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Nickel-Catalyzed Transfer Semihydrogenation and Hydroamination of Aromatic Alkynes Using Amines As Hydrogen Donors

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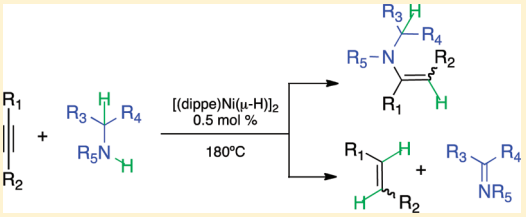
Supporting Information

ABSTRACT: The transfer hydrogenation of diphenylacetylene to yield *cis*- and *trans*-stilbenes was achieved using a variety of amines as hydrogen donors and the complex **1** ([(dippe)Ni(μ-H)]$_2$) in catalytic amounts (0.5% mol). The use of nucleophilic amines such as pyrrolidine in neat conditions afforded the hydroamination of diphenylacetylene, in moderate to high yields. Cyclization of 2-ethynylaniline also was carried out under similar conditions, with **1** in catalytic amounts, but in low yield, mainly due to the formation of homocoupling products of the starting material. The hydrogenation of diphenylacetylene by using other nitrogenated compounds such as aromatic N-heterocycles was addressed to give a metal-mediated process, using **1** in stoichiometric amounts.



1. INTRODUCTION

Hydrogenation of alkynes to afford alkenes can be carried out by using hydrogen and a homogeneous or heterogeneous catalyst, such as the one developed by Lindar.[1] Transfer hydrogenation has became an alternative to the use of dihydrogen on the small and middle scale, due to its simplicity and reduction of risks and operational difficulties associated with the use of gaseous hydrogen, along with the environmentally friendly properties of some hydrogen donors.[2] Synthesis of alkenes through the semihydrogenation of alkynes is an important process since alkene derivatives are valuable building blocks for both academia and industry. In recent years, the research on homogeneous transfer semihydrogenation of alkynes has been focused on the use of complexes of noble metals such as iridium,[3] ruthenium,[4] and palladium,[5] with methanol, 2-propanol, or the azeotropic mixture of HCOOH and NEt_3 being the most common hydrogen sources. In this context, although the catalyzed dehydrogenation of amines is a well-known topic,[6] their use in the reduction of alkynes has been scarcely studied,[7] and one of the closest approaches to this process is the use of alkenes such as *tert*-butylethylene as hydrogen acceptors in the dehydrogenation of amines.[6d] Regarding the latter transformation, the hydrogen abstraction can be attained by the amino or aliphatic dehydrogenation[8] depending on the substitution of the amine, resulting in the formation of imines or enamines as oxidation products, respectively. A further study on the hydrogen transfer from amines to alkynes would lead to a better understanding of their potential use as hydrogen donors as well as contribute to the implementation of synthetic methods for the synthesis of imines through the dehydrogenation of amines.[9]

On the other hand, a second pathway for the activation of alkynes is to achieve their hydroamination aimed to obtain imines, amines, and N-heterocycles.[10] This has been a process of interest due to the relative availability of the starting materials and the occurrence of derivatives of the synthesized compounds in many biological systems or their vast applications in pharmaceutical[11] and agrochemical products.[10a,12] Most of the developed work in the hydroamination of alkynes has largely been achieved by using palladium complexes,[10b,13] even though there are many reports in which other metals such as titanium,[10b,14] rare earth metals,[15] and some late transition metals[16] have been widely employed. However, despite the variety of developed organometallic catalysts, to date, few are examples of the use of complexes of nonexpensive metals such as nickel in the hydroamination of alkynes.[16e,17]

Herein we wish to report the semihydrogenation and hydroamination of diphenylacetylene and 2-ethynylaniline using complex **1** ([(dippe)Ni(μ-H)]$_2$) along with amines and aromatic N-heterocyles as hydrogen sources. The relatively scarce use of amines as hydrogen sources as well as the nonexpensive metal based catalyst is spotlighted.

