A Family of Active Iridium Catalysts for Transfer Hydrogenation of Ketones

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The air-stable iridium chlorodihydride complex $IrH_2Cl[(^iPr_2PC_2H_4)_2NH]$, **1**, was prepared from the reaction of $[IrCl(coe)_2]_2$ with the pincer ligand $(^iPr_2PC_2H_4)_2NH$ in 2-propanol at 80 °C. Reaction of **1** with KO^{t}Bu in THF resulted in the formation of the air-sensitive amidodihydride complex $IrH_2[(^iPr_2PC_2H_4)_2N]$, **2**, which in the presence of 2-propanol readily forms the moderately air-stable trihydride complex $IrH_3[(^iPr_2PC_2H_4)_2NH]$, **3**. The trihydride and amidodihydride complexes in the absence of a base are exceptionally active catalysts for the transfer hydrogenation of ketones in 2-propanol.

Introduction

Catalytic hydrogenation of ketones is a fundamental and indispensable process for the production of a wide range of alcohols including chiral compounds, which are useful as valuable end products and precursors for the pharmaceutical, agrochemical, flavor, fragrance, material, and fine chemical industries.[1] The catalytic hydrogenation processes developed by Noyori and co-workers are very attractive, since the precatalysts consist of well-defined air-stable $RuCl_2(PR_3)_2$(diamine) and $RuCl_2$(diphosphine)(diamine) complexes for the generation of active species for the homogeneous and asymmetric hydrogenation of ketones[1,2] and imines[3] in the presence of a base and hydrogen gas. It has been proposed and subsequently mechanistically elucidated that the key modus operandi of these catalysts is the presence of mutually cis N−H and Ru−H moieties of the dihydride catalytic species that electronically activate hydrogen gas and facilitate reduction by an outer-sphere hydrogen-transfer mechanism.[3a,4,5] Other ruthenium and iridium catalysts containing tetradentate diaminodiphosphine[6−8] and aminophosphine[9] ligands have also been shown to be very effective for the hydrogenation[7,9b,c] and transfer hydrogenation[6−8,9a] of ketones.

Transfer hydrogenation, whereby a hydrogen donor solvent such as 2-propanol or triethylammonium formate serves as the reducing agent, though currently not as highly developed as catalytic hydrogenation, is widely recognized as a potentially lucrative niche technology that is particularly significant and attractive whenever pressure hydrogenation, for whatever reason, is not applicable or practical.[6−8,10] Hence, transfer hydrogenation is complementary to pressure hydrogenation processes, especially for small- to medium-scale transformations. In most cases, 2-propanol is the conventional hydrogen donor solvent of choice because it is stable, is nontoxic, has a moderate boiling point (82 °C), is readily available, inexpensive, and environmentally friendly.[11] The presence of a strong base such as KO^{t}Bu is usually necessary for most transfer hydrogenation processes

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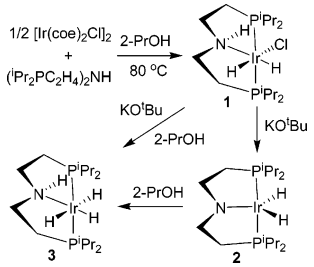
Scheme 1. Preparation of Complexes



in 2-propanol. However, the presence of a base can adversely affect stereoselectivity and it cannot be used for base-sensitive ketones.[5d,10a]

There are several previous reports on the preparation of aminodiphosphine ligands of the type $(R_2PC_2H_4)_2NR$, their transition metal complexes, and even their use in catalysis.[12−14] A noteworthy example is the work by Bianchini and co-workers on the use of iridium catalysts containing aminodiphosphine ligands (where R represents an alkyl substituent) for the transfer hydrogenation of ketones.[14] The authors also reported the characterization of several hydride-containing compounds, which were possibly the true catalytic species or their intermediates.

As an extension of research toward elucidating the role of the bifunctional proton-hydride motif in catalysis, we decided to investigate hydride-containing complexes containing aminodiphosphine ligands of the type $(R_2PC_2H_4)_2NH$ on the premise that coordination of the NH moiety and its interactions with hydrides could influence the catalytic properties of the complexes. Here we report that the air-stable complex $IrH_2Cl[(^iPr_2PC_2H_4)_2NH]$, **1**, serves as a convenient shelf-stable precursor to the catalytically active compounds $IrH_2[(^iPr_2PC_2H_4)_2N]$, **2**, and $IrH_3[(^iPr_2PC_2H_4)_2NH]$, **3**, which are effective for the transfer hydrogenation of ketones under base-free conditions.

