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FULL PAPER

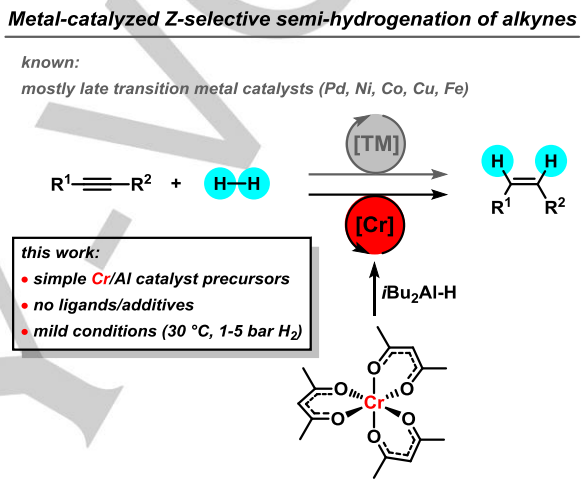
Stereoselective Chromium-Catalyzed Semi-Hydrogenation of Alkynes

Bernhard J. Gregori,[a] Michal Nowakowski,[b] Anke Schoch,[b] Simon Pöllath,[c] Josef Zweck,[c] Matthias Bauer,[b] and Axel Jacobi von Wangelin[a]*

Abstract: Chromium complexes have found very little applications as hydrogenation catalysts. Here, we report a Cr-catalyzed semi-hydrogenation of internal alkynes to the corresponding *Z*-alkenes with good stereocontrol (up to 99/1 for dialkyl alkynes). The catalyst comprises the commercial reagents chromium(III) acetylacetonate, $Cr(acac)_3$, and diisobutylaluminium hydride, DIBAL-H, in THF. The semi-hydrogenation operates at mild conditions (1-5 bar H_2, 30 °C).

Introduction

Alkenes are ubiquitous motifs in numerous organic molecules including natural products, fragrances, pharmaceuticals, agrochemicals, fine chemicals, and polymers. The meticulous control over the stereochemistry of the C=C bond enables distinct structural and functional properties of the alkene unit.[1] An especially attractive access to both stereoisomers of alkenes from the same starting material is the semi-hydrogenation of alkynes.[2] High reactivities, mild reaction conditions, and good levels of stereocontrol of this atom-economical reaction have been reported in the presence of various transition metal catalysts. The first and foremost method is the Lindlar-type *Z*-selective hydrogenation[3] with Pd@$CaCO_3$ catalysts that are poisoned with quinoline and lead acetate. Later, the Nickel-P2 catalyst[4] ($Ni(OAc)_2$, $NaBH_4$, ethanol) was reported to give similar selectivities. Recently, major progress has been achieved toward the application of late 3d transition metal catalysts (Fe,[5] Co,[6] Ni,[4,7] Cu[8]), whereas much less attention has been devoted to earlier 3d metals (Sc,[9] V,[10] Mn,[11] Cr[12]). Only two examples of chromium-catalyzed semi-hydrogenation of alkynes were reported: With (arene)tricarbonylchromium complexes[12a] at harsh conditions (120 °C, 70 bar H_2); with metallated porous organic polymers but narrow scope and low selectivity.[12b,c]
Unlike the many applications of chromium complexes to polymerizations,[13] oxidations,[14] and organometallic chemistry,[15] there is very little knowledge of the activity of chromium catalysts in hydrogenation reactions.[12,16] Here, we report an operationally facile protocol for the semi-hydrogenation of alkynes based on a catalyst comprising of commercially available chromium tris(acetylacetonate), $Cr(acac)_3$, and diisobutylaluminium hydride, DIBAL-H, at very mild conditions (Scheme 1, bottom).



Scheme 1. Chromium-catalyzed *Z*-selective semi-hydrogenation of alkynes.

