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Stereoselective Hydrogenation of Aromatic Alkynes Using Water, Triethylsilane, or Methanol, Mediated and Catalyzed by Ni(0) Complexes

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The use of complexes of the type [(P-P)Ni(η^2-*C*,*C*-alkyne)] (P-P = 1,2-bis(di-isopropyl-phosphinoethane or 1,2-bis(diterbutylphosphino-ethane) in the presence of water, triethylsilane/water, or methanol as hydrogen sources yields the selective production of E- or Z- aromatic alkenes from the corresponding alkynes. For instance, in the case of diphenylacetylene (dpa) and water, a metal-mediated process was found to yield *trans*-stilbene stoichiometrically, whereas in the case of triethylsilane/water and methanol, a catalytic system (1% mol) was found. The catalytic systems gave >95% conversion to *cis*- or *trans*-stilbene, respectively. The use of a variety of substituents on the aromatic ring was also assessed. Deuterium-labeling studies using D_2O allowed the confirmation of water as the hydrogen source for the alkyne reduction.

Introduction

The development of novel catalysts for the activation of small molecules such as water,[1] alcohols,[2] or ammoniaboranes[3] generating or transferring dihydrogen to unsaturated compounds is an important area in contemporary chemistry. Inexpensive, environmentally friendly, and readily available materials are particularly important features that are sought and highlighted for such purposes, and this puts them in perspective for conversion into potentially useful fuel sources[4] or, alternatively, for their use in synthetic work where these molecules are incorporated into other substrates by means of stoichiometric[1a,b,5] or catalytically[6] driven reactions (e.g., hydrogen transfer).[7] In the case of water, traditional splitting methods involve photochemical,[8]electrochemical,[9] and combined photochemical/electrochemical processes[10] in the presence of a sacrificial agent where dihydrogen is ultimately generated.

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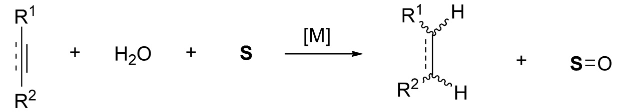
Scheme 1



To the best of our knowledge, little is known about the use of transition metals in stoichiometric or catalytic reactions that involve the splitting of water molecules, from which the transfer of dihydrogen into organic molecules in solution and under thermal conditions could be performed. Relevant examples of metal-mediated hydrogen transfer to unsaturated compounds such as alkenes or alkynes that yield the corresponding alkanes or alkenes making use of water, a transition metal (Co, Rh, and Pd), and a sacrificial agent (**S**)[11] have been reported, although only in a handful of examples (Scheme 1).

The use of 2 equiv of a $Cp_2Ti(Cl)(H_2O)$ compound for the reduction of alkenes using a second palladium or rhodium compound in catalytic proportion has been reported.[11a] In another report, a series of alkynes were reduced to olefins displaying only the trans configuration using 5 mol% of the palladium precursor compound $[Pd(Cl)(\eta^3\text{-}C_3H_5)]_2$, 10 mol% of PPh_3, D_2O (10 equiv) or water (2.5 equiv), and hexamethyldisilane ($Me_3Si{-}SiMe_3$, 1.5 equiv) as a sacrificial agent.[11b] A variation of the latter methodologies that consisted of the reductive coupling of activated alkenes in the presence of alkynes to yield cross-coupled products when using the cobalt catalyst, $[Co(I)_2(PPh_3)_2]$, and a mixture of Zn and ZnI_2 (as sacrificial agents) has also been reported.[11c]

The selective semihydrogenation of alkynes to yield *cis*-alkenes selectively is a very important topic that still needs to be developed in order to overcome several practical inconveniences during the synthesis, along with the undesired isomerization of the produced *cis*-alkene to the corresponding trans one in the reaction mixture. A search for simple preparative methods that may afford the *cis*-alkenes readily and in high yield is badly needed in order to make the process sustainable, and in this regard, some recent examples using a zero-valent palladium catalyst reported by Elsevier and co-workers can be highlighted.[12] Other relevant examples adressing the production of *cis*-alkenes through the use hydrosilanes and palladium catalysts in acid media have also been presented by Trost and Braslau.[13]

In the case of alcohols, their use as hydrogen-transfer agents has been found to be effective in the reduction of unsaturated polar moieties such as carbonyls or imines, unlike water. The use of methanol has afforded the catalytic and enantioselective preparation of alcohols and amines when starting from the latter substrates,[2i−k] and also, examples that address the reduction of alkenes or alkynes using methanol and related media have been reported.[2a−e] In the case of acetylenes, the search for improved systems that may drive their selective and efficient reduction using water, hydrosilanes/water, or methanol in the presence of an inexpensive metal catalyst still represents a major challenge for sustainable chemistry.

Table 1.[15]

entry[a]	ligand	solvent	T (°C)	time (d)[b]	conv. (%)[c]	ratio, *trans*-stb:**3a**[d]
1	dippe	benzene-d_6	100	8		
2	dippe	toluene-d_8	100	8	40	20:1
3	dippe	THF-d_8	100	8	100	12:1
4	dippe	toluene-d_8	140	7	100	15:1
5	dtbpe	toluene-d_8	140	12	100	only *trans*-stb([e])

[a] All reactions were monitored by ^1H and $^{31}P\{^1H\}$ NMR. A total of 350 equiv of water were used in all these reactions. [b] Heating was stopped when the signals of the starting complex disappeared in the $^{31}P\{^1H\}$ NMR spectrum. [c] Yields were primarily determined on the basis of the isolated product and corroborated by ^1H NMR and GC-MS. [d] Relative ratios were determined by ^1H NMR (see Supporting Information). [e] Only free *trans*-stb was observed as a result of the hydrogen transfer reaction using **2b**.

The present work describes the reactivity of $[(P\text{-}P)Ni(\eta^2\text{-}C,C\text{-alkyne})]$ complexes (P-P = 1,2-bis(diisopropyl-phosphinoethane, dippe, or 1,2-bis(diter-butyl-phosphinoethane, dtbpe), in the presence of (a) water, (b) triethylsilane/water, and (c) methanol, as hydrogen sources. The results show that the selective production of the corresponding *cis*- or *trans*-alkene from the corresponding alkyne is feasible under such conditions and may give rise to high yields of products.