Results and Discussion

The iridium chlorodihydride complex **1** was prepared by warming a stoichiometric mixture of the ligand $(^iPr_2PC_2H_4)_2NH$[12a] with $[Ir(coe)_2Cl]_2$ (Scheme 1, coe = cyclooctene). Extensive refluxing of the reaction mixture or prolonging the reaction time resulted in some decomposition of the product and the formation of some byproducts, including the 16-electron chlorohydridoamido species $IrHCl[(^iPr_2PC_2H_4)_2N]$, due to loss of H_2 from **1**. Precipitation of the product by the addition of hexane to the reaction mixture resulted in a white, crystalline solid.

Complex **1** is air-stable in the solid state and in solution; soluble in most common organic solvents, including dichloromethane, benzene, toluene, THF, and alcohols; and insoluble in ether and hexane. The single-crystal X-ray structure of **1** is shown in Figure 1. The complex crystallizes as a distorted octahedron with trans phosphines (P1−Ir−P2 = 167.20(4)°). The two hydrides are mutually cis, with one (H1Ir) being trans to the chloride and the other (H2Ir) trans to the nitrogen of the ligand. The chloride ligand is bent toward the nitrogen (N1−Ir−Cl = 86.54(9)°) and forms a classical hydrogen bond, with a Ir−Cl···H−N bond distance of 2.58(7) Å. This hydrogen bonding is consistent with the broad and intense νNH band in the infrared (Nujol) spectrum of **1** at 3171 cm^{-1}. The infrared spectrum also shows two intense νIrH bands at 2164 and 2087 cm^{-1}.

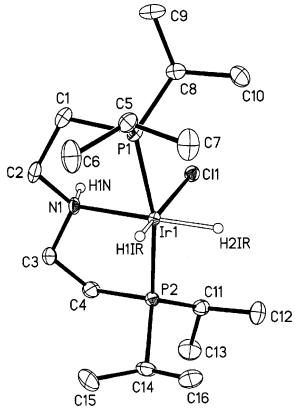


Figure 1. Structure of $IrH_2Cl[(^iPr_2PC_2H_4)_2NH]$, **1**.

Upon treating a THF solution of **1** with a base in an aprotic solvent such as THF, ether, toluene, or benzene, the amidodihydride complex $IrH_2[(^iPr_2PC_2H_4)_2N]$, **2**, readily and quantitatively forms. Filtration of the mixture to remove KCl, concentration of the filtrate, and addition of hexane resulted in precipitation and isolation of **2** as an air-sensitive, yellow, crystalline solid. Exposure of a solution of **2** to hydrogen gas or to 2-propanol resulted in the formation of **3**, which is isolated as a moderately air-stable, white crystalline solid. Alternatively, **3** can be prepared directly from **1** in the presence of KO^tBu in 2-propanol.

The ^1H NMR spectrum of **1** shows two distinct hydride chemical shifts, while that of **2** shows a single chemical shift for the two hydrides. The ^1H NMR spectrum of **3** shows three distinct hydride resonances, while the $^{31}P\{^1H\}$ and ^{31}P NMR spectra show singlet and quartet patterns, respectively, at 62.7 ppm.

The infrared spectrum of **3** shows three very intense iridium hydride bands at 2101, 1943, and 1702 cm^{-1}. The low νIrH vibration mode at 1702 cm^{-1} may be indicative of a hydride forming a nonclassical Ir−H···H−N hydrogen bond[15] with the amine proton of the pincer ligand. This is consistent with the comparatively low νNH vibration mode of 3140 cm^{-1} relative to those observed in **1** (3171 cm^{-1}) and the free ligand (3285 cm^{-1}).[16]

In the presence of 2-propanol and catalytic amounts of a base such as KO^tBu at room temperature, **1** facilitates the efficient transfer hydrogenation of acetophenone to phenylethanol. In the absence of a base, no hydrogenation was observed, clearly demonstrating that **1** is not the true catalyst. An NMR tube reaction mixture (S:C = 83:1) containing acetophenone (100 mg), 2-propanol (600 mg), and catalytic amounts of **3** (5 mg)

