Selective Hydrogenation of Cinnamaldehyde and Other α,β-Unsaturated Substrates Catalyzed by Rhodium and Ruthenium Complexes

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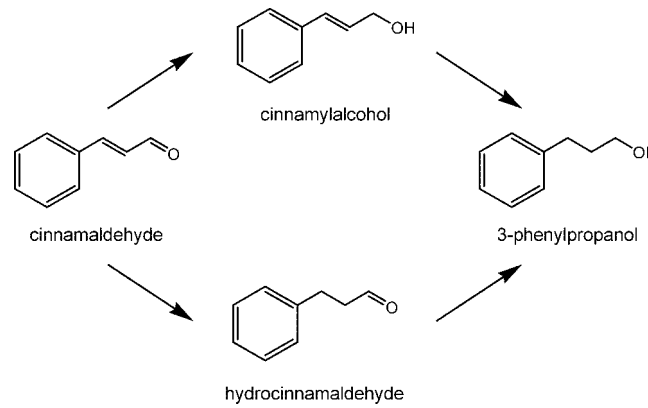
The complexes [Rh(PhBP$_3$)(cod)] (**1**) and [{Ru(PhBP$_3$)(μ-Cl)}$_2$] (**8**), containing the tripodal phosphanoborate ligand [PhB(CH$_2$PPh$_2$)$_3$]$^-$, are efficient catalysts for the selective hydrogenation of cinnamaldehyde to the corresponding allyl alcohol. Complex **8** is one of the most efficient catalysts reported to date for this reaction, in terms of activity (TOF 527 h^{-1}) and selectivity (≥97%) under mild reaction conditions (6.8 atm H$_2$, 75 °C). The rhodium system also displays good catalytic features in the hydrogenation of cinnamaldehyde (TOF 219 h^{-1}), particularly a high selectivity (81%) for this metal in the reduction of the C═O bond. Crotonaldehyde can also be reduced, although the selectivities are not as high as for cinnamaldehyde; 2-cyclohexenone is rapidly and specifically reduced to cyclohexanone by both catalysts. The ruthenium catalyst **8** operates via heterolytic activation of hydrogen, involving monohydride intermediates and possibly ionic hydrogen transfer, while the rhodium complex **1** involves oxidative addition of dihydrogen to form dihydride intermediates and follows a substrate route. Indeed, complex **1** reacts with hydrogen in acetonitrile to give the dihydride complex [Rh(PhBP$_3$)(H)$_2$(NCMe)] (**3**), while protonation of one of the phosphane arms of the ligand occurs on treatment of complex **1** with HBF$_4$ to give the cationic species [Rh{PhB(PH)P$_2$}(cod)]BF$_4$. The hydride ligands in **3** are easily removed as molecular hydrogen by reaction with CO under atmospheric pressure to give the rhodium(I) complex [Rh(PhBP$_3$)(CO)$_2$]. In this reaction, the replacement of acetonitrile by CO takes place previously to the elimination of hydrogen, which indicates that substrates can coordinate to the metal in **3** by replacement of the labile acetonitrile ligand. Under an atmosphere of argon, complex **3** reacts with chloroform to give an equimolecular mixture of the *cis* and *trans* isomers of [{Rh(PhBP$_3$)(H)(μ-Cl)}$_2$] and, eventually, complex [Rh(PhBP$_3$)Cl$_2$] in one day.

Introduction

The chemoselective reduction of α,β-unsaturated aldehydes is of considerable importance in the synthesis of fine chemicals, particularly intermediates for the fragrance and pharmaceutical industries.[1] The possible reaction pathways and products that are available in the hydrogenation of *trans*-cinnamaldehyde are depicted in Scheme 1; although the unsaturated alcohol (cinnamyl alcohol) is highly desirable, its formation is often accompanied by the products of C═C bond hydrogenation (hydrocinnamaldehyde) and/or total reduction (3-phenylpropanol). Selective reduction of the C═O bond can be brought about stoichiometrically with boron and aluminum hydrides,[2] but such methods are inadequate for large-scale applications, particularly in view of the increasing demand for greener processes involving more atom-economic catalytic reactions and more straightforward workup procedures. Selective catalytic hydrogenation with molecular hydrogen is a more attractive synthetic method in terms of atom economy, but reduction of C═C bonds is often thermodynamically favored over C═O reduction in the intramolecular competition between olefinic and

Scheme 1. Possible Hydrogenation Pathways for *trans*-Cinnamaldehyde



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(1) (a) *Ullman's Encyclopedia of Technical Chemistry, Electronic Release*, 6th ed.; Wiley-VCH: Weinheim, 2000. (b) Kraft, P.; Bajgrowicz, J. A.; Denis, C.; Fráter, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 2980–3010. (c) Bauer, K.; Garbe, D.; Surburg, H. *Common Fragrance and Flavor Materials: Preparation, Properties and Uses*, 3rd ed.; Wiley-VCH: Weinheim, 1977.

(2) (a) Fukuzawa, S. I.; Fujinami, T.; Ymauchi, S.; Sakai, S. *J. Chem. Soc., Perkin Trans.* **1986**, 1929–1932. (b) Gemal, A. L.; Luche, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 5454–5459.

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carbonyl groups,[3] and consequently hydrogenation of the C=C bond is often achieved under mild conditions with high specificity.[4,5]

Nevertheless, the design of suitable catalysts can open kinetically viable pathways for the hydrogenation of the carbonyl group in α,β-unsaturated carbonyl compounds, and therefore the search for new selective systems remains an important challenge. Reduction with molecular hydrogen may be achieved by use of heterogeneous catalysts,[4,6] which are not always selective enough or tolerant to functional groups. Soluble transition metal complexes are known to promote the chemoselective reduction of α,β-unsaturated aldehydes under hydrogen transfer conditions with primary or secondary alcohols serving as hydrogen donors;[7,8] some examples are known of homogeneous catalysts promoting the preferential formation of unsaturated alcohols by use of molecular hydrogen,[9−11] perhaps the most notable being Noyori's ruthenium-based systems including diamino and diphosphine ligands,[8] water-soluble catalysts containing ruthenium and sulfonated triphenylphosphine,[12] and bis-phosphine ruthenium(II) arene complexes.[13] Nevertheless, the development of new selective catalysts capable of promoting this important transformation under mild reaction conditions continues to be an interesting challenge.

The anionic tripodal phosphanoborate ligand $[PhB(CH_2PPh_2)_3]^-$ (henceforth referred to as $PhBP_3$) displays interesting structural and electronic properties that have been exploited in the synthesis of new complexes of Fe, Ru, Co, Ir, Rh, and Ni with interesting reactivity.[14−17] In particular, iridium complexes bearing $PhBP_3$ can activate C−H and Si−H bonds;[16] the unusual ground state geometry of the pseudotetrahedral complex $[Co(PhBP_3)I]$ can correlate with novel modes of reactivity[15] that could be exploited in unusual catalytic transformations. The chemistry of complexes of rhodium with this anionic type of ligand has been scarcely explored.[16a,17] Although a good number of hydrogenation catalysts are based on group VIII metals with phosphane ligands, including neutral tripodal ligands such as $[CH_3C(CH_2PPh_2)_3]$ and $[PhP(CH_2PPh_2)_3]$,[18,19] to our knowledge no applications of "$PhBP_3M$" systems in catalysis have been previously reported.

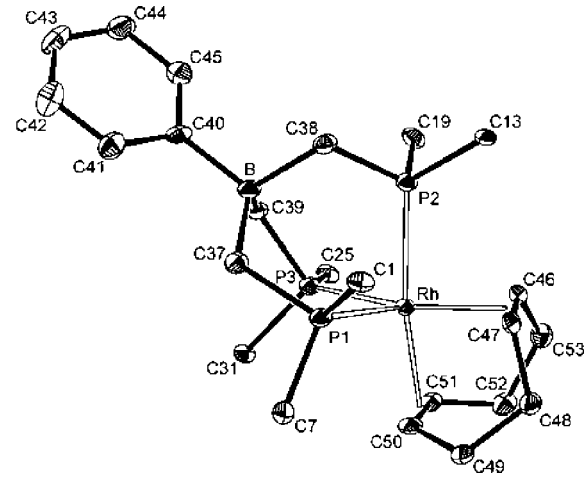


Figure 1. Structure (ORTEP at 50% level) of complex **1** (only the *ipso* carbons from the phenyl groups are shown for clarity).

In this paper we describe the synthesis and some reactions of rhodium complexes with the anionic $PhBP_3$ ligand as well as the regioselective hydrogenation of *trans*-cinnamaldehyde by $[\{Ru(PhBP_3)(\mu\text{-}Cl)\}_2]$ and $[Rh(PhBP_3)(cod)]$, to yield preferentially the allylic alcohol. The effects of various reaction parameters on the hydrogenation activity and selectivity are also discussed. Finally, applications to other α,β-unsaturated carbonyl compounds (crotonaldehyde, 2-cyclohexenone) are also examined.

