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# Nickel-Catalyzed Transfer Hydrogenation of Ketones Using Ethanol as Solvent and Hydrogen Donor

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## ABSTRACT

We report a nickel(0)-catalyzed direct transfer hydrogenation (TH) of a variety of alkyl-aryl, diaryl, and aliphatic ketones with ethanol. This protocol implies a reaction in which a primary alcohol serves as a hydrogen atom source and solvent in a one-pot reaction without any added base. The catalytic activity of the nickel complex [(dcype)Ni(COD)] **(e)** (dcype: 1,2-bis(dicyclohexyl-phosphine)ethane, COD: 1,5-cyclooctadiene), towards transfer hydrogenation (TH) of carbonyl compounds using ethanol as the hydrogen donor was assessed using a broad scope of ketones; giving excellent results (up to 99 % yield) compared to other homogeneous phosphine-nickel catalysts. Control experiments and a mercury poisoning experiment support a homogeneous catalytic system; the yield of the secondary alcohols formed in the TH reaction was monitored by gas chromatography (GC) and NMR spectroscopy.

*Keywords*: Homogeneous catalysis, nickel, transfer hydrogenation, ketones, ethanol, secondary alcohols.

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## 1. INTRODUCTION

The catalytic transfer hydrogenation (TH) of ketones is currently recognized as one of the most valuable synthetic methods for obtaining a number of value-added products including alcohols, due to its operational simplicity, easy access to hydrogen sources, lower cost, and safety.[1] Regularly, the catalysts used for the transfer hydrogenation of ketones are based on Ru,[2] Rh,[3] Ir,[4] Fe,[5] and Co,[6] exhibiting very good activity and selectivity under low to higher temperatures (generally 20 – 150 ºC).

Ruthenium and Rhodium compounds with N-heterocyclic carbenes (NHCs) have been widely used as catalysts in the transfer hydrogenation process of carbonyl compounds.[2b, 3d, 6d] Albrecht et al. reported the first rhodium(III) complexes bound to C4-coordinating N-heterocyclic dicarbenes.[2d] The exceptionally strong donor ability of carbenes in such a C4-coordination mode increases the catalytic activity of the rhodium center and allows the efficient TH of benzophenone in 2 h using *i*PrOH/KOH and 1 mol % catalyst loading. Recently, Ding et al. found that the phosphine bis-benzothienyl iridium(III) complex can be used in the hydrogenation of acetophenone.[3a] A secondary alcohol was obtained by using 2 mol % of catalyst, *t*BuOK, at 110 ºC, and 2-propanol as a hydrogen source, and the product was obtained with 65 % conversion. However, the limited availability, high cost, and toxicity of these precious metals demand their replacement with earth-abundant, inexpensive, and nontoxic metals. For this reason, reactions catalyzed by first-row metals such as nickel have attracted increasing attention.[1d, 8]

Some complexes of nickel have also been used in the transfer hydrogenation of carbonyl compounds although in a lesser extent;[8] furthermore, several reports emerged describing the application of supported nickel nanoparticles (NiNPs), [8c, 8d, 8f] and a few homogeneous nickel-

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based catalysts have been reported for the transfer hydrogenation of ketones; for example, Sattar et al. reported the use 10 mol % of $[Ni(P(OPh)_3)_4]$ to catalyze the TH of alkyl and aryl ketones using $HCOONH_4$.[8a] This is the first example of a homogeneous Ni(0) catalyst being active in the reduction of ketones in high yields (68 - 97 %) at 110 ºC with a reaction time of 5 to 24 h and acetic acid as the solvent. Varghese et al. investigated the use of $[NiCl_2(PPh_3)_2]$ as a catalyst for the reduction of ketones and aldehydes.[8g] As a result, phenylmethyl alcohol was produced in high yield (82 %) using a load of 15 mol % of the nickel complex, NaOH, and reflux for 30 h. This reaction did not proceed in the absence of NaOH.

The reduction of ketones furnishes secondary alcohols as the principal products;[9] they are key structural units present in various biologically and pharmaceutically active compounds.[1c, 1d] Direct hydrogenation of ketones with $H_2$ is a widely used method employed for secondary alcohols.[1e, 6a, 20.] In previous work, our group reported one of the few examples using nickel in homogeneous hydrogenation of ketones using dihydrogen to give the corresponding secondary alcohols or alkanes successfully.[20] However, the use of hazardous pressurized $H_2$ and its limited availability demand their replacement with other hydrogen donors. Hence, developing more efficient and green transfer hydrogenation methodologies utilizing non-hazardous and easily available starting materials would be most desirable for sustainable processes.[10] Recently, less toxic and more readily available molecules such as alcohols,[11, 7] formic acid-triethylamine mixture[12], and HCOONa in water[13] were used as the hydrogenation agents of carbonyl compounds for synthesis of secondary alcohols as an alternative to $H_2$.

In most of the cases, 2-propanol is the conventional hydrogen donor/solvent of choice and is also readily available and inexpensive. Also, the presence of bases such as $KO^tBu$ or KOH are usually necessary for most TH processes in 2-propanol,[11] the presence of a strong base can

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adversely affect selectivity, and it cannot be used for base-sensitive ketones. Primary alcohols (*i.e.*, ethanol or methanol) are generally not employed as hydrogen donors because of the unfavorable redox potential of the primary vs. secondary alcohols.[11c] However, in the last few years, ethanol has been used efficiently as a reducing agent in TH with formation of acetaldehyde or ethyl acetate[4h], but its use as hydrogen source and solvent has been relatively less explored.[11]

Thus, we focused our study on developing a simple catalytic system that works under relatively mild conditions as well as challenging substrates. We have been interested in the design of phosphine-nickel(0) complexes and their application in transfer hydrogenation of molecules such as alkynes[14, 15] and α,β-unsaturated ketones[16, 17] using ammonia-borane, sodium borohydride, water, triethylsilane, methanol, and amines as hydrogen sources.[14-17] For these reactions, we found that the best catalysts were nickel (0) complexes using chelating bisphosphines with electron-donor ligands. Herein, we disclose the use of homogeneous nickel catalysts, in which [(dcype)Ni(COD)] (dcype: 1,2ethylene-bis(dicyclohexylphosphine)ethane, COD: 1,5-cyclooctadiene) was used as catalytic precursor showing high catalytic activity for easily oxidizable alcohols and their use in TH of a variety of ketones using moderate reaction conditions and high conversions.

