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Z-Selective, Catalytic Internal Alkyne Semihydrogenation under H_2/CO Mixtures by a Niobium(III) Imido Complex

Thomas L. Gianetti, Neil C. Tomson, John Arnold,* and Robert G. Bergman*

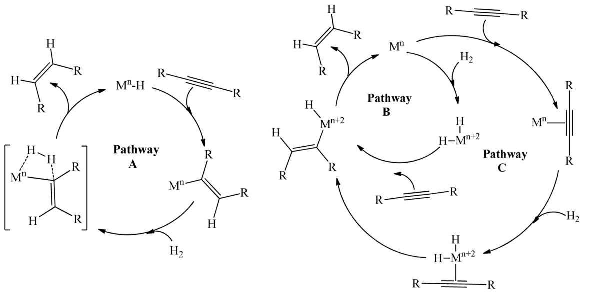
Department of Chemistry, University of California, Berkeley, California 94720, United States

Supporting Information

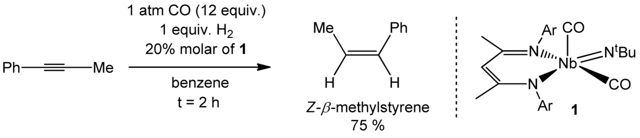
ABSTRACT: The discovery of a Nb(III)-mediated catalytic hydrogenation of internal alkynes to (*Z*)-alkenes that proceeds through an unprecedented mechanism is reported. The mechanistic proposal involves initial reduction of the alkyne by the Nb(III) complex (BDI)Nb(N^{t}Bu)(CO)$_2$ to provide a Nb(V) metallacyclopropene, itself capable of σ-bond metathesis reactivity with H_2. The resulting alkenyl hydride species then undergoes reductive elimination to provide the (*Z*)-alkene product and regenerate a metal complex in the Nb(III) oxidation state. Support for the proposed mechanism is derived from (*i*) the dependence of the product selectivity on the relative concentrations of CO and H_2, (*ii*) the isolation of complexes closely related to those proposed to be part of the catalytic cycle, (*iii*) H/D crossover experiments, and (*iv*) DFT studies of multiple possible reaction pathways.

Homogeneous hydrogenation reactions catalyzed by transition-metal complexes are some of the most extensively studied in organometallic chemistry. Many of these systems operate via one of two common mechanisms, namely, the monohydride and dihydride mechanisms shown in Scheme 1.[1] The development of new catalysts that can access alternative hydrogenation pathways constitutes an attractive area of research for discovering reagents capable of providing control over selectivity and substrate scope. The selective conversion of alkynes to (*Z*)-alkenes, typically accomplished by the heterogeneous Lindlar's catalyst,[2] is difficult to achieve because of *E*/*Z* isomerization and overhydrogenation.[1−3] The development of effective molecular catalysts for this transformation remains an area of intense study with recent notable successes.[1,4] Here we report a mechanistic investigation of a selective semihydrogenation reaction catalyzed by a d^2 transition metal under a mixture of H_2 and CO. Since most of the H_2 produced industrially must be separated from CO, the lack of hydroformylation reactivity of the catalyst presented herein constitutes an interesting step in designing effective hydrogenation catalysts that are able to function in the presence of unpurified syngas.[5]

Scheme 1. Monohydride Mechanism (Pathway A) and Dihydride Mechanism (Pathways B and C)



Scheme 2. Hydrogenation of 1-Phenyl-1-propyne with 1 (0.2 equiv) under a H_2/CO Atmosphere (1:12 Ratio)



Many low-valent early transition metals, such as d^2 metal complexes, are known to oxidatively couple alkynes to form metallacyclopentadiene species.[3,6] Because of this reactivity, the use of d^2 transition-metal complexes as hydrogenation catalysts is rare.[7] Only one d^2 system, reported by Boncella and co-workers,[8] efficiently catalyzes hydrogenation of an unsaturated substrate (internal alkene), but the mechanism of this d^2 molybdenum imido-catalyzed reaction has not been reported. We recently showed that treatment of the Nb(III) dicarbonyl complex (BDI)Nb(N^{t}Bu)(CO)$_2$ (**1**) with 1-phenyl-1-propyne does not result in alkyne−alkyne coupling but instead yields the metallacyclopropene complex (BDI)Nb(N^{t}Bu)(η^2-MeC≡CPh)(CO) (**2**).[9] Acidification of **2** in methanol leads to the formation of (*Z*/*E*)-β-methylstyrene along with the starting alkyne in a 2:1 ratio. The formation of β-methylstyrene focused our attention on the potential use of **1** as a hydrogenation catalyst.