Results and Discussion

Compounds **2a** and **2b** were prepared following methodologies similar to the one reported originally by Jones et al. using the nickel(I) hydride dimers, $[(P\text{-}P)Ni(\mu\text{-}H)]_2$ (P-P = dippe, dtbpe; compounds **1a** and **1b**, respectively).[14] The formation of the nickel(0) compounds **2a** and **2b** was confirmed by NMR using closed tubes equipped with J. Young's valves (see Supporting Information).

When reacted with water (eq 1), **2a** evolves slowly to a coordinated *trans*-stb analogue of the type $[(dippe)Ni(\eta^2\text{-}C\text{-}C\text{-}\{trans\text{-}C(H)(Ph){=}C(Ph)(H)\}]$ (**3a**), which after 8 days at 100 °C in THF-d_8, toluene-d_8, or benzene-d_6 or 7 days at 140 °C in toluene-d_8 (see Table 1) yields free *trans*-stb, $Ni(OH)_2$, and diphosphine monoxide, $(^iPr)_2P\text{-}CH_2{-}CH_2{-}P({=}O)\ (^iPr)_2$ (dippeO, see Supporting Information). $Ni(OH)_2$ and dippeO correspond to the final fate of oxygen in this reaction. In the case of **2b**, its use also drives the formation of the free *trans*-stb, although only under persistent heating at a higher temperature (140 °C) and for a longer period of time (12 days in toluene-d_8). The formation of the nickel(0) analogue bearing the coordinated *trans*-stb moiety, $[(dtbpe)Ni(\eta^2\text{-}(C,C)\text{-}\{trans\text{-}C(H)(Ph){=}C(Ph)(H)\}]$ (**3b**), was elusive under the reaction conditions used, and in this instance, the stability of the resulting compound turned out to be very

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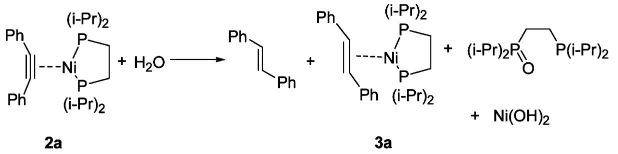
low. A significant formation of $Ni(OH)_2$ was formed over time.



(1)

As indicated in Table 1, the overall processes exhibited a strong dependence on temperature, solvent polarity, and steric hindrance of the auxiliary ligands. Heating to 140 °C was required to achieve complete reduction of dpa using **2b**. In the case of **2a**, the reactions performed in nonpolar solvents such as toluene-d_8 or benzene-d_6 (entries 1 and 2, Table 1) resulted in poor to null conversions. Only the reaction using THF reached completion, resulting in formation of a 12:1 ratio of free *trans*-stb-to-**3a** (entry 3). The immiscibility of water in the systems was overcome by increasing the temperature for the process from 100 to 140 °C (entries 2 and 4), which resulted in a significant improvement (entry 4).

In order to verify the hypothesis of water being the hydrogen source for the alkyne reduction, a deuterium labeling experiment using deuterium oxide (D_2O) instead of water was undertaken at 140 °C. The experiment was performed using toluene-d_8 following the conditions described in entry 4 of Table 1 (fully described in the Supporting Information); 100% deuterium incorporation into *trans*-stb was observed, also producing the d_2-*trans*-stb analogue. No d_2-*cis*-stb was formed in the process. A tentative mechanistic proposal for the reduction of dpa to *trans*-stb starting with the nickel(0) compound **2a** is shown in Scheme S1 (Supporting Information).

X-ray-quality crystals for compound **3a** were found to spontaneously crystallize from the H_2O/THF reaction mixture described in entry 3 of Table 1. An X-ray diffraction study of these crystals[16] allowed the confirmation of such an intermediate, as produced from the catalytic process (Figure 1, Table 2).

An independent preparation of **3a** using [(dippe)Ni(μ-H)$_2$] (**1a**) and *trans*-stb (described in the Supporting Information) allowed full characterization of the former compound. A reactivity study involving the replacement of the coordinated *trans*-stb ligand in **3a** by dpa was also addressed. The latter study confirmed a partial substitution at room temperature (24 h in THF), producing **2a**. The reaction reached completion after heating the system to 50 °C for a period of 6 h in THF, or 100 °C for 2 h in toluene. The observation of going from **3a** to **2a** under heating is consistent with the proposal illustrated in Scheme S1 (Supporting Information) for the catalytic process, even if ultimately hampered by the oxidation of the catalyst intermediates (vide supra). The step, in turn, is probably driven by the better π acceptance of the dpa ligand versus *trans*-stb when coordinated to nickel(0), provided that a considerable back-donation is excerpted by the [(dippe)Ni^0] moiety over these two.[17,18]

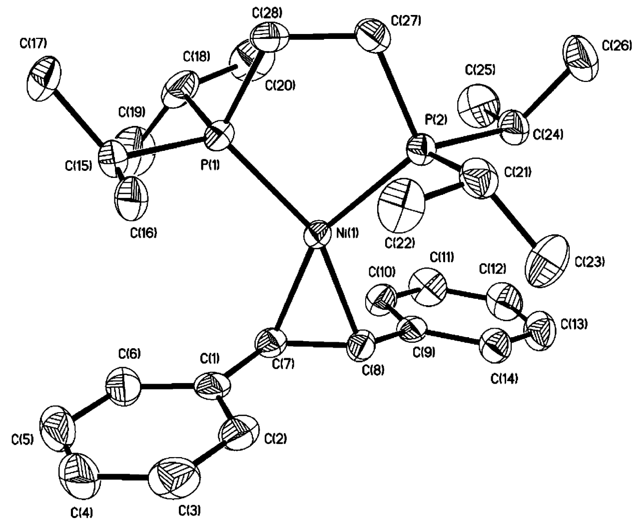


Figure 1. ORTEP representation of complex **3a**·0.5THF showing thermal ellipsoids at the 50% probability level. Selected bond distances in angstroms: Ni(1)−C(7) 1.979(4), Ni(1)−C(8) 1.983(4), Ni(1)−P(2) 2.1484(12), Ni(1)−P(1) 2.1504(13), C(7)−C(8) 1.426(6), C(1)−C(7) 1.473(6), C(8)−C(9) 1.469(6). Selected angles in degrees: P(2)−Ni(1)−P(1) 91.99(5), C(7)−Ni(1)−C(8) 42.20(16), C(8)−Ni(1)−P(2) 112.66(13), C(7)−Ni(1)−P(1) 113.35(13).