Results and Discussion

Synthesis and Reactivity Studies of $[Rh(PhBP_3)(cod)]$ (1). Complex **1** was prepared straightforwardly in high yield by metathesis of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (cod = 1,5-cyclooctadiene) with $[Li(tmen)][PhBP_3]$ (tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine) in dichloromethane. The X-ray structure of **1** (Figure 1) shows a pentacoordinated rhodium center bonded to the three phosphorus atoms of the anion $[PhBP_3]^-$ and a chelating 1,5-cyclooctadiene ligand. The geometry around the rhodium can be described as a distorted trigonal bipyramid with

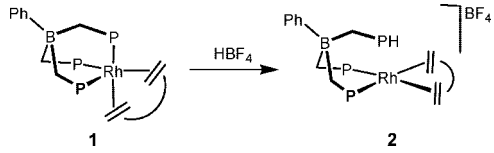
(3) Mertens, P. G. N.; Poelman, H.; Ye, X.; Vankelecom, I. F. J.; Jacobs, P. A.; De Vos, D. E. *Catal. Today* **2007**, *122*, 352–360.
(4) (a) Rylander, P. N. *Hydrogenation Methods*; Academic Press: London, 1985; p 70. (b) Rylander, P. N. *Catalytic Hydrogenation in Organic Synthesis*; Academic Press: London, 1979; p 74.
(5) (a) Nuithitikul, K.; Winterbottom, M. *Chem. Eng. Sci.* **2004**, *59*, 5439–5447. (b) López-Linares, F.; Agrifoglio, G.; Labrador, A.; Karam, A. *J. Mol. Catal. A: Chem.* **2004**, *207*, 117–122. (c) Kostas, I. D. *J. Organomet. Chem.* **2001**, *634*, 90–98.
(6) (a) Serrano-Ruiz, J. C.; López-Cudero, A.; Solla-Gullón, J.; Sepúlveda-Escribano, A.; Aldaz, A.; Rodriguez-Reinoso, F. *J. Catal.* **2008**, *253*, 159–166. (b) Meric, P.; Yu, K. M. K.; Kong, A. T. S.; Tsang, S. C. *J. Catal.* **2006**, *237*, 330–336. (c) Mäki-Arvela, P.; Hájek, J.; Salmi, T.; Murzin, D. Y. *Appl. Catal. A: Gen.* **2005**, *292*, 1–49. (d) Zhao, F.; Ikushima, Y.; Chatterjee, M.; Shirai, M.; Arai, M. *Green Chem.* **2003**, *5*, 76–79. (e) Yu, W.; Lui, H.; Liu, M.; Liu, Z.; Milone, C. *React. Funct. Polym.* **2000**, *44*, 21–29, and references therein.
(7) (a) Farnetti, E.; Nardin, G.; Graziani, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1264–1265. (b) Visintin, M.; Spogliarich, R.; Kaspar, J.; Graziani, M. *J. Mol. Catal.* **1985**, *32*, 349–351.
(8) (a) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc.* **2006**, *128*, 8724–8725. (b) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40–73.
(9) Clarke, M. L.; Roff, G. J. In *Handbook of Homogeneous Hydrogenation*; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, 2007; Vol. 1, p 413.
(10) Li, R.-X.; Wong, N.-B.; Li, X.-J.; Mak, T. C. W.; Yang, Q.-C.; Tin, K.-C. *J. Organomet. Chem.* **1998**, *571*, 223–229.
(11) (a) Hotta, K. *J. Mol. Catal.* **1985**, *29*, 105–107. (b) Farnetti, E.; Kašpar, J.; Spogliarich, R.; Graziani, M.; Pesce, M. *J. Chem. Soc., Chem. Commun.* **1986**, 746–747.
(12) (a) Hernández, M.; Kalck, Ph. *J. Mol. Catal. A: Chem.* **1997**, *116*, 131–146. (b) Grosselin, J. M.; Mercier, C.; Allmang, G.; Grass, F. *Organometallics* **1991**, *10*, 2126–2133. (c) Joó, F. *Acc. Chem. Res.* **2002**, *35*, 738–745.
(13) Chaplin, A. B.; Dyson, P. J. *Organometallics* **2007**, *26*, 4357–4360.
(14) (a) Hou, H.; Rheingold, A. L.; Kubiak, C. P. *Organometallics* **2005**, *24*, 231–233. (b) Thomas, J. C.; Peters, J. C. *Polyhedron* **2004**, *23*, 489–497. (c) MacBeth, C. E.; Thomas, J. C.; Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2004**, *43*, 4645–4662. (d) Brown, S. D.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 4538–4539. (e) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6252–6254. (f) Jenkins, D. M.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 11162–11163. (g) Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5074–5084. (h) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 10782–10783. (i) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 11238–11239. (j) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322–323.
(15) Jenkins, D. M.; Di Bilio, A. J.; Allen, M. J.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 15336–15350.
(16) (a) Turculet, L.; Feldman, J. D.; Tilley, T. D. *Organometallics* **2004**, *23*, 2488–2502. (b) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4050–4064. (c) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4065–4075. (d) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871–9872.
(17) Tejel, C.; Ciriano, M. A.; Jiménez, S.; Passarelli, V.; López, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 2093–2096.
(18) de Vries, J. G., Elsevier, C. J., Eds. *Handbook of Homogeneous Hydrogenation*; Wiley-VCH: Weinheim, 2007; Vol. 1.
(19) (a) Hierso, J.-C.; Amardeil, R.; Bentabet, E.; Broussier, R.; Gautheron, B.; Meunier, P.; Kalck, P. *Coord. Chem. Rev.* **2003**, *236*, 143–206. (b) Simpson, M. C.; Cole-Hamilton, D. J. *Coord. Chem. Rev.* **1996**, *155*, 163–207.

Table 1. Bond Distances (Å) and Angles (deg) for Complex 1[a]

Rh−P1	2.4464(10)	P1−Rh−Ct1	120.19(10)
Rh−P2	2.3236(10)	P2−Rh−Ct1	89.36(10)
Rh−P3	2.3910(10)	P3−Rh−Ct1	148.38(10)
Rh−C46	2.179(4)	P1−Rh−Ct2	103.18(10)
Rh−C47	2.153(3)	P2−Rh−Ct2	167.21(10)
Rh-Ct1	2.046(4)	P3−Rh−Ct2	96.95(10)
Rh−C50	2.230(3)	Ct1-Rh-Ct2	83.12(14)
Rh−C51	2.271(3)	P1−Rh−P2	89.53(3)
Rh-Ct2	2.140(4)	P1−Rh−P3	90.92(3)
C46−C47	1.417(5)	P2−Rh−P3	85.04(3)
C50−C51	1.383(5)		

[a] Ct1 and Ct2 are the middle points of C46−C47 and C50−C51, respectively.

Scheme 2. Protonation of Compound 1 to Produce the Cationic Complex 2



1 2

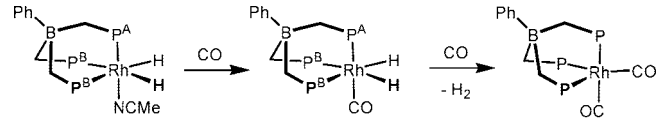
P2 and one of the C═C bonds (that formed by C50−C51) at the apical positions (see Table 1) and two P atoms (P1 and P3) and the other C═C bond at the equatorial plane forming P−Rh−P angles close to 90°, probably due to steric requirements of the tripodal ligand. The Rh−P bond distances are in the normal range, with the phosphorus at the apical position (Rh−P2) being the shortest.

In solution, complex **1** was found to be a fluxional species showing a doublet in the $^{31}P\{^{1}H\}$ NMR spectrum. The fluxional behavior that makes the three phosphorus nuclei equivalent could be attributed to an easy turnstile rotation movement, although the dissociation of one of the phosphane arms leading to a square-planar transient species cannot be excluded. In fact, one of the phosphane arms of the ligand is protonated on treatment of complex **1** with HBF_4 to give the square-planar cationic species $[Rh\{PhB(PH)P_2\}(cod)]BF_4$ (**2**) (Scheme 2). The phosphanium proton in **2** was clearly detected by ^{1}H NMR spectroscopy, giving rise to a doublet of triplets at $\delta = 6.29$ ppm due to the coupling with the phosphorus nucleus ($J_{H-P} = 481$ Hz) and two methylenic protons ($J_{H-H} = 7.1$ Hz), while one of the two signals in the $^{31}P\{^{1}H\}$ NMR spectrum lacks the coupling with the rhodium atom, as expected.

In spite of containing a coordinative and electronically saturated metal center, complex **1** was found to be a reactive species undergoing oxidative−addition reactions with, for example, oxygen and hydrogen. The product of the reaction with oxygen is the previously reported dinuclear peroxo complex $[\{Rh(PhBP_3)(O)_2\}_2]$,[17] while the reaction with hydrogen in a coordinating solvent such as acetonitrile produces the mononuclear dihydride complex $[Rh(PhBP_3)(H)_2(NCMe)]$ (**3**). Complex **3** was isolated as an air-stable yellow solid with two equivalent *cis*-hydrido ligands and the anionic triphosphane ligand coordinated in a *fac* mode. This structure is consistent with a signal at high field in the ^{1}H NMR spectrum and two resonances (AM_2X spin system, $X = {}^{103}Rh$) in the $^{31}P\{^{1}H\}$ NMR spectrum. Noticeably, the signal corresponding to the phosphorus atoms *trans* to the hydride ligands (P^B) is shifted to high field (see Experimental Section). Spin−lattice relaxation time measurements for the hydride resonance of **3** at δ −7.08 ppm gave a $T_{1\ min}$ value of 321(16) ms (5 °C), in accordance with the expected hydride nature of these ligands.

