DOI: 10.1002/ange.201205946

VIP Hydrogenation

A Functional-Group-Tolerant Catalytic *trans* Hydrogenation of Alkynes**

*Karin Radkowski, Basker Sundararaju, and Alois Fürstner**

The catalytic semihydrogenation of alkynes to *Z* alkenes is widely practiced textbook knowledge.[1] Amongst the various heterogeneous or homogenous catalysts capable of effecting this transformation, the use of palladium on $CaCO_3$ doped with lead is particularly popular, and is commonly called Lindlar catalyst after its discoverer;[2–4] variants using $BaSO_4$ as the support material and quinoline as additive are also popular. The major role of the catalyst poisons is to prevent over-reduction of the alkene primarily formed,[5] whereas the *Z* selectivity is an intrinsic feature: transition metal catalysts, be they homogenous or heterogeneous, usually deliver the two hydrogen atoms of H_2 suprafacially to the π system of the substrate by a sequence of hydrometalation/reductive elimination as the elementary step (although the exact processes on a metallic surface, where multimetallic sites may be engaged, are still not understood in full detail).[1,5,6] The small amounts of isomeric by-products that typically accompany the *Z* alkenes are thought to derive from secondary processes.

Because of this well-established stereochemical course, the formation of *E* alkenes by catalytic hydrogenation is inherently difficult and no broadly applicable protocol is known to date.[7,8] In fact, all commonly practiced methods for the direct conversion of alkynes to *E* alkenes are stoichiometric in nature, with Birch-type reductions using dissolving metals being the classical incarnation. The use of alkali metals in liquid ammonia or amines, however, obviously prevents applications to polyfunctionalized, base-labile and/or sensitive substrates.[9,10] The arguably best catalytic alternative is a two-step protocol, in which the alkyne is first subjected to a ruthenium-catalyzed *trans* hydrosilylation[11] followed by gentle protodesilylation of the resulting alkenylsilanes with stoichiometric amounts of a suitable fluoride source.[12] Although this indirect approach is largely superior to the Birch reduction in terms of functional group compatibility and has served our program well in the past,[13,14] we sought to develop a more direct solution. Outlined herein are our preliminary results on a rather unique ruthenium-catalyzed *trans*-selective alkyne hydrogenation. As this method is stereocomplementary to the classical Lindlar reduction and tolerates a host of reducible functional groups, we believe that it holds great promise for future applications.

The *trans* hydrosilylation alluded to above uses $[Cp^*Ru(MeCN)_3]PF_6$ (**1**; Cp* = pentamethylcyclopentadienyl; see Scheme 1) as precatalyst.[11,12] With the isolobal relationship between R_3Si and H in mind, one might envisage that this or similar complexes could possibly effect *trans*-hydrogenation reactions as well. In a pioneering NMR study, Bargon and co-workers indeed demonstrated that the related cationic sorbic acid complex $[Cp^*Ru(\eta^4\text{-}CH_3CH{=}CH{-}CH{=}CHCOOH)]^+ OTf^-$ (**2**) catalyzes the *trans* reduction of substrates such as 2-pentyne or 1-phenyl-1-propyne in $[D_4]$methanol under a hydrogen atmosphere (1 bar); terminal acetylenes were found to be unreactive.[15] Parahydrogen-induced polarization (PHIP) experiments demonstrated that the *E* alkene formation was intrinsic and not caused by posterior $Z \rightarrow E$ isomerization. The PHIP spectra also implied a pair-wise delivery of the hydrogen atoms of H_2. To account for these results, the authors proposed a mechanism involving μ-bridged dinuclear complexes, but emphasized the somewhat speculative nature of their proposal.[15] This suggestion was also based on earlier evidence from the rhodium series.[7]

Free alcohols, a diethyl acetal, and a conjugated ketone were found to be compatible with this method, although no yields of isolated products were reported.[15,16] Unfortunately, however, our attempts to translate this methodology to the semihydrogenation of the lactonic cycloalkyne **5**, which serves as a model compound in our ongoing studies on the development of ever more effective catalysts for alkyne metathesis,[17] only met with limited success (Scheme 1).