Table 2. Summary of Crystallographic Data Obtained for **3a**·0.5THF

empirical formula	$C_{30}H_{48}NiOP_2$
fw	537.33
temperature	100(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*P*2(1)/*c*
unit cell dimensions	$a = 11.2062(15)$ Å $b = 15.874(2)$ Å $c = 16.660(2)$ Å $\alpha = 90°$ $\beta = 94.364(3)°$ $\gamma = 90°$
volume	2955.0(7) Å^3
Z	4
density (calculated)	1.208 Mg/m3
abs coeff	0.783 mm^{-1}
F(000)	1160
cryst size	0.23 × 0.21 × 0.16 mm^3
θ range for data collection	1.77−25.00°
index ranges	$-13 \le h \le 12$, $-18 \le k \le 18$, $-19 \le l \le 16$
reflns collected	13604
ind reflns	5189 [R(int) = 0.0590]
completeness to $\theta = 25.00°$	99.9%
refinement method	full-matrix least-squares on F^2
data/restraints/params	5189/173/371
goodness-of-fit on F^2	1.155
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0688, wR2 = 0.1310
R indices (all data)	R1 = 0.0887, wR2 = 0.1386
largest diff. peak and hole	0.557 and −0.487 e Å^{-3}

In addition to the latter points, studies were also undertaken addressing the issue of selectivity toward *trans*-stb, whose formation is indicative of a metal-mediated process as the

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(15) Only minute amounts of *cis*-stilbene (*cis*-stb), apart from the main product *trans*-stb, were observed in experiments described in entries 4 and 5. No traces of the phenylbencylketone expected from a competing hydration reaction in these reactions was observed, all of which confirms a preference for the selective reduction of dpe to yield *trans*-stb.

(16) Crystallographic data for **3a** has been deposited at the Cambridge Crystallographic Data Centre, CCDC 686568.

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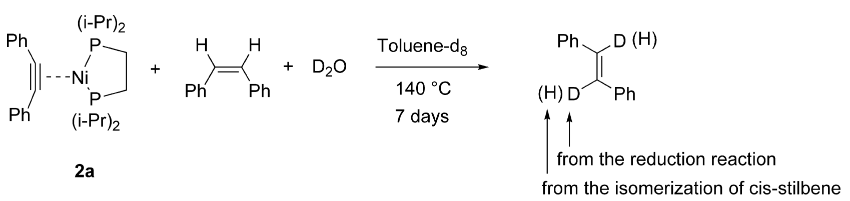
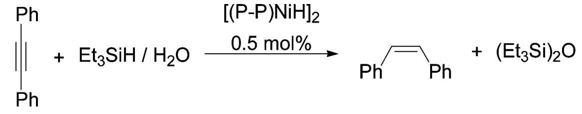
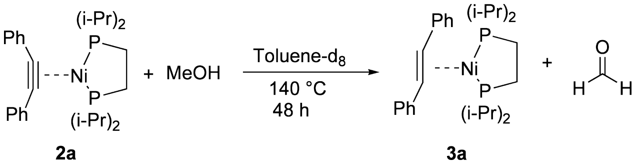
Scheme 2



Scheme 3



Scheme 4



direct addition of water to the coordinated dpa in **2a** or **2b**—if occurring similarly to what has been speculated for the nitrile hydration processes using nickel(0) compounds[17,19] —would be expected to result in the production of enols or ketones but certainly not alkenes.[20] The preference for the formation of *trans*-stb over *cis*-stb or even a mixture of the two suggested a thermodynamically driven process, as the expected kinetic product, *cis*-stb, had not been observed at this point. An experiment addressing the isomerization of *cis*- to *trans*-stb in the presence of nickel(0) was undertaken using a toluene-d_8 mixture of the π-bound alkyne complex **2a** in the presence of *cis*-stb and D_2O.[11b,21] The mixture was heated to 140 °C for 7 days following the optimized conditions described in entry 4 of Table 1. The incorporation of proton residues over the final *trans*-stb proceeding from **2a**, namely, *trans*-(D/H)(Ph)C═C(Ph)(D/H) instead of *trans*-(D)(Ph)C═C(Ph)(D), was confirmed by ^{1}H NMR. A sharp singlet at δ 7.12, slightly deshielded from the original one at δ 6.51, which is related to *cis*-stb, gradually appeared in the ^{1}H spectrum of the heated solution, confirming the presence of the protiated *trans*-(D/H)(Ph)C═C(Ph)(D/H) analogue. Its presence validated the reduction of dpa as a thermodynamically driven process. Scheme 2 summarizes these findings.

With the aim of optimizing the reduction of dpa using nickel catalysts, it became clear that the use of an additional sacrificial agent would be required, as in fact the P-P ligand had been acting as a sacrificial agent in all the experiments using water as the hydrogen source. Consequently, the use of a silane as a sacrificial agent was envisaged as a useful option and was explored. Scheme 3 summarizes the results obtained under catalytic conditions.

The use of Et_3SiH/H_2O in THF allowed the selective preparation of *cis*-stb in 98% yield at 180 °C, within 48 h. GC-MS analysis of the crude reaction allowed confirmation of the presence of $(Et_3Si)_2O$, and a $^{31}P\{^1H\}$ NMR followup allowed for ruling out the presence of phosphine oxide. A variety of reaction conditions was addressed after this result, the complete tables for which are included in the Supporting Information. A mechanistic proposal for the reduction of dpa using Et_3SiH/H_2O is illustrated in Scheme S2 (Supporting Information).

The use of methanol as a hydrogen source for the reduction of dpa was also addressed as an alternative. The latter substrate was expected to act as both a hydrogen source and a sacrificial agent while readily oxidizing to formaldehyde.[22] Scheme 4 summarizes our findings after 48 h at 140 °C, under stoichiometric conditions.

As in the case in which Et_3SiH was used, the reaction time required to ensure complete conversion of dpa was found to be shorter than with all of the previous experiments using water (see Table 1). No catalyst decomposition took place. The reaction was addressed in catalysis, which yielded 99.5% of *trans*-stb by GC-MS (100% conversion of dpa; Table S3, Supporting Information), and no oxidation of the [(dippe)Ni^0] catalyst was observed at the 1 mol % catalytic proportion, after 24 h. Analysis of the GC profile of the crude reaction mixture confirmed the additional formation of *cis*-stb and the enolether,[20] (MeO)(Ph)C═C(H)(Ph), in minute amounts of 0.49 and 0.01%, respectively. As a result of this, an extremely selective reductive process to form *trans*-stb when using the [Ni(0)] catalyst was devised. A proposal of a competitive mechanism for the formation of the enolether operating at a much slower rate than the one leading to *trans*-stb is presented in Scheme S3 (Supporting Information). The formation of *trans*-stb using 1 mol % of the nickel(0) catalyst was achieved in 88.6% yield (95% overall conversion) at a time as short as 12 h.

With the aim of extending the scope of this reaction to other alkynes, the use of a variety of substituted aromatic alkynes was assessed under catalytic conditions, using Et_3SiH/H_2O and methanol. The results are sumarized in Tables 3 and 4, respectively.

As shown, most of the systems gave high yields of the corresponding alkene under similar reaction conditions. In general, the use of Et_3SiH/H_2O selectively favors the production of *cis*-alkenes, and the use of MeOH favors the formation of *trans*-alkenes, with exception of 1-chloro-4-

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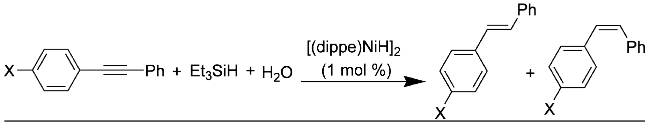
(22) A positive chromotropic acid test for formaldehyde presence was observed: Zhang, J.; Thickett, D.; Green, L. *J. Am. Inst. Conservation* **1994**, *33*, 1,–47.

Table 3. Results for Substituted Aromatic Alkynes Used under Catalytic Conditions, Using Et_3SiH/H_2O[a]



entry	X	conv. (%)	yield, alkyne/*trans*-alkene/*cis*-alkene[b]
1	CHO	100	0:0:100
2	*p*-F−C_6H_4−CO	95	5:0:95
3	OMe	20	80:0:20
4	Cl	100	0:99:0
5[c]	OMe	91	9:3:88

[a] All reactions were performed in stainless reactor vessels (Parr) equipped with internal magnetic drive stirring using 20 mL of THF at 180°C, over 48 h, using ratios of $[(dippe)NiH]_2$/alkyne/Et_3SiH/H_2O of 1:200:268:60 000, respectively. [b] Yields determined by GC-MS and ^1H NMR. [c] Reaction was performed at 200 °C.

(phenyl-ethynyl)benzene, the last giving in both systems the corresponding *trans*-alkane, probably due to the formation of minute amounts of HCl, allowing the *cis* to *trans* isomerization of the olefin.[11b]