Although complex **3** does not eliminate hydrogen spontaneously, the hydride ligands are easily removed as hydrogen and

Scheme 3. Formation of the Dicarbonyl Complex 4 through the Dihydride Intermediate 5



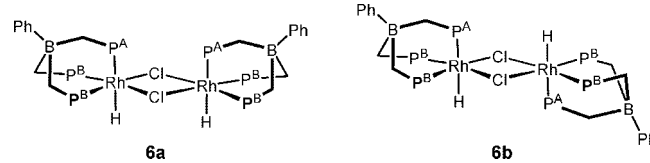
3 5 4

replaced by CO under atmospheric pressure to give the rhodium(I) complex $[Rh(PhBP_3)(CO)_2]$ (**4**) (Scheme 3). Alternatively, complex **4** was straightforwardly prepared from the reaction of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ with $[Li(tmen)][PhBP_3]$ (see Experimental Section). Complex **4** was characterized according to its analytical and spectroscopic data as having two carbonyl groups, which give two μ(CO) bands at 1966 and 2037 cm^{-1} in the IR spectrum, and a triphosphane ligand coordinated in a *fac* fashion. The equivalence of the phosphorus nuclei, which give a doublet at δ 20.7 ppm ($J_{P-Rh} = 99$ Hz) in the $^{31}P\{^{1}H\}$ NMR spectrum, can be again attributed to a fluxional behavior of the pentacoordinated species.

A confirmation of the way in which this reaction proceeds was obtained by monitoring the uptake of ^{13}CO by NMR spectroscopy. The intermediate $[Rh(PhBP_3)(H)_2(^{13}CO)]$ (**5**) (Scheme 3), resulting from the replacement of acetonitrile by CO in a first step, was detected and characterized spectroscopically. Complex **5** subsequently eliminates hydrogen (detected by ^{1}H NMR) in the presence of CO to give the dicarbonyl complex **4**. A consequence of this reaction pathway is the evidence that the acetonitrile ligand in complex **3** is labile, which opens the possibility to coordinate substrates at the site provided by replacement of acetonitrile in **3**.

The structure of complex **5** depicted in Scheme 3 is consistent with the spectroscopic features of the complex labeled with ^{13}CO. The mutually *cis* equivalent hydride ligands give a high-field resonance centered at δ −7.41 ppm in the ^{1}H NMR spectrum, while the phosphane arms (P^B) in *trans* position produce a double doublet of doublets in the $^{31}P\{^{1}H\}$ NMR spectrum by coupling with rhodium, one phosphorus nucleus (P^A), and the carbonyl group. Meanwhile, the fine structure of the signal due to the carbonyl group in the $^{13}C\{^{1}H\}$ NMR spectrum is consistent with its disposition *trans* to one of the phosphane arms and *cis* to the other two.

Complex **3** reacts readily with chloroform in minutes to produce the replacement of hydride by chloride. Monitoring the reaction of **3** in $CDCl_3$, the spectra corresponding to complexes **6a** and **6b** (Figure 2) in equimolecular amounts along with $CHDCl_2$ were observed a few minutes after mixing. This reaction proceeds further to produce the full replacement of the hydrido ligands to give $[Rh(PhBP_3)Cl_2]$ (**7**) quantitatively in one day. Replacement of hydride by chloride by using a chlorocarbon such as carbon tetrachloride is a well-known reaction of metal hydrides,[20] but as the degree of chlorination of the chlorocarbon decreases, this reaction is less frequent or disappears. Therefore, we have studied the progress of the reaction of **3** in CD_2Cl_2 since some of the catalytic studies were carried



6a 6b

Figure 2. *Cis* (**6a**) and *trans* (**6b**) isomers of complex $[\{Rh(PhBP_3)(\mu\text{-}Cl)(H)\}_2]$.

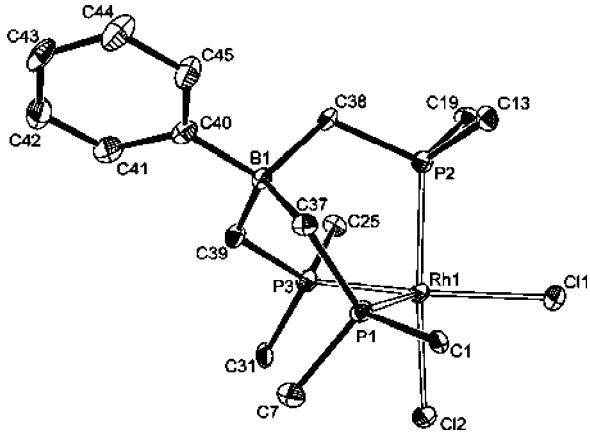


Figure 3. Structure (ORTEP at 50% level) of complex **7** (only the *ipso* carbons from the phenyl groups are shown for clarity).

Table 2. Bond Distances (Å) and Angles (deg) for the Two Independent Molecules of Complex 7

Rh1−P1	2.2332(13), 2.2342(13)	P1−Rh1−Cl1	113.88(5), 121.67(5)
Rh1−P2	2.3290(14), 2.3193(13)	P2−Rh1−Cl1	90.27(5), 86.82(4)
Rh1−P3	2.2729(14), 2.2647(13)	P3−Rh1−Cl1	156.18(5), 151.62(5)
Rh1−Cl1	2.3715(13), 2.3646(12)	P1−Rh1−Cl2	98.17(5), 96.73(5)
Rh1−Cl2	2.3460(13), 2.3497(13)	P2−Rh1−Cl2	171.40(5), 171.46(5)
		P3−Rh1−Cl2	90.20(5), 91.60(5)
		Cl1−Rh1−Cl2	86.33(4), 86.78(4)
		P1−Rh1−P2	90.42(5), 91.45(5)
		P1−Rh1−P3	89.94(5), 86.68(5)
		P2−Rh−P3	89.74(5), 91.34(5)

out in this solvent. The mixture of complexes **6** can be detected by NMR in solutions of **3** in CD_2Cl_2, but this reaction proceeds more slowly than in $CDCl_3$. The half-life of **3** to give **6** is ca. 5 h, while the reaction is completed in 24 h. Moreover, the mixture of isomers **6** is scarcely soluble in dichloromethane, and it precipitates as formed, in such a way that the replacement of hydride by chloride in **6** to give **7** does not take place in dichloromethane. Spectroscopic data of **6a** and **6b** (see Experimental Section) were found to be similar to those of the related dicationic analogous complex $[\{Rh(triphos)(\mu\text{-}Cl)(H)\}_2](BPh_4)_2$ containing the neutral tripodal ligand triphos ($MeC(CH_2PPh_2)_3$).[21]

Complex $[Rh(PhBP_3)Cl_2]$ (**7**) was fully characterized (see Experimental Section) including an X-ray structure determination. Figure 3 shows the molecular structure of **7**, while Table 2 lists selected bond distances and angles.

The rhodium atom in **7** shows an approximately square-pyramidal coordination polyhedron with one of the phosphorus atoms, P1, at the apical position and the other two phosphorus atoms and the two chloride ligands at the base. The tripodal $PhBP_3^-$ ligand coordinates to the rhodium in a *fac* mode similar to that described above for **1**. Nevertheless, the average Rh−P bond distance in **7** is shorter than in $[Rh(PhBP_3)(cod)]$ (**1**), as expected for the higher oxidation state of the metal in the former. Interestingly, complex **7** is mononuclear, while related complexes with anionic *fac* ligands such as $[\{Rh(Tp^{Me2})Cl(\mu\text{-}Cl)\}_2]$[22a] and $[\{Rh(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$[22b] were found to be dinuclear chloride-bridged species. In solution, complex **7** is fluxional, showing a single signal in the $^{31}P\{^1H\}$ NMR spectrum. The coupling constant J_{P-Rh} (108 Hz) was found to be similar to that observed for the Rh(I) derivatives (105 and 99 Hz for complexes **1** and **4**, respectively), apparently being insensitive to the oxidation state of the metal.

Table 3. Hydrogenation of *trans*-Cinnamaldehyde Catalyzed by $[\{Ru(PhBP_3)(\mu\text{-}Cl)\}_2]$ (8)[a]

entry	solvent	[cat] (mM)	[subst] (M)	[NEt_3] (M)	TOF (h^{-1})	select.[b] (%)
1	1,2-dichloroethane	0.6	1.33	0	31	81
2	1,2-dichloroethane	0.6	1.33	0.6	258	77
3	THF	0.6	1.33	0.6	203	92
4	ethyl acetate	0.6	1.33	0.6	488	90
5	toluene	0.6	1.33	0.6	448	90
6	THF	0.2	0.88	0.3	114	95
7	1,2-dichloroethane	0.2	0.88	0.3	70	94
8	toluene	0.2	0.88	0.3	51	51

[a] 95 °C; 13.6 atm H_2. [b] Selectivity: % of *trans*-cinnamyl alcohol in total product.