## 2. RESULTS AND DISCUSSION

We previously reported[20] the synthesis of nickel complexes [(dippe)Ni($\eta^2$-*O,C*-ketone)] by the reaction of [(dippe)Ni(μ-H)]$_2$ with a variety of ketones or 1,2-diketone at room temperature. Thus, considering the exceptional activity of bisphosphine-nickel(0) complexes in homogeneous hydrogenation of ketones using $H_2$, we are interested in developing active nickel catalysts for efficient and green transfer hydrogenation of ketones using alcohols as hydrogen sources.

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We initially focussed on using primary and secondary alcohols as hydrogen donors for the reduction of ketones. The results showed that on using 2 mol % of [Ni(COD)$_2$] and 3 mol % of chelating bisphosphine (dippe: 1,2-bis(di-isopropylphosphino)ethane) performed better using alcohols as reagent and solvent, for the reduction of acetophenone (**Table 1**). As seen in **Table 1**, the use of methanol resulted in poor conversion of the substrate **1a**, and the yield of α-methylbenzyl-alcohol is low (13 %) (entry 1). The reaction using ethanol as the hydride donor gave the best conversion and the highest selectivity (entry 2), and the α-methylbenzyl-alcohol (**2a**) was produced with a 95 % yield. Using secondary alcohols such as isopropanol and isobutanol under the same reaction conditions, the yield of product **2a** in both cases decreases, showing that isobutanol is more reactive compared with isopropyl alcohol (53 %) (entry 4). Furthermore, monitoring the reaction by GC-MS, the corresponding aldehydes were observed by dehydrogenation of the used alcohols. Dehydrogenative oxidations of the primary alcohols can proceed in the absence of a base, and generally, secondary alcohols require sub-stoichiometric amounts of base.[11c, 18] Thus, ethanol was converted to acetaldehyde and acetic acid ethyl ester (ethyl acetate) according to GC-MS analysis (SI, Fig. S39-S40).

Therefore, we focused on performing the transfer hydrogenation under neat conditions with ethanol and then assessed different amounts of catalyst, time, and temperature for this nickel-catalyzed methodology (**Table 2**).

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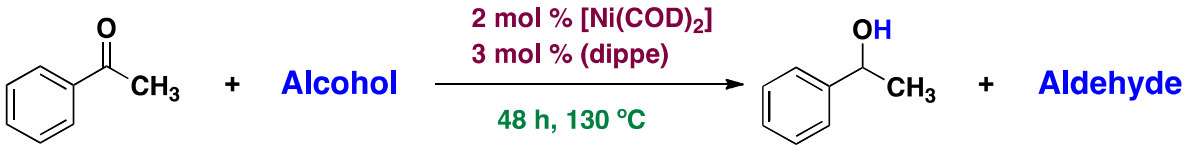
**Table 1. Metal-Mediated TH Results with Acetophenone Using Alcohols as the Hydrogen Source** [a]




1a 2a

| Entry | Alcohol [b] | Conversion (%) | 2a (%) |
|---|---|---|---|
| 1 | $H_3C-OH$ Methanol | 13 | 13 |
| 2 | $CH_3$ OH Ethanol | 95 | 95 |
| 3 | $CH_3$ $H_3C$ OH Isopropanol | 4 | 4 |
| 4 | $CH_3$ $H_3C$ OH Isobutanol | 53 | 53 |

[a] **1a** (1.1 mmol, 130.8 mg), **Alcohol** (7 mL), **[Ni(COD)$_2$]** (0.022 mmol, 6 mg), (**dippe**) (0.033 mmol, 8.7 mg); All reactions were completed in 130 ºC and 48 h; Yields were determined by GC-MS. [b] The alcohol was used as reactant and solvent.

In order to further improve the catalytic system, we investigated a variety of reaction conditions for the reaction of acetophenone **1a** and ethanol, with catalytic amounts of [Ni(COD)$_2$] and the ligand dippe. On decreasing the temperature to 100 ºC, the reaction gave a low yield of **2a** (2 %) **Table 2**, entry 1. In this case, ~97% acetophenone remained unchanged. As mentioned previously, a high yield of **2a** was observed when the temperature was increased at 130 ºC during 48 h (entry 2). Increasing the temperature to 150 ºC both conversion and yield of **2a** were quantitative. A screening of different alkyl phosphines (dcype and dtbpe) at 130 ºC showed that

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dcype performed better, achieving a quantitative yield of **2a** (entry 6). These reactions occurred homogeneously, as confirmed by a mercury drop test (entries 4 and 7) without significant loss of activity.

The use of aryl phosphines [dppf, dppe, $P(C_6H_5)_3$] or phosphites [$P(OC_2H_5)_3$] gave, in general, low conversion of **2a** (entries 9-12) with selectivity to the formation of the α-alkylation product (**3a**). The catalytic α-alkylation of **1a** with ethanol consists of catalytic oxidation of the primary alcohol into the corresponding aldehyde (acetaldehyde), which undergoes aldol condensation with the ketone substrate **1a**. Subsequent dehydration and catalytic reduction of the α,β-unsaturated enone furnishes the saturated ketone product **3a**.[11c] Thus, the transfer hydrogenation of **2a** was favored by using σ donor ligands, and the α-alkylation of ketone was favored by using σ donor / π acceptor ligand under the used reaction conditions.