Catalytic hydrogenation of 1-phenyl-1-propyne to (*Z*)-β-methylstyrene (2 h, 1.0 equiv of H_2, 75% yield) was achieved in the presence of **1** (20 mol %) and an excess of CO (12 equiv) in benzene at room temperature (Scheme 2). Increasing the H_2 loading to 3.0 equiv led to a marginal increase in the yield of (*Z*)-β-methylstyrene (85%) and produced trace amounts of *n*-propylbenzene (^{n}PrPh, 3%). Higher CO loadings (40 equiv) led to a drop in catalytic activity but no decrease in selectivity, providing (*Z*)-β-methylstyrene in 45% yield after 2 h. Previous reports of both CO exchange on **1** and the isolation of the tris(isocyanide)Nb(III) complex (BDI)Nb(N^{t}Bu)(CNXyl)$_3$ (Xyl = 2,6-Me $_2$C$_6$H$_3$) suggest[9b] that higher CO loadings result

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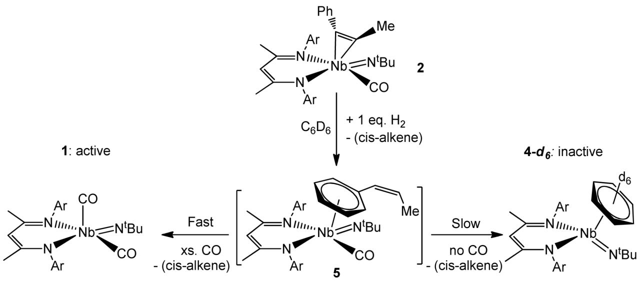
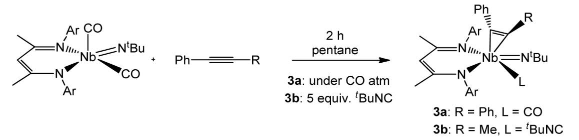
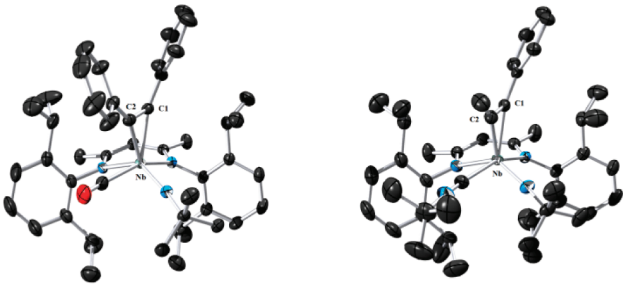
Scheme 3. Role of CO To Maintain High Reactivity and Selectivity



Scheme 4. Synthesis of Complexes 3a and 3b





Complex **3a** Complex **3b**

Figure 1. Molecular structures of **3a** and **3b** determined by single-crystal X-ray diffraction. H atoms have been omitted for clarity; the thermal ellipsoids are at the 50% probability level.

in the formation of the electronically and coordinatively saturated tricarbonyl complex (BDI)Nb(N^{t}Bu)(CO)$_3$.

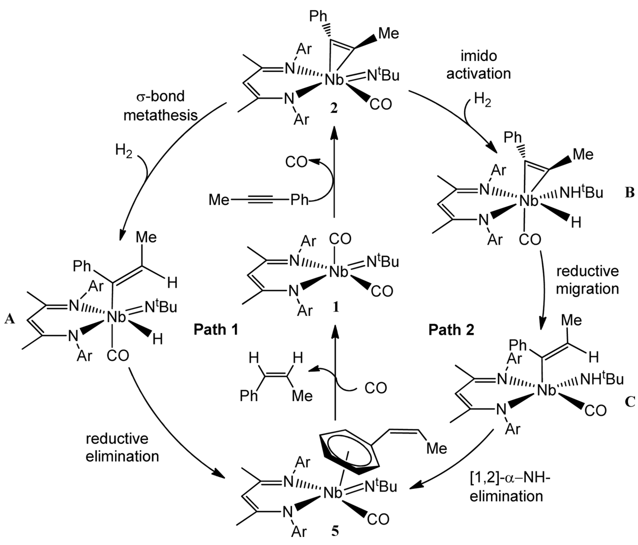
Decreasing the CO loading also resulted in lower yields of (*Z*)-*β*-methylstyrene (~12%) but concurrently led to the formation of both ^{n}PrPh (~16%) and allylbenzene (~6%). Under these conditions, ^{1}H NMR monitoring of the reaction mixture indicated that the catalytic activity stopped after 2 h, at which time the metal complex had been converted into a new, catalytically inactive species, complex **4-*d*$_6$** [see the Supporting Information (SI)]. Analysis using ^{1}H and ^{2}H NMR spectroscopy led to the assignment of **4-*d*$_6$** as a C_6D_6-coordinated complex (Scheme 3), based in part on the presence of a characteristic singlet at 3.7 ppm in the ^{2}H NMR spectrum. A related η^6-arene Mo complex was observed by Boncella and co-workers.[8] Over the course of the reaction leading to **4-*d*$_6$**, the intermediate complex **5** was also observed. The latter species displayed three resonances with a 1:2:2 ratio between 3.6 and 4.1 ppm. This pattern is consistent with a monosubstituted arene ligand bound to the metal center; **5** was therefore assigned as a catalyst–product π complex (Scheme 3), similar to **4-*d*$_6$**. The presence of this η^6-arene intermediate in hydrogenation mechanisms is not unusual and has been observed with several catalysts.[8,10] Separate experiments showed that treatment of **1** with (*Z*)-*β*-methylstyrene provided no observable reaction; thus, the excess CO required for efficient catalysis may be needed to drive catalyst turnover via displacement of the product alkene from the catalyst–product π complex.

Monitoring the course of the most-selective and highest-yielding catalytic reaction (12:1 CO/H_2) by NMR spectroscopy allowed us to observe that the metallacyclopropene complex **2** maintained a constant concentration, suggesting that this complex is the resting state of the catalytic cycle. This hypothesis was supported by a half-turnover experiment wherein treatment of **2** with 1.0 equiv of alkyne and 0.5 equiv of H_2 gave 0.5 equiv of (*Z*)-*β*-methylstyrene, 0.5 equiv of alkyne, and 1.0 equiv of **2**. We note that the formation of **2** by treatment of **1** with 1-phenyl-1-propyne was rapid within the concentration range used during catalysis and that complex **2** was the only transition-metal-containing species observed in solution during the course of the reaction.

Obtaining structural information on **2** was hampered by its thermal instability, but closely related analogues were isolable. Treatment of **1** with 1,2-diphenylacetylene yielded the metallacyclopropene complex (BDI)Nb(N^{t}Bu)(η^2-PhC≡CPh)(CO) (**3a**) in 71% yield (Scheme 4). The higher ν_{CO} absorption frequency for **3a** (2052 cm^{-1}) relative to that for **2** (2039 cm^{-1}) correlates with the π acidity of the two alkynes, but the high ν_{CO} for both complexes [ν_{CO}(free CO) = 2143 cm^{-1}] suggests little π back-bonding from the metal into the π* orbitals of CO, consistent with a high oxidation state at the metal center. Complexes **2** and **3a** are two of the few examples in which CO is coordinated to a formally d^0 group 5 transition-metal complex.[11] Substitution of the CO on **2** by the more strongly *σ*-donating ligand ^{t}BuNC yielded the thermally stable complex (BDI)Nb(N^{t}Bu)(η^2-PhC≡CMe)(CN^{t}Bu) (**3b**; Scheme 4) in 52% yield. Similar to complex **3a**, weak-to-nonexistent π back-donation from the metal to the isocyanide in **3b** was indicated by IR spectroscopy [ν_{CN}(**3a**) = 2167 cm^{-1}, ν_{CN}(free ^{t}BuCN) = 2125 cm^{-1}]. The crystal structures of **3a** and **3b** exhibit distorted square-pyramidal geometries (Figure 1; τ_{3a} = 0.32 , τ_{3b} = 0.33).[12] In both structures, the C_1–C_2 bond lengths of the metallacyclopropene unit show significant elongation from those of the uncoordinated alkyne to values consistent with C–C double bonds [C_1–C_2(**3a**), 1.308(4) Å; C_1–C_2(**3b**), 1.309(3) Å; C(sp^2)–C(sp^2), 1.31–1.34 Å].[13] The Nb–C distances [Nb–C_1(**3a**), 2.144(3) Å; Nb–C_2(**3a**), 2.175(3) Å; Nb–C_1(**3b**), 2.144(2) Å; Nb–C_2(**3b**), 2.143(2) Å] are within the range of Nb(V)–C(alkyl) bonds reported previously.[14] Because complexes **3a** and **3b** both exhibit considerable metallacyclopropene–Nb(V) character, the oxidative addition of H_2 to such formally oxidized complexes (**2**, **3a**, **3b**) is unlikely.