Results and Discussion

Lead discovery

We have recently reported the use of co-catalytic iron(II) bis(acetylacetonate) and DIBAL-H in alkyne semi-hydrogenations.[5a] A brief survey of 3d transition metal salts revealed distinct activities in the model reaction of 1-phenyl-1-propyne under low H_2 pressure (2 bar): While $Ni(acac)_2$ and $Co(acac)_2$ underwent complete hydrogenations to the alkanes, chemoselective hydrogenation to the alkenes with high *Z*-stereocontrol was observed with $Fe(acac)_2$[5a] and $Cr(acac)_3$ (Table 1, entries 1-4). To the best of our knowledge, the latter protocol constitutes the first application of a simple Cr salt/metal hydride co-catalyst to efficient alkyne semi-hydrogenations. $CrCl_2$ and $CrCl_3$ afforded slightly higher stereoselectivities (*Z*/*E* = 17/1) but with significantly lower yields (Table 1, entries 5, 6). For further studies, we used the readily soluble, bench-stable, and commercially available $Cr(acac)_3$ (see ESI for further optimization experiments).

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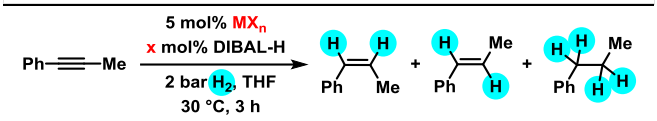
Table 1. Selected optimization experiments.[a]

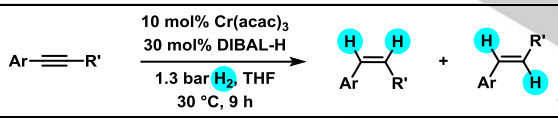


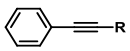
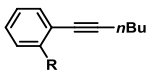
Entry	MX_n	x	Alkenes [%]	*Z*/*E*	Alkane [%]
1	$Fe(acac)_2$	10	98	18/1	<1
2	$Co(acac)_2$	10	<1	-	>99
3	$Ni(acac)_2$	10	<1	-	>99
4	**$Cr(acac)_3$**	**15**	**51**	**12/1**	**2**
5	$CrCl_2$	10	19	17/1	<1
6	$CrCl_3$	15	28	16/1	1
7	-	15	<1	-	-

[a] Conditions: 0.2 mmol alkyne, 0.4 mL THF. Yields and *Z*/*E* ratios were determined by ^{1}H-NMR and GC-FID.

Substrate Scope. The optimized conditions (10 mol% $Cr(acac)_3$, 30 mol% DIBAL-H) were then applied to the semi-hydrogenation of various aryl-substituted alkynes at very mild conditions (1.3-5 bar H_2, 30 °C) and reaction times up to 24 h to assure (near) quantitative conversions. 1-Aryl-2-alkyl acetylenes (Table 2) and 1,2-diaryl acetylenes (Table 3) showed high conversions but only moderate *Z*/*E*-stereoselectivities (up to 10/1). Terminal alkynes were not tolerated (Table 2, entry 3) while the reaction was compatible with F, Cl, Br, NH_2, OCF_3, ester, TMS, and cyclopropyl.

Table 2. Semi-hydrogenation of aryl-alkyl substituted alkynes.[a]

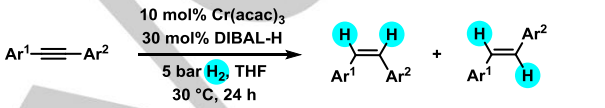


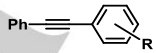
Entry	Alkyne	R	Alkenes [%]	*Z*/*E*
1[b]		Me	95	6/1
2		Et	94	6/1
3[c]		H	0	-
4[d]		*c*-Propyl	96	6/1
5[b]		*c*-Hexyl	73	9/1
6		TMS	58[e]	4/1
7		H	87	6/1
8[f]		Me	96	7/1
9[g]		OMe	43[e]	2/1
10[h]		Cl	96	3/1
11[h]		NH_2	87	6/1

[a] Conditions: 0.2 mmol alkyne, 0.4 mL THF. Yields and *Z*/*E* ratios were determined by ^{1}H-NMR and GC-FID. [b] 5 h. [c] 5 bar H_2, 3 h. [d] 3 bar H_2, 16 h. [e] Incomplete conversion. [f] 14 h. [g] 12 h. [h] 5 bar H_2, 24 h.