Screening of different phosphine nickel precursors such as $[(P\text{-}P)Ni(\mu\text{-}H)]_2$ using alkyl di-phosphines (dippe, dcype, and dtbpe), gave a high yield of □**a**. However, the TH with these catalytic precursors requires a high reaction temperature (150 ºC) to achieve a quantitative yield of **2a** (entries 16-18). Consequently, we selected the system $[Ni(COD)_2]$ / alkyl-phosphines (dippe or dcype) for further investigation and the study of substrate scope, since this system is relatively inexpensive and readily commercially available. Control experiments showed no product formation in the absence of any ligand, $[Ni(COD)_2]$ or both (entries 13-15).

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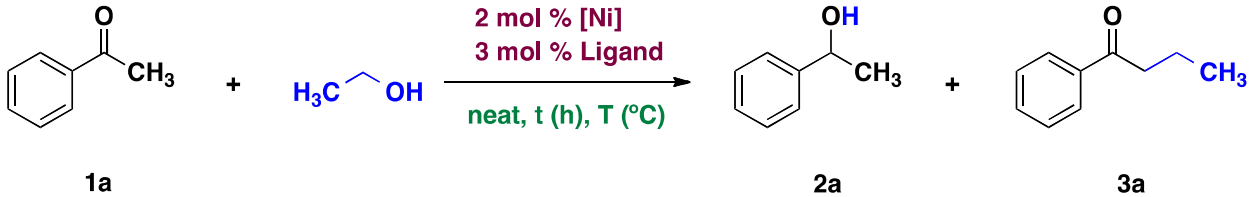
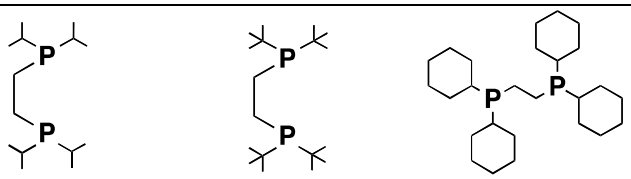
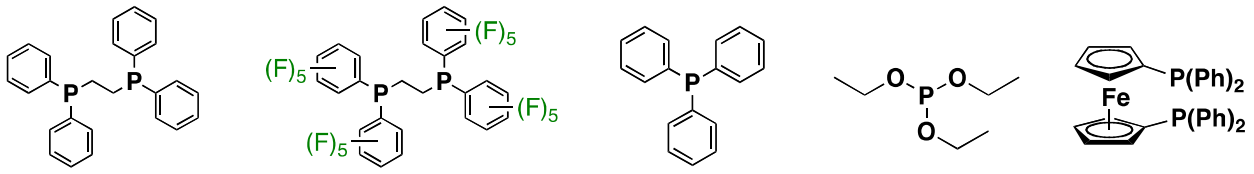
**Table 2. Optimization of Catalyst and Condition for Transfer Hydrogenation of Acetophenone Using Ethanol** [a]




1a 2a 3a



dippe dtbpe dcype



dppe $[(C_6F_5)_2PCH_2\text{-}]_2$ $P(C_6H_5)_3$ $P(OC_2H_5)_3$ dppf

| Entry | [Ni] | Ligand | T (°C) | t (h) | Conv. (%) | 2a (%) | 3a (%) |
|---|---|---|---|---|---|---|---|
| 1 | $Ni(COD)_2$ | dippe | 100 | 24 | 2 | 2 | - |
| 2 | $Ni(COD)_2$ | dippe | 130 | 48 | 95 | 95 | - |
| 3 | $Ni(COD)_2$ | dippe | 150 | 48 | 100 | 100 | - |
| 4[b] | $Ni(COD)_2$ | dippe | 150 | 48 | 94 | 94 | - |
| 5 | $Ni(COD)_2$ | dtbpe | 130 | 48 | 90 | 90 | - |
| 6 | $Ni(COD)_2$ | dcype | 130 | 48 | 100 | 100 | - |
| 7[b] | $Ni(COD)_2$ | dcype | 130 | 48 | 96 | 96 | - |
| 8 | $Ni(COD)_2$ | dppe | 130 | 48 | 3 | - | 3 |
| 9 | $Ni(COD)_2$ | $[(C_6F_5)_2PCH_2\text{-}]_2$ | 130 | 48 | 15 | - | 15 |
| 10 | $Ni(COD)_2$ | $P(C_6H_5)_3$ | 130 | 48 | 0 | - | - |

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 11 | $Ni(COD)_2$ | $P(OC_2H_5)_3$ | 130 | 48 | 13 | - | 13 |
| 12 | $Ni(COD)_2$ | dppf | 130 | 48 | 0 | - | - |
| 13[c] | $Ni(COD)_2$ | - | 130 | 48 | 0 | - | - |
| 14[d] | - | dippe | 130 | 48 | 0 | - | - |
| 15 | - | - | 130 | 48 | 0 | - | - |
| 16 | $[(dippe)Ni(\mu\text{-}H)]_2$ | | 150 | 48 | 96 | 96 | - |
| 17 | $[(dcype)Ni(\mu\text{-}H)]_2$ | | 150 | 48 | 98 | 98 | - |
| 18 | $[(dtbpe)Ni(\mu\text{-}H)]_2$ | | 150 | 48 | 89 | 89 | - |

[a] **1a** (1.1 mmol, 130.8 mg), **ethanol** (119.88 mmol, 7 mL), [**Ni**] (0.022 mmol), **Ligand** (0.033 mmol); Conversion and yields were determined by GC-MS. [b] Hg drop test (0.30 mmol). [c] **$[Ni(COD)_2]$** (0.022 mmol).[d] **dippe** (8.7 mg, 0.033 mmol).

