Catalytic Hydrogenation

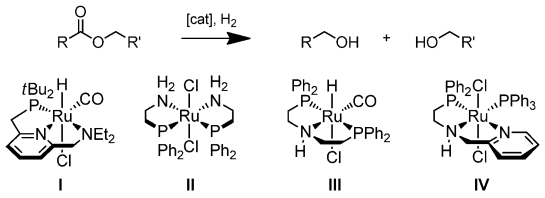
DOI: 10.1002/anie.201209218

Replacing Phosphorus with Sulfur for the Efficient Hydrogenation of Esters**

*Denis Spasyuk, Samantha Smith, and Dmitry G. Gusev**

The reduction of carboxylic esters is a common organic reaction that is often accomplished with the help of aluminium hydrides.[1] Another known approach is Bouveault–Blanc reduction of esters with alkali metals in ethanol.[2] Both classical reduction methods present problems: With aluminium hydrides, the reactions are hazardous and have challenging workups owing to the highly exothermic hydrolysis step that yields voluminous precipitates. In the Bouveault–Blanc method, the drawbacks include excessive foaming and the risk of fires. Both methods produce large amounts of waste.

An attractive "green" alternative to the classical methods is the catalytic hydrogenation shown in Scheme 1, a method which has attracted much recent interest for the reduction of esters under H_2.[3–7] The disclosure of Milstein's catalysts in 2006 (such as complex **I**; Scheme 1)[3] was quickly followed by



I II III IV

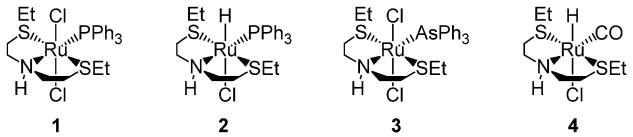
Scheme 1. Ester hydrogenation catalysts.

the development of the Firmenich catalysts in 2007,[4] among which $[RuCl_2(H_2NC_2H_4PPh_2)_2]$ (**II**) is effective at 100 °C at a 0.05 mol % catalyst loading.[4a] In 2011, a new catalyst, Ru-MACHO (**III**), was patented by Takasago chemists.[5] Ru-MACHO is useful at a 0.05 mol % loading for the hydrogenation of methyl lactate and methyl menthoxyacetate, giving high yields of (*R*)-1,2-propanediol and 2-(L-menthoxy)ethanol, respectively. The most recent additions to this list of efficient catalysts are osmium and ruthenium complexes from our group,[6] particularly the air-stable complex $[RuCl_2(PPh_3)\{PyCH_2NHC_2H_4PPh_2\}]$ (**IV**), which demonstrated unprecedented activity in the hydrogenation of esters and imines at [Ru] loadings as low as 50 ppm at 40 °C.

It can be seen that all of the ester hydrogenation catalysts in Scheme 1 possess amino–phosphine ligands. More generally, many Noyori-type catalysts incorporate a combination of phosphorus and nitrogen donors.[8] Despite the widespread application and tremendous success of phosphines in catalysis, they have well-known disadvantages. Their preparations are often far from trivial and require handling under an inert atmosphere. As a result, the amino–phosphines are costly chemicals that can be challenging to make on a large scale. Not surprisingly, catalysts **I**–**III** (available from Strem Chemicals) are very expensive, especially **I**, which costs $680 per gram. Considering that ruthenium contributes less than 1 % to this cost, it is apparent that the development of practical ester hydrogenation calls for using practical ligands, preferably ones containing no phosphorus.

Intrigued by the recent observation of the superior catalytic activity of $[CrCl_3\{HN(C_2H_4SEt)_2\}]$ over $[CrCl_3\{HN(C_2H_4PEt_2)_2\}]$ for the trimerization of ethylene to 1-hexene,[9a] we became interested in the preparation of ruthenium complexes with the $HN(C_2H_4SEt)_2$ (SNS) ligand and the evaluation of their catalytic activity for ester hydrogenation. The SNS ligand is obtained nearly quantitatively by adding bis-(2-chloroethyl)amine hydrochloride to a solution of ethanethiol and NaOH in ethanol.[9b] This synthesis has the practical advantages of being straightforward and scalable; it can be conveniently performed in air, and it provides the SNS ligand at a small fraction of the cost of the amino–phosphines used in catalysts **I**–**IV**. Herein, we report the preparation of a readily available, air-stable ruthenium–SNS complex that is the most efficient catalyst for ester hydrogenation to date, outperforming the known catalytic systems **I**–**III** by a large margin. The significance of this finding goes beyond ester hydrogenation. It is now apparent that a new class of catalysts for the Noyori-type hydrogenation of compounds with C=X bonds can be made based on amino–sulfides that have the potential to replace the ubiquitous phosphorus-based ligands used in this area.

The ruthenium complexes of Figure 1 were obtained by the conventional ligand substitution reactions of $HN(C_2H_4SEt)_2$ with $[RuCl_2(PPh_3)_3]$, $[RuHCl(PPh_3)_3]$, $[RuCl_2$-



1 2 3 4

Figure 1. New SNS catalysts.

[*] Dr. D. Spasyuk, S. Smith, Prof. D. G. Gusev
Department of Chemistry, Wilfrid Laurier University
75 University Ave. W., Waterloo, ON N2L3C5 (Canada)
E-mail: dgoussev@wlu.ca
dgoussev@hotmail.com
Homepage: http://wlu.ca/homepage.php?grp_id=366

[**] We are grateful to NSERC Canada, the Ontario Government and Wilfrid Laurier University for financial support

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201209218.

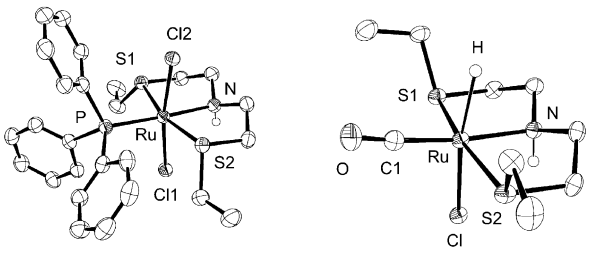


Figure 2. Ortep plots of **1** and **4** with most hydrogens omitted for clarity. Thermal ellipsoids set at 50%.

$(AsPh_3)_3$], and [RuHCl(CO)$(PPh_3)_3$], as documented in the Supporting Information. Complexes **1** and **4** have been crystallographically characterized and their molecular geometries are presented in Figure 2.[10]

The catalytic results of this paper are organized in Tables 1 and 2. First, we compare the effectiveness of catalysts **I**–**IV** and our newly developed complexes **1**–**4**. Two typical substrates were selected for the comparative study: methyl benzoate and methyl hexanoate. The hydrogenations were performed at 40 °C, under H_2 (50 bar), using a catalyst loading of 0.05 mol% in all cases. The reaction mixtures were analyzed by ^{1}H NMR spectroscopy after 3 h of hydrogenation. In all cases, they were found to contain the product alcohols together with varied amounts of byproduct from transesterification, as well as methanol and unreacted starting material. The results in Table 1 demonstrate that the Milstein and Takasago catalysts **I** and **III** are the least effective in the group and produce little product under the test conditions. The Firmenich catalyst **II** shows a moderate performance, whereas complex **IV** is the most effective of the known systems. The new catalysts **1**–**4** are all active for ester hydrogenation; among these, the dichloride and hydrido–chloride complexes **1** and **2** give the best conversions to products, accompanied by formation of the smallest amounts of the symmetrical ester byproducts. To gain a broader understanding of the catalytic performance of **1**, we tested this complex in the hydrogenation of the diverse group of substrates shown in Figure 3, accompanied by variation of the reaction temperature, time, and substrate-to-catalyst (S/C) ratios.

The data in Table 2 support the assessment of complex **1** as an outstanding hydrogenation catalyst possessing unsurpassed efficiency and distinguished by excellent thermal stability and longevity in catalytic solutions. Large turnover numbers were observed for methyl and ethyl benzoates **E1** and **E2**, respectively. For methyl hexanoate (**E6**), a high TON

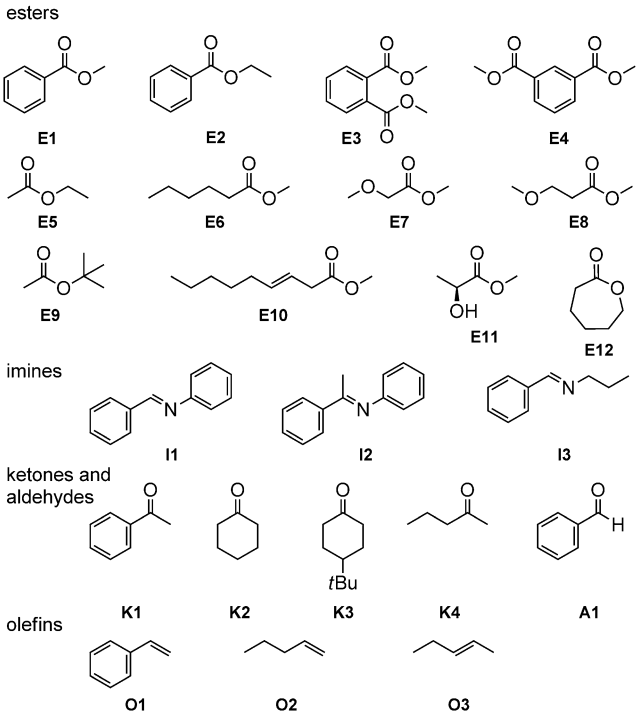


Figure 3. Substrates tested in this work.

of 9800 is achieved in 2 h at 100 °C with **1**, whereas Firmenich catalyst **II** is known to be 6.5 times slower at this temperature for a similar substrate, methyl octanoate, giving a TON of 1880 after 2.5 h.[4a] The reduction of neat ethyl acetate (**E5**) is particularly impressive with **1**, affording a TON of 58400 after 21 h under very mild reaction conditions ($T = 40$ °C). A relatively difficult substrate, methyl phthalate (**E3**) is also rapidly reduced with **1** (0.1 mol%) at 100 °C.

Catalyst **1** has also been successfully tested for the hydrogenation of typical imines and ketones shown in Figure 3, where TONs up to 40000 have been observed when running the reactions at 23–40 °C. Catalyst **1** also has some activity for olefin hydrogenation. Styrene was reduced relatively rapidly at 40 °C with **1** (0.05 mol%). However, the reduction of 1-pentene was considerably slower, and 2-pentene was largely unchanged even after 48 h at 40 °C. The latter observation is promising for the selective hydrogenation of esters, ketones, and imines containing internal C=C bonds. For example, the hydrogenation of methyl 3-nonenoate at 40 °C afforded *trans*-3-nonen-1-ol in a 73% yield. Such selectivity is rare among catalysts that are active

Table 1: Comparative hydrogenation with catalysts **I**–**IV** and **1**–**4**.[a]

Substrate	Catalyst							
	I	**II**	**III**	**IV**	**1**	**2**	**3**	**4**
$PhCO_2Me$	4 (3)[b]	63 (6)[b]	4 (3)[b]	75 (6)[b]	86 (2)[b]	84 (3)[b]	57 (6)[b]	45 (7)[b]
$C_5H_{11}CO_2Me$	18 (7)[c]	55 (16)[c]	23 (8)[c]	89 (10)[c]	98 (1)[c]	96 (1)[c]	75 (13)[c]	66 (17)[c]

[a] Conditions: ester (0.1 mol), catalyst (0.05 mol%), KOMe (5 mol%) in THF (15 mL) under H_2 (50 bar) for 3 h at 40 °C. [b] Concentration (mol%) of benzyl alcohol in the product mixture; data in parentheses is the concentration (mol%) of benzyl benzoate. The balance of material present was unreacted starting material. [c] Concentration (mol%) of 1-hexanol in the product mixture; data in parentheses is the concentration (mol%) of hexyl hexanoate. The balance of material present was unreacted starting material.

Table 2: Hydrogenation of the substrates shown in Scheme 3 catalyzed by **1**.[a]

Entry	Substrate	S/C[b]	Base	Solvent	*t* [h]	*T* [°C]	Conv. [%]
1	**E1**	4000	*t*BuOK	THF	6	40	95
2	**E2**	20000	EtONa	THF	16	40	85[c]
3	**E3**	1000	MeOK	THF	1.2	100	96
4	**E4**	2000	MeOK	THF	16	40	93
5	**E4**	1000	MeOK	THF	1	100	100
6	**E5**	40000	EtONa	neat	14	40	95[d]
7	**E5**	80000	EtONa	neat	21	40	73[d]
8	**E6**	20000	MeOK	THF	24	40	81[c,e]
9	**E6**	10000	MeOK	THF	2	100	98[c]
10	**E7**	10000	MeOK	THF	16	60	100[c]
11	**E8**	2000	MeOK	THF	21	23	97
12	**E9**	4000	*t*BuOK	neat	1	100	100
13	**E10**	2000	*t*BuOK	THF	8	40	100[f]
14	**E11**	2000	MeOK[g]	toluene	1	100	93
15	**E12**	10000	MeOK	toluene	2	100	99
16	**I1**	20000	*t*BuOK	THF	1.5	23	100
17	**I2**	50000	MeOK	THF	1	40	63
18	**I3**	2000	*t*BuOK	toluene	6	40	100
19	**K1**	40000	*t*BuOK	THF	24	40	100[c,h]
20	**K2**	20000	*t*BuOK	THF	1	23	100[c,h]
21	**K3**	20000	*t*BuOK	THF	2	23	100[c,h,i]
22	**K4**	20000	*t*BuOK	THF	1	40	100[c,h]
23	**A1**	10000	MeOK	toluene	1.5	100	94
24	**O1**	2000	*t*BuOK	THF	20	40	100
25	**O2**	2000	MeOK	THF	48	40	75
26	**O3**	2000	MeOK	THF	48	40	13

[a] Unless otherwise noted, the reaction was carried out on substrate (0.02 mol) with base additive (1 mol%) in solvent (6 mL) in a 75 mL Parr high-pressure vessel. [b] Substrate to catalyst ratio. [c] Substrate (0.1 mol) was hydrogenated in a 0.3 L vessel. [d] Substrate (0.2 mol) was hydrogenated in a 0.3 L vessel. [e] The product also contained hexyl hexanoate (9%). [f] *Trans*-3-nonen-1-ol/1-nonanol = 73:27. [g] 5 mol% of base was used. [h] In 15 mL of THF. [i] *Cis*/*trans* product ratio = 87:13.

for ester hydrogenation. So far, only one ruthenium catalyst from Firmenich[4] and an osmium catalyst from our group[6a] have shown good selectivity for the reduction of esters with internal C=C bonds.

As we commented recently,[6b] high catalytic efficiency in ester hydrogenation is expected to correlate with activity in the reverse reaction of acceptorless dehydrogenative coupling (ADC) of alcohols, affording symmetrical esters. Indeed, when tested in the ADC reaction of ethanol under reflux, with S/C = 2000 and 10000, complex **1** gave 97% and 89% conversion to ethyl acetate in 16 and 24 h, respectively. This performance is similar to that of catalyst **IV**, and complexes **1** and **IV** are currently among the most efficient ADC catalysts.[11]

When studying the reactions of **1** upon heating in basic ethanol, we observed a quantitative conversion of the dichloride into species **5**, which was isolated and characterized as $[RuH(OEt)(PPh_3)\{HN(C_2H_4SEt)_2\}]$ and crystallized with one equivalent of hydrogen-bonded ethanol, **5**·EtOH (Figure 4). The preparation of **5** containing no ethanol was also possible by treating hydrido–chloride species **2** with EtONa in toluene. Interestingly, whereas **5** is thermally stable in solution, **5**·EtOH is readily and selectively converted into $[RuH_2(PPh_3)\{HN(C_2H_4SEt)_2\}]$ (**6**) and ethyl acetate upon

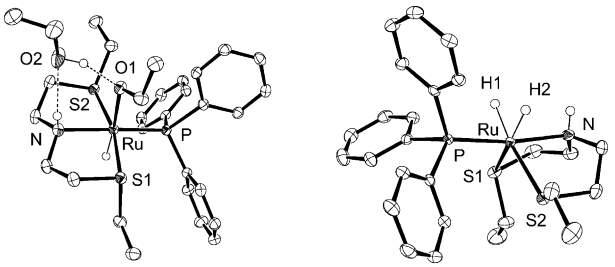
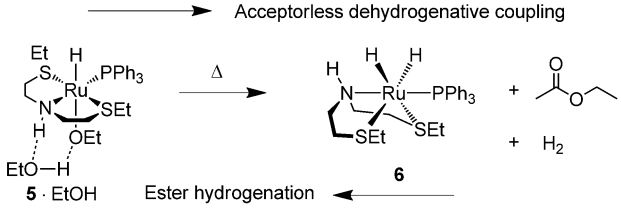


Figure 4. Ortep plots of **5**·EtOH (left) and **6** (right). Thermal ellipsoids set at 50%.

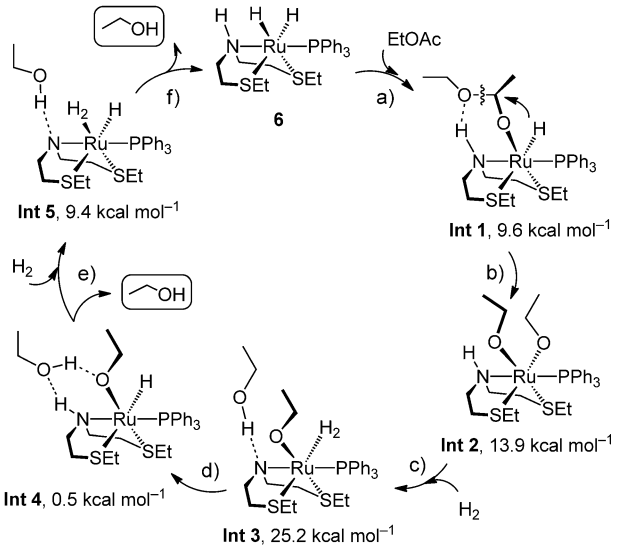


Scheme 2. Formation of dihydride **6** from **5**·EtOH.

mild heating in toluene, as shown in Scheme 2.[12] The molecular structure of **6** is presented in Figure 4; unlike the related *mer*-SNS compounds **1**–**5**, the dihydride **6** adopts a *fac*-SNS geometry.

Scheme 2 has mechanistic implications, as the forward reaction is part of the ADC process, whereas the reverse reaction is ester hydrogenation. Complex **5**·EtOH rapidly hydrogenates ethyl acetate at room temperature (23°C), giving 77% conversion into ethanol within 1 h, under H_2 (50 bar), with [Ru] (0.02 mol%) and NaOEt (1 mol%) and with an efficiency corresponding to TOF = 3850 h^{-1}. We believe that dihydride **6** is the hydrogenation catalyst involved in this process, as well as in the reactions of Table 2, where **6** is presumably produced under H_2 from **1** and base. We further note that the NH group is crucial for catalysis. We synthesized two analogues of catalyst **1**: $[RuCl_2(PPh_3)\{O(C_2H_4SEt)_2\}]$ (**7**) and $[RuCl_2(PPh_3)\{MeN(C_2H_4SEt)_2\}]$ (**8**), and these complexes proved to be inactive in the hydrogenation of methyl benzoate at 40–100°C, under the reaction conditions given in Table 1.

The mechanism of ester hydrogenation is poorly understood.[7i] According to Milstein et al[3a] and Saudan et al,[4a] the concerted transfer of a metal hydride and a ligand proton to the C=O group of the substrate first takes place, affording a hemiacetal intermediate. Dissociation of the hemiacetal gives rise to an aldehyde, which is hydrogenated again by the catalyst, thus completing the reduction process. In our hands, examination of the reaction mixtures by ^{1}H NMR spectroscopy gave no evidence of the presumed hemiacetal or aldehyde intermediates of ester hydrogenation, ethanol dehydrogenation reactions, or the reaction shown in Scheme 2. It is likely that no free organic intermediate, hemiacetal or aldehyde, is released into the reaction solution during the reactions catalyzed by the SNS complexes presented herein.



Scheme 3. Base-free reduction of ethyl acetate catalyzed by **6**.

A tentative mechanism for the base-free hydrogenation of ethyl acetate catalyzed by **6** is presented in Scheme 3. Free energies for all of the intermediates shown in Scheme 3 were calculated in ethyl acetate using the M06-L functional. Among the proposed key steps is the insertion of ethyl acetate into a Ru–H bond of **6**, to afford **Int 1**, which is analogous to the hemiacetaloxide formation in the reaction of *trans*-[RuH_2{(*R*)-BINAP}{(*R*,*R*)-dpen}] with γ-butyrolactone, as documented by Bergens et al.[7g] Inspection of the DFT-optimized structure of **Int 1** reveals an interesting feature: **Int 1** has a six-membered cycle formed by the H-N-Ru-O-CH(Me)-OEt groups and closed by an NH···O hydrogen bond ($d_{O\cdots H} = 1.92$ Å). The single C–O bond of **Int 1** is elongated to 1.493 Å from the corresponding 1.345 Å distance in ethyl acetate. It is conceivable that intramolecular nucleophilic substitution in step b results in the formation of bis(ethoxide) **Int 2**, which rearranges in step c to afford the dihydrogen complex **Int 3**. Heterolytic splitting of the η^2-H_2 ligand in step d gives **Int 4**. Ethanol elimination accompanied by H_2 coordination and heterolysis in steps e and f regenerate dihydride **6**. The isolated complex **5**·EtOH (a *mer*-SNS isomer of **Int 4**) is apparently a resting state of the catalyst. Formation of **5**·EtOH from **6**, ethyl acetate, and H_2 is favorable by $\Delta G = -6.2$ kcal mol^{-1}, which is 6.7 kcal mol^{-1} more stable than **Int 4**.

Base has a tremendous accelerating effect on the hydrogenation rate. Without base, **5**·EtOH (0.02 mol%) gave only 4% conversion into ethyl acetate in 2 h at 40 °C under H_2 (50 bar), which corresponds to TOF = 100 $^{-1}$ vs. TOF = 4100 h^{-1} with NaOEt (1 mol%) in 1 h under otherwise identical conditions. According to Bergens et al,[13] base helps by labilizing the alkoxide intermediates (such as **Int 2** and **Int 4**) for EtO^- substitution, through deprotonation of the NH group. Elucidating all of the complex mechanistic features of catalytic ester hydrogenation should be the subject of a dedicated computational study.

In conclusion, herein we report the development of a novel catalyst type based on the $HN(C_2H_4SEt)_2$ ligand. The readily available, air-stable complex [$RuCl_2(PPh_3)${HN-$(C_2H_4SEt)_2$}] (**1**) shows outstanding efficiency for the hydrogenation of a broad range of substrates with C=X bonds (esters, ketones, imines) as well as for the acceptorless dehydrogenative coupling of ethanol to ethyl acetate. This study has demonstrated that the phosphorus groups of Noyori-type catalysts can be successfully replaced by sulfide groups, thus overcoming the many drawbacks of working with phosphines and phosphine-based catalysts, such as high synthetic costs and the need for handling under inert atmosphere. Complex **1** is the first practical and highly active green hydrogenation catalyst for substrates with C=X (X = O, N) bonds, and has a high potential to replace the use of main-group hydrides for the reduction of esters in the chemical industry and academic laboratories.

Received: November 16, 2012
Revised: January 2, 2013
Published online: January 28, 2013

Keywords: dehydrogenative coupling · esters · hydrogenation · imines · thioethers

[1] a) *Comprehensive Organic Synthesis*, *Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, New York, **1991**; b) J. Seyden-Penne, *Reductions by the Alumino- and Borohydride in Organic Synthesis*, 2nd ed., Wiley-VCH, New York, **1997**.
[2] P. Vogt, B. Bodnar, *Spec. Chem. Mag.* **2009**, *29/7*, 22–24.
[3] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131–1133; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113–1115; b) E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* **2011**, *3*, 609–614; c) E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon, D. Milstein, *Organometallics* **2011**, *30*, 3826–3833; d) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588–602; e) D. Milstein, E. Balaraman, C. Gunanathan, B. Gnanaprakasam, J. Zhang, WO 2012/052996A2, **2012**.
[4] a) L. A. Saudan, C. M. Saudan, C. Debieux, P. Wyss, *Angew. Chem.* **2007**, *119*, 7617–7620; *Angew. Chem. Int. Ed.* **2007**, *46*, 7473–7476; b) L. Saudan, P. Dupau, J.-J. Riedhauser, P. Wyss (Firmenich SA), WO 2006106483, **2006**; c) L. Saudan, P. Dupau, J.-J. Riedhauser, P. Wyss (Firmenich SA), US 2010280273, **2010**.
[5] a) W. Kuriyama, Y. Ino, O. Ogata, N. Sayo, T. Saitoa, *Adv. Synth. Catal.* **2010**, *352*, 92–96; b) Y. Ino, W. Kuriyama, O. Ogata, T. Matsumoto, *Top. Catal.* **2010**, *53*, 1019–1024; c) W. Kuriyama, T. Matsumoto, Y. Ino, O. Ogata, N. Saeki (Takasago Int. Co.), WO 2011048727, **2011**.
[6] a) D. Spasyuk, S. Smith, D. G. Gusev, *Angew. Chem.* **2012**, *124*, 2826–2829; *Angew. Chem. Int. Ed.* **2012**, *51*, 2772–2775; b) D. Spasyuk, D. G. Gusev, *Organometallics* **2012**, *31*, 5239–5242.
[7] a) Y. Sun, C. Koehler, R. Tan, V. T. Annibale, D. Song, *Chem. Commun.* **2011**, *47*, 8349–8351; b) F. Stempfle, D. Quinzler, I. Heckler, S. Mecking, *Macromolecules* **2011**, *44*, 4159–4166; c) M. J. Hanton, S. Tin, B. J. Boardman, P. Miller, *J. Mol. Catal. A* **2011**, *346*, 70–78; d) W. W. N. O, A. J. Lough, R. H. Morris, *Chem. Commun.* **2010**, *46*, 8240–8242; e) T. Touge, T. Hakamata, H. Nara, T. Kobayashi, N. Sayo, T. Saito, Y. Kayaki, T. Ikariya, *J. Am. Chem. Soc.* **2011**, *133*, 14960–14963; f) M. Ito, T. Ootsuka, R. Watari, A. Shiibashi, A. Himizu, T. Ikariya, *J. Am. Chem. Soc.* **2011**, *133*, 4240–4242; g) S. Takebayashi, S. H. Bergens, *Organometallics* **2009**, *28*, 2349–2351; h) I. Carpenter, S. C. Eckelmann, M. T. Kuntz, J. A. Fuentes, M. B. France, M. L. Clarke, *Dalton Trans.* **2012**, *41*, 10136–10140; i) M. L. Clarke,

Catal. Sci. Technol. **2012**, *2*, 2418 – 2423; j) W. W. N. O, R. H. Morris, *ACS Catal.* **2013**, *3*, 32 – 40.

[8] For recent reviews, see: a) C. Wang, X. F. Wu, J. L. Xiao, *Chem. Asian J.* **2008**, *3*, 1750 – 1770; b) S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226 – 236; c) J. S. M. Samec, J. E. Backvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237 – 248; d) T. Ikariya, K. Murata, R. Noyori, *Org. Biomol. Chem.* **2006**, *4*, 393 – 406; e) S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201 – 2237; f) R. Noyori, *Angew. Chem.* **2002**, *114*, 2108 – 2123; *Angew. Chem. Int. Ed.* **2002**, *41*, 2008 – 2022.

[9] a) D. S. McGuinness, P. Wasserscheid, D. H. Morgan, J. T. Dixon, *Organometallics* **2005**, *24*, 552 – 556; b) M. Konrad, F. Meyer, K. Heinze, L. Zsolnai, *J. Chem. Soc. Dalton Trans.* **1998**, 199 – 205.

[10] The *mer*-SNS complexes form isomers in solution. This is due to the different arrangements of the SEt groups relative to the SNS ligand plane. Two of the isomers have eclipsed SEt groups (arranged on one side of the SNS plane), and the third isomer has staggered SEt groups (occupying the opposite sides of the SNS plane).

[11] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840 – 10841; b) J. Zhang, M. Gandelman, L. J. W. Shimon, D. Milstein, *Dalton Trans.* **2007**, 107 – 113; c) J. Zhang, E. Balaraman, G. Leitus, D. Milstein, *Organometallics* **2011**, *30*, 5716 – 5724; d) C. Gunanathan, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2009**, *131*, 3146 – 3147; e) C. del Pozo, M. Iglesias, F. Sánchez, *Organometallics* **2011**, *30*, 2180 – 2188; f) S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, *Angew. Chem.* **2011**, *123*, 3595 – 3599; *Angew. Chem. Int. Ed.* **2011**, *50*, 3533 – 3537; g) M. Nielsen, A. Kammer, D. Cozzula, H. Junge, S. Gladiali, M. Beller, *Angew. Chem.* **2011**, *123*, 9767 – 9771; *Angew. Chem. Int. Ed.* **2011**, *50*, 9593 – 9597; h) M. Nielsen, H. Junge, A. Kammer, M. Beller, *Angew. Chem.* **2012**, *124*, 5809 – 5811; *Angew. Chem. Int. Ed.* **2012**, *51*, 5711 – 5713.

[12] A related transformation of a ruthenium isopropoxide into a hydride species, facilitated by isopropanol, has been studied; see: W. Baratta, M. Ballico, G. Esposito, P. Rigo, *Chem. Eur. J.* **2008**, *14*, 5588 – 5595.

[13] R. J. Hamilton, S. H. Bergens, *J. Am. Chem. Soc.* **2006**, *128*, 13700 – 13701; see also Ref. [7g].