Hydrogenation of *trans*-Cinnamaldehyde with $[\{Ru(PhBP_3)(\mu\text{-}Cl)\}_2]$ (8). The dinuclear complex $[\{Ru(PhBP_3)(\mu\text{-}Cl)\}_2]$ (**8**), previously reported by Peters,[14g] was found to be a very efficient catalyst for the reduction of *trans*-cinnamaldehyde in a variety of solvents at 95 °C and 13.6 atm H_2, as shown by the data contained in Table 3. A marked enhancement of the catalytic activity (measured as TOF) is accomplished by addition of triethylamine (compare entries 1 and 2); this is a good indication that this catalyst operates by a mechanism involving heterolytic hydrogen splitting, something rather common for ruthenium(II) complexes containing chloride ligands.[18]

The most striking feature of this system is the very high selectivity toward *trans*-cinnamyl alcohol observed in all cases, which seems to be favored in more dilute solutions in polar solvents to reach values as high as 94% and 95% in 1,2-dichloroethane and THF, respectively, although at some expense of reaction rate (compare entries 2/7 and 3/6, Table 3). Further optimization, together with rapid and controlled internal stirring of the reaction mixture, led to a maximum TOF value of 527 h^{-1} in the hydrogenation of *trans*-cinnamaldehyde in 1,2-dichloroethane under mild conditions (75 °C, 6.8 atm H_2, [Ru] = 0.32 mM; [substrate] = 1.28 M) with 97% selectivity for the reduction of the C=O bond. It is important to note that this remarkable selectivity was maintained up to 100% conversion.

Such high efficiency in the hydrogenation of α,β-unsaturated aldehydes is very seldom encountered for homogeneous transition metal catalysts, with the notable exception of Noyori's Ru-phosphane-diamine system, which functions very well at room temperature and 4 atm H_2, producing unsaturated alcohols with 100% selectivity, although it requires also the addition of a KOH/*i*-PrOH mixture as an activator.[8] A more atom-economic and therefore more desirable approach is the selective reduction using molecular hydrogen, for which only a few examples have been reported. The complex $[Ru(bdna)(CO)(H)_2(PPh_3)]$ (bdna = 1,8-bis(diphenylphosphinomethyl)naphthalene) reduces citral and *trans*-cinnamaldehyde to the corresponding unsaturated alcohols with >95% selectivity under rather drastic conditions (50 atm H_2 and 70−80 °C).[10] Similarly, arene-ruthenium(II) complexes with PPh_3 and $P(p\text{-tol})_3$ ligands reduce *trans*-cinnamaldehyde selectively to *trans*-cinnamyl alcohol with TOF values around 250−400 h^{-1} and selectivities >99% under 50 atm H_2 at 50 °C.[13] Ruthenium complexes of water-soluble phosphines (tppms, tppts, triphenylphosphine monosulfonate or trisulfonate, respectively) also reduce the C=O bond of *trans*-cinnamaldehyde with selectivities over 90% in an aqueous biphasic medium under 20 atm of H_2.[13] Other known catalysts

(20) Tejel, C.; Ciriano, M. A.; Millaruelo, M.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **2003**, *42*, 4750–4758.
(21) Bianchini, C.; Meli, A.; Laschi, F.; Ramirez, J. A.; Zanello, P.; Vacca, A. *Inorg. Chem.* **1988**, *25*, 4429–4435.
(22) (a) May, S.; Reinsalu, P.; Powell, J. *Inorg. Chem.* **1989**, *19*, 1582–1589. (b) Churchill, M. R.; Julis, S. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 1137–1141.

Table 4. Hydrogenation of *trans*-Cinnamaldehyde Catalyzed by [Rh(PhBP$_3$)(cod)] (1)[a]

entry	solvent	[subst] (M)	additive (M)	TOF (h^{-1})	select.[b] (%)
1	no solvent	7.95	0	150	51
2	1,2-dichloroethane	1.33	0	130	81
3	1,2-dichloroethane/HBF_4	1.33	0.74×10^{-3}	138	64
4	1,2-dichloroethane/HBF_4	1.33	1.7×10^{-2}	24	7
5	1,2-dichloroethane/NEt_3	1.33	0.6	42	12
6	ethyl acetate	1.33	0	80	56
7	THF	1.33	0	47	69
8	toluene	1.33	0	71	51

[a] 95 °C; 13.6 atm H_2; [Rh] = 0.74×10^{-3} M. [b] Selectivity: % of cinnamyl alcohol in total product.

are in general less active, are less selective, or require considerably higher temperatures and pressures to operate than complex **8**.[9]

Hydrogenation of *trans*-Cinnamaldehyde with [Rh(PhBP$_3$)(cod)] (1). Table 4 displays the results of hydrogenating *trans*-cinnamaldehyde with the rhodium complex [Rh(PhBP$_3$)(cod)] (**1**) in different solvents at 95 °C and 13.6 atm H_2. The best combination of activity and selectivity for C=O bond reduction was obtained in 1,2-dichloroethane (TOF 130 h^{-1}; 81% *trans*-cinnamyl alcohol, 6% hydrocinnamaldehyde, 13% 3-phenylpropanol). Other polar solvents (ethylacetate, THF) produce lower activity and selectivity, perhaps by competing with the substrate for coordination sites. In toluene, the catalyst shows moderate activity for the production of the unsaturated alcohol TOF (71 h^{-1}) and low selectivity (51%). We also performed solventless reactions, which are generally preferred as "greener" alternatives. In this case, although the catalytic activity is somewhat enhanced when pure *trans*-cinnamaldehyde is employed (TOF 150 h^{-1}), the selectivity for *trans*-cinnamyl alcohol is drastically reduced (51%) with respect to the reaction in 1,2-dichloroethane. The higher selectivity observed in dilute solution suggests that the C=O bond binds preferentially to the rhodium center, but when the pure substrate is used, coordination of the metal to both the C=O and C=C bonds is likely to be enhanced in a more competitive manner, thereby resulting in a selectivity drop. Addition of triethylamine has a detrimental effect on both the activity and selectivity of complex **1** for the hydrogenation of *trans*-cinnamaldehyde, which indicates that this catalyst does not operate through heterolytic activation of hydrogen, as is the case of the ruthenium derivative **8**. Thus, oxidative addition of H_2 seems a more plausible reaction pathway, to form an 18-e Rh(III) catalytically active species of the type [Rh(PhBP$_3$)(H)$_2$L], similar to [Rh(PhBP$_3$)(H)$_2$(NCMe)] (**3**), where L is a substrate molecule.

Addition of 1 equiv of HBF_4 to the catalytic mixture in 1,2-dichloroethane results in a slight improvement of the activity (TOF 138 h^{-1}) together with a drop in the selectivity toward cinammyl alcohol from 81% to 64%. This is due to protonation of one of the phosphorus atoms of the PhBP$_3$ ligand to form [Rh{PhB(PH)P$_2$}(cod)]BF_4 (**2**) with an additional vacant site in the catalytically active species, which would thereby become less constrained, making coordination of the sterically hindered C=C bond of cinnamaldehyde more facile. If acid in excess over the stoichiometric amount is added to the reaction medium, both the activity and selectivity are decreased, which suggests the decomposition of the catalyst under strongly acidic conditions.

In an attempt to optimize the catalytic performance of complex **1** to a level comparable to that obtained with complex **8**, a systematic variation of various reaction parameters was undertaken. Figure 4 shows the results of hydrogenating *trans*-cinnamaldehyde with complex **1** in 1,2-dichloroethane solution under different H_2 pressures at 95 °C. Within the range 6.8−34 atm H_2 the activity increased in an approximately linear fashion with the reaction pressure (Figure 4a) up to a value of 430 h^{-1}, while a slight increase in the selectivity for the production of *trans*-cinnamyl alcohol from 76% to 83−85% was observed (Figure 4b). A log $P(H_2)$ vs log TOF plot shows that the reaction rate is close to first-order in hydrogen pressure within the range studied.

The effect of catalyst concentration on the hydrogenation activity and selectivity is reported in Figure 5. TOF values increase linearly with catalyst concentration up to 219 h^{-1} at 0.89×10^{-3} M, beyond which no further increase in the reaction rate was observed (Figure 5a); the selectivity also increased from 71% to 81% with increasing catalyst concentration up to the saturation point (Figure 5b). The reason for this saturation value may be that at high concentrations the catalyst could be involved in dimerization equilibria to form dinuclear species of the type [{Rh(PhBP$_3$)(μ-H)H}$_2$], similar to iridium complexes described by Peters.[16b] Such dimerization processes would not allow a higher effective concentration of the monomeric active species that operates in the hydrogenation cycle.

Figure 6 shows the effect of the substrate concentration on the TOF values and the selectivity toward *trans*-cinnamyl alcohol. The selectivity remained unchanged at ca. 81% within the range of *trans*-cinnamaldehyde concentrations employed, while the TOF values increase with increasing substrate concentration up to a maximum value of 219 h^{-1} (at 1.3 M *trans*-cinnamaldehyde and beyond).

The experimental data are suggestive of *saturation kinetics*, in agreement with a rapid equilibrium being established between the substrate and the catalyst, followed by an irreversible rate-determining reaction with H_2 (Scheme 4).

This behavior is very common for enzyme-catalyzed reactions (Michaelis−Menten kinetics) and corresponds to the classical *substrate route* that predominates in a number of homogeneous catalytic hydrogenation reactions with other rhodium complexes.[18]

Direct Comparison of the Properties of [Rh(PhBP$_3$)(cod)] (1) and [{Ru(PhBP$_3$)(μ-Cl)}$_2$] (8) in the Hydrogenation of *trans*-Cinnamaldehyde. It is interesting to compare both catalytic systems under similar reaction conditions. As shown in Table 5, both complexes display good reaction rates and high selectivity for the formation of *trans*-cinnamyl alcohol, which is the most valuable product of the hydrogenation. It is important to note that the high selectivity is maintained at conversions as high as 99% and 90% for complexes **8** and **1**, respectively. At 75 °C and 6.8 atm H_2 the hydrogenation proceeds with a much higher turnover frequency for the ruthenium catalyst **8** (527 h^{-1}) as compared to the rhodium complex **1** (TOF = 43 h^{-1}). The selectivity is also considerably higher in the case of ruthenium (compare entries 1/2). By using the optimal reaction conditions developed for the rhodium catalyst **1** (95 °C, 13.6 atm H_2, entry 3) both the activity and selectivity are enhanced but not to the same level as for **8**.

In general, ruthenium complexes are more selective for the reduction of the C=O bond of α,β-unsaturated aldehydes, while rhodium catalysts tend to hydrogenate the C=C bond preferentially, although a few examples are known of Rh complexes that are moderately selective for C=O bond reduction.[23] In this study we have found that the rhodium complex **1** containing the rigid anionic tripodal ligand [PhBP$_3$]$^-$ displays very good catalytic features in the hydrogenation of *trans*-cinnamaldehyde,

(23) Nomura, K. *J. Mol. Catal. A: Chem.* **1998**, *130*, 1–28.

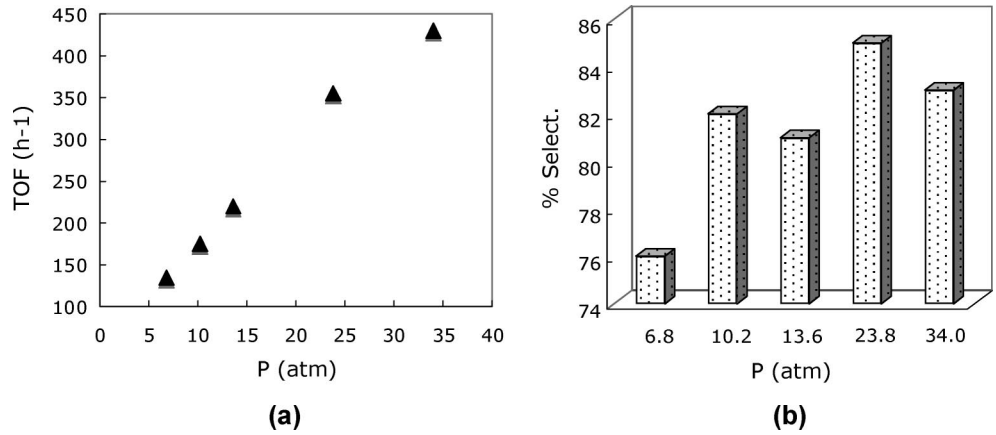


Figure 4. Effect of the hydrogen pressure on the rate and selectivity of the hydrogenation of cinnamaldehyde by complex **1** (1,2-dichloroethane 95 °C, [cat] = 0.89 × 10^{-3} M, [subst] = 1.4 M).

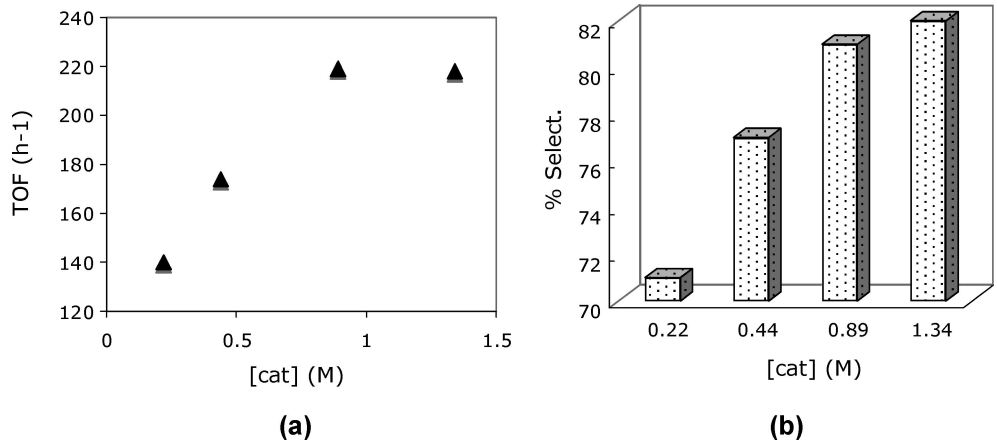


Figure 5. Effect of catalyst concentration on the rate and selectivity in the hydrogenation of cinnamaldehyde by complex **1** (in 1,2-dichloroethane, 95 °C, 13.6 atm H_2, [subst] = 1.4 M).

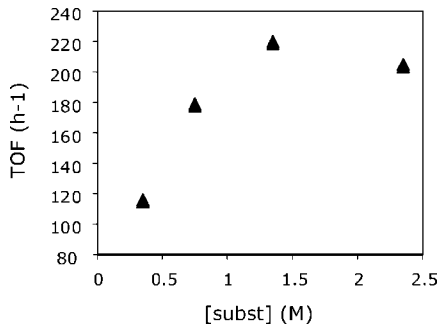
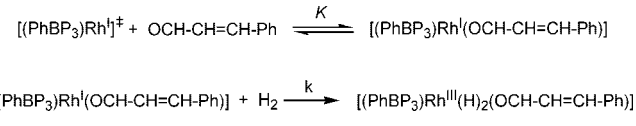


Figure 6. Effect of initial substrate concentration on the rate of hydrogenation of *trans*-cinnamaldehyde by complex **1** (in 1,2-dichloroethane, 95 °C, 13.6 atm H_2, [cat] = 0.89 × 10^{-3} M).

Scheme 4. Possible Steps in the Hydrogenation of *trans*-Cinnamaldehyde Catalyzed by 1



particularly an unusually high selectivity for this metal in the reduction of the C=O bond. Nevertheless, it is clear that the ruthenium complex **8** is superior to **1** and no doubt one of the most efficient catalysts reported to date for the hydrogenation of *trans*-cinnamaldehyde, in terms of activity (TOF 527 h^{-1}) and selectivity (≥97%) under very mild reaction conditions (6.8 atm H_2, 75 °C).

Table 5. Catalytic Hydrogenation of *trans*-Cinnamaldehyde in 1,2-Dichloroethane

entry	catalyst	[M] (mM)	P (H_2) (atm)	T (°C)	TOF (h^{-1})	select. (%)[a]
1	[{Ru($PhBP_3$)(μ-Cl)}$_2$]	0.30	6.8	75	527	97
2	[Rh($PhBP_3$)(cod)]	0.71	6.8	75	43	78
3	[Rh($PhBP_3$)(cod)]	0.71	13.6	95	219	81

[a] Selectivity: % of cinnamyl alcohol in total product.

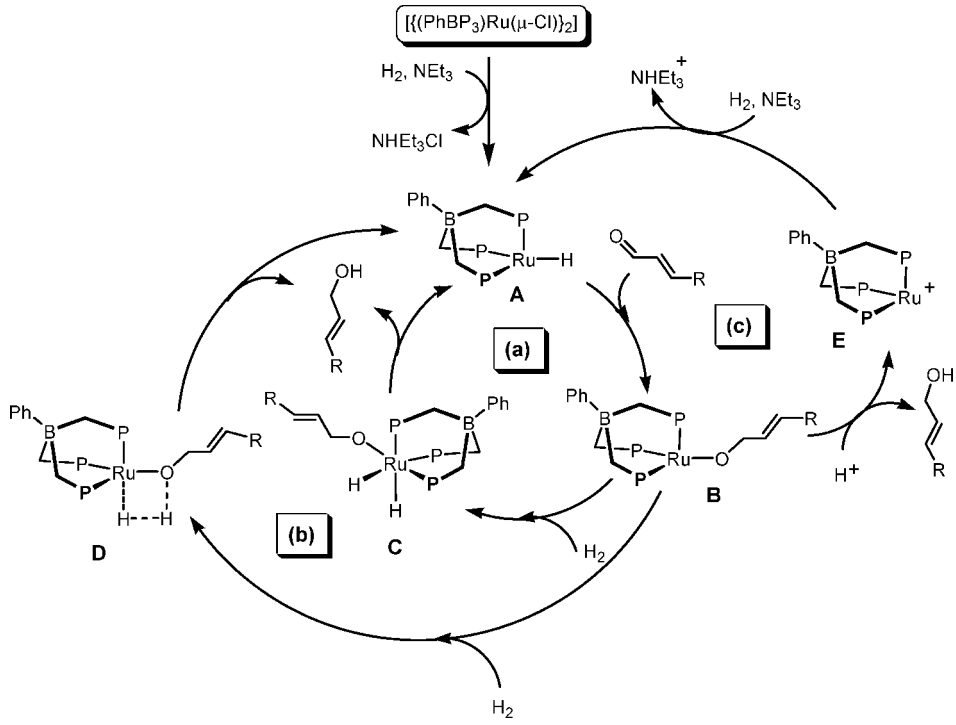
Hydrogenation of Other α,β-Unsaturated Aldehydes and Ketones with [Rh($PhBP_3$)(cod)] (1) and [{Ru($PhBP_3$)(μ-Cl)}$_2$] (8). The results presented above encouraged us to extend our studies to other α,β-unsaturated aldehydes and ketones (see Table 6). In the case of crotonaldehyde the selectivity when using the ruthenium complex **8** is lower than the one observed for *trans*-cinnamaldehyde but still attractive; the rhodium complex **1**, on the other hand, was found to be rather unselective in the reduction of crotonaldehyde. A possible explanation for the lower selectivities observed lies in the fact that the C=C bond in crotonaldehyde is much less sterically constrained than the one in *trans*-cinnamaldehyde, and this probably results in a poorer discrimination of the metal between coordination of the C=O bond against the C=C bond; electronic effects, however, cannot be ruled out. Previous reports involving other ruthenium and rhodium catalysts that compared cinnamaldehyde and crotonaldehyde follow a similar trend.[9]

Table 6. Hydrogenation of Other α,β-Unsaturated Substrates Catalyzed by Complexes 1 and 8

catalyst	substrate	[M] (mM)	[subst] (M)	T (°C)	$P(H_2)$ (atm)	TOF (h^{-1})	select. (%)
$[\{Ru(PhBP_3)(\mu\text{-}Cl)\}_2]$	crotonaldehyde	0.41	1.14	75	6.8	443	68[a]
$[Rh(PhBP_3)(cod)]$	crotonaldehyde	0.74	2.03	95	13.6	74	15[b]
$[\{Ru(PhBP_3)(\mu\text{-}Cl)\}_2]$	2-cyclohexenone	0.40	1.68	75	6.8	1475	100[c]
$[Rh(PhBP_3)(cod)]$	2-cyclohexenone	0.74	1.75	95	6.8	1153	100[c]

[a] Selectivity is % of crotyl alcohol in total product. Other products were butyraldehyde (0.5%) and butanol (16.4%). [b] Selectivity is % of crotyl alcohol in total product. Other products were butyraldehyde (14%) and butanol (9%). [c] Selectivity is % of cyclohexanone in total product.

Scheme 5. Possible Mechanistic Pathways in the Hydrogenation of *trans*-Cinnamaldehyde Catalyzed by Complex 8



In the case of 2-cyclohexenone, the C═O bond is not readily reduced with either one of these two catalysts under mild reaction conditions. Instead, both complexes rapidly and specifically reduce the C═C bond to yield cyclohexanone as the sole product of the reaction.

Mechanistic Considerations. Although the experimental data available do not allow us to accurately describe the mechanistic details of the hydrogenation of *trans*-cinnamaldehyde with complexes **1** and **8**, it is interesting to consider the possible routes available to each catalyst that are consistent with the experimental results. In the case of ruthenium, it is clear that the presence of a base is required for the activation of the catalyst, which points to a heterolytic splitting of dihydrogen together with a bridge cleavage reaction to produce a reactive 14-electron monomeric monohydride active species **A**, which enters the catalytic cycle depicted in Scheme 5.[24]

Interaction of the substrate with the metal center probably takes place preferentially through the C═O bond, in accord with the high selectivity observed, particularly for *trans*-cinnamaldehyde; in the case of the less sterically demanding crotonaldehyde, coordination of the C═C bond is not as disfavored. Stepwise or concerted hydride transfer to the C═O bond leads to the alkoxide intermediate **B**, which may generate the product by several reaction pathways: In a "classical" mechanism (path a, Scheme 5), oxidative addition of hydrogen to generate the Ru(IV) species **C** and subsequent reductive elimination of the allyl alcohol regenerates **A** and completes the catalytic cycle.[25] Alternatively, the electron-deficient alkoxy intermediate **B** could react with molecular hydrogen by a heterolytic mechanism (path b, Scheme 5) in which the coordinated oxygen atom acts as the base,[8,12,24] as in species **D**. An intermolecular ionic mechanism can also be envisaged (path c, Scheme 5), involving protonolysis of the alkoxy intermediate **B** to liberate the product and a highly reactive cationic Ru(II) intermediate **E**, capable of rapidly interacting with dihydrogen via heterolytic splitting (aided by triethylamine) to regenerate **A** and a proton that would be captured by triethylamine.[24] All these possibilities have precedent in the chemistry of ruthenium, and any one of them could be consistent with our data; at present, we do not have enough information to distinguish a preferred pathway.

In the case of the rhodium catalyst the experimental data point to a dihydride active species and a classical "substrate mechanism" (Scheme 6); this is in agreement with the saturation kinetics observed with respect to substrate concentration, the close to first-order dependence on the hydrogen pressure, and a wealth of knowledge on rhodium-catalyzed hydrogenation reactions.[26]

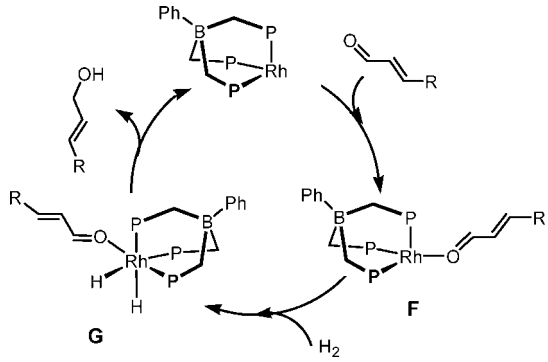
The high selectivity for the reduction of *trans*-cinnamaldehyde again suggests that the substrate must likely bind to the metal

(24) Stanley, G. G. *Comprehensive Organometallic Chemistry III*; Crabtree, R. H.; Mingos, D. M., Eds.; Elsevier: New York, 2007; Vol. 1, pp 119−140.

(25) Sánchez-Delgado, R. A.; Rosales, M. *Coord. Chem. Rev.* **2000**, *196*, 249–280.

(26) Oro, L. A.; Carmona, D. In *Handbook of Homogeneous Hydrogenation*; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, 2007; Vol. 1, pp 3−30.

Scheme 6. Possible Mechanism for the Hydrogenation of *trans*-Cinnamaldehyde Catalyzed by 1



through the C═O bond; although an end-on coordination is represented for species **F** in Scheme 6, η^2-C═O side binding is also possible. A less sterically demanding situation, as in the case of crotonaldehyde or of protonation of one phosphorus atom, would lead to a loss in selectivity, as observed. Oxidative addition of hydrogen forms the rhodium(III) intermediate **G**. Subsequently, transfer of the two hydrides to the C═O bond yields the allylic alcohol as the major product and regenerates the catalyst. An analogous set of the reactions on a C═C coordinated substrate would produce the saturated aldehyde, which is always observed with the rhodium system. However, an alternative explanation for the presence of hydrocinnamaldehyde in the final reaction mixture could be the isomerization of cynnamyl alcohol, but this point was not investigated in detail. Finally, it should be indicated that, in the absence of a hydrogen atmosphere, complex **3** decarbonylates *trans*-cinnamaldehyde to styrene probably through the intermediate **F**.

Conclusion

We have demonstrated that the complexes [Rh(PhBP$_3$)(cod)] (**1**) and [{Ru(PhBP$_3$)(μ-Cl)}$_2$] (**8**), containing the anionic tripodal phosphanoborate ligand [PhB(CH$_2$PPh$_2$)$_3$]$^-$, are efficient catalysts for the regioselective hydrogenation of *trans*-cinnamaldehyde to the corresponding allyl alcohol. Complex **8** turned out to be one of the most active and selective catalysts reported so far for the mild hydrogenation of the C═O bond of *trans*-cinnamaldehyde using molecular H$_2$, exhibiting higher activity and selectivity than the rhodium complex **1**, provided that NEt$_3$ is added to the reaction mixture. Side reactions that often take place concurrently with the hydrogenation of aldehydes, such as decarbonylation, which is promoted by a number of phosphane rhodium[27−29] or ruthenium[30] complexes, or condensation reactions that are catalyzed by rhodium[31] and ruthenium[32] phosphane complexes, are not observed in this case. Crotonaldehyde can also be reduced with catalysts **1** and **8**, although the selectivity for the unsaturated alcohol is lower than in the case of *trans*-cinnamaldehyde. 2-Cyclohexenone was rapidly and specifically reduced at the C═C bond with both systems.

The ruthenium catalyst **8** operates via heterolytic activation of hydrogen, involving monohydride intermediates and possibly ionic hydrogen transfer, while the rhodium complex **1** follows a substrate route and involves oxidative addition of dihydrogen to form dihydride intermediates.