In order to identify some of the catalytically active species in the TH of acetophenone, we carried out the stoichiometric reaction between $[Ni(COD)_2]$ and dippe. As depicted in **Scheme 1**, complexes [(dippe)Ni(COD)] **(c)** and $[(dippe)_2Ni]$ **(d)** were observed as the main products when using 2 equivalents of $[Ni(COD)_2]$ **(a)** and 3 equivalents of 1,2-bis(di-isopropyl-phosphino)ethane (dippe) **(b)** in THF-$d_8$ at room temperature. The $^{31}P\{^1H\}$ spectrum of this mixture showed a singlet at 53.92 ppm, which is characteristic of complex $[(dippe)_2Ni]$ [19, 20] (**Figure 1**). The $^{31}P\{^1H\}$ singlet at 70.15 ppm was assigned to the complex [(dippe)Ni(COD)] **(c)**. Thus, we synthetized complexes **(c)** and **(b)** independently, and their reactivity with acetophenone was investigated in order to identify the possible active species in the TH of ketone **1a** (**Figures 2-3**).

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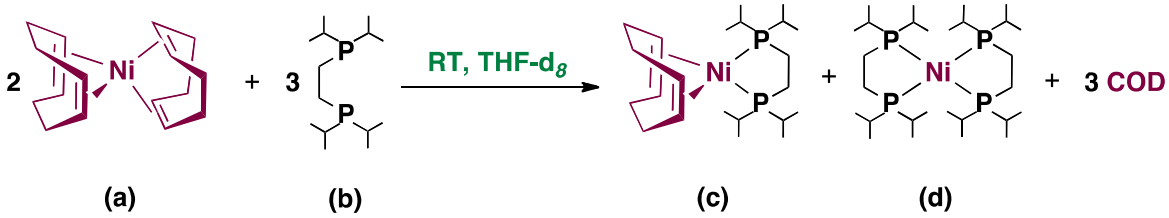
**Scheme 1. Coordination of the dippe Ligand to [Ni(COD)$_2$]**



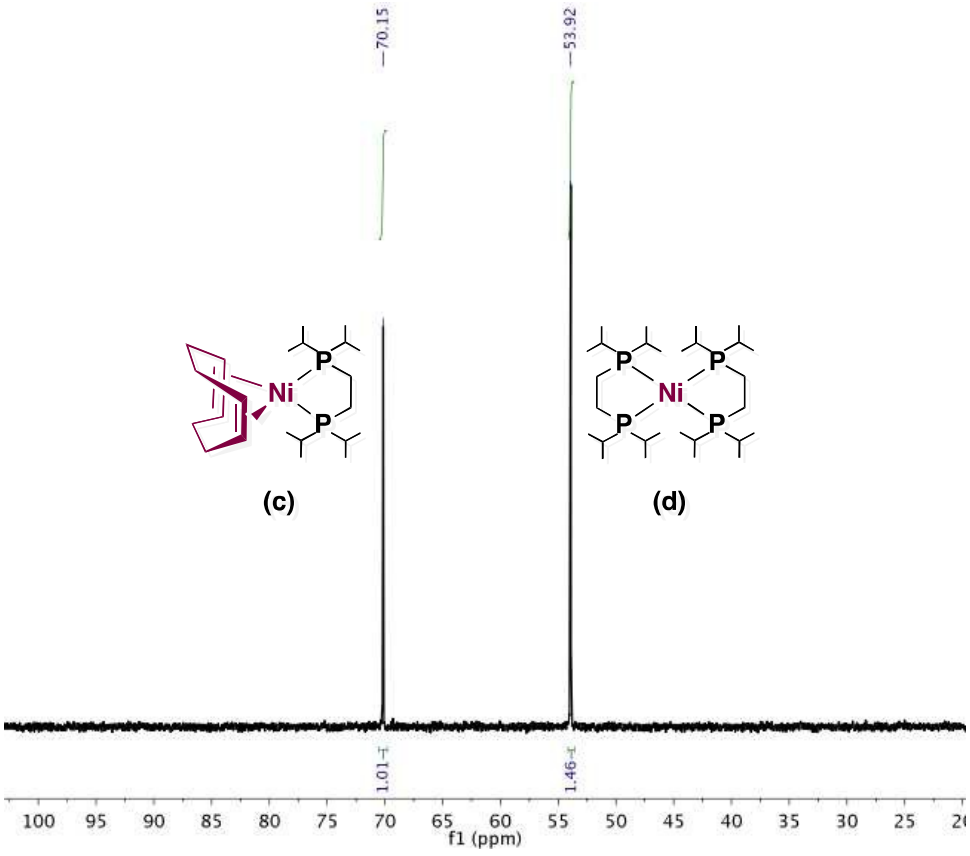




**Figure 1.** $^{31}P\{^{1}H\}$-NMR spectrum of reaction between 2 equiv of **(a)** and 3 equiv of **(b)** at RT in THF-$d_8$.

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Freund et al.[21] reported the use of 1 equiv of (dcype) and 1 equiv of [Ni(COD)$_2$] in THF at room temperature to produce [(dcype)Ni(COD)] in high yields. Thus, we followed a similar procedure to prepare [(dippe)Ni(COD)] **(c)** with an isolated yield of 89 % (see the experimental section and SI, Fig. S2-S3). Then, the reaction of **(c)** with acetophenone **1a** in THF-$d_8$ was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (**Figure 2**). The mixture of acetophenone **1a** and complex **(c)** was gently heated, increasing the temperature from 25 to 130 ºC. The $^{31}P\{^1H\}$ NMR spectrum at room temperature shows the signal assigned to [(dippe)Ni(COD)], at □□□□□ □□□. The spectrum at 50 ºC shows two doublets between 71 and 65 ppm with $^2J_{P\text{-}P}$ = 70.36 Hz, characteristic of similar nickel(0) complexes with diphosphine ligands,[19, 20] in agreement with $\eta^2$-C=O coordination of ketones proposed for complex [(dippe)Ni($\eta^2$-C,O-$C_8H_8O$)] **3**. When the temperature was increased to 130 ºC, the original small doublets increased due to the formation of complex [(dippe)Ni($\eta^2$-C,O-$C_8H_8O$)] **3** (**Figure 2**).