2. RESULTS AND DISCUSSION

In order to assess the general reactivity of complex **1** toward the transfer hydrogenation and/or the hydroamination of diphenylacetylene (DPA), complex [(dippe)Ni(η^2-C,C-DPA)] was synthesized according to the reported methodology[18] using **1** and diphenylacetylene. Reaction of [(dippe)Ni(η^2-C,C-DPA)] with 4 equiv of cyclohexylamine at 140 °C yielded the corresponding hydrogenation products. NMR spectra of the reaction mixture are evidence for the presence of complex [(dippe)Ni(η^2-C,C-*trans*-stilbene)]. Key signals for this complex were assigned in the $^{31}P\{^1H\}$ NMR at 66.94 ppm (s) and in the ^1H NMR at

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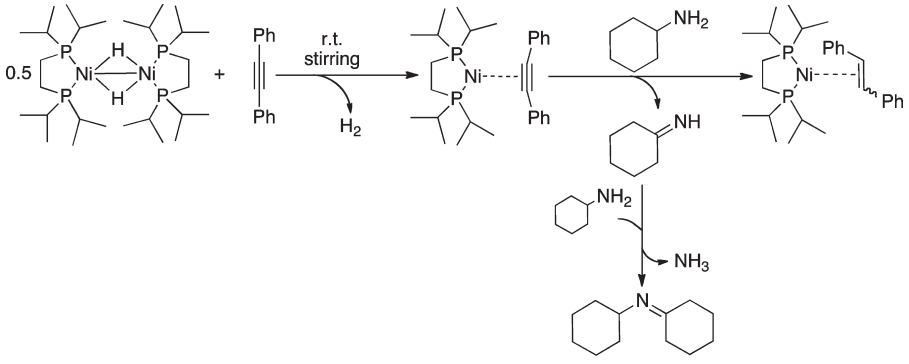
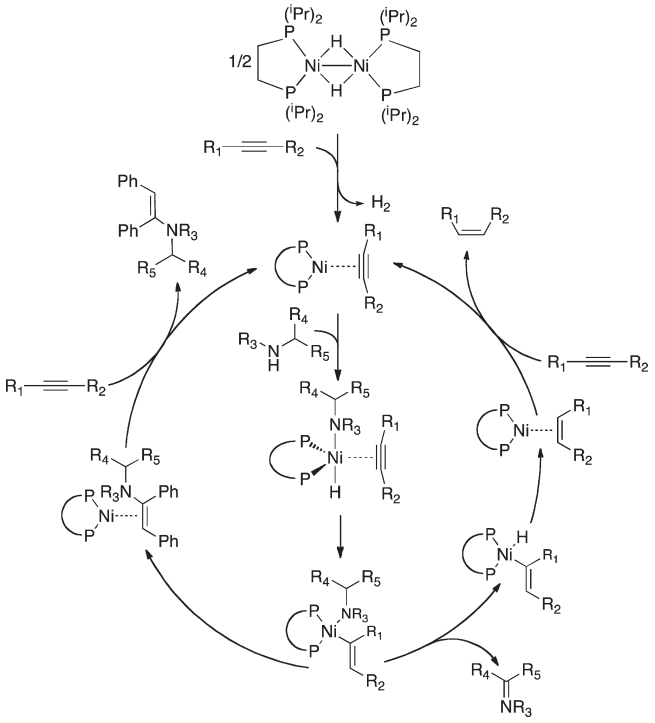
Scheme 1



Scheme 2

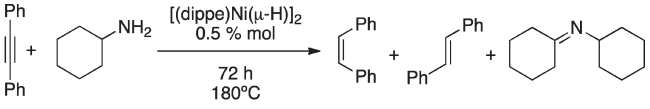


4.49 ppm (s, br); also, based on the ^{1}H NMR spectra, free *cis*- (s, 6.40 ppm) and *trans*-stilbene (s, 6.95 ppm) were formed as represented in Scheme 1 (see Scheme 2 and Scheme S1, SI, for mechanistic proposals). After 77 h, the reaction was completed and the crude was analyzed by GC-MS. Chromatographic data showed complete hydrogenation of diphenylacetylene and the formation of *cis*- (17.5%) and *trans*-stilbene (82.5%) (Figure S3). To note, no hydroamination products were detected.

Considering the above, experiments under catalytic conditions were assayed using a variety of solvents, temperatures, and proportions of cyclohexylamine, in order to find the optimized conditions for the hydrogenation of diphenylacetylene. The main results for these experiments are summarized in Table 1.