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Table 1. Transfer Hydrogenation of Ketones in 2-Propanol Using Iridium Complexes as Catalyst[a]

entry	substrate	temp (°C)	S:C	time (h)	conv (%)	yield (%)
1[b]		25	5,000	2	>99	98
2[b]		60	100,000	12	92	90
3[c]		25	5,000	2	>99	98
4[d]		25	5,000	2	>99	98
5[b,e]		25	5,000	2	>99	95
6[b]		25	10,000	2.5	>99	97
7[b]		25	5,000	1	>99	98
8[b]		40	2,500	2	98	90
9[b]		40	2,500	2	95	81
10[b]		40	2,500	2	92	82
11[b]		40	2,500	2	94	90
12[b]		80	1,000	1	93	90

[a] A weighed amount of the catalyst (**3**, **2**, or **1**/KO^{t}Bu) was added to a solution of the substrate in 2-propanol and the mixture stirred at the desired temperature. After attainment of equilibrium the solvent was removed by evaporation under reduced pressure. Yields are based on the amount of substrate. [b] Catalyst = **3**. [c] Catalyst = **2**. [d] Catalyst = **1**/KO^{t}Bu (1:10). [e] Saturated alcohol is the only product.

showed efficient transfer hydrogenation of the ketone to the alcohol at room temperature without the addition of a base and with the concomitant formation of acetone. Likewise a scaled-up reaction (S:C = 5000:1) containing acetophenone (6.0 g, 50 mmol), 2-propanol (30 g), and **3** (5 mg, 0.01 mmol) resulted in the formation of 80% phenylethanol in 2 h at room temperature. Evaporation of the solvent under vacuum resulted in further conversion of the ketone to the alcohol, with greater than 99% conversion being observed after complete removal of 2-propanol and acetone (Table 1). Excellent conversions were also observed at higher temperatures, even at a molar S:C ratio of 100 000 to 1.

Other ketone substrates were readily converted to their respective alcohols (Table 1) under similarly mild and base-free reaction conditions using **3** as a catalyst. The transfer hydrogenation of benzalacetone (entry 5) gave the saturated alcohol 4-phenyl-2-butanol as the sole product. The transfer hydrogenation of the aldimine (entry 12, Table 1) to the amine was accomplished using **3** as a base-free catalyst, but required heating the mixture to 80 °C. The amidodihydride complex **2** also functions as a base-free transfer hydrogenation catalyst and displays catalytic activity similar to **3** under comparable reaction conditions (entry 3). Similarly **1**/KO^{t}Bu can be used directly as a catalyst (entry 4).

A preliminary kinetic study was also conducted to demonstrate the catalytic activity of **3**. Aliquots of a catalytic mixture in 2-propanol containing acetophenone and **3** (S:C = 7500:1) were transferred to an NMR tube, and the transfer hydrogenation reaction was followed as a function of time and temperature by monitoring the change in intensity of the methyl chemical shift

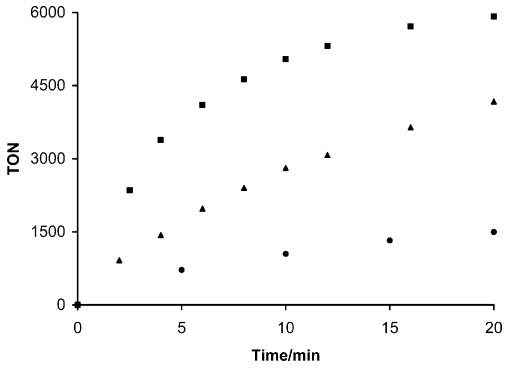
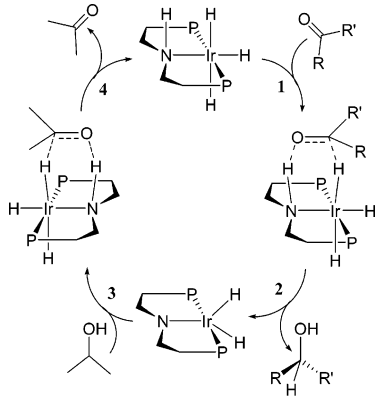


Figure 2. Kinetic study of the transfer hydrogenation of acetophenone catalyzed by **3** in 2-propanol. S:C = 7500; ● = 25 °C; ▲ = 50 °C; ■ = 60 °C.

Scheme 2. Proposed Transfer Hydrogenation Mechanism



of both the ketone and phenylethanol. The results are illustrated in Figure 2. Turnover frequencies of 13 000 and 43 000 h^{-1} at 50% conversion were calculated for the transfer hydrogenation of acetophenone at 50 and 60 °C, respectively.