Experimental Section

Starting Materials and Physical Methods. All the operations were carried out under an argon atmosphere using standard Schlenk-tube technique. Solvents were purified by standard procedures. [Li(tmen)][PhB(CH$_2$PPh$_2$)$_3$],[33] [{Rh(μ-Cl)(cod)}$_2$],[34] and [{Ru(PhBP$_3$)(μ-Cl)}$_2$][14g] were prepared according to the literature methods. HBF$_4$ (Aldrich, 54% w/w in Et$_2$O) was commercially available and was used as received. Elemental analyses were performed using a Perkin-Elmer 2400 microanalyzer. Mass spectra (MALDI) were recorded with a Bruker MicroFlex spectrometer using DCTB (1,1-dicyano-4-*tert*-butylphenyl-3-methylbutadiene) as matrix and in a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ mode. NMR spectra were recorded on a Bruker AV 300 spectrometer operating at 300.13 MHz, respectively, for ^{1}H. IR spectra were recorded with a Nicolet 550 spectrophotometer. Conductivities were measured in acetone solutions using a Philips PW 9501/01 conductimeter.

Synthesis of the Complexes: [Rh(PhBP$_3$)(cod)] (1). Solid [{Rh(μ-Cl)(cod)}$_2$] (133 mg, 0.27 mmol) was added to a solution of [Li(tmen)][PhB(CH$_2$PPh$_2$)$_3$] (436 mg, 0.54 mmol) in dichloromethane (8 mL) to give an orange solution and a white solid in 1 h at rt. The solvent was evaporated under vacuum, the residue was extracted with a 1:1 mixture of toluene/dichloromethane (30 mL), and the LiCl was removed by filtration. Evaporation of the extract to ca. 5 mL and addition of hexane (20 mL) produced the crystallization of **1** as a yellow solid. The solid was washed with hexane (2 × 5 mL) and vacuum-dried. Yield: 380 mg, 80%. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 7.61 (d, 7.6 Hz, 2H; H^o), 7.28 (t, 7.6 Hz, 2H; H^m) and 7.09 (t, 7.6 Hz, 1H; H^p) *Ph*B, 7.19 (m, 18 H, H^{o+p}) and 7.06 (t, 37.3 Hz, 12 H; H^m) Ph$_2$P, 3.70 (br s, 4H; HC═), 2.65 (m, 4H; H$_2$C) and 2.28 (m, 4H; H$_2$C) cod, 1.46 (br s, 6H; H$_2$C-P). ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$, 25 °C): δ 17.8 (d, J_{P-Rh} = 105 Hz). MS (Maldi): *m*/*z* (%): 788 (100) [M$^+$ − cod]. Anal. Calcd (%) for C$_{53}$H$_{53}$BP$_3$Rh: C 71.00, H 5.96. Found: C 71.03; H 6.08.

[Rh{PhB(PH)P$_2$}(cod)]BF$_4$ (2). HBF$_4$·Et$_2$O (21 mL, 0.13 mmol) was added to a solution of [Rh(PhBP$_3$)(cod)] (**1**) (116 mg, 0.13 mmol) in dichloromethane (4 mL) to produce an orange solution. Addition of hexane (10 mL) led to the crystallization of an orange solid corresponding to **2**. The solid was washed with hexane (2 × 5 mL) and vacuum-dried. Yield: 110 mg, 87%. ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.8−6.6 (35H, PhB+Ph$_2$P), 6.29 (dt, J_{H-P} = 481 Hz, J_{H-H} = 7.1 Hz, 1H, PH), 4.34 (br, 2H, ═CH), 4.10 (br, 2H, ═CH), 2.27 (m, 2H, CH$_2$), 2.15 (m, 2H, CH$_2$), 2.11 (br, 4H, CH$_2$), 1.67 (m, δ_A, 2H) and 1.40 (m, δ_B, 2H, J_{A-B} = 12.5 Hz, CH$_2$PRh), 0.68 (dd, J_{H-H} = 16 Hz, J_{H-P} = 7.1 Hz, 2H, CH$_2$PH). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ 24.0 (dd, J_{P-Rh} = 140 Hz, J_{P-P} = 5 Hz, 2P), 13.2 (t, J_{P-P} = 5 Hz, 1P). MS (FAB$^+$, NBA): *m*/*z* (%): 897 (53) [M$^+$]. Anal. Calcd (%) for C$_{53}$H$_{54}$B$_2$F$_4$P$_3$Rh·1.5CH$_2$Cl$_2$: C 58.87, H 5.16. Found: C 58.51; H 5.25. Λ_M (5.16 × 10^{-4} M in acetone) = 69 S·mol^{-1}·cm^{-1}.

[Rh(PhBP$_3$)(H)$_2$(NCMe)] (3). A yellow suspension of [Rh(PhBP$_3$)(cod)] (**1**) (116 mg, 0.13 mmol) in acetonitrile was stirred at 70 °C under an atmosphere of hydrogen at 3 bar overnight (15 h) to give a white precipitate after the starting material had

(27) (a) Tsuji, J.; Ohno, K. *Tetrahedron Lett.* **1965**, *6*, 3969–3971. (b) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99–107. (c) Tsuji, J.; Ohno, K. *J. Am. Chem. Soc.* **1968**, *90*, 94–98.

(28) Abu-Hasanayn, F.; Goldman, M. E.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 2520–2524.

(29) Beck, C. M.; Rathmill, S. E.; Park, Y. J.; Chen, J.; Crabtree, R. H.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5311–5317.

(30) Van Der Sluys, L. S.; Kubas, G. J.; Caulton, K. G. *Organometallics* **1991**, *10*, 1033–1038.

(31) Burkhardt, E. R.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30–34.

(32) Ito, T.; Horino, H.; Koshiro, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 504–512.

(33) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4050–4064.

(34) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88–90.

become a solution. The suspension was concentrated to ca. 1 mL, and the solid was isolated by filtration under argon, washed with cold diethyl ether (2 × 5 mL), and vacuum-dried. Yield: 86 mg, 80%. ^{1}H NMR (C_6D_6, 25 °C): δ 8.17 (d, 7.2 Hz, 2H, H^o, PhB), 8.06 (m, 4H, H^o, Ph$^B_2$-P^B), 7.94 (m, 4H, H^o, Ph$^A_2$-P^A), 7.68 (t, 7.2 Hz, 2H, H^m, PhB), 7.42 (t, 7.2 Hz, 1H, H^p, PhB), 7.14 (t, 7.8 Hz, 4H, H^o, Ph$^B_2$-P^B), 6.92 (m, 6H, H^{m+p}, Ph$^B_2$-P^B), 6.38 (m, 12H, H^{m+p}, Ph$^B_2$-P^B + H^{m+p}, Ph$^A_2$-P^A), 2.11 (m, δ^A, 2H) and 1.81 (m, δ^B, $J_{A\text{-}B}$ = 12.2 Hz; CH_2P^B), 1.59 (d, J_{H-P} = 13.6 Hz; CH_2P^A), 0.27 (s, 3H, MeCN), − 7.08 (m, J_{H-P^B} = 157 Hz, J_{H-Rh} = 15 Hz, J_{H-H} = 4 Hz, J_{H-P^A} = − 2 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 53.8 (dt, J_{P-Rh} = 129 Hz, J_{P-P} = 28 Hz, P^A), 24.0 (dd, J_{P-Rh} = 79 Hz, J_{P-P} = 28 Hz, P^B). IR (KBr, cm^{-1}): 1946 (s), 1918 (s). Anal. Calcd (%) for $C_{47}H_{46}NBP_3Rh$: C 67.89, H 5.58, N 1.68. Found: C 67.36; H 5.80, N 1.53.

[Rh(PhBP$_3$)(CO)$_2$] (4). Solid [{Rh(μ-Cl)(CO)$_2$}$_2$] (23 mg, 0.06 mmol) was added to a solution of [Li(tmen)][PhB(CH$_2$PPh$_2$)$_3$] (93 mg, 0.12 mmol) in toluene (5 mL) to give a yellow solution, from which a yellow solid crystallized in 20 min. Toluene (10 mL) was added to extract the solid, and then, the suspension was filtered over kieselguhr to remove LiCl. Concentration of the filtrate and addition of hexane gave complex **4** as yellow crystals after two days at −25 °C. The solid was washed with cold hexane (2 × 5 mL) and vacuum-dried. Yield: 90 mg, 93%. ^{1}H NMR (C_6D_6, 25 °C): δ 8.05 (d, 7.2 Hz, 2H, H^o, PhB), 7.64 (t, 7.2 Hz, 2H, H^m, PhB), 7.38 (m, 1 + 12H, H^p, PhB + H^o, Ph$_2$P), 6.80 (m, 18H, H^{m+p}, Ph$_2$P), 1.75 (d, J_{H-P} = 10.8 Hz, 6H, CH$_2$P). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 20.7 (d, J_{P-Rh} = 99 Hz). IR (Nujol, cm^{-1}): 2037 (s), 1966 (s). MS (FAB$^+$, NBA): *m/z* (%) 788 (100) [M$^+$ − 2CO]. Anal. Calcd (%) for $C_{47}H_{41}BO_2P_3Rh$: C 66.85, H 4.89. Found: C 66.54; H 4.79.