According to these results, there is a low conversion when a coordinating solvent such as THF was used despite the increase in the quantity of the amine or temperature (entries 1 to 4). Catalytic conversion is enhanced when low coordinating solvents such as toluene or dioxane are used (entries 5 and 7). Imine **1e** is a characteristic dehydrogenation−transamination product from the transfer hydrogenation reaction,[6a] detected by GC-MS

Table 1. Catalytic Hydrogenation of Diphenylacetylene Using Cyclohexylamine As Hydrogen Source[a]

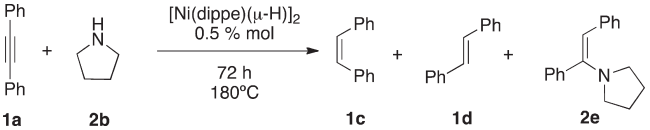


1a **1b** **1c** **1d** **1e**

entry	T (°C)	solvent	**1b** (equiv)	yield (%)[b]	**1c** (%)	**1d** (%)
1	100	THF	400	2	0	2
2	140	THF	400	4	0	4
3	180	THF	1000	15	5	10
4	180	THF	2000	11	5	6
5	180	dioxane	2000	100	15	85
6	180	acetonitrile	2000	2	2	0
7	180	toluene	2000	69	10	59

[a] All reactions were carried out in a stainless steel Parr reactor using 15 mL of solvent. A molar proportion of 1:200 of [(dippe)Ni(μ-H)]$_2$ and diphenylacetylene, respectively, was employed. [b] Chromatographic yields.

Table 2. Catalytic Hydrogenation of Diphenylacetylene Using Pyrrolidine As Hydrogen Source[a]



1a **2b** **1c** **1d** **2e**

entry	solvent	yield (%)[b]	**1c** (%)	**1d** (%)	**2e** (%)
1	THF	46	28	16	2
2	toluene	91	51	37	3
3	dioxane	100	26	71	3
4	neat	59	16	6	37

[a] All reactions were carried out in a stainless steel Parr reactor using 15 mL of solvent. A molar proportion of 1:200:1000 of [(dippe)Niμ-H]$_2$, diphenylacetylene, and amine, respectively, was used. [b] Chromatographic yields.

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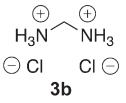
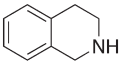
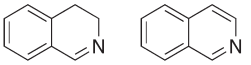
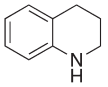
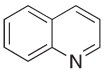
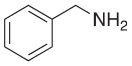
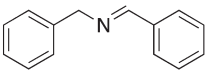
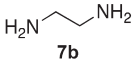
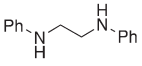
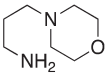
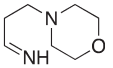
Table 3. Catalytic Hydrogenation of Diphenylacetylene Using Different Amines As Hydrogen Sources[a,b,c,d]

Entry	Amine	Yield (%)[b]	**1c** (%)	**1d** (%)	Observed dehydrogenation-transamination product
1	 **3b**	8	4	3	ND
2	 **4b**	32	14	18	
3	 **5b**	11	3	8	
4	 **6b**	91	14	77	
5	 **7b**	4	1	3	ND
6	 **8b**	6	1	5	ND
7	 **9b**	47	15	32	
8[c]	 **10b**	40	21	19	ND
9	CH_3NH_2 **11b**	19[d]	14	4	$CH_3N{=}CH_2$

[a] All reactions were carried out in a stainless steel Parr reactor using 15 mL of dioxane at 180 °C. A molar proportion of 1:200:1000 of $[(dippe)Ni(\mu\text{-}H)]_2$, diphenylacetylene, and amine, respectively, was used. ND = not determined. [b] Chromatographic yields. [c] Reaction at 160 °C. [d] 6.5 g of methylamine. One percent of the hydroamination product was also formed.

(Figures S4 and S5, SI). When the reaction is carried out in acetonitrile (entry 6), the yield decreases dramatically probably due to the oxidative addition of this nitrile to nickel.[19] As can be seen in Table 1 and also considering the results from the use of stoichiometric quantities of **1** (*vide supra*), the formation of *trans*-stilbene (thermodynamic product) suggests a Ni-catalyzed *cis*−*trans* isomerization of the initially formed *cis*-stilbene (Scheme S1, SI).[20]

On using a different hydrogen donor, such as pyrrolidine (**2b**), rather similar results were obtained, as shown in Table 2. As seen before, a high conversion of diphenylacetylene to its corresponding hydrogenation products is attained by using low-coordinating solvents (toluene and dioxane), unlike the use of solvents such as THF. It is noticeable that in these experiments low amounts of the hydroamination product could be obtained (entries 1 to 3). Improved yields for the hydroamination process to produce **2e** are obtained under neat conditions (entry 4, Table 2); this is a good result considering the low favored intermolecular hydroaminations.[10] Clearly, the presence of these products shows the effect of the increase in the nucleophilicity of the hydrogen donor in the formation of condensation products.