Performing the hydrogenation reaction with mixtures of H_2 and D_2 under the conditions found to produce (*Z*)-*β*-methylstyrene exclusively (12:1 CO/H_2) revealed that only the d_0 and d_2 isotopomers were formed, irrespective of the H_2/D_2 ratio employed (see the SI). This finding is consistent with a mechanism involving the hydrogenation of one molecule of alkyne by one molecule of H_2. This contrasts with many early-transition-metal hydrogenation mechanisms (Scheme 1, pathway A), in which two separate molecules of H_2 formally provide one H atom a piece when reducing an unsaturated hydrocarbon by one bond order. The mechanisms for late-metal-mediated hydrogenation reactions typically involve oxidative addition of H_2 to the metal

Scheme 5. Mechanistic Hypotheses



center (Scheme 1, pathways B and C). While **1** appears to serve as a catalyst for the formation of HD from mixtures of H_2 and D_2 in the absence of an alkyne substrate, no HD was observed during the course of the hydrogenation reaction under the conditions for selective alkyne reduction described above. A mechanism involving initial H_2 oxidative addition to the metal center is therefore deemed unlikely under the catalytic conditions.[15] Thus, both the metal hydride mechanism common to early-metal hydrogenation catalysts and the oxidative addition mechanisms common to late-metal catalysts are unlikely in this case.

We propose two possible mechanisms, both of which are consistent with our data (Scheme 5). In the first pathway (Scheme 5, pathway 1), the alkyne substrate oxidizes the metal center of complex **1** to give the Nb(V) metallacyclopropene complex **2**. Subsequent σ-bond metathesis of one of the Nb−C bonds with H_2 forms alkenyl Nb(V) hydride complex **A**. Reductive elimination of the alkene generates the catalyst−product adduct **5**, in which external CO may replace the alkene to regenerate **1**. The second proposed mechanism (Scheme 5, pathway 2) involves the same initial addition of the alkyne to **1** as a means of generating **2**, but H_2 addition in this case occurs across the Nb=N^{t}Bu bond to form amido niobium hydride complex **B**.[4b] Insertion of the coordinated alkyne into the newly formed M−H bond yields amino alkenyl complex **C**, from which [1,2]-α-NH elimination results in the same catalyst−product adduct (complex **5**) as described for pathway 1. We currently favor pathway 1 on the basis of our computational investigations (see below) as well as the following precedents: (*i*) The Nb(V) dimethyl complex (BDI)Nb(N^{t}Bu)Me_2 was observed to react rapidly and cleanly with H_2 in THF to give a product whose identity strongly suggested a Nb(III) intermediate.[9b] (*ii*) Reaction-site-selectivity studies on related neutral and cationic alkyl Nb(V) and alkyl Ta(V) imido complexes indicated a preference for both polar and nonpolar substrates to undergo reaction at the alkyl group as opposed to the imido group.[16]

Density functional theory (DFT) calculations were performed to probe the potential energy surface describing the interaction of (BDI′)Nb(NMe)$(CO)_2$ (**I-1**; BDI′ = HC[C(Me)NPh$]_2$) with MeC≡CPh and H_2 (see the SI).[17] At this level of theory, the rate-determining step (rds) of pathway 1, **TS-3a-1**, which corresponds to σ-bond metathesis of the Nb−$C_{(\alpha\text{-}CH_3)}$ bond with H_2, was favored by ~30 kcal/mol over the rds of pathway 2, **TS-3c**, itself comprising the [1,2] addition of H_2 across the Nb=N^{t}Bu bond (Figures 2 and 3). Alternative pathways were considered, including a five-membered-ring transition state (TS) formed by interaction of the alkyne and the imido group as well as a TS for σ-bond metathesis with the Nb−$C_{(\alpha\text{-}Ph)}$ bond, but they were all found to lie significantly higher in energy than **TS-3a-1** (see the SI). The CO moiety, which during **TS-3a-1** was displaced to a trans position relative to the alkyne to give **I-4**, was found to relax to a basal position (**I-5**) prior to C−H reductive elimination. The proximity of CO and the hydride led to a nonproductive CO insertion pathway to generate a formyl alkenyl complex (**I-8b**). However, the small difference in the calculated energies of **I-5** and **I-8a/b** suggest that formation of the latter may be reversible and difficult to detect. Whether C−C reductive elimination from **I-8a/b** is kinetically or thermodynamically disfavored is not currently known, but we found no experimental evidence for hydroformylation products under the studied conditions. Finally, the calculations suggest that the product−metal adduct **I-7** and a hypothetical four-coordinate monocarbonyl Nb(III) complex (BDI′)Nb(NMe)(CO) (**I-9s**; $S = 0$[18]) are essentially equienergetic (see the SI).