Conclusions

We have shown that the selective reduction of dpa to *trans*-stb using nickel(0) complexes of the type $[(P\text{-}P)Ni(\eta^2\text{-}C,C\text{-}dpa)]$ can be successfully achieved using water (metal-mediated case) or methanol (metal-mediated and catalytically) in high yields. The use of triethylsilane/water (catalytic) allowed the selective preparation of *cis*-stb, also in high yields. In the first case, the diphosphine is ultimately oxidized in the process and acts as a sacrificial agent, whereas in the case of triethylsilane, the decomposition is prevented as the latter acts as both a hydrogen source and sacrificial agent that traps oxygen as $(Et_3Si)_2O$. In the case of methanol, a similar system was found in which it acted as a hydrogen source and a reductive agent, the latter having been oxidized to formaldehyde during the catalytic process. The use of methanol allowed the reaction to occur at a much faster rate, 100% conversion of dpa into *trans*-stb being observed after 24 h of heating at 180 °C. Other aromatic alkynes can be selectively reduced. The use of Et_3SiH/H_2O allows the production of *cis*-alkenes, and the use of MeOH allows the formation of *trans*-alkenes with the exception of 1-chloro-4-(phenyl-ethynyl)benzene, the last giving in both systems the corresponding *trans*-alkane. The use of nickel as an inexpensive active catalyst for the reduction of dpa is highlighted. Further studies are currently underway to fully elucidate the mechanistic pathway that operates for this process.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were performed using standard Schlenk and glovebox techniques under high-purity argon (Praxair, 99.998%) using an MBraun glovebox (<1 ppm H_2O and O_2). Parr Series 4590 and 4561M stainless steel autoclaves (T316SS), bench top mini reactors (100, 300 mL), and 4750 general purpose vessels (125 mL) were used for catalysis experiments. Liquid substrates were reagent-grade and were degassed using the freeze−thaw−pump method prior to their use. All alkyne standards, *cis* and *trans*-stilbene (*cis*-stb and *trans*-stb), were purchased from Aldrich and were stored in a glovebox for their use. All water used was distilled. Toluene and methanol were dried by standard methods and stored over 4 Å molecular sieves, under argon. Protiated solvents (THF and hexanes, J.T. Baker) were reagent-grade and were dried and deoxygenated by distillation from purple benzophenone ketyl solutions, under argon. Toluene was refluxed over sodium for 1 day under an argon atmosphere to ensure complete dryness and was distilled and stored in the glovebox. Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratories and were stored over 3 Å molecular sieves in the glovebox for at least 24 h, prior to their use. The chelating bisphosphine ligand, dippe,[23] was synthesized from 1,2-bis(dichlorophosphino)ethane (Aldrich) and the corresponding isopropylmagnesium chloride solution (2.0 M) in THF (Aldrich). The nickel(I) dimer, $[(dippe)NiH]_2$ (**1**), was prepared from a hexane slurry of $[(dippe)NiCl_2]$[24] using superhydride ($LiHBEt_3$), similarly to the literature procedure.[25] Neutral alumina was used for the preparation of complex **1** and was first dried under a vacuum at 200 °C for a period of 48 h. All other substances, filters, and chromatographic materials were reagent-grade and were used as received. The organometallic complexes and organics produced in this work were purified either by crystallization or by column chromatography. Reactor vessels for catalysis were charged in the glovebox. The crude reaction mixtures were recovered from these and were immediately analyzed by GC-MS. The catalytic conversions of substrates were determined by the integration of areas in the respective chromatograms. The retention times of all products were compared against pure standards of the same substances. NMR spectra of complexes and products in this work were recorded at ambient temperature using a 300 MHz Varian Unity spectrometer. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the complexes were obtained from concentrated THF-d_8, benzene-d_6, and toluene-d_8 solutions of the pure compounds. All air- and moisture-sensitive samples in this work were handled under an inert atmosphere using thin-wall (0.38 mm) WILMAD NMR tubes equipped with J. Young's valves. Heating of the charged NMR tubes was done using stirred thermostatted silicon oil baths. The ^1H and $^{13}C\{^1H\}$ NMR spectra of all purified products were obtained at room temperature from concentrated $CDCl_3$ or CD_2Cl_2 solutions. ^1H chemical shifts (δ, ppm) are reported relative to residual proton resonances in the deuterated solvent. $^{13}C\{^1H\}$ NMR spectra are reported relative to the reference signal of the corresponding deuterated solvent. $^{31}P\{^1H\}$ NMR spectra are of nickel compounds, and free phosphines are reported relative to external 85% H_3PO_4. Coupling constants (*J* values) are given in hertz. GC-MS determinations were performed using a Varian Saturn 3 equipped with a 30m DB-5MS capillary column. Melting points of purified organics were determined in a capillary using an electrothermal digital melting point apparatus. MS-EI$^+$ analyses were performed by USAI-UNAM using a Thermo-Electron DFS. Mass spectrometric and elemental analyses of pure compounds **2a**, **2b**, and **3a** showed variable inconsistencies due to their high oxygen sensitivity and were not reported.

Reduction of dpa with $[(dippe)Ni(\eta^2\text{-}C,C\text{-}dpa)]$ (2a) Using Water As a Hydrogen Source. Into NMR tubes with Young's valves were charged solutions of complex **2a** (45 mg, 0.09 mmol) in 0.7 mL of deuterated solvents (toluene-d_8 or THF-d_8), and to these were added 300 equiv of water (0.45 mL, 0.45 mg, 27 mmol).

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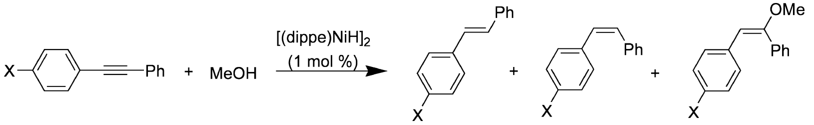
(23) Cloke, F. G. N.; Gibson, V. C.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1988**, *2227*, 2229.

(24) Scott, F.; Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113.

(25) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855–10856.

Table 4. Results for Substituted Aromatic Alkynes Used under Catalytic Conditions, Using Methanol[a]



entry	X	conv. (%)	yield, alkyne/*trans*-alkene/*cis*-alkene/enolether[b]
1	CHO	100	0:85:0:15
2	*p*-F$-$C$_6$H$_4-$CO	94	6:64:14:16
3	OMe	91	9:90:1:0
4	Cl	100	0:99:1:0
5[c]	*p*-F$-$C$_6$H$_4-$CO	98	2:82:11:5

[a] All reactions were performed in stainless reactor vessels (Parr) equipped with internal magnetic drive stirring using 30 mL of toluene/MeOH in a ratio of 2:1 at 180 °C, over 24 h, using ratios of [(dippe)NiH]$_2$/alkyne of 1:200. [b] Yields determined by GC-MS and ^{1}H-NMR. [c] Reaction was performed at 200 °C.

Everything was then heated in a thermostatted silicon oil bath. For toluene-d_8 at 100 °C, the reaction was heated and monitored over 8 days by NMR (Figures S1 and S2, Supporting Information). Formation of the free *trans*-stilbene and [(dippe)Ni(η^2-(*C*-*C*)-{*trans*-*C*(H)(Ph)=*C*(Ph)(H)}] (**3a**) in a ratio of 20:1 was found by integral comparisons in the ^{1}H spectrum, comparing vinylic protons of free *trans*-stilbene (*s*, 7.05 ppm) and those coordinated to [(dippe)Ni^0] (*s*, 4.5 ppm), respectively. ^{1}H NMR of vinylic protons (toluene-d_8): δ 7.05 (*s*, *trans*-*C*(**H**)(Ph)=*C*(Ph)(**H**)), 6.5 (*s*, *cis*-*C*(**H**)(Ph)=*C*(Ph)(**H**)), 4.57 (s, [(dippe)Ni(η^2-(*C*-*C*)-{*trans*-(**H**)(Ph)=*C*(Ph)(**H**)}]). ^{31}P{^{1}H} NMR data for the mixture at the end of the reaction (toluene-d_8): δ 77.4 (*s*, **2a**), 67.07 (*s*, **3a**), 51.7 (*d*, $^2J_{P-P}$ = 36.8 Hz, (^{i}Pr)$_2$P-CH$_2$-CH$_2$-**P**(=O)(^{i}Pr)$_2$), 8.35 (*d*, $^2J_{P-P}$ = 36.8 Hz, (^{i}Pr)$_2$**P**-CH$_2-$CH$_2-$P(=O) (^{i}Pr)$_2$).

Preparation of [(dippe)Ni(η^2-*C*,*C*-dpa)] (2a). To a dark red solution of [(dippe)Ni(μ-H)]$_2$, **1a**, (0.120 g, 0.138 mmol) in toluene (5.0 mL) was added dpa (0.064 g, 0.372 mmol). The mixture was stirred at room temperature for 15 min, and all hydrogen gas produced was vented away from the system into the glovebox. After 30 min of stirring, a yellow solution was obtained. The solvent was removed in vacuo, and the remaining residue was further dried under a vacuum for 3 h. The residue was redissolved in hexane, and the solution was filtered through a canula into a second Schlenk flask, from which the solvent was again stripped. The remaining yellow solid was dried for 4 h under a vacuum. Yield of **2a**: 95% (0.176 g). ^{1}H NMR (THF-d_8): δ 7.35 (d, J_{H-H} = 7.4 Hz, 4H), 7.18 (t, J_{H-H} = 7.4 Hz, 4H), 7.01 (t, J_{H-H} = 7.3 Hz, 4H), 2.12 (septuplet, J_{H-H} = 7.2 Hz, 2H, *CH*Me$_2$), 1.65 (d, J_{H-P} = 9.2 Hz, 4H, P*CH$_2$CH$_2$*P), 1.08 (quintet, J_{H-H} = 7.2 Hz, J_{H-P} = 7.2 Hz, 24H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (THF-d_8): δ 141.3 (t, $^2J_{C-P}$ = 7.1 Hz, *C*-Ph,), 132.1 (s, Ar CH), 128.3 (d, $^2J_{C-P}$ = 8.6 Hz, *C*-Ph), 127.3 (s, Ar CH), 124.9 (s, Ar CH), 26.7 (t, J_{C-P} = 10.4 Hz), 22.2 (t, J_{C-P} = 19.1 Hz), 20.4 (t, J_{C-P} = 4.0 Hz), 19.1 (s). ^{31}P{^{1}H} NMR (THF-d_8): δ 80.9 (s).

Preparation of [(dtbpe)Ni(η^2-*C*,*C*-dpa)] (2b). The preparation of this compound was performed following the procedure described above for **2a**, using [(dtbpe)Ni(μ-H)]$_2$ (**1b**; 0.045 g, 0.059 mmol) and dpa (0.021 g, 0.119 mmol) in 5.0 mL of toluene. Yield of **2b**: 93% (0.613.0 g). ^{1}H NMR (benzene-d_6): δ 7.58 (d, J_{H-H} = 7.4 Hz, 4H), 7.24 (t, J_{H-H} = 7.4 Hz, 4H), 7.06 (t, J_{H-H} = 7.3 Hz, 2H), 1.45 (m, 4H, P*CH$_2$CH$_2$*P), 1.18 (d, CH$_3$, 36H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 143.97 (t, $^2J_{C-P}$ = 8.25 Hz, *C*-Ph), 138.89 (t, $^2J_{C-P}$ = 19.95 Hz), 128.24 (s, Ar CH), 127.39 (s, Ar CH), 124.23 (s, Ar CH), 34.50 (t, J_{P-C} = 7.05 Hz, *C*Me$_3$), 30.81 (t, J_{P-C} = 3.15 Hz, C*Me$_3$*), 23.97 (t, J_{P-C} = 16.5 Hz, P*CH$_2$CH$_2$*P). ^{31}P{^{1}H} NMR (benzene-d_6): δ 94.09 (s).

Preparation of [(dippe)Ni(η^2-*C*,*C*-*trans*-stb)] (3a). To a dark solution of **1a** (0.030 g, 0.046 mmol) in 5 mL of toluene was added *trans*-stb (0.016 g, 0.093 mmol). The mixture was allowed to stir for a period of 8 h, during which time a yellow solution was obtained. The solvent was evaporated and the remaining residue dried in vacuo. Yield of **3a**: 98% (0.045 g). ^{1}H NMR (toluene-d_8): δ 7.25 (d, J_{H-H} = 7.8 H, 4H), 7.11 (t, J_{H-H} = 7.8 Hz, 4H), 6.89 (t, J_{H-H} = 7.8 Hz, 2H), 4.46 (s, 2H, vinylic protons), 2.09 (septuplet, J_{H-H} = 7.2 Hz, 2H, *CH*Me$_2$), 1.65 (d, J_{H-P} = 9.2 Hz, 4H, P*CH$_2$CH$_2$*P), 1.05 (quintet, J_{H-H} = 7.2 Hz, J_{H-P} = 7.2 Hz, 24H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (toluene-d_8): 147.56 (s, Ar CH), 126.8 (s, Ar CH), 124.59 (s, Ar CH), 121.3 (s, Ar CH), 50.9 (t, $^2J_{C-P}$ = 8.5 Hz, =*C*(H)(Ph)), 25.6 (t, J_{C-P} = 9.5 Hz), 23.8 (t, J_{C-P} = 9.52 Hz), 18.9 (t, J_{C-P} = 3.5 Hz), 17.1 (s). ^{31}P{^{1}H} NMR (toluene-d_8): δ 65.8 (s).

Metal-Mediated Experiments for the Reduction of dpa Using Water, Performed in Closed NMR Tubes. Reduction of dpa with [(dippe)Ni(η^2-*C*,*C*-dpa)] (2a) Using Water As a Hydrogen Source. NMR tubes with J. Young's valves were charged in different runs with solutions of **2a** (45 mg, 0.09 mmol) using 0.7 mL of deuterated solvents (toluene-d_8 or THF-d_8), and to these was added 300 equiv of water (0.45 mL, 0.45 mg, 27 mmol). The mixtures were then heated in a thermostatted silicon oil bath.

For the reaction in toluene-d_8 at 100 °C, the NMR tube was heated and monitored over 8 days (Figures S1and S2, Supporting Information). The formation of free *trans*-stb and [(dippe)Ni(η^2-(*C*-*C*)-{*trans*-*C*(H)(Ph)=*C*(Ph)(H)}] (**3a**) in a ratio of 20:1 was determined by ^{1}H NMR, comparing the integrals of the respective vinylic protons of free *trans*-stb and those of the coordinated ligand to [(dippe)Ni^0] (7.04 and 4.5 ppm, respectively). ^{1}H NMR of vinylic protons (toluene-d_8): δ 7.05 (s, *trans*-*C*(**H**)(Ph)=*C*(Ph)(**H**)), 6.5 (s, *cis*-*C*(**H**)(Ph)=*C*(Ph)(**H**)), 4.57 (s, [(dippe)Ni(η^2-(*C*$-$*C*)-{*trans*-(**H**)(Ph)=*C*(Ph)(**H**)}]). ^{31}P{^{1}H} NMR (toluene-d_8): δ (ppm) 77.4 (s, **2a**), 67.07 (s, **3a**), 51.7 (d, J_{P-P} = 36.8 Hz, (^{i}Pr)$_2$P-CH$_2$-CH$_2$-**P**(=O) (^{i}Pr)$_2$), 8.35 (d, J_{P-P} = 36.8 Hz, (^{i}Pr)$_2$**P**-CH$_2$-CH$_2-$P(=O) (^{i}Pr)$_2$). After reaction completion, the tube was opened in the air, and the remaining volatiles were removed in vacuo using a Schlenk line. The corresponding free olefin was purified by column chromatography in silica gel, eluting with hexanes. Yield of *trans*-stb after workup: 40% of white crystals (0.0065 g). Mp: 112 °C. MS-EI$^+$, *m*/*z* (%): 180 (M$^+$). ^{1}H (CDCl$_3$): δ 7.49 (*d*, J_{H-H} = 6.9 H, 4H), 7.33 (*t*, J_{H-H} = 7.2 Hz, 4H), 7.24 (*t*, J_{H-H} = 8.7 Hz, 2H), 7.09 (*s*, 2H, vinylic protons). ^{13}C{^{1}H} NMR (CDCl$_3$): 137.5 (*s*, Ar CH), 128.8 (*s*, Ar CH), 127.8 (overlapping *s*, Ar CH and =*C*(Ph)(H)), 126.7 (*s*, Ar CH). Formation of a small amount of a green solid was detected during the course of the reaction. The solid was identified as $Ni(OH)_2$, characterized by solubility and reactivity with ammonium hydroxide according to trials reported in the existing literature[26] and comparing it with an authentic sample of this compound.

For the reaction in toluene-d_8 at 140 °C, a NMR tube was charged in a glovebox using complex **2a** (45 mg, 0.09 mmol) in 0.7 mL of deuterated solvents (toluene-d_8 or THF-d_8), and to it was added 300 equiv of water (0.45 mL, 0.45 mg, 27 mmol), following the procedure described above. The reaction was heated and monitored for 7 days using NMR spectroscopy, after which time, compound **2a** had reacted completely. As in the case of the system heated at 100 °C (vide supra), the formation of free *trans*-stb and **3a** were detected, however, in a ratio of 15:1, on the basis of ^{1}H NMR analysis. Formation of the phosphine monoxide, $(^i\mathrm{Pr})_2P\text{-}CH_2\text{-}CH_2\text{-}P(=O)\ (^i\mathrm{Pr})_2$ (Figure S1, Supporting Information) and $Ni(OH)_2$ were also observed.

For the reaction using THF-d_8 at 100 °C, a reaction system was set up following the same scheme described above, although using THF-d_8. The system was heated to 100 °C and monitored over 8 days, after which time **2a** reacted completely. Formation of free *trans*-stb and **3a** in a relative ratio of 12:1 was confirmed by ^{1}H NMR. The mentioned phosphine monoxide and $Ni(OH)_2$ were also observed to form progressively in the same reaction mixture. Incidentally, **3a** was isolated from this mixture as crystals suitable for X-ray diffraction.

Reduction of dpa with [(dtbpe)Ni(η^2-C,C-dpa)] (2b) Using Water. Compound **2b** (0.03 g, 0.054 mmol) was reacted with water (0.3 mL, 16 mmol) in a toluene-d_8 solution (0.7 mL) at 140 °C following the methodology described for compound **2a**. Heating was resumed until complete consumption of **2b** was reached, according to $^{31}P\{^1H\}$ NMR followup, which occurred after 12 days at that temperature. The reaction was quenched by exposing the system to air, and all volatiles were removed in a Schlenk line, under a vacuum. Produced *trans*-stb was purified by column chromatography as described already. Yield of *trans*-stb: 98% of white crystals.

Deuterium Labeling Using D_2O. An NMR tube fitted with a J. Young's valve was charged in a glovebox using a toluene-d_8 (0.7 mL) solution of **2a** (0.045 g, 0.09 mmol) and 300 equiv of D_2O (0.3 mL, 27 mmol). The mixture was heated to 140 °C over 7 days, after which time it was exposed to air. The produced volatiles were removed in vacuo, and the product was purified by chromatography. Yield of *trans*-(Ph)(D)C=C(Ph)(D), after work up: 100%. MS-EI$^+$, *m/z* (%): 182 (100%).

Figure S3, Supporting Information, shows the corresponding ^{1}H spectrum of this product. The signal that corresponds to the vinyl protons is absent in the spectrum, which is a confirmation of 100% incorporation of deuterium.

Displacement of *trans*-stb by dpa in Complex 3a. A solution of **3a** (0.03 g, 0.059 mmol) in toluene-d_8 (0.7 mL) was charged into a NMR tube equipped with a Young's valve in a glovebox, and to it was added 1 equiv of dpa (0.01 g, 0.059 mmol). The tube was closed and stirred at room temperature for 1 day, during which time only a very small amount of **2a** was observed to be formed by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction was then heated to 100 °C in a stirred oil bath, and progression of the reaction was continuously monitored. After 3.5 h, **3a** was found to be converted entirely into **2a**, confirming a complete displacement of *trans*-stb (Figure S4, Supporting Information). Similar results were observed using THF-d_8.