Highly electrophilic and reduction-sensitive functional groups underwent competing reduction which led to catalyst deactivation. (4-Bromophenyl)ethynylbenzene gave minor dehalogenation (<5%) which could be suppressed by higher catalyst loadings (Table 3, entry 4). Carboxylate groups were fully preserved while ketones, nitriles, and nitro substituents were reactive under the conditions (traces of corresponding alcohol and amine products detected by GC-MS). Internal alkynes bearing 1,2-dialkyl substitution gave high yields and near perfect stereoselectivities in most cases (Table 4). Several functionalized alkynes with chloro, acetate, trimethylsilyloxy, and phthalimido substituents afforded the desired *Z*-alkenes with >99/1 stereocontrol.

Table 3. Semi-hydrogenation of diaryl alkynes.[a]



Entry	Alkyne	R	Alkenes [%]	*Z*/*E*
1[b]		-	98	3/1
2		2-F	87	7/1
3[b]		4-Cl	96	3/1
4		4-Br	22 (98)[c]	6/1 (4/1)[c]
5[d]		2-OMe	97	1/1
6[d]		3-OMe	92	3/1
7[d]		4-OMe	87	2/1
8		4-OCF_3	85	4/1
9		4-COMe	30[e]	3/1
10[f]		4-CO_2Me	97	10/1
11		4-NH_2	0	-
12[g]		4-NO_2	0	-

[a] Conditions: 0.2 mmol alkyne, 0.4 mL THF. Yields and *Z*/*E* ratios were determined by ^{1}H-NMR and GC-FID. [b] 3 bar H_2. [c] 20 mol% [Cr], 60 mol% DIBAL-H. [d] 3 bar H_2, 16 h. [e] Incomplete conversion. [f] 2 bar H_2, 12 h. [g] 3 bar H_2, 20 h.

Catalyst characterization. In an effort to elucidate the nature of the active catalyst, we performed several spectroscopic studies. The strongly reducing conditions (DIBAL-H, H_2) and the absence of stabilizing ligands may facilitate catalyst reduction to a low-valent or naked metal species which ultimately may nucleate and grow to larger particles. However, the clear distinction between homogeneous and heterogeneous metal catalysts is not trivial,[17] yet reaction progress analyses and kinetic poisoning experiments can provide useful insight.[18] The semi-hydrogenation of 1-phenyl-1-propyne with 10 mol% [Cr] under standard conditions displayed quite effective catalyst inhibitions when 5 mol% tri-methylphosphite, $P(OMe)_3$, or trimethylphosphine, PMe_3, respectively, were added after 30 min reaction. As the observed catalyst inhibitions were not complete, these results may indicate the presence of a major portion of active heterogeneous catalysts which are in equilibrium with homogeneous catalyst species.

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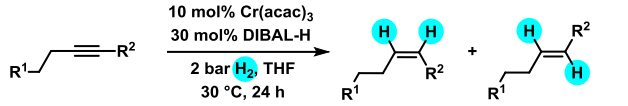
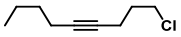
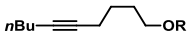
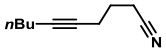
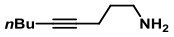
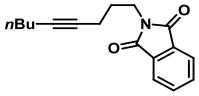
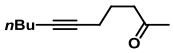
Table 4. Semi-hydrogenation of dialkyl-substituted alkynes.[a]



Entry	Alkyne	R	Alkenes [%]	*Z*/*E*
1[b]		*n*-C_5H_{11}	99	>99/1
2			18 (42)[c] (58)[d]	>99/1
3		Me	99	>99/1
4		Ac	73	>99/1
5[e]		TMS	35	>99/1
6[f]			0	-
7[g]			0	-
8[e]			91	>99/1
9[g]			0	-
10[g]			89	6/1

[a] Conditions: 0.2 mmol alkyne, 0.4 mL THF. Yields and *Z*/*E* ratios were determined by ^{1}H-NMR and GC-FID. [b] 1.3 bar H_2, 14 h. [c] 20 bar H_2, 24 h. [d] 5 bar H_2, 48 h. [e] 20 bar H_2, 48 h. [f] 1.3 bar H_2, 20 h. [g] 5 bar H_2.

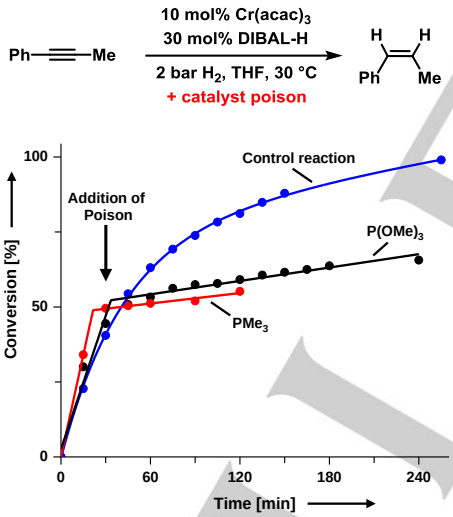


Figure 1. Kinetic catalyst poisoning experiments with PMe_3 and $P(OMe)_3$, respectively (each 0.5 equiv. per [Cr]; addition after 30 min of hydrogenation).

The catalyst activation by addition of DIBAL-H was studied by in-operando X-ray absorption spectroscopy (XAS) at the chromium K-edge.[14d,19] Figure 2 shows the XANES (X-ray absorption near edge structure) spectra for the successive additions of up to 6 equiv. DIBAL-H to a solution of $Cr(acac)_3$ in THF (in the absence of alkyne and H_2). At higher DIBAL-H concentrations, minor amounts of a precipitate formed which is in accordance with the particle formation monitored by transmission electron microscopy (TEM, *vide infra*). The recorded set of spectra exhibits an isosbestic point so that a steady conversion of a homogeneous solution is dominant in the XAS data. The magnitude of band shifts induced by the addition of DIBAL-H is becoming lesser when approaching the 5th and 6th equivalent. The continuous band shifts - and the fact that the most active Cr catalyst involves 3 equiv. DIBAL-H - may be indicative of the presence of multiple equilibrating species among which the fully reduced species is not the active catalyst.[5a,19] The comparison with the XAS spectrum of a bulk Cr(0) foil (Figure 2, gray curve) demonstrates that reduction by the co-catalyst DIBAL-H does not exclusively take place at Cr under the catalytic conditions. In agreement with earlier observations in the closely related $Fe(acac)_2$-catalyzed semi-hydrogenation,[5a] we postulate the operation of ligand-centered reduction events. The XANES curvature of the reduced species (with 6 equiv. DIBAL-H) showed the characteristic features of elemental chromium (mainly the intense and broad pre-peak and edge signals in the range of 5988-5998 eV) but still was significantly different from the XANES spectrum of Cr(0). This supports the notion that potentially formed Cr(0) particles remaining in solution are rather small, in low concentration, or occurring in a different coordination environment. Further, the doublet-like white line between 6005-6020 eV did not disappear completely so that the presence of acac or related ligands at chromium ions cannot be excluded. This behavior is also reflected in the EXAFS (extended X-ray absorption fine structure) analysis (please see the ESI for details) which clearly document constantly decreasing Cr-O coordination numbers upon addition of DIBAL-H. In the same direction, the Cr-C contributions from the acac-backbone decrease, while the Cr-O and Cr-C distances slightly increase. Importantly, no Cr-Cr pairs of potential clusters could be observed under the catalytic reaction conditions. In combination with the XANES results, we therefore postulate that the major reduction by the co-catalyst DIBAL-H occurs at the acac ligands in solution phase.[5a]

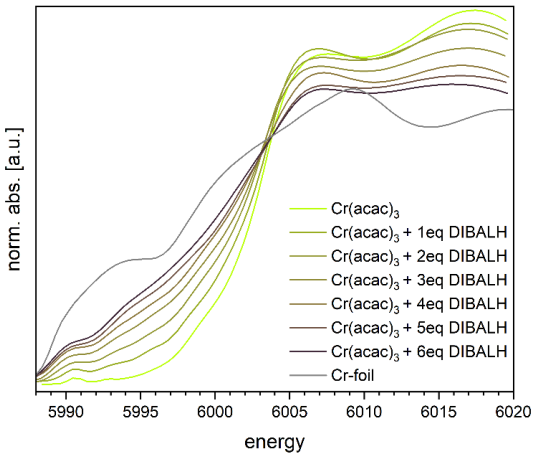


Figure 2. XANES spectra of co-catalyst mixtures of $Cr(acac)_3$ with DIBAL-H. Spectrum of bulk Cr(0) foil shown for comparison.

The notion of significant ligand reduction is further supported by a detailed quantification of the by-products of the binary pre-catalyst mixture (Scheme 2). Stoichiometric reaction of tris(benzoyl-acetonato)chromium(III), $Cr(bzac)_3$, and DIBAL-H afforded mostly

ligand reduction by hydride addition and deoxygenation (Scheme 2b). In comparison with our earlier report of an iron-catalyzed semi-hydrogenation protocol,[5a] the extent of ligand-centered reduction is higher for Cr, which appears to reflect the inherent redox potentials and Lewis acid character. The reaction order of the semi-hydrogenation was determined to be ~1 in [Cr] catalyst under the catalytic reaction conditions and slightly higher (approaching 2.5) at lower catalyst concentrations (see the ESI). Scheme 2c illustrates potential homogeneous and heterogeneous catalyst species. We speculate that DIBAL-H acts as activator for the pre-catalyst by ligand and Cr reduction. The softer metal Cr, even more so in low oxidation states, engages in coordination of the soft Lewis base alkyne to effect π-bond activation.

We further wished to study the formation of nanoparticles from reactions of $Cr(acac)_3$ with 3 equiv. DIBAL-H (upon ageing for >30 min and solvent evaporation). Transmission electron microscopy (TEM) measurements were performed to evaluate the size, elemental composition, and structure of the resultant heterogeneous species. Figures 3a and 3b show the TEM images of isolated Cr-nanoparticles before the Cu/C grid. An energy dispersive X-ray (EDX) spectrum on particles in a ~1.5 µm² area is given in Figure 3c. Beside the metal background noise of the TEM device (Fe, Co, Cu; see ESI), only two clear Cr peaks are present, proving the particles' Cr content. The background does not contain any Cr and Al. Electron diffraction measurements further indicated a crystalline structure of the Cr(0) particles (see ESI). Analysis of 225 particles gave an average particle size of 5.2 ± 0.1 nm with a standard deviation σ = 1.9 nm (Figure 3d).

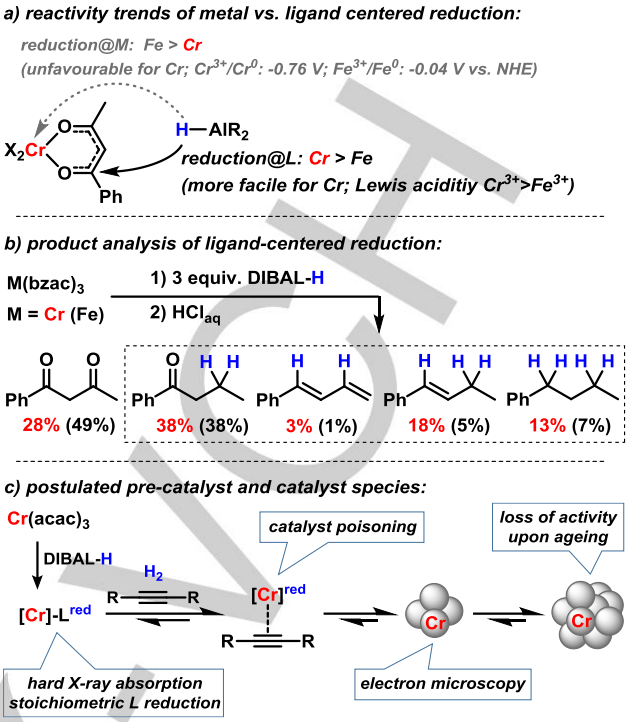
Conclusions

Among the rich literature of chromium catalysis in organic transformations, there are only very few reports of chromium-catalyzed hydrogenations. This work has demonstrated the catalytic potential of the simple pre-catalyst mixture $Cr(acac)_3$/DIBAL-H in the stereoselective semi-hydrogenation of alkanes. The protocol involves mild conditions (<5 bar H_2, 30 °C) and can be applied to various arylalkynes and alkylalkynes including functionalized substrates bearing halogen, ester, and amine groups. Spectroscopic studies indicate a significant operation of ligand-centered reduction events en route to the active Cr catalyst species, which most likely are both homogeneous and heterogeneous in nature, and possibly equilibrate under the conditions.

Experimental Section

Catalyst preparation: Under an atmosphere of argon (Schlenk line or glove box), an oven-dried vial was charged with a stir bar, $Cr(acac)_3$ (17.6 mg, 50 µmol), and dry THF (0.85 mL). The mixture was stirred for 10 min at r.t. and DIBAL-H was added dropwise (150 µL, 1.0 M in toluene, 150 µmol, 3.0 equiv.). The resultant mixture was stirred for 20 min prior to hydrogenation reactions (color-change from purple to black after 5 min).

General procedure of catalytic semi-hydrogenations: Under argon (Schlenk line or glove box), an oven-dried 4 mL vial with a stir bar was



Scheme 2. a) Trends of metal vs. ligand reduction in pre-catalyst mixtures of $M(bzac)_3$ and DIBAL-H. b) Analysis of products derived from ligand-centered reduction of $M(bzac)_3$ with DIBAL-H (relative GC-MS peak areas of products are given). c) Potential catalyst species and catalyst characterization studies.

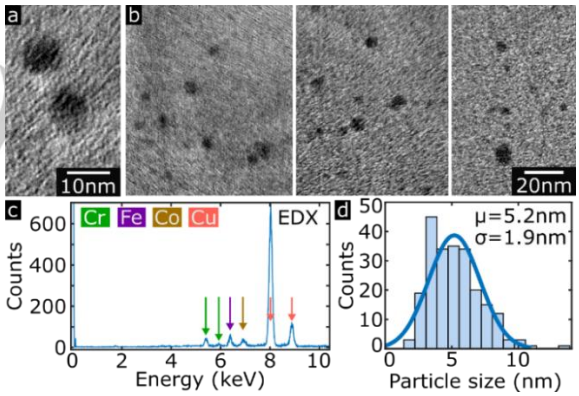


Figure 3. a) High-resolution TEM of two Cr nanoparticles; b) Overview images of several nanoparticles; c) EDX spectrum; d) Size distribution of 225 particles.

charged with alkyne (0.2 mmol) and *n*-pentadecane (internal GC reference, 0.2 mmol, 42.5 mg). The catalyst suspension (see above, 0.4 mL, 0.02 mmol [Cr], 10 mol%) was added, the vial sealed with a septum, punctured by a short needle, and transferred to a pressure-resistant reactor equipped with a gas inlet. The reactor was purged with H_2 for 1 min while stirring the reaction. After three short cycles of (de)pressurizing (2.0 bar, 5 sec, 1.3 bar), H_2 pressure and temperature were set (1.3 bar, 30 °C). After 3-48 h, the reactor was cooled and the pressure released. The vials were retrieved, saturated aqueous $NaHCO_3$ (1.5 mL) and ethyl acetate (1.5 mL) were added. The resulting suspension was stirred for 20 min, the organic phase separated and filtered through a SiO_2 plug. Yields and selectivities were determined by flash chromatography (SiO_2, *n*-pentane, ethyl acetate), quantitative GC, and NMR vs. internal reference.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: chromium • hydrogenation • alkynes • stereoselectivity • nanoparticles

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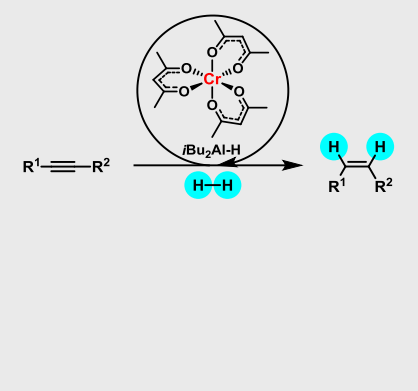
FULL PAPER

Stereoselective semi-hydrogenations of alkynes were developed with a simple [Cr(acac)$_3$/DiBAL-H] catalyst mixture. The reactions operate under mild conditions (30°C, 1-5 bar H_2) and display very good yields and *Z*/*E* ratios (>99/1 for alkyl substituents).



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