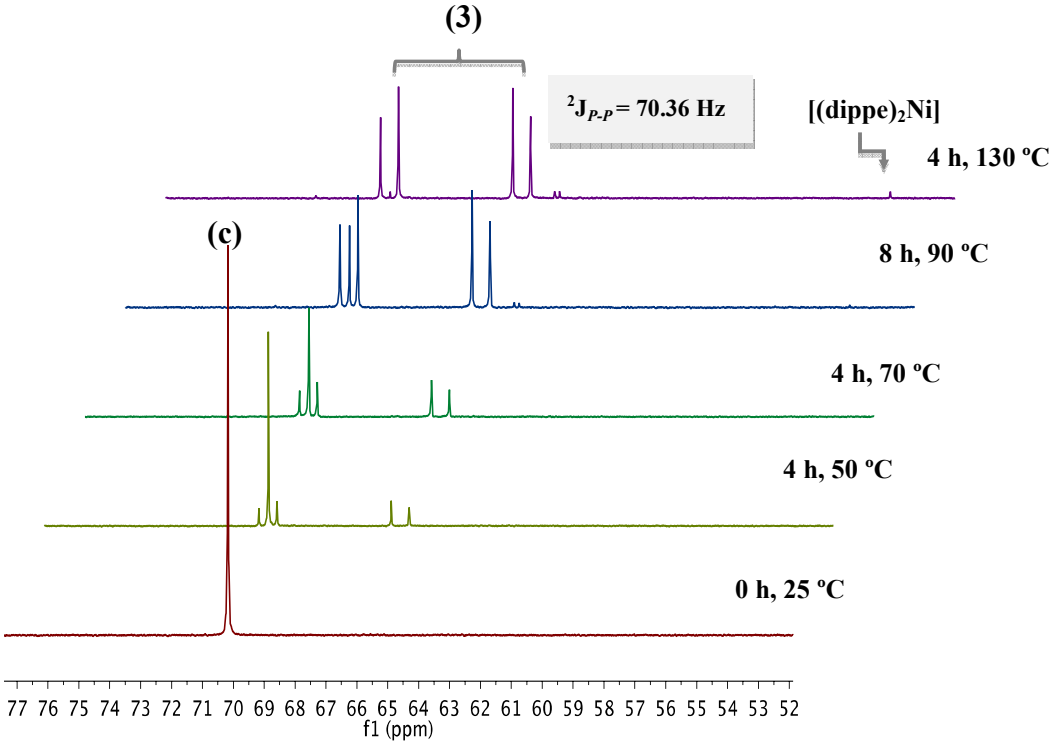


**Figure 2.** $^{31}P\{^1H\}$ NMR spectra of reaction between complex **(c)** and acetophenone **1a** (THF-$d_8$, 121.32 MHz).

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The complex [(dippe)$_2$Ni] **(d)** was obtained in good yield (92 %) using 1 equiv of [Ni(COD)]$_2$ and 2 equiv of (dippe) at room temperature (see the Experimental section and SI, Fig. S4-S5). As seen in **Figure 3**, the reaction of complex **d** with acetophenone **1a** does not proceed at low temperatures, formation of **3** was detected at high temperatures (90 ºC) and longer reaction times compared to the reaction time with the complex **c**, and the $^{31}P\{^1H\}$ NMR spectrum shows the appearance of two doublets between 71 and 65 ppm with $^2J_{P\text{-}P}$ = 70.36 Hz assigned to complex [(dippe)Ni($\eta^2$-C,O-$C_8H_8O$)] **3**.

The coordination of other ketones such as 4-fluoroacetophenone and 2-furyl-methyl-ketone to **c** was also assessed in THF-$d_8$ at 100 ºC during 24 h, allowing the complete formation of $\eta^2$-C,O complexes with formula [(dippe)Ni($\eta^2$-C,O-ketone)] (**3-5**), **Scheme 2**.