The effect of structure and substitution of the hydrogen donor for different amines was also addressed using the conditions for **2b**, summarized in Table 3. With the use of primary or secondary amines with α-H to the nitrogen atom, such as in **6b**, the catalytic conversion can be successfully achieved as in the case of cyclohexylamine or pyrrolidine. For diamines **7b** and **8b** the conversion was decreased presumably because of the displacement of the substrate **1a** from the metal center by the chelating diamines, resulting in the formation of [(dippe)Ni (diamino)] complexes, inhibiting the catalytic activity. Low to moderate yields are obtained on using aromatic N-heterocycles, such as **5b** (entry 3), probably due to their low nucleophilicity. This effect also can be drastically noticed when protonated amines are used (entry 1).

A mechanistic proposal for both catalytic hydroamination and transfer hydrogenation of alkynes is depicted in Scheme 2.

A different set of hydrogen donors, such as *tert*-butylamine, indole, carbazole, and pyrrole, was tested. Nevertheless, none of these reagents afforded a catalytic reduction of **1a**, and such transformation could be achieved only with the use of complex **1** in stoichiometric amounts. The lack of catalytic activity of these

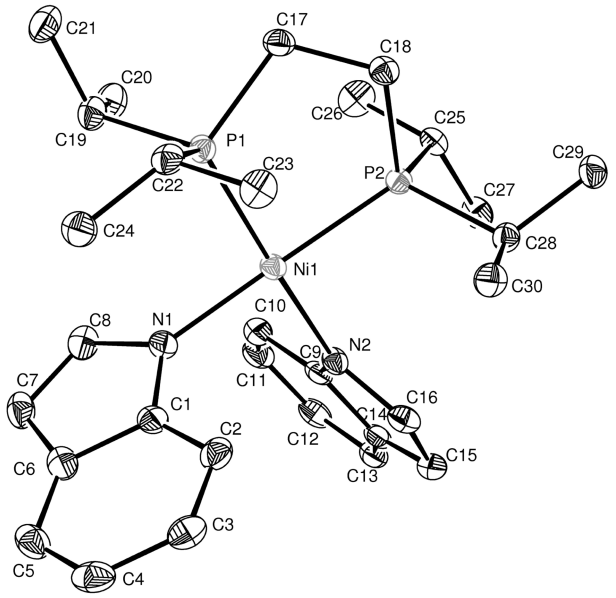
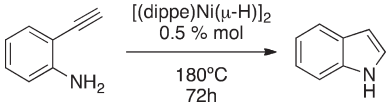


Figure 1. ORTEP drawing (50% probability) of [(dippe)Ni (κ^1-$C_8H_6N)_2$]. Selected bond lengths (Å) and angles (deg): N(1)−Ni(1) 1.9307(16), N(2)−Ni(1) 1.9339(15), P(1)−Ni(1) 2.1836(5), P(2)−Ni(1) 2.1834(5), N(1)−Ni(1)−N(2) 90.53(7), N(1)−Ni(1)−P(2) 176.59(5), N(2)−Ni(1)−P(2) 90.35(5), N(1)−Ni(1)−P(1) 91.76(5), N(2)−Ni(1)−P(1) 175.94(5), P(2)−Ni(1)−P(1) 87.55(2).

Table 4. Catalytic Cyclization of 2-Ethynilaniline[a]



entry	solvent	yield (%)[b]
1	dioxane	8
2	toluene	15
3	neat	25

[a] All reactions were carried out in a stainless steel Parr reactor using 15 mL of dioxane, except for neat conditions, where 0.5 mL of **13b** was used. A molar proportion of 1:200 of [Ni(dippe)μ-H]$_2$ and 2-ethynilaniline was used. [b] Chromatographic yields.

systems is mainly due to the formation of rather stable N-coordinated complexes, like the one isolated when indole was employed as hydrogen source (Figure 1); here a Ni(II) complex in a square-planar geometry was observed. This complex was prepared independently in high yield reacting **1** with indole (see Experimental Section) and was highly thermally stable under argon.

To further extend the reactivity found in the addition of amines to alkynes, the intramolecular cyclization of 2-ethynylaniline was explored in the conditions shown in Table 4. After 72 h, there was a complete conversion of the starting material; however, depending on the solvent, only 8% to 25% yield corresponds to the cyclization product and the remainder corresponds to other byproducts. GC-MS determinations are consistent with the formation of homocoupling products derived from the starting material via C−H bond activation in the terminal alkyne (Figures S9 to S13, SI), along with hydroamination products between the produced indole and the starting material.

3. CONCLUSIONS

We have shown a new methodology for the transfer hydrogenation of internal aromatic alkynes catalyzed by a nickel complex exhibiting moderate to excellent yields depending on the structure of the hydrogen donor. Transfer hydrogenation under the described conditions is sensitive to the use of coordinating solvents and hydrogen donors such as diamines, N-heterocycles, and THF due to the deactivation of the catalyst by those species linked to the formation of rather stable intermediates. Hydroamination is performed with better yields on using an excess of nucleophilic amine. The use of a substrate containing both a N−H donor moiety and a terminal alkyne allowed cyclization, but there is a strong competence of C(sp)−H bond activation by the metal center leading to homocoupled products. Studies are underway to decrease or avoid homocoupling.

4. EXPERIMENTAL SECTION

Unless otherwise noted, all experiments were carried out using standard Schlenk techniques in a double vacuum-argon manifold or in a glovebox (MBraun Unilab) under high-purity argon (Praxair 99.998), with controlled concentrations of water and oxygen (<1 ppm). Catalytic experiments were carried out in a stainless steel Parr (T315SS) reactor. All liquid reagents were purchased in reagent grade and were degassed before use. Diphenylacetylene and alkene standards were purchased from Aldrich and were stored in the glovebox for further use. Solvents were dried using standard techniques and stored in the glovebox before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were stored under 4 Å molecular sieves for 24 h before use. Nickel dimer [(dippe)Ni(μ-H)]$_2$ was synthesized according to the procedure reported in the literature.[21] NMR spectra of complexes and organic products were acquired at room temperature using a 300 MHz Varian Unity Inova spectrometer. Samples and reactions were manipulated under an inert atmosphere and charged in thin-wall (0.33 mm) Wilmad NMR tubes, equipped with J. Young valves, and were heated in silicon oil baths at the desired temperature. Chemical shifts in ^{1}H MNR spectra (δ, ppm) are reported according to the residual protio-solvent. $^{13}C\{^1H\}$ NMR spectra are referenced to the carbon signal of each solvent. $^{31}P[^1H\}$ NMR spectra are referenced to external 85% H_3PO_4. GC-MS determinations were performed using an Agilent 5975C equipped with a 30 m DB-5MS capillary (0.32 mm i.d.) column. Elemental analyses were also performed by USAI-UNAM using a Perkin-Elmer 2400 microanalyzer.

Synthesis of [(dippe)Ni(η^2-C,C-DPA)]. Following the reported procedure by Jones et al,[18] to a dark red solution of [(dippe)Ni(μ-H)]$_2$ (0.053 g, 0.0822 mmol) in THF (5.0 mL) was added DPA (0.0292 g, 0.164 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 under vacuum, and the remaining yellow residue was further dried under vacuum for 4 h. ^{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, $CHMe_2$), 1.65 (d, J_{H-P} = 9.2 Hz, 4H, PCH_2CH_2P), 1.08 (quintet, J_{H-H} = 7.2 Hz, J_{H-P} = 7.2 Hz, 24H, $CHMe_2$). $^{13}C\{^1H\}$ 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). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 80.9 (s). Yield: 90%. Satisfactory elemental analysis was also obtained for this sample.

Reduction of Diphenylacetylene in [(dippe)Ni(η^2-C,C-DPA)] Using Cyclohexyamine as Hydrogen Source. Into a NMR tube with a Young's valve was charged a solution of [(dippe)Ni-(η^2-C,C-DPA)] (45 mg, 0.09 mmol) in 0.7 mL of toluene-d_8, and to this was added 4 equiv of cyclohexylamine (0.046 mL, 0.360 mmol). The tube was closed and heated at 140 °C. The formation of [(dippe)Ni-(η^2-C,C-*trans*-stilbene)] was detected by the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, as a singlet at 66.9 ppm (see Figure S1, SI). After 77.5 h the heating was stopped and the reaction mixture was analyzed by GC-MS (*cis*-stilbene: 17.5, *trans*-stilbene: 82.5).

Catalytic Reduction of Diphenylacetylene Using Cyclohexylamine As Hydrogen Source. A typical experiment for the catalytic reduction of diphenylacetylene was performed as follows: A stainless steel reactor (T316SS) with inner magnetic stirring was charged in a glovebox with diphenylacetylene (0.166 g, 0.92 mmol, 200 equiv), **1** (0.0032 g, 0.0045 mmol, 1 equiv), and cyclohexylamine (0.532 mL, 4.5 mmol for 1000 equiv) in 15 mL of solvent (THF, MeCN, toluene, or 1,4-dioxane). The reactor was heated in an oil bath at different temperatures (100, 140, 180 °C) for 72 h. At the end of that reaction time, the reaction was analyzed by GC-MS.