Proof of Isomerization of *cis*-stb into *trans*-stb. A toluene-d_8 solution of **2a** (45 mg, 0.09 mmol) was charged in a NMR tube equipped with a Young's valve, and to it were added 300 equiv of D_2O (0.3 mL, 0.45 mg, 27 mmol) and 1 equiv of *cis*-stb (15 μL, 0.016 g, 0.09 mmol). The reaction was heated to 140 °C for a period of 7 days, after which time it was exposed to air, and the crude mixture was analyzed by ^{1}H ($CDCl_3$). Figure S5 (Supporting Information) shows the corresponding spectrum. The singlet at 7.09 ppm corresponds to the vinylic protons of *trans*-stb.

Metal-Mediated Experiments for the Reduction of dpa Using Water, Performed in Stainless Steel Reactor Vessels. Catalysis Assessment Using a 10:1 Molar Ratio of dpa/[Ni(0)]. A stainless steel autoclave (T316SS, 100 mL) equipped with an inner magnetic stirring drive was charged in a glovebox with a toluene solution (20 mL) of dpa (0.16 g, 0.92 mmol), **1a** (0.03 g, 0.045 mmol), and H_2O (5.0 mL, 277 mmol). The vessel was heated at 180 °C for 7 days, after which time heating was resumed, and the vessel was allowed to cool down to room temperature before its opening in a fume hood. The vessel was then opened and its contents examined. The crude reaction mixture was recovered from the vessel and analyzed by GC-MS (chromatogram included as Figure S7, Supporting Information). Conversion of dpa into *trans*-stb was determined directly by GC-MS analysis. Yield of *trans*-stb after reaction: 20%.

Catalysis Assessment Using a 100:1 Molar Ratio of dpa/[Ni(0)]. A vessel was charged with a toluene solution (20 mL) of dpa (0.16 g, 0.92 mmol), **1a** (0.003 g, 0.0045 mmol), and H_2O (5.0 mL, 277 mmol) and the system heated at 180 °C for 7 days following the reaction scheme described for the 1:10 molar ratio experiment. Yield of *trans*-stb after reaction: 5%.

Metal-Mediated Experiments for the Reduction of dpa Using Methanol. Stoichiometric Reduction of dpa in [(dippe)Ni(η^2-C,C-dpa)] (2a), Using Methanol in a Closed NMR Tube. Using a toluene-d_8 solution of **2a** (0.045 g, 0.09 mmol) and 80 equiv of MeOH (0.3 mL, 7 mmol) a NMR tube equipped with a Young's valve was charged, and the closed tube was heated in an oil bath to 140 °C for 48 h. A complete conversion of **2a** into **3a** was confirmed to take place after this time.

Catalytic Reduction of Alkynes Using [Ni(0)] in the Presence of Methanol, Using a Reactor Vessel. A typical experiment for each alkyne was made as follows: A series of reactor vessels were charged in separate runs with charges of dpa (0.16 g, 0.92 mmol), **1a** (0.003 g, 0.0045 mmol), and MeOH (5.0 mL, 123 mmol) in 20 mL of toluene. The vessels were heated to 180 °C for different periods of time (12, 24, and 72 h), and their contents were analyzed by GC-MS after each completion of each reaction time. The evolution of each system is illustrated in Figures S9−S11 (Supporting Information) by their corresponding chromatograms. At the end of each reaction, three products were observed, namely, *trans*- and *cis*-stb and minute amounts of the enol-ether, illustrated in Figure S6 (Supporting Information). Table S1 (Supporting Information) indicates the respective ratios obtained for these products.

Reduction of dpa using methanol and [(dtbpe)Ni] catalysts in a reactor vessel. A reactor vessel was charged in a glovebox with dpa (0.14 g, 0.79 mmol), **2a** (0.003 g, 0.0039 mmol), and MeOH (5 mL, 123 mmol), in 20 mL of toluene. The vessel was heated to 180 °C for 12 h, and the crude mixture was analyzed by GC-MS, as done for previous experiments. Conversion of

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(26) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley Interscience: New York, 1988; p 743.

dpa after reaction: 1% (chromatogram in Figure S12, Supporting Information) of a mixture of *cis*- and *trans*-stb.

Isomerization of cis to *trans*-stilbene using methanol and [(dippe)Ni]. A toluene solution (20 mL) of *cis*-stb (0.158 mL, 0.16 g, 0.90 mmol), **1a** (0.003 g, 0.0045 mmol), and MeOH (5.0 mL, 123 mmol) was heated to 180 °C, for 5 h. Conversion of *cis*-stb into *trans*-stb, after reaction: 37% (figure S13, Supporting Information).

Catalytic reduction of alkynes using Et_3SiH/H_2O. A typical experiment for each alkyne was conducted as follows: dpa (0.165 g, 0.93 mmol), **1a** (0.003 g, 0.0045 mmol), Et_3SiH (0.297 mL, 1.86 mmol), and H_2O (5.03 mL, 270 mmol) were dissolved in 20 mL of THF (a similar procedure described for methanol, vide supra). At the end of the reaction, the crude mixture was analyzed and quantified by GC-MS. A representative chromatogram is illustrated in Figure S14 (Supporting Information), showing the presence of *cis*-stb.

Acknowledgment. We thank CONACyT (Grant F80606) and DGAPA-UNAM (Grant IN202907-3) for the financial support of this work. We also thank Dr. Miguel Muñoz-Hernández (X-ray), Dr. Alma Arévalo, and Marco G. Crestani for their technical assistance. R.B.-F. also thanks CONACyT for a Ph.D. grant.

Supporting Information Available: Complementary experimental procedures, GC-MS determinations, and CIF file for **3a**·0.5THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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