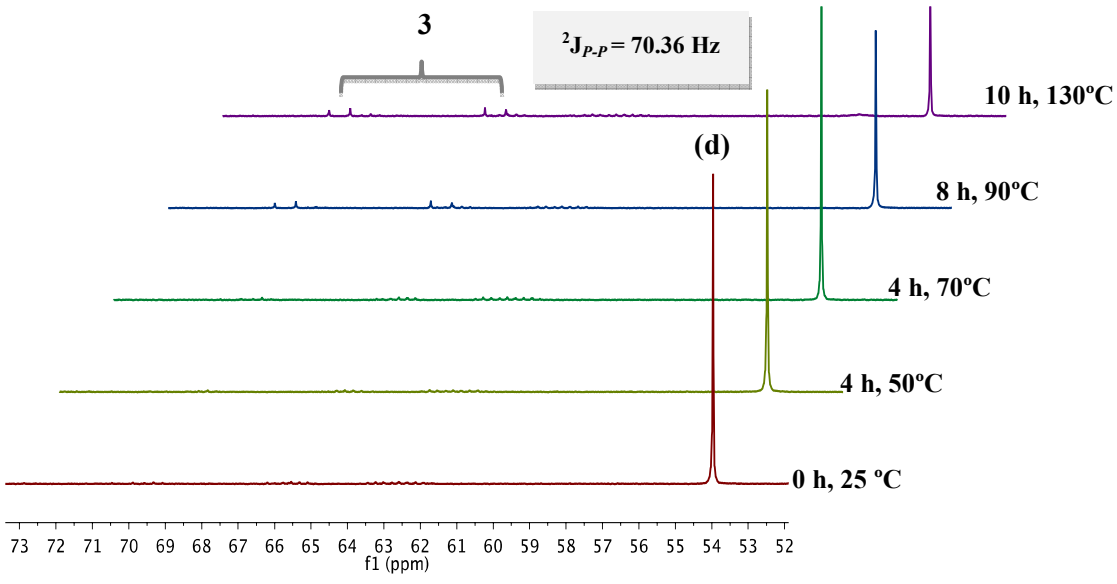


**Figure 3.** $^{31}P\{^1H\}$ NMR spectra of reaction between **d** and **1a** (THF-$d_8$, 121.32 MHz).

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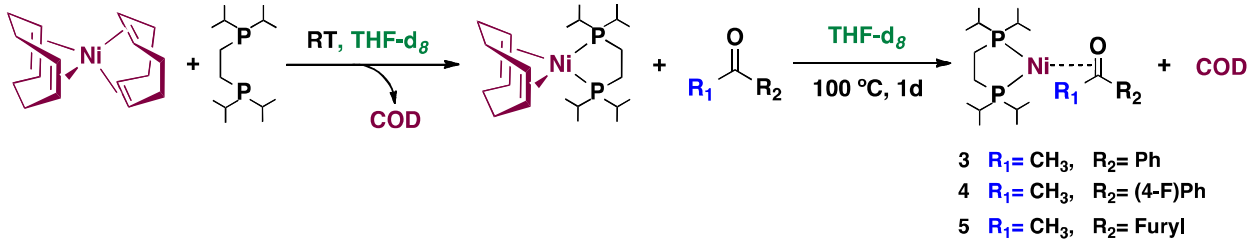
Complexes **3-5** typically display two doublets in the range 60-75 ppm with $^{2}J_{P\text{-}P}$ around 68-71 Hz. These doublets are characteristic of two non-equivalent phosphorus atoms coordinated to a metal center and the magnitude of the $^{2}J_{P\text{-}P}$ characteristic of coordination to a Ni(0) center (see the Experimental Section and SI, Fig. S6-S14).[20]

**Scheme 2. Formation of [(dippe)Ni($\eta^2$-C,O-ketone)] complexes 3-5**




With these results, we decided to explore the possibility that the phosphine-nickel(0) derivatives could activate ethanol and possibly generate hydride species that would be active in the base-free transfer hydrogenation process. Additionally, to optimize the hydrogenation reaction conditions and explore the catalytic activity of our Ni catalyst, several nickel phosphine complexes **(c)** – **(f)** were prepared following the method of Freund *et al*.[21] The complexes were isolated as brown or yellow solids in good yields (79 % - 92 %) and characterized by $^{1}H$ and $^{31}P\{^{1}H\}$ NMR spectroscopy. The corresponding signals are consistent with experimental values reported from the literature[21] (see Supporting Information). **Scheme 3** shows the complexes used in TH of acetophenone.

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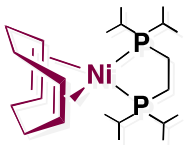
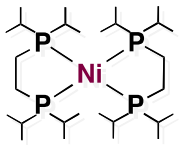
**Scheme 3. Phosphine Nickel Complexes evaluated in Transfer Hydrogenation Catalysis**



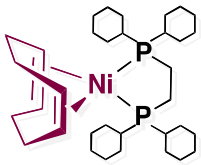

**[(dippe)Ni(COD)]**

**(c)**



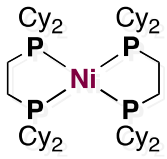

**[(dippe)$_2$Ni]**

**(d)**




**[(dcype)Ni(COD)]**

**(e)**




**[(dcype)$_2$Ni]**

**(f)**

When using 2 mol % of Ni catalyst for 12 h and 130 ºC, not conversion of acetophenone was observed in all cases (**Figure 4**). The complex [(dippe)Ni(COD)] **(c)** displayed similar activity as complex [(dcype)Ni(COD)] **(e)** to yield **2a** in 78 % and 95 % for 24 h, respectively, as seen in **Figure 4**. On the other hand, complexes [(dippe)$_2$Ni] (**d**) and [(dcype)$_2$Ni] (**f**) were also tested, but they were found to be less effective at 24 h. Only when increasing the reaction time to 36 h were some acceptable yields observed (**Figure 4**). It is important to note that 99 % yield of **2a** was observed after 36 h using the pre-catalyst (**e**) and a lower conversion was achieved with (**c**) (90 %). Due to the relatively high temperature of reaction and the induction period up until 24 h, selected experiments were performed at 36 h using the mercury drop test to confirm the homogeneity of the system (see SI, Table S1) and no significant differences in yields of **2a** were observed. These results suggest that nickel catalyst was performed by molecular nickel complexes and not by nickel nanoparticles.

A decrease in catalyst load to 1 mol % resulted in a significant decrement to produce **2a** in moderate yields (52 % to 72 %) at 48 h and 130 ºC (**Figure 5**). A catalytic load of 1 mol % turned out to be ineffective at 36 h; consequently, the most efficient conditions for hydrogenation

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of acetophenone are 2 % mol of [(dcype)Ni(COD)] **(e)**, 130 ºC, and 36 h using ethanol as the hydrogen source and solvent.

Considering these optimized conditions, we turned our attention in the TH of challenging aliphatic, alkyl-aryl and diaryl ketones, which are difficult to reduce by other nickel catalysts[8b, 8g, 8k] to obtain the corresponding secondary alcohols (**Table 3**).