In summary, we have reported the efficient and selective catalytic semihydrogenation of 1-phenyl-1-propyne into

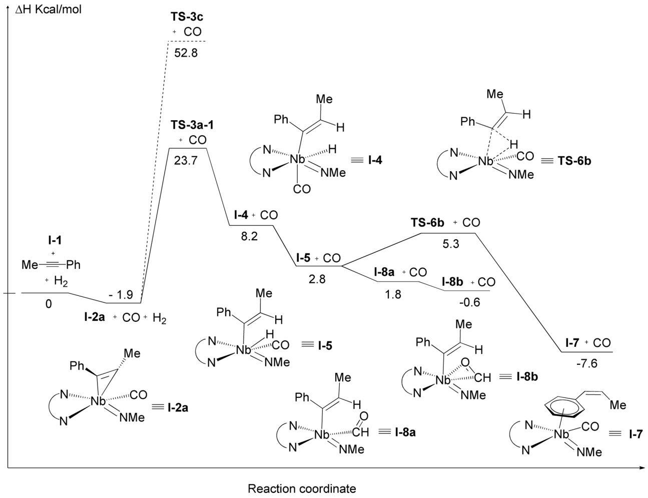
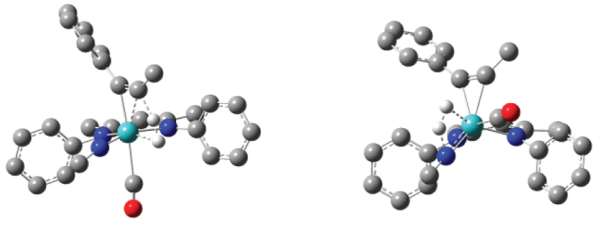


Figure 2. Enthalpy profile for the hydrogenation mechanism.



ΔH° = 23.7 kcal/mol

Pathway 1, **TS-3a-1**

ΔH° = 52.8 kcal/mol

Pathway 2, **TS-3c**

Figure 3. Calculated transition states for the rate-limiting steps of the two proposed mechanisms.

(*Z*)-β-methylstyrene by a d^2 niobium complex under H_2/CO mixtures. The experimental data are supported by DFT calculations, which suggest a novel mechanism for the hydrogenation reaction that involves coordination of an alkyne to form a metallacyclopropene Nb(V) complex followed by σ-bond metathesis with H_2 and subsequent reductive elimination to yield the product (*Z*)-alkene. An excess of CO is required for catalyst stability and proposed to function as a means of displacing the product alkene from a Nb(III) intermediate for achieving catalyst turnover. We are currently performing further synthetic, mechanistic, and kinetic studies in order to support our preliminary results on the mechanism and intermediates involved in this reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, analytical data, NMR spectra, crystal data, CIF files for **3a** and **3b**, and DFT methods and results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

arnold@berkeley.edu; rbergman@berkeley.edu

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(7) However, some group 5 and 6 transition-metal complexes show a tendency to form stable η^2-alkyne/alkene adducts; their reactivity has also been studied. See: (a) Biasotto, F.; Etienne, M.; Dahan, F. *Organometallics* **1995**, *14*, 1870. (b) Etienne, M.; Carfagna, C.; Lorente, P.; Mathieu, R.; de Montauzon, D. *Organometallics* **1999**, *18*, 3075. (c) Hirpo, W.; Curtis, M. D. *Organometallics* **1994**, *13*, 2706. (d) Ison, E. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **2006**, *25*, 1557.

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(12) As determined using the continuous symmetry parameter $\tau = (\alpha - \beta)/60°$, where α and β are the largest and second-largest angles about the metal center, respectively, See: Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

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(15) In addition to this result, DFT calculations showed that dihydride intermediate **I-10** is +27.5 kcal/mol from dicarbonyl complex **1** and thus +3.8 kcal/mol from the σ-bond metathesis TS (see the SI).

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(17) All structures were fully optimized with Gaussian 09 using the B3LYP hybrid functional. The LANL2DZ basis set was used for the metal center, and the 6-31G* basis set with a 5d diffusional was used for the H, C, N, and O atoms. All optimized geometries were compared using their zero-point energies. For computational expediency, the aryl groups of the BDI ligand were replaced with phenyl groups and the tBu imido ligand was replaced by a methylimido group.

(18) The triplet state was found to be 9.4 kcal/mol higher in energy.