Catalytic Hydroamination and Reduction of Diphenylacetylene Using Pyrrolidine As Hydrogen Source. A stainless steel reactor was charged with diphenylacetylene (0.166 g, 0.92 mmol, 200 equiv), **1** (0.0032 g, 0.0045 mmol, 1 equiv), and pyrrolidine (0.389 mL, 4.5 mmol) in 15 mL of solvent (THF, toluene, 1,4-dioxane, or cyclohexylamine). The reactor was heated in an oil bath at 180 °C for 72 h. At the end of that time, the reaction was analyzed by GC-MS.

Catalytic Hydroamination and Reduction of Diphenylacetylene Using Different Amines As Hydrogen Source. A stainless steel reactor was charged with diphenylacetylene (0.166 g, 0.92 mmol, 200 equiv), **1** (0.0032 g, 0.0045 mmol, 1 equiv), and 1000 equiv of amine. The reactor was heated in an oil bath at 180 °C for 72 h. At the end of that time, the reaction was analyzed by GC-MS.

Synthesis of [(dippe)Ni(κ^1-$C_8H_6N)_2$]. A THF solution of **1** (0.060 g, 0.093 mmol) was mixed with indole (0.109 g, 0.933 mmol) and heated to 80 °C for 16 h, during which the solution color changed from wine red to orange. The solvent was eliminated *in vacuo* and characterized by NMR. $^{31}P\{^1H\}$ NMR (acetone-d_6, 121.32 MHz, 25 °C): δ 57.2 . ^1H NMR (acetone-d_6, 300 MHz, 25 °C): δ 7.59 (d, J_{H-H} = 8.1 Hz, 1H), 7.45 (d, J_{H-H} = 7.8 Hz, 1H), 7.31 (d, J_{H-H} = 3.0 Hz, 1H), 7.11 (t, J_{H-H} = 7.8 Hz, 1H), 7.02 (t, J_{H-H} = 7.8 Hz, 1H), 6.48 (d, J_{H-H} = 3.0 Hz, 1H), 2.5 (m, CH, 2H), 1.7 (m, CH_2, 2H), 1.35 (m, CH_3, 12H). Anal. Calcd for $C_{30}H_{44}N_2NiP_2$: C 65.12, H 8.01, N 5.06. Found: C 65.2, H 8.09, N 5.0.

Stoichiometric Reduction of DPA Using 1 and N-Heterocycles. A typical experiment was performed as follows: Using a stainless steel Parr reactor, to a 1,4-dioxane solution (15 mL) of complex **1** (30 mg, 0.046 mmol) were added DPA (16 mg, 0.093 mmol) and the corresponding N-heterocycle (0.093 mmol, 11 mg of indole, 15.5 mg of carbazole, 6.5 μL of pyrrole); the reactor was heated to 200 °C for 72 h. The formation of *cis*-stilbene and *trans*-stilbene was determined by GC-MS. Yield: (a) pyrrole: 100% *trans*-stilbene; (b) indole: 5% *cis*-stilbene, 95% *trans*-stilbene; (c) carbazole: 13% *cis*-stilbene, 30% *trans*-stilbene.

X-ray Structure Determination. For [(dippe)Ni(κ^1-$C_8H_6N)_2$], a crystal mounted on a glass fiber was studied with an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector ($\lambda_{Mo\,K\alpha}$ = 0.71073 Å, monochromator: graphite) equipped with a sealed tube X-ray source at 130 K. CrysAlisPro and CrysAlis RED software packages[22] were used for data collection and data integration. Structure solution and refinement were carried out with the programs SHELXS97[23] and SHELXL97. ORTEP-3 for Windows[24] was used for molecular graphics. The software used to prepare material for publication was WinGX version 1.80.05.[25]

Full-matrix least-squares refinement was carried out by minimizing $(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined anisotropically. H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C−H distances fixed to 0.95 (aromatic CH) with U_{iso} = 1.2U_{eq}(C), 0.98 (methyl CH_3) with U_{iso} = 1.5U_{eq}(C), and 1.00 (methyne CH) with U_{iso} = 1.2U_{eq}(C). Goodness-of-fit on F^2 = 0.960.

■ ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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