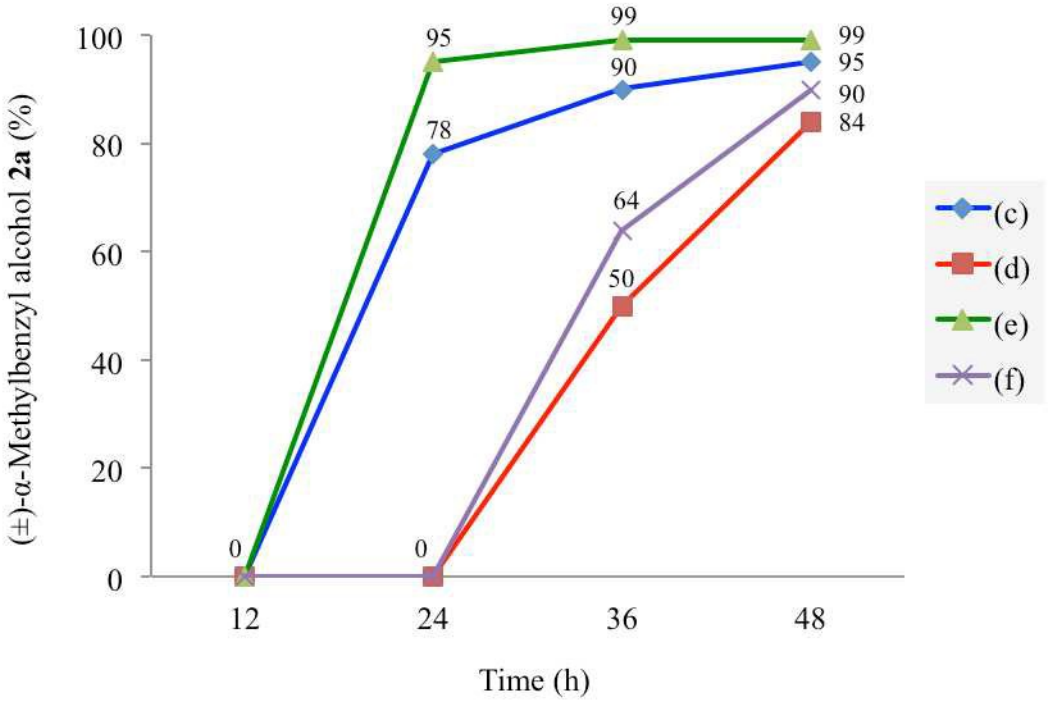


**Figure 4.** Activity of different nickel pre-catalysts at 130 ºC.

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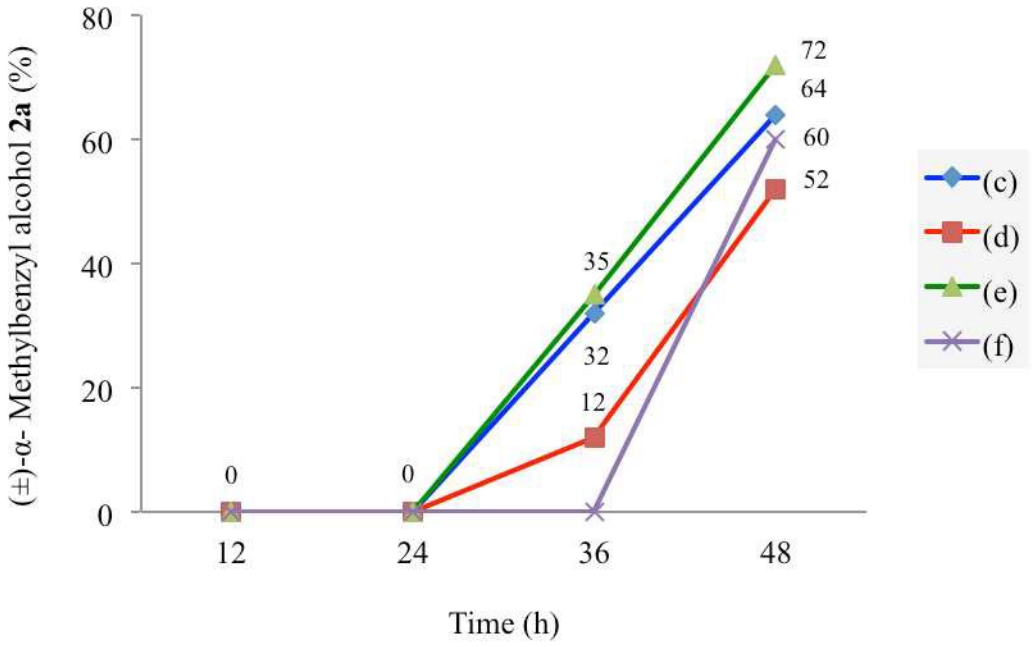


**Figure 5.** Activity of different nickel pre-catalysts using lower catalyst load at 130 ºC.

Key results for the substrate screening are shown in **Table 3.** Complex **(e)** catalyzed hydrogenation of acetophenone to 1-phenylethanol with 99 % conversion at 130 ºC and 36 h. (entry 1). The yields were also high with the use of acetophenones with electron-donor and electron-withdrawing substituents (entries 2-4). The details of percent yields, TONs and TOFs are given in **Table 3**.

Likewise, good to excellent yields were achieved for the transfer hydrogenation of diaryl ketones, (entries 6-7). In the case of heteroaromatic ketones such as 2-furyl-methyl-ketone and di-(2-pyridyl) ketone, yields of 99 % and 95 % were obtained for the secondary alcohol products 1-(furan-2-yl) ethanol and di(pyridine-3-yl)methanol, respectively (entries 7-8).