To account for the relatively mild reaction conditions for this transfer hydrogenation process involving the trihydride catalyst, the bifunctional ionic mechanism shown in Scheme 2 is proposed. The first step in the catalytic cycle involves the concerted transfer of a hydride and the NH proton to the carbonyl carbon and oxygen of the ketone, respectively, via a six-membered pericyclic transition state. Liberation of the alcohol product is followed by abstraction of hydrogen from 2-propanol by the highly reactive 16-electron amidodihydride intermediate. This transfer hydrogenation mechanism, in which the trihydride catalyst is regenerated from 2-propanol, is similar to the transfer hydrogenation process reported for the Noyori-type RuH(η^6-arene)(tosyldiamine) complexes,[17] which also require a hydrogen donor solvent such as 2-propanol or triethylammonium formate.

Conclusion

In summary, this report has demonstrated that iridium complexes containing an aminodiphosphine ligand are useful as catalysts for the transfer hydrogenation of ketones under very mild reaction conditions. The cis Ir−H···H−N bifunctional motif of the iridium catalysts in this study may be a key feature

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for the higher rate of catalytic activity observed for these compounds relative to those previously reported that contain N-substituted ligands.[14] Our ongoing research will further explore the kinetics and the mechanism of the transfer hydrogenation process and the development of chiral ligands and catalysts for asymmetric transformations.

Experimental Section

All preparations and manipulations were carried out under hydrogen, nitrogen, or argon atmospheres with the use of standard Schlenk, vacuum line, and glovebox techniques in dry, oxygen-free solvents. Tetrahydrofuran (THF), diethyl ether (Et_2O), and hexanes were dried and distilled from sodium benzophenone ketyl. Deuterated solvents were degassed and dried before use. Potassium *tert*-butoxide, chlorodiisopropylphosphine, bis(chloroethyl)amine hydrochloride, ketones, and amines were supplied by Aldrich Chemical Co. NMR spectra were recorded on either a Varian Unity Inova 300 MHz spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121.5 for ^{31}P) or a Bruker Avance 500 MHz DRX spectrometer. All ^{31}P chemical shifts were measured relative to 85% H_3PO_4 as an external reference. ^{1}H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. The alcohol products obtained from the catalytic transfer hydrogenation of ketones were characterized by their ^{1}H and ^{13}C NMR spectra. All Infrared spectra were obtained on a Perkin-Elmer Spectrum BXII FT IR spectrometer. The ligand $(^iPr_2PC_2H_4)_2NH$ is a known compound. The synthesis below is a modification of the reported procedure.[12a]

Synthesis. $(^iPr_2PC_2H_4)_2NH$. Chlorodiisopropylphosphine (11.0 g, 72 mmol) was added in 2 g portions to a suspension of lithium granules (1.5 g, 216 mmol) in THF (40 mL) (CAUTION!! Each subsequent 2 g portion must be added only after the mixture becomes and retains a yellow-green coloration and cools to or near room temperature). The resulting suspension was stirred vigorously at room temperature for 72 h. It was then filtered and cooled to −80 °C, and a solution of bis(chloroethyl)trimethylsilylamine (7.75 g, 36 mmol) in 10 mL of THF was slowly added, with vigorous stirring. The mixture was then allowed to warm to room temperature and refluxed for 1 h. Water (15 mL) was added and the mixture stirred at room temperature for 1 h. The aqueous layer was removed and 15 mL of hexanes and 15 mL of water added. The mixture was refluxed for 4 h, cooled to room temperature and the aqueous layer removed. The solvent was removed by evaporation, and the crude diphosphine product was purified by distillation under vacuum. The fraction that boiled at 120−140 °C was collected. The purity (>98% by NMR) was sufficient for the applications below. Yield = 9.72 g, 88%. ^{1}H NMR (C_6D_6): δ 0.99 (dd, J_{HH} = 7.2 Hz, J_{HP} = 11.1 Hz, 12H, CH_3); 1.03 (dd, J_{HH} = 7.2 Hz, J_{HP} = 14.1 Hz, 12H, CH_3); 1.25 (s, br, 1H, NH); 1.51 (td, J_{HH} = 7.5 Hz, J_{HP} = 3 Hz, 4H, CH_2); 1.58 (septet of doublet, J_{HH} = 7.2 Hz, J_{HP} = 1.9 Hz, 4H, CH); 2.82 (quart, $J_{HH} \approx J_{HP}$ = 7.8 Hz, 4H, CH_2). ^{31}P{^{1}H} NMR (C_6D_6): δ −0.91 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.8 (d, J_{CP} = 10.0 Hz, CH_3); 20.17 (d, J_{CP} = 16.6 Hz, CH_3); 23.23 (d, J_{CP} = 19.2 Hz, CH_2); 23.61 (d, J_{CP} = 13.7 Hz, CH); 49.22 (d, J_{CP} = 24.4 Hz, CH_2). IR (neat): 3285 cm^{-1} (w, NH).

$IrH_2Cl[(^iPr_2PC_2H_4)_2NH]$, 1. A 3 mL aliquot of 2-propanol was added to a mixture of $[IrCl(coe)_2]_2$ (1.5 g, 1.6 mmol) and $(^iPr_2PC_2H_4)_2NH$ (1.02 g, 3.3 mmol) and the resulting suspension warmed for 45 min at 80 °C. Hexane (6 mL) was then added, and the resulting white precipitate was filtered, washed with hexanes, and dried under vacuum. Yield = 1.52 g, 89%. ^{1}H NMR (C_6D_6): δ −25.13 (td, J_{HH} = 8.0 Hz, J_{HP} = 14.7 Hz, 1H, IrH); −19.83 (td, J_{HH} = 8.0 Hz, J_{HP} = 13.5 Hz, 1H, IrH); 0.84 (dd, J_{HH} = 7.0 Hz, J_{HP} = 14.1 Hz, 6H, CH_3); 1.13 (m, 12H, CH_3); 1.59 (dd, J_{HH} = 7.0 Hz, J_{HP} = 14.1 Hz, 6H, CH_3); 1.65−1.87 (m, 8H); 2.93 (m, 4H, CH_2); 3.99 (br, 1H, NH). ^{31}P{^{1}H} NMR (C_6D_6): δ 54.17 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 16.85 (s, CH_3); 19.01 (s, CH_3); 21.68 (t, J_{CP} = 2.85 Hz, CH_3); 21.88 (t, J_{CP} = 3.7 Hz, CH_3); 22.74 (t, J_{CP} = 15.1 Hz, CH); 24.66 (t, J_{CP} = 14.0 Hz, CH); 32.95 (t, J_{CP} = 11.4 Hz, CH_2); 55.38 (t, J_{CP} = 3.1 Hz, CH_2). IR (Nujol): 3172 cm^{-1} (strong, NH); 2164, 2087 cm^{-1} (strong, IrH). Anal. Calcd for $C_{16}H_{39}ClIrNP_2$: C,35.91; H, 7.35; N, 2.62. Found: C, 35.75; H, 7.22; N, 2.50.

$IrH_2[(^iPr_2PC_2H_4)_2N]$, 2. Tetrahydrofuran (2 mL) was added to a mixture of $IrH_2Cl(^iPr_2PC_2H_4)_2NH$ (250 mg, 0.47 mmol) and KO^{t}Bu (75 mg, 0.67 mmol) and the mixture stirred for 30 min at room temperature. The mixture was filtered to remove KCl and excess base and the filtrate evaporated to near dryness. Hexane (5 mL) was then added and the suspension stirred for 1 h. A yellow crystalline product resulted, which was filtered, washed with hexane, and dried under vacuum. Yield = 223 mg, 96%. ^{1}H NMR (toluene-d_8): δ −22.35 (triplet of quintet, J_{HH} = 3.2 Hz, J_{HP} = 10.8 Hz, 2H, IrH); 0.99 (dd, J_{HH} = 6.9 Hz, J_{HP} = 13.9 Hz, 12H, CH_3); 1.13 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.4 Hz, 12H, CH_3); 1.80 (m, 8H); 3.20 (dtt, J_{HH} = 3.05 Hz, J_{HH} = 6.41 Hz, J_{HP} = 13.4 Hz, 4H, CH_2). ^{31}P{^{1}H} NMR (toluene-d_8): δ 80.58 (s). Anal. Calcd for $C_{16}H_{38}IrNP_2$: C, 38.54; H, 7.68; N, 2.81. Found: C, 38.41; H, 7.49; N, 2.64.

$IrH_3[(^iPr_2PC_2H_4)_2NH]$, 3: Method A. 2-Propanol (1 mL) was added to a solution of $IrH_2(^iPr_2PC_2H_4)_2N$ (800 mg, 1.5 mmol) in THF (5 mL) and the mixture stirred for 30 min at room temperature. Hexane (10 mL) was then added, precipitating the product as a crystalline white solid, which was dried under vacuum. Yield = 628 mg, 84%.

Method B. 2-Propanol (5 mL) was added to a mixture of $IrH_2Cl(^iPr_2PC_2H_4)_2NH$ (500 mg, 0.95 mmol) and KO^{t}Bu (150 mg, 1.34 mmol) and the mixture stirred for 30 min at room temperature. The solvent was removed under reduced pressure and tetrahydrofuran (5 mL) added. The mixture was filtered and the filtrate concentrated (2 mL) under reduced pressure. Hexane (10 mL) was then added and the suspension stirred for 1 h. The white crystalline product was filtered, washed with hexane, and dried under vacuum. Yield = 421 mg, 90%. ^{1}H NMR (THF-d_8): δ −22.58 (tt, J_{HH} = 4.8 Hz, J_{HP} = 14.4 Hz, 1H, IrH); −12.59 (td, J_{HH} = 5.1 Hz, J_{HP} = 17.7 Hz, 1H, IrH); −12.07 (td, J_{HH} = 5.7 Hz, J_{HP} = 16.5 Hz, 1H, IrH); 1.07 (dd, J_{HH} = 7.0 Hz, J_{HP} = 15.0 Hz, 6H, CH_3); 1.17 (m, 18H, CH_3); 1.56 (ttd, J_{HH} = 14.4, 5.7 Hz, J_{HP} = 2.7 Hz, 2H); 1.75 (m, 4H, CH); 1.98 (m, 2H), 2.14 (tdd, J_{HH} = 14.1, 4.0 Hz, J_{HP} = 3.9 Hz, 2H); 3.22 (m, 2H); 4.39 (br, 1H, NH). ^{31}P{^{1}H} NMR (THF-d_8): δ 62.73 (s). ^{13}C{^{1}H} NMR (THF-d_8): δ 17.41 (t, J_{CP} = 1.42 Hz, CH_3); 17.89 (t, J_{CP} = 1.72 Hz, CH_3); 18.29 (t, J_{CP} = 2.25 Hz, CH_3); 18.56 (t, J_{CP} = 3.45 Hz, CH_3); 23.97 (t, J_{CP} = 14.9 Hz, CH); 26.22 (t, J_{CP} = 15.1 Hz, CH); 30.19 (t, J_{CP} = 10.5 Hz, CH_2); 55.69 (t, J_{CP} = 4.0 Hz, CH_2). IR (Nujol): 3140 cm^{-1} (strong, NH); 2101, 1943, 1702 cm^{-1} (strong, IrH). Anal. Calcd for $C_{16}H_{40}IrNP_2$: C, 38.38; H, 8.05; N, 2.80. Found: C, 38.26; H, 7.81; N, 2.59.

X-ray Structure Analysis. Crystals of **1** were obtained by the slow diffusion of hexane into THF solutions of the desired compounds under a nitrogen atmosphere. Data were collected on a Nonius Kappa-CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The CCD data were integrated and scaled using the DENZO-SMN software package, and the structures were solved and refined using SHELXTL V5.0. The hydrides were located and refined with isotropic thermal parameters.

Procedure for Catalytic Transfer Hydrogenation of Ketones. In a typical catalytic transfer hydrogenation procedure, a weighed amount of the respective catalyst (**1**/KO^{t}Bu, **1**/NaOEt, **2**, or **3**)[18] was added to a solution of the substrate in 2-propanol and the mixture stirred at the desired temperature under an inert atmosphere of nitrogen or argon. The reaction progress was monitored using

(18) Note: whenever **1** and a base were used as the catalyst, the ratio of complex to base (KO^{t}Bu or NaOEt) varied from 1:8 to 1:15.

NMR. After attainment of an equilibrium conversion (80−95%) or the allotted time, the solvent was removed by evaporation under reduced pressure. The alcohols were purified by filtering a hexane solution of the crude product through a pad of silica, then removing the solvent and remaining ketone under reduced pressure.

Procedure for Kinetic Studies. A stock solution of the catalyst was prepared by dissolving 5 mg (0.01 mmol) of the trihydride complex **3** in 10 mL of 2-propanol. A 2.0 mL aliquot of this stock solution was then diluted to 10 mL with 2-propanol, and 0.50 g of the diluted catalyst solution and 0.11 g (0.91 mmol) of acetophenone were quickly added to a NMR tube, which was then shaken vigorously and quickly transferred to the probe of the NMR spectrometer. The progress of the reaction was monitored as a function of time by following the increase in intensity of the chemical shift of the methyl protons of the phenylethanol product and the concurrent decrease in intensity of the chemical shift of the methyl protons of acetophenone.

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Supporting Information Available: Experimental procedures for transfer hydrogenations, table of kinetic results, and crystallographic data for **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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