As can be seen from the selected data shown in Table 1, the hydrogenation of alkyne **5** in the presence of complexes **1** or **2** proceeded with appreciable *E* selectivity. However, the sorbic acid complex **2** failed to bring about full conversion even at a loading of 25 mol% and the reaction was not very clean either (Table 1, entry 1). Although the commercial acetonitrile adduct **1** was more effective,[16] the mass recovery was poor in most cases (Table 1, entries 3–5) and the *E*/*Z* ratio provided room for improvement. Careful inspection of the crude mixtures indicated substantial oligomerization by transesterification before and/or after the semireduction. This competing pathway is attributed to an effective activation of the carboxyl groups by the evidently fairly Lewis acidic ruthenium species derived from **1** under the reaction conditions. This side reaction was more pronounced in MeOH than in CH_2Cl_2, which was therefore chosen as the solvent for further optimization.[18]

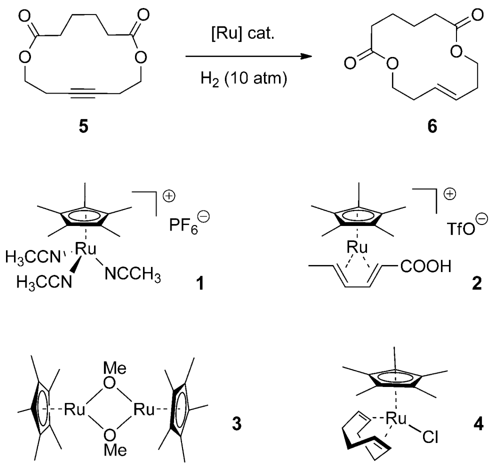
Another important piece of information came from experiments with the methoxide-bridged dimer **3**. On treatment with TfOH (Tf = trifluoromethanesulfonyl) in CH_2Cl_2,

---

[*] K. Radkowski, Dr. B. Sundararaju, Prof. A. Fürstner
Max-Planck-Institut für Kohlenforschung
45470 Mülheim/Ruhr (Germany)
E-mail: fuerstner@kofo.mpg.de

[**] Generous financial support by the Max-Planck-Gesellschaft, the Fonds der Chemischen Industrie, and the Alexander von Humboldt-Stiftung (fellowship to B.S.) is gratefully acknowledged. We thank the analytical departments of our Institute for excellent assistance.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205946.



Scheme 1. Model reaction for the investigation of the *trans*-selective alkyne hydrogenation effected by [Cp*Ru]-based precatalysts; for the results, see Table 1.

Table 1: Optimization of the *trans*-selective alkyne hydrogenation shown in Scheme 1.[a]

Entry	[Ru]	mol %	Additive (mol %)	Solvent	*t* [h]	*E*/*Z*[b]	Yield [%][c]	By-products[d] [%]
1	**2**[e,h]	25		MeOH	0.5	87:13	55[f]	5
2	**1**[e,h]	25		MeOH	0.5	96:4	35	<2
3	**1**	10		MeOH	1	94:6	45	2
4	**1**	5		MeOH	1	94:6	48	12[g]
5	**1**[h]	25		CH_2Cl_2	1	88:12	55	11[g]
6	**1**	2		CH_2Cl_2	0.5	85:15	86	19[g]
7	**3**	5	TfOH (10)	CH_2Cl_2	1	58:42	n.d.	1
8	**3**	5	TfOH/ COD (10)	CH_2Cl_2	2.5	82:18	82	8
9	**4**	5		CH_2Cl_2	1	98:2	89	15
10	**4**	5.5	AgOTf (5)	CH_2Cl_2	0.5	98:2	89–96[i]	7–10[i]
11	**4**	2.2	AgOTf (2)	CH_2Cl_2	0.5	98:2	89	15

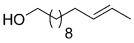
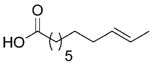
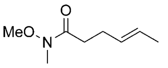
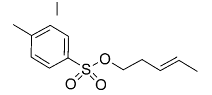
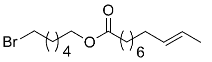
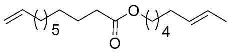
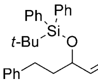
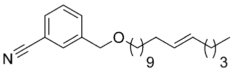
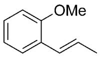
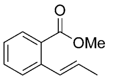
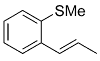
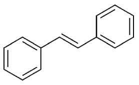
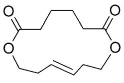
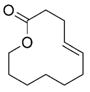
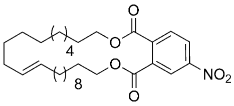
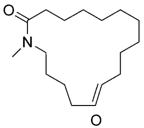
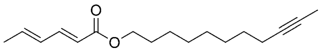
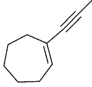
[a] Unless stated otherwise, all reactions were performed under H_2 (10 bar) at ambient temperature. [b] Ratio observed in the crude product prior to work-up. Determined by GC analysis. [c] Combined yield of the isolated alkenes and alkane. [d] Sum of alkane and isomeric alkenes formed by double bond migration, which co-elude as a single peak. Determined by GC analysis. [e] At 55 °C. [f] Yield determined by GC analysis; the reaction did not proceed further when stirred for additional 2 h. [g] GC–MS results suggest that the by-products largely consisted of isomeric alkenes formed by double-bond migration. [h] At 1 bar H_2 pressure. [i] Range observed in several independent reactions on different scale (0.2–1.3 mmol); n.d. = not determined.

this complex releases unligated $[Cp^*Ru]^+$ into the solution.[19] Whereas this free species on its own performed poorly (Table 1, entry 7), the selectivity was largely restored and the product yield good when 1,5-cyclooctadiene (COD) was present (Table 1, entry 8).[20] These results suggested that a chelating diene ligates the active species without interrupting the hydrogenation; in so doing, it tempers the Lewis acidity of the Cp^*Ru^{II} entity and hence ensures high productivity, while assisting the *trans*-selective course of the reduction.

As a consequence, we focused our efforts on the use of commercial [Cp*Ru(cod)Cl] (**4**) as a defined precatalyst. At a loading of 5 mol % and a hydrogen pressure of 10 bar,[21] this complex cleanly effected the reduction of **5** to **6**, to afford an excellent *E*/*Z* ratio of no less than 98:2 (Table 1, entry 9). Some over-reduction was noticed, but the alkane by-product could be partly removed by flash chromatography. Importantly and in striking contrast to the experiments with **1** or **2**, the competing oligomerization was largely suppressed and the mass recovery was therefore excellent (89 % combined yield of alkene and alkane). The reaction could be further improved upon ionization of **4** with AgOTf[22] prior to the actual hydrogenation step. This allowed the reaction time to be reduced, without compromising the yield and selectivity (Table 1, entries 10–11).[23] A control experiment confirmed that the *E* selectivity is inherent to the reduction and not the result of rapid *Z*→*E* isomerization.[24]

This favorable outcome encouraged us to investigate the scope of the method in more detail. As can be seen from the results compiled in Table 2, a mixture of **4** (5.5 mol %) and AgOTf (5 mol %) in CH_2Cl_2 allowed an assortment of substrates to be reduced with excellent levels of *E* selectivity. Importantly, the yields of the isolated products were high in all cases investigated and the method was compatible with a variety of polar substituents, including esters, amides, free carboxylic acids, ketones,[18] a primary alcohol, and methyl and silyl ethers, as well as an elimination-prone primary tosylate. Moreover, reducible sites such as a nitro group, an alkyl bromide, the N–O bond of a Weinreb amide, an aromatic nitrile, and a terminal alkene remained intact. Even a thioether moiety in vicinity to the alkyne did not poison the catalyst; actually, the formation of the sulfide shown in entry 11 (Table 2) worked particularly well, as virtually no over-reduction was observed in this case but the high *E* selectivity remained uncompromised. In contrast, substrates containing a 1,3-diene or a 1,3-enyne unit could not be hydrogenated (Table 2, entries 19 and 20), most likely because of the tight coordination of such conjugated π systems to the active ruthenium species formed in situ (compare the sorbic acid complex **2** and complex **11** shown in Scheme 3); likewise and in analogy to the report by Bargon and co-workers,[15] the attempted reduction of a terminal alkyne did not work well. In all cases investigated, the *E* configuration of the major product was assigned by NMR spectroscopy and confirmed by direct comparison with the corresponding *Z* alkene made by Lindlar reduction. It is informative to look at the spectra (see the Supporting Information), which show that the amount of over-reduced and/or isomeric by-products present in the crude mixtures is not higher than that obtained in the classical Lindlar reductions using a commercial $Pd(Pb)/CaCO_3$ sample. The over-reduction of the substrate was typically in the range of 5–15 %; for reasons that are not entirely clear, however, it was more significant in the reduction of tolane (Table 2, entry 12), a propargylic silyl ether (Table 2, entry 7), and the strained cycloalkynes that form the products shown in entries 14 and 18 (Table 2). Despite this minor drawback, the new method

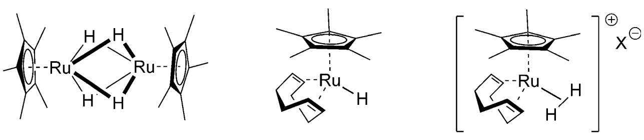
Table 2: *trans*-Selective reduction of internal alkynes.[a]

Entry	Major Product	*t* [h]	*E*/*Z*[b]	Yield [%][c]
1		0.5	98:2	96
2		0.5	95:5	88
3		4	96:4	66[d]
4		2.5	93:7	95
5		0.5	95:5	87
6		0.5	97:3	60[d]
7		4	93:7	96 (33)[c,d]
8		0.5	87:13	95 (21)[c]
9		2.5	96:4	86
10		0.5	97:3	67
11		1.5	97:3	88[e]
12		21	95:5	82 (34)[c]
13		0.5	98:2	89[f]
14		0.5	96:4	64 (27)[c,d]
15		16[g]	97:3	81[d]
16		3	92:8	80
17		34[g]	91:9	85
18		1[g]	97:3	77 (26)[c,d]
19				n.r.
20				n.r.

[a] Unless stated otherwise, the reactions were performed with **4** (5.5 mol%) and AgOTf (5 mol%) in CH_2Cl_2 at RT under H_2 (10 bar initial pressure); for representative procedures, see the Supporting Information. [b] Determined by GC analysis. [c] Combined yield of alkenes and the alkane (5–15%, as determined by GC analysis); if the amount of alkane by-product (and/or isomeric alkenes formed by double-bond migration) exceeds 15%, the measured GC% are indicated in brackets. [d] Alkene isomers formed by double-bond migration were detected. [e] No alkane was detected. [f] 1.3 mmol scale, see the Supporting Information. [g] Using the neutral complex **4** without AgOTf; n.r. = no reaction.

constitutes the first practical, efficient, functional-group-tolerant, broadly applicable, and highly *E*-selective semihydrogenation protocol for alkynes. As such, it is strictly stereocomplementary—but otherwise very well comparable—to the classical repertoire.

The unorthodox stereochemical course of this hydrogenation raises important questions as to the actual mechanism. Although a final answer cannot be given at this point, several findings bear relevant information. First, it must be noticed that a solution of **4** and AgOTf in CD_2Cl_2, when kept in the absence of the alkyne substrate under H_2 atmosphere (10 bar) in an NMR pressure tube for 1–5 h, gives rise to a mixture containing several discrete species. Three distinct signals in the high-field region (δ_H (CD_2Cl_2): −4.96, −8.02, −13.42 ppm) indicate that more than one ruthenium hydride complex is formed. Some reasonable candidates are shown in Scheme 2; however, they could not be unambiguously identified by comparison with literature data, because the reported spectra were recorded in a different solvent or at a significantly different temperature. Therefore we decided to prepare these complexes by unambiguous routes and individually test their catalytic performance.



7 δ_H = -13.98 ppm (C_6D_6)

8 δ_H = -5.74 ppm (C_6D_6)

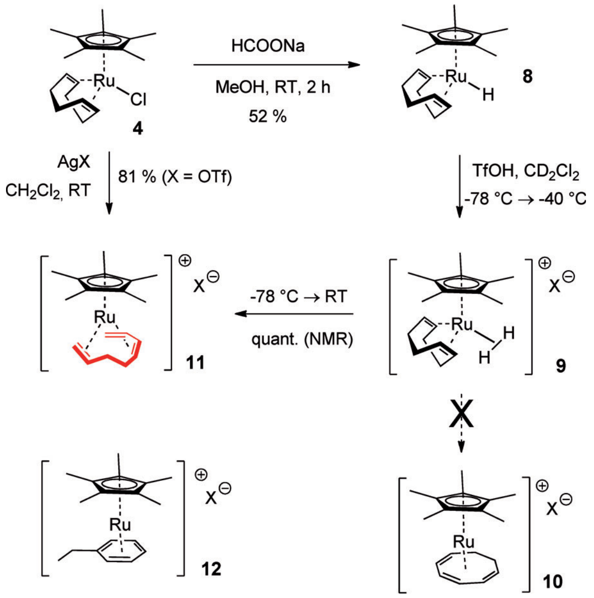
9 δ_H = -4.81 ppm (CD_2Cl_2 at 200K)

Scheme 2. Known ruthenium hydride (or hydrogen) complexes that might possibly form in situ from **4**/AgOTf under the conditions of the catalytic hydrogenation.

The conspicuous signal below −13 ppm suggested that the dimeric dihydride species **7** might be generated from the precatalyst, if the COD ligand is hydrogenated off (or replaced by solvent prior to reaction with H_2).[25] Recalling that Bargon and co-workers had proposed a bimetallic mechanism,[15] this species seemed a particularly hot candidate. Therefore complex **7** was prepared according to a literature route[26] but it was found to afford only a disappointingly low selectivity ($E/Z = 55:45$) when used as catalyst for the reduction of **5** to **6** under standard conditions (10 bar H_2, CH_2Cl_2, RT).

Likewise, our control experiments exclude that the monohydride complex **8**[27] is the operative *E*-selective catalyst. This species, for which a convenient new synthesis route was found using sodium formate as the hydride source (Scheme 3), resulted only in poor conversion and an unfavorable *E*/*Z* ratio of 45:55.

Should any complex **8** be formed from [Cp*Ru(cod]OTf and H_2, however, one equivalent of TfOH must also be generated. Therefore we checked whether the acid plays any role in the catalytic process. To this end, preformed hydride **8** was protonated with TfOH in CD_2Cl_2 at −78 °C to give the known cationic dihydrogen complex **9** (Scheme 3).[28] This species is only stable below −40 °C, at which temperature it did not effect any noticeable hydrogenation of the model substrate **5**. In contrast, when a mixture containing **9**



Scheme 3. Fate of the cationic [Cp*Ru(cod)] fragment.

(10 mol%) and alkyne **5** was allowed to reach ambient temperature under H_2 (10 bar), product **6** was quantitatively formed with excellent selectivity ($E/Z = 95{:}5$).[29] This result corresponds closely to the outcome under the standard conditions used in the preparative experiments (Table 1, entry 10), thus suggesting that either the cationic dihydrogen complex **9** itself is in the catalytic cycle and effects the *trans* hydrogenation before it decomposes, or that this complex first transforms into another species, which then serves as the actual catalyst.[30]

To check this latter possibility, the fate of complex **9a** (X = OTf) was further investigated (Scheme 3). It has previously been reported that its sister compound **9b** ($X = BF_4$) converts into the 1,3,5-cyclooctatriene complex **10b** ($X = BF_4$).[28] Surprisingly though, we observed a different outcome: thus, **9a** was found to afford complex **11a** as the only product detectable by NMR spectroscopy, when a solution in CD_2Cl_2 was allowed to warm from −78°C to ambient temperature. This remarkable transformation, during which the COD ring transforms into an acyclic η^4,η^2-1,3,7-octatriene ligand by C−C bond cleavage,[31,32] was also observed upon stirring of the cationic species generated from [Cp*RuCl(cod)] (**4**) and AgOTf for 4 h in CH_2Cl_2 under Ar. Moreover, we confirmed that it is not the escorting counterion that accounts for this unusual result, as ionization of **4** with $AgBF_4$ furnished the analogous complex **11b** ($X = BF_4$) together with the arene complex **12b** derived thereof.[33]

Because the complexes **11** and **12** form on a timescale similar to that of the actual hydrogenation reaction, we tested whether they exert any catalytic activity. In fact, the use of the isolated complex **11a** (5 mol%) resulted in an *E*-selective hydrogenation of the model substrate **5**, albeit the *E*/*Z* ratio (86:14) was somewhat less favorable than that obtained with the in situ mixture **4**/AgOTf (Table 1, entry 10). In contrast, the arene adduct **12b** was inactive, which likely explains why toluene had been found unsuitable as (co)solvent in the present hydrogenation.[18]

In any case, the method described above seems to be the first practical and truly functional-group-tolerant procedure for the catalytic semihydrogentaion of alkynes to *E* alkenes, which is stereocomplementary to the classical Lindlar reduction or its synthetic equivalents. The active catalyst is generated in situ from [Cp*RuCl(cod)] (**4**) and AgOTf under hydrogen pressure. Although no detailed picture of the operative mechanism can yet be drawn, the available data suggest that neither the mononuclear nor the dinuclear hydride complexes, [Cp*RuH(cod)] and [Cp*Ru(μ-H)$_4$RuCp*], respectively, account for the observed results. Rather, the cationic dihydrogen complex [Cp*Ru(H_2)(cod)]OTf (**9**) and/or products derived from this labile entity seem to play a role. We intend to scrutinize this notion, with the hope of identifying ligand frameworks that impart more stability onto the active species and hence better lend themselves to mechanistic investigations.

Received: July 25, 2012

Keywords: alkenes · alkynes · hydrogenation · ruthenium · *trans* reduction

---

[1] a) A. M. Kluwer, C. J. Elsevier in *Handbook of Homogeneous Hydrogenation*, *Vol. 1* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, pp. 375–411; b) H.-U. Blaser, A. Schnyder, H. Steiner, F. Rössler, P. Baumeister in *Handbook of Heterogeneous Catalysis*, *Vol. 7*, 2nd ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3284–3308; c) S. Siegel in *Comprehensive Organic Synthesis Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 417–442; d) H. Takaya, R. Noyori in *Comprehensive Organic Synthesis*, *Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 443–469; e) P. N. Rylander, *Hydrogenation Methods*, Academic Press, London, **1985**; f) Á. Molnár, A. Sárkány, M. Varga, *J. Mol. Catal. A* **2001**, *173*, 185–221; g) E. N. Marvell, T. Li, *Synthesis* **1973**, 457–468.

[2] a) H. Lindlar, *Helv. Chim. Acta* **1952**, *35*, 446–450; b) H. Lindlar, R. Dubuis, *Org. Synth.* **1966**, *46*, 89–91.

[3] a) D. J. Cram, N. L. Allinger, *J. Am. Chem. Soc.* **1956**, *78*, 2518–2524; b) J.-J. Brunet, P. Caubere, *J. Org. Chem.* **1984**, *49*, 4058–4060; c) J. Rajaram, A. P. S. Narula, H. P. S. Chawla, S. Dev, *Tetrahedron* **1983**, *39*, 2315–2322; d) K. R. Campos, D. Cai, M. Journet, J. J. Kowal, R. D. Larson, P. J. Reider, *J. Org. Chem.* **2001**, *66*, 3634–3635; e) M. Gruttadauria, L. F. Liotta, R. Noto, G. Deganello, *Tetrahedron Lett.* **2001**, *42*, 2015–2017; f) Y. Lee, Y. Motoyama, K. Tsuji, S.-H. Yoon, I. Mochida, H. Nagashima, *ChemCatChem* **2012**, *4*, 778–781.

[4] For other functional-group-tolerant *Z*-selective semihydrogenation methods, see the following for leading references and literature cited therein: a) R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1976**, *98*, 2143–2147; b) M. W. van Laren, C. J. Elsevier, *Angew. Chem.* **1999**, *111*, 3926–3929; *Angew. Chem. Int. Ed.* **1999**, *38*, 3715–3717; c) M. Sodeoka, M. Shibasaki, *J. Org. Chem.* **1985**, *50*, 1147–1149; d) C. A. Brown, V. K. Ahuja, *J. Org. Chem.* **1973**, *38*, 2226–2230; e) P. Hauwert, G. Maestri, J. W. Sprengers, M. Catellani, C. J. Elsevier, *Angew. Chem.* **2008**, *120*, 3267–3270; *Angew. Chem. Int. Ed.* **2008**, *47*, 3223–3226; f) H. S. La Pierre, J. Arnold, F. D. Toste, *Angew. Chem.* **2011**, *123*, 3986–3989; *Angew. Chem. Int. Ed.* **2011**, *50*, 3900–3903;

g) B. M. Choudary, G. V. M. Sharma, P. Bharathi, *Angew. Chem.* **1989**, *101*, 506–507; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 465–466.

[5] For leading studies on the structure of Lindlar catalysts and the effect of the additives, see: a) A. B. McEwen, M. J. Guttieri, W. F. Maier, R. M. Laine, Y. Shvo, *J. Org. Chem.* **1983**, *48*, 4436–4438; b) R. Schlögl, K. Noack, H. Zbinden, A. Reller, *Helv. Chim. Acta* **1987**, *70*, 627–679.

[6] W. A. Maier, *Angew. Chem.* **1989**, *101*, 135–146; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 135–145.

[7] Dinuclear hydridorhodium complexes were shown to be intrinsically selective catalysts for the semihydrogenation of alkynes to *E* alkenes; unfortunately, the lifetime of the catalyst clusters is very limited and *Z*-alkene formation takes over after a few minutes under catalytic conditions. It seems that this method has not found any applications to advanced synthesis, see: a) R. R. Burch, E. L. Muetterties, R. G. Teller, J. M. Williams, *J. Am. Chem. Soc.* **1982**, *104*, 4257–4258; b) R. R. Burch, A. J. Shusterman, E. L. Muetterties, R. G. Teller, J. M. Williams, *J. Am. Chem. Soc.* **1983**, *105*, 3546–3556.

[8] For an *E*-selective transfer hydrogenation of unfunctionalized alkynes with an iridium catalyst, see: a) K. Tani, A. Iseki, T. Yamagata, *Chem. Commun.* **1999**, 1821–1822; a catalyst formed from [$RhCl_3$(pyridine)$_3$] and $NaBH_4$ in DMF allowed for the *trans* hydrogenation of diphenylacetylene to (*E*)-stilbene, although functionalized alkynes gave the corresponding *Z* alkenes, see: b) P. Abley, F. J. McQuillin, *J. Chem. Soc. D* **1969**, 1503–1504.

[9] a) K. N. Campbell, L. T. Eby, *J. Am. Chem. Soc.* **1941**, *63*, 216–219; b) R. A. Benkeser, G. Schroll, D. M. Sauve, *J. Am. Chem. Soc.* **1955**, *77*, 3378–3379; c) I. Kovářová, L. Steinz, *Synth. Commun.* **1993**, *23*, 2397–2404; d) review: D. J. Pasto in *Comprehensive Organic Synthesis*, *Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 471–488.

[10] For the use of (over)stoichiometric Cr^{II}, which is more functional group tolerant, see: a) C. E. Castro, R. D. Stephens, *J. Am. Chem. Soc.* **1964**, *86*, 4358–4363; b) A. B. Smith III, P. A. Levenberg, J. Z. Suits, *Synthesis* **1986**, 184–189; c) E. M. Carreira, J. Du Bois, *J. Am. Chem. Soc.* **1995**, *117*, 8106–8125.

[11] The term "*trans* hydrosilylation" of an alkyne is used here to denote a reaction in which the H and the R_3Si unit of R_3SiH end up *trans* to each other; because of the formalism of nomenclature, however, the resulting alkenylsilanes are correctly termed *cis* configured.

[12] a) B. M. Trost, Z. T. Ball, T. Jöge, *J. Am. Chem. Soc.* **2002**, *124*, 7922–7923; b) B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2005**, *127*, 17644–17655; c) B. M. Trost, M. R. Machacek, Z. T. Ball, *Org. Lett.* **2003**, *5*, 1895–1898; d) review: B. M. Trost, Z. T. Ball, *Synthesis* **2005**, 853–887.

[13] a) A. Fürstner, K. Radkowski, *Chem. Commun.* **2002**, 2182–2183; b) F. Lacombe, K. Radkowski, G. Seidel, A. Fürstner, *Tetrahedron* **2004**, *60*, 7315–7324; c) A. Fürstner, M. Bonnekessel, J. T. Blank, K. Radkowski, G. Seidel, F. Lacombe, B. Gabor, R. Mynott, *Chem. Eur. J.* **2007**, *13*, 8762–8783.

[14] a) K. Lehr, R. Mariz, L. Leseurre, B. Gabor, A. Fürstner, *Angew. Chem.* **2011**, *123*, 11575–11579; *Angew. Chem. Int. Ed.* **2011**, *50*, 11373–11377; b) K. Micoine, A. Fürstner, *J. Am. Chem. Soc.* **2010**, *132*, 14064–14066.

[15] D. Schleyer, H. G. Niessen, J. Bargon, *New J. Chem.* **2001**, *25*, 423–426.

[16] The selective *trans* hydrogenation of more robust peptidic alkyne substrates, with the aid of [Cp*Ru(MeCN)$_3$]PF_6 as catalyst, is described in a patent, although no yields are given, see: A. Robinson, S. Goodwin, WO 2011/146974A1, May 25, **2010**.

[17] a) J. Heppekausen, R. Stade, R. Goddard, A. Fürstner, *J. Am. Chem. Soc.* **2010**, *132*, 11045–11057; b) J. Heppekausen, R. Stade, A. Kondoh, G. Seidel, R. Goddard, A. Fürstner, *Chem. Eur. J.* **2012**, *18*, 10281–10299; c) A. Fürstner, C. Mathes, C. W. Lehmann, *Chem. Eur. J.* **2001**, *7*, 5299–5317.

[18] Acetone could also be used, whereas no reaction was observed in toluene or CH_2Cl_2/toluene.

[19] D. Rondon, B. Chaudret, X.-D. He, D. Labroue, *J. Am. Chem. Soc.* **1991**, *113*, 5671–5676.

[20] Phosphines and arenes instead of COD shut the reaction off.

[21] To ensure high rates, H_2 pressures of ≥ 2 bar were necessary; the isomer ratio did not change much with pressure.

[22] $AgPF_6$ and $AgNTf_2$ gave similar results, whereas $AgBF_4$, $AgSbF_6$, and $AgB(Ar_F)_4$ ($Ar_F = 3,5\text{-}(CF_3)_2C_6H_3$) led to lower selectivity and/or (significantly) lower yields.

[23] The rate difference between reactions catalyzed by the neutral complex **4** or by the cationic species formed from **4**/AgOTf was actually much more pronounced in the cases shown in Table 2, entries 14 and 15, and 16 and 17.

[24] This finding concurs with the conclusions drawn by Bargon and co-workers, see Ref. [15]. Specifically, when the *Z* alkene derived from alkyne **5** by Lindlar reduction ($Z/E = 93{:}7$) was exposed to the standard reaction conditions (**4** (5.5 mol%), AgOTf (5.5 mol%), CH_2Cl_2, H_2 (10 bar)), no isomerization whatsoever was noticed after 30 min; even after 15 h, the Z/E ratio was still ≥ 84:16.

[25] COD ligated to [Cp*Ru] is kinetically rather labile, see: M. O. Albers, D. J. Robinson, A. Shaver, E. Singleton, *Organometallics* **1986**, *5*, 2199–2205.

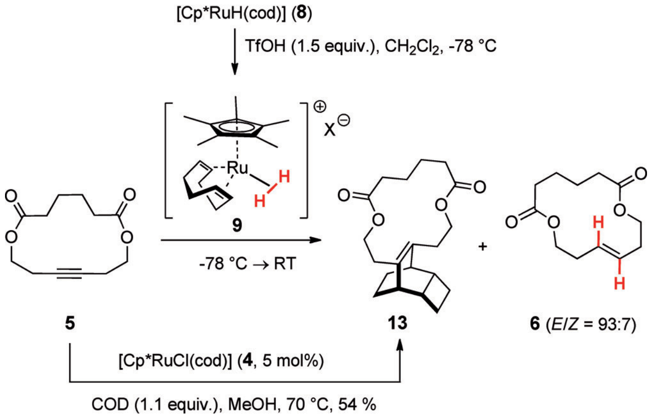
[26] a) H. Suzuki, H. Omori, D. H. Lee, Y. Yoshida, M. Fukushima, M. Tanaka, Y. Moro-oka, *Organometallics* **1994**, *13*, 1129–1146; for the reaction of this complex with diphenylacetylene to give μ-alkyne-bridged complexes, see: b) H. Omori, H. Suzuki, T. Kakigano, Y. Moro-oka, *Organometallics* **1992**, *11*, 989–992; c) review: H. Suzuki, *Eur. J. Inorg. Chem.* **2002**, 1009–1023.

[27] U. Kölle, B.-S. Kang, G. Raabe, C. Krüger, *J. Organomet. Chem.* **1990**, *386*, 261–266. This paper reports a hydride shift for complex **8** of $\delta_H = -5.2$ ppm in C_6D_6, whereas we record $\delta_H = -5.74$ in C_6D_6 and -6.2 in CD_2Cl_2.

[28] G. Jia, W. S. Ng, C. P. Lau, *Organometallics* **1998**, *17*, 4538–4540.

[29] 6% (as determined by GC) of alkane were concomitantly formed.

[30] The notion that the cationic hydrogen complex **9** itself is the active catalyst or an immediate precursor to it is corroborated by a stoichiometric control experiment. When substrate **5** was exposed to one equivalent of **9** (generated from **7** and TfOH) under Ar, alkene **6** was formed with excellent E/Z selectivity (93:7). However, the yield was low because product **13** was produced in equal amounts. This compound derives from a ruthenium-catalyzed cycloaddition process that has precedent in the literature, see: B. M. Trost, K. Imi, A. F. Indolese, *J. Am. Chem. Soc.* **1993**, *115*, 8831–8832. In fact, reaction of **5** with



COD (1.1 equiv) in the presence of [Cp*RuCl(cod)] (**4**, 5 mol %) delivered **13** in 54 % yield.

[31] **11** is a known complex previously prepared by coupling of two butadiene units in the coordination sphere of ruthenium, see: K. Itoh, K. Masuda, T. Fukahori, K. Nakano, K. Aoki, H. Nagashima, *Organometallics* **1994**, *13*, 1020 – 1029.

[32] For the cleavage of norbornadiene within the coordination sphere of [Cp*Ru], see: H. Suzuki, T. Kakigano, H. Fukui, M. Tanaka, Y. Moro-oka, *J. Organomet. Chem.* **1994**, *473*, 295 – 301.

[33] **11** might convert into **12** by isomerization/electrocyclization/aromatization. The conversion of COD to ethylbenzene with modified (cyclopentadienyl)ruthenium templates has precedent in the literature, although no mechanism was proposed, see: B. Dutta, R. Scopelliti, K. Severin, *Organometallics* **2008**, *27*, 423 – 429.