Similarly, the use of aliphatic ketones such as 2-adamantanone and cyclohexanone gave the corresponding secondary alcohols in excellent yields of 98 % (entries 9-10). Interestingly, under

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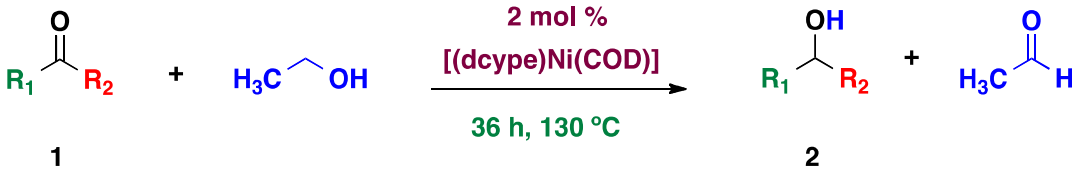
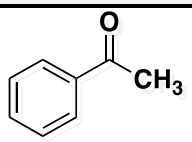
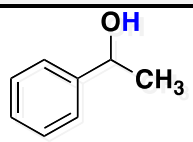
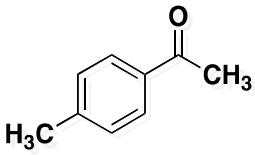
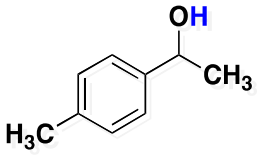
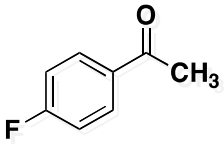
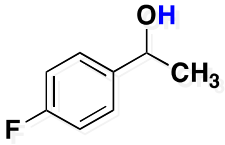
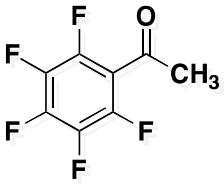
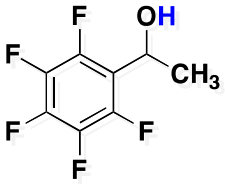
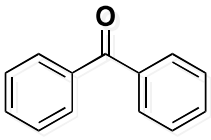
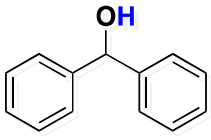
the same reaction conditions, benzyl shows 100 % conversion but 65 % selectivity to 1,2-diphenylethane-1,2-diol (entry 11), 29 % of 1,2-diphenyl ethane, and 6 % of 1,2-diphenyl ethanol (see SI, Fig. S35-S38). To the best of our knowledge, a Ni-catalyzed TH of ketones using ethanol as the hydrogen donor and solvent has not been reported so far.[8]

**Table 3. Scope of substrates** [a]




| Entry | Ketone (1) | Alcohol (2) | Yield (%) | TON | TOF ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 |  |  | 99 | 50 | 1.5 |
| 2 |  |  | 98 | 49 | 1.4 |
| 3 |  |  | 96 | 48 | 1.3 |
| 4 [b] |  |  | 99 | 50 | 1.5 |
| 5 |  |  | 99 | 50 | 1.5 |

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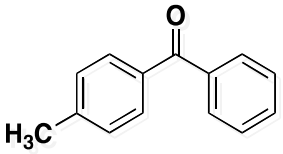
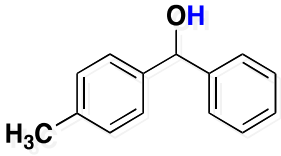
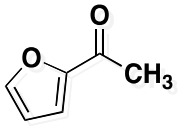
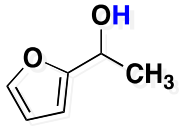
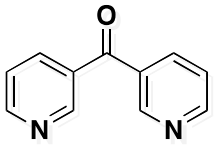
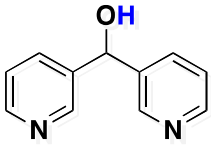
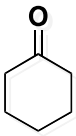
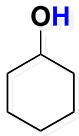
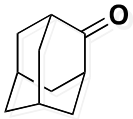
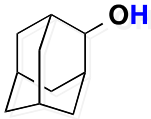
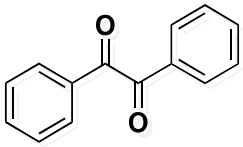
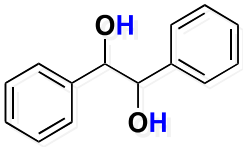
| | | | | | |
|---|---|---|---|---|---|
| 6 |  |  | 98 | 49 | 1.4 |
| 7 |  |  | 99 | 50 | 1.5 |
| 8 |  |  | 95 | 48 | 1.3 |
| 9 |  |  | 98 | 49 | 1.4 |
| 10 |  |  | 99 | 50 | 1.5 |
| 11 |  |  | 65 | 33 | 1 |

[a] **Carbonyl compound** (1.1 mmol), **ethanol** (119.88 mmol, 7 mL), **[(dcype)Ni(COD)]** (0.022 mmol); Conversion and yields were determined by GC-MS. [b] Reaction carried out at 150 ºC.

At the beginning of the reaction ethanol was consumed to produce acetaldehyde during the induction period (12-24 h), then ethyl-acetate began to be produced to yield a final (1:1) ratio. Thus, we believe the induction period is associated with the production of hydrides involved in catalysis, and then acetaldehyde reacts with ethanol to yield ethyl-acetate with hydrogen release (see SI, Scheme1). [4h, 3f]

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A comprehensive mechanistic proposal that illustrates the TH reaction of ketones using low-valent nickel is included in the SI section, it considers the results obtained herein and closely reports on similar transfer hydrogenation process [11c, 17, 18] (see SI, **Scheme 1**).

## 3. CONCLUSIONS

In summary, we report an easily accessible, inexpensive, and highly active Ni catalysts for the homogeneous hydrogenation of C=O bonds to selectively produce alcohols. The used chelating phosphines with electron-donor ligands allowed a fine-tuning of the catalyst's performance. The best catalytic precursor [(dcype)Ni(COD)] operated under relative mild conditions and addