds) (Table 3).

A low telomerisation conversion was observed in ethanol after extended reaction time, while 1-propanol and 1-butanol showed similar conversions and TONs to those observed for 1,3-pentadiene, albeit at an increased reaction temperature. In terms of catalytic activity, little difference between the C_3 and C_4 alcohols was observed. C_3 secondary alcohols, such as isopropanol, also did not show any conversion. In common with reactions using the 1,3-pentadiene substrate, the increased telomerisation conversion in the presence of longer chain alcohols is believed to be associated with the higher stability and/or solubility of the catalytic species derived from Pd(IMes)(dvds) in those solvents.

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Table 3 The influence of nucleophiles on the telomerisation of 1,3-hexadiene

Catalyst	Nucleophile	$T/°C$	TON @ 21 h	Conversion @ 7 h (%)	Conversion @ 21 h (%)
Pd(IMes)(dvds)	MeOH	90	—	—	—
Pd(IMes)(dvds)	EtOH	90	78.1	—	14.3
Pd(IMes)(dvds)	1-Propanol	90	281.3	36.1	51.8
Pd(IMes)(dvds)	1-Butanol	90	263.1	39.2	48.4

Reaction conditions: 0.5 mL 1,3-hexadiene (0.6 M), solvent 5 mL 1% NaOMe in the alcohol, 0.5 mL decane as internal standard. Catalyst: 8×10^{-6} mol of Pd(IMes)(dvds).

Table 4 The influence of the initial concentration of 1,3-pentadiene

Initial concentration/M	$-r_{A\,max}$/ mol h^{-1} L^{-1}	TON	Conversion @ 7 h (%)	Selectivity @ 7 h (%)
4.3	0.093	608	14.9	95.9
3.3	0.054	361	11.6	97.2
2.0	0.024	157	8.4	98.2
1.0	0.015	99	10.6	97.9

Reaction conditions: solvent up to a total volume of 6.5 mL dry 1% NaOMe in MeOH, 1 mL decane as internal standard, time 7 h, catalyst 8×10^{-6} mol of Pd(IMes)(dvds).

3.3. Influence of initial concentration of 1,3-pentadiene

The influence of the initial concentration of 1,3-pentadiene (between 1.0 to 4.3 M) on conversion and selectivity in the telomerisation with methanol using Pd(IMes)(dvds) as the catalyst was investigated. Low conversion values were obtained for all reactant concentrations, and although TONs were improved at higher concentrations, no significant effect of 1,3-pentadiene concentration on the conversion was observed (Table 4). Similarly, there was no influence on the selectivity towards telomerisation products.

4. Conclusions

Conjugated C_5 and C_6 dienes were successfully telomerised with 1-propanol and 1-butanol nucleophiles using a Pd(II)-carbene complex, Pd(IMes)(dvds). Conversions of up to 48% were attained with high selectivity towards telomerisation products. The carbene complex was shown to be active under conditions where Pd(acac)$_2$-3PPh$_3$ was completely inactive, suggesting that the longer chain alcohol nucleophiles/solvents were able to stabilise the active catalytic species derived from the carbene complex.

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References

1 E. J. Smutny, *J. Am. Chem. Soc.*, 1967, **89**, 6793–6794.
2 S. Takahashi, T. Shibano and N. Hagihara, *Tetrahedron Lett.*, 1967, **8**, 2451–2453.
3 A. Zapf and M. Beller, *Top. Catal.*, 2002, **19**, 101–109.
4 B. Cornils, *J. Mol. Catal. A: Chem.*, 1999, **143**, 1–10.
5 R. Jackstell, M. G. Andreu, A. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Röttger, O. Briel, R. Karch and M. Beller, *Angew. Chem., Int. Ed.*, 2002, **41**, 986–989.
6 R. Jackstell, A. Frisch, M. Beller, D. Röttger, M. Malaun and B. Bildstein, *J. Mol. Catal. A: Chem.*, 2002, **185**, 105–112.
7 J. Muzart, *Tetrahedron*, 2005, **61**, 5955–6008.
8 A. Krotz, F. Vollmüller, G. Stark and M. Beller, *Chem. Commun.*, 2001, 195–196.
9 A. Grotevendt, M. Bartolome, A. Spannenberg, D. J. Nielsen, R. Jackstell, K. J. Cavell, L. A. Oro and M. Beller, *Tetrahedron Lett.*, 2007, **48**, 9203–9207.
10 S. M. Maddock and M. G. Finn, *Organometallics*, 2000, **19**, 2684–2689.
11 F. Leca and R. Réau, *J. Catal.*, 2006, **238**, 425–429.
12 M. S. Viciu, F. K. Zinn, E. D. Stevens and S. P. Nolan, *Organometallics*, 2003, **22**, 3175–3177.
13 G. Santos Fonseca, R. F. de Souza and J. Dupont, *Catal. Commun.*, 2002, **3**, 377–380.
14 T. Antonsson and C. Moberg, *Organometallics*, 1985, **4**, 1083–1086.
15 T. Prinz and B. Driessen-Hölscher, *Chem.–Eur. J.*, 1999, **5**, 2069–2076.
16 W. Keim, K.-R. Kurtz and M. Röper, *J. Mol. Catal.*, 1983, **20**, 129–138.
17 T. Mitsuyasu, M. Hara and J. Tsuji, *J. Chem. Soc. D*, 1971, 345.
18 V. Desvergnes-Breuil, C. Pinel and P. Gallezot, *Green Chem.*, 2001, **3**, 175–177.
19 B. Estrine, S. Bouquillon, F. Henin and J. Muzart, *Appl. Organomet. Chem.*, 2007, **21**, 945–946.
20 B. Estrine, S. Bouquillon, F. Hénin and J. Muzart, *Green Chem.*, 2005, **7**, 219–223.
21 F. Hénin, A. Bessmertnykh, A. Serra-Muns, J. Muzart and H. Baillia, *Eur. J. Org. Chem.*, 2004, 511–520.
22 A. Behr and M. Urschey, *Adv. Synth. Catal.*, 2003, **345**, 1242–1246.
23 A. Behr and M. Urschey, *J. Mol. Catal. A: Chem.*, 2003, **197**, 101–113.
24 R. Palkovits, I. Nieddu, R. J. M. K. Gebbink and B. M. Weckhuysen, *ChemSusChem*, 2008, **1**, 193–196.
25 A. Behr, P. Bahke, B. Klinger and M. Becker, *J. Mol. Catal. A: Chem.*, 2007, **267**, 149–156.
26 N. Yoshimura, in *Applied Homogeneous Catalysis with OrganometallicComplexes*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, Germany, 1996, pp. 351.
27 R. Jackstell, S. Harkal, H. J. Jiao, A. Spannenberg, C. Borgmann, D. Rottger, F. Nierlich, M. Elliott, S. Niven, K. Cavell, O. Navarro, M. S. Viciu, S. P. Nolan and M. Beller, *Chem.–Eur. J.*, 2004, **10**, 3891–3900.
28 N. D. Clement, L. Routaboul, A. Grotevendt, R. Jackstell and M. Beller, *Chem.–Eur. J.*, 2008, **14**, 7408–7420.
29 F. Benvenuti, C. Carlini, M. Lami, M. Marchionna, R. Patrini, A. M. Raspolli Galleti and G. Sbrana, *J. Mol. Catal. A: Chem.*, 1999, **144**, 27–40.
30 R. Jackstell, A. Grotevendt, D. Michalik, L. E. Firdoussi and M. Beller, *J. Organomet. Chem.*, 2007, **692**, 4737–4744.
31 D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J. P. Melder, K. Ebel and S. Brode, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1021–1023.
32 A. Gordillo, L. Duran Pachon, E. de Jesus and G. Rothernberg, *Adv. Synth. Catal.*, 2009, **351**, 325–330.
33 R. Palkovits, A. N. Parvulescu, P. J. C. Hausoul, C. A. Kruithof, R. J. M. Klein Gebbink and B. M. Weckhuysen, *Green Chem.*, 2009, **11**(8), 1155–1160.

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