Monitoring the Reaction of Complex 3 with ^{13}CO by NMR. A solution of [Rh(PhBP$_3$)(H)$_2$(NCMe)] (**3**) in C_6D_6 was exposed to a ^{13}CO atmosphere for 20 min in a NMR tube. Examination of the solution by NMR revealed the complete transformation of the starting material into hydrogen and a mixture of the complexes [Rh(PhBP$_3$)(H)$_2$(^{13}CO)] (**5**) and [Rh(PhBP$_3$)(^{13}CO)$_2$] (**4′**) in a 1:2.5 molar ratio. Further exposure to an atmosphere of ^{13}CO gave eventually a solution of [Rh(PhBP$_3$)(^{13}CO)$_2$] and hydrogen. Selected spectroscopic data of **5**: ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 38.6 (ddt, J_{P-C} =109 Hz, J_{P-Rh} = 97 Hz, J_{P-P} = 35 Hz), 21.6 (ddd, J_{P-Rh} = 80 Hz, J_{P-P} = 35 Hz, J_{P-C} =6 Hz). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6, 25 °C): δ 194.1 (ddt, J_{C-P} = 109 Hz, J_{C-Rh} = 53 Hz, J_{C-P} =6 Hz).

Reaction of Complex 3 with CD_2Cl_2. [Rh(PhBP$_3$)(H)$_2$(NCMe)] (**3**) (25 mg, 0.030 mmol) was dissolved in CD_2Cl_2 (0.5 mL) in a NMR tube with a small amount of silicone as internal standard. Examination of the solution by ^{1}H and ^{31}P{^{1}H} NMR revealed slow transformation of **3** into the complexes **6a/6b**. A pale yellow solid precipitates from this solution in one day. After centrifugation of the tube, the solvent was removed and the residue was dried under vacuum. Yield: 18 mg, 73%. ^{1}H NMR (C_6D_6, 25 °C): δ 8.11−6.58 (35H, PhB+Ph$_2$P), 2.19 (d, J_{H-P} = 11.6 Hz, 2H, CH$_2$P), 1.96 (d, J_{H-P} = 11.9 Hz, 2H, CH$_2$P), 1.89 (m, δ_A, 1H) and 1.70 (t, δ_B, J_{H-P} = 11.1 Hz, $J_{A\text{-}B}$ = 14.6 Hz, 1H, CH$_2$P), 1.85 (m, δ_A, 1H) and 1.53 (Brt, δ_B, $J_{A\text{-}B}$ = 12.0 Hz, 1H, CH$_2$P), −5.34 (dm, J_{H-P} = 205.0 Hz, 1H, H-Rh), −6.29 (dm, J_{H-P} = 210.1 Hz, 1H, H-Rh). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 48.9 (dd, J_{P-Rh} = 126 Hz, J_{P-P} = 22 Hz), 46.6 (dd, J_{P-Rh} = 124 Hz, J_{P-P} = 20 Hz), 1,98 (dt, J_{P-Rh} = 43 Hz, J_{P-P} = 22 Hz), −5.61 (dt, J_{P-Rh} = 40 Hz, J_{P-P} = 20 Hz). IR (KBr, cm^{-1}): 2014 (m), 1995 (m). Anal. Calcd (%) for $C_{45}H_{42}BClP_3Rh\cdot 3CH_2Cl_2$: C 58.63, H 4.76. Found: C 58.85; H 5.32.

[Rh(PhBP$_3$)Cl$_2$] (7). A solution of complex **3** (103 mg, 0.124 mmol) in chloroform (5 mL) was left for 1 day at room temperature. Evaporation of the solvent to ca. 2 mL and addition of hexane rendered complex **8** as an orange crystalline solid in two days in the freezer. The solid was isolated by decantation of the mother liquid and washing with diethyl ether. Yield: 96 mg, 90%. ^{1}H NMR (C_6D_6, 25 °C): δ 7.63 (d, 7.2 Hz, 2H, H^o, PhB), 7.50 (dd, 12H, H^o, Ph$_2$P), 7.37 (t, 7.6 Hz, 2H, H^m, PhB), 7.19 (t, 4.8 Hz, 1H, H^p, PhB), 7.16 (t, 6H, 7.2 Hz, H^p, Ph$_2$P), 6.98 (t, 12H, 7.6 Hz, H^m, Ph$_2$P), 1.57 (d, J_{H-P} = 7.6 Hz, 6H, CH$_2$P). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 52.3 (d, J_{P-Rh} = 108 Hz). MS (FAB$^+$, NBA): *m/z* (%) 823 (100) [M$^+$ − Cl]. Anal. Calcd (%) for $C_{45}H_{41}BCl_2P_3Rh\cdot 0.5CHCl_3$: C 59.50, H 4.55. Found: C 60.02; H 4.27.

Table 7. Crystallographic Data for Compounds 1·2CH$_2$Cl$_2$ and 7

	1·2CH$_2$Cl$_2$	7
chem formula	$C_{55}H_{57}BCl_4P_3Rh$	$C_{45}H_{41}BCl_2P_3Rh$
fw	1066.44	859.31
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	12.0712(8)	9.6633(7)
b [Å]	13.5583(9)	18.6168(13)
c [Å]	15.4578(11)	22.0862(15)
α [deg]	91.3980(10)	104.400(1)
β [deg]	94.1190(10)	93.131(1)
γ [deg]	103.3790(10)	90.810(1)
V [Å^3]	2452.7(3)	3841.1(5)
Z	2	4
ρ_{calcd} [g cm^{-3}]	1.444	1.486
μ(Mo Kα) [mm^{-1}]	0.702	0.742
min/max transmn	0.8587/0.9391	0.7951/0.9638
F(000)	1100	1760
cryst size [mm]	0.16 × 0.11 × 0.09	0.36 × 0.05 × 0.05
θ range [deg]	2.27−25.39	2.22−26.02
reflns collected	29 190	42 014
indep reflns	10 649	15 011
R_{int}	0.0449	0.0753
reflns [$F^2 > 2\sigma(F^2)$]	8168	10 784
data/restraints/params	10 649/7/590	15 011/0/937
$R(F)$ [$F^2 > 2\sigma(F^2)$]	0.0478	0.0587
$wR(F^2)$ [all data]	0.1122	0.1149
GOF(F^2) [all data]	0.977	1.051
largest diff peak/hole [e Å^{-3}]	0.886/−1.187	0.950/−0.796

Structural Analysis of 1·2CH$_2$Cl$_2$ and 7. A summary of crystal data and refinement parameters is reported in Table 7. X-ray data were collected with a Bruker Smart Apex CCD diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using ω scans (0.3°). The crystals were covered with inert oil, mounted on glass fibers, and cooled to the data collection temperature (100 K). Data were corrected for absorption using a multiscan method applied with the SADABS program.[35] The structures were solved by direct methods and refined by full-matrix least-squares on F^2, with the program SHELX97[36] in the WINGX[37] package. All non-hydrogen atoms except those of a disordered solvent molecule were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions refined riding on the corresponding atom with a isotropic displacement parameter related to that of the bonded atom. The program ORTEP-3[38] was used for diagrams.

Procedure for Catalytic Reactions. Solvents (analytical grade, Aldrich) were dried and degassed by use of an Innovative Technology solvent purification unit; substrates and other reagents (Aldrich) were used as received. In preliminary experiments the catalyst, the substrate, the solvent, any additive desired, and a stirring bar were placed in a 4793 Parr reactor (100 mL) inside a glovebox. The reactor was purged with hydrogen three times, then charged to the desired pressure and immersed in an oil bath pre-equilibrated at the desired temperature. The reaction was stopped at the appropriate time by placing the reactor in ice; excess hydrogen

(35) Sheldrick, G. M. *SADABS version 2.03*; University of Göttingen: Germany, 2002.
(36) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis*, Release 97-2; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.
(37) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(38) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

was removed at room temperature, the reactor was opened, and the products were immediately analyzed by GC.

Once the desired reaction conditions were determined, further hydrogenation experiments were performed by use of a 5513 Parr reactor (100 mL) fitted with internal stirring and thermocouple, a sampling valve, and a high-pressure buret and coupled to a Parr 4836 controller. The reactor was loaded with the catalyst, the substrate, any additive desired, and the solvent, flushed three times with hydrogen, charged to the desired pressure, and placed in an electric oven pre-equilibrated at the desired temperature. Samples of the reaction mixture were periodically withdrawn through the sampling valve; the pressure was readjusted to maintain a constant value throughout the experiment, and the samples were immediately analyzed by GC, using a Shimadzu 2010 chromatograph with an FID detector. Each experiment was repeated at least twice in order to ensure reproducibility of the results. Average values of two or more runs are reported in the tables and figures.

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Supporting Information Available: Full ORTEP drawings for complexes **1** · $2CH_2Cl_2$ and **7**. Single-crystal X-ray diffraction data in CIF format for complexes **1** · $2CH_2Cl_2$ and **7** are available free of charge via the Internet at http://pubs.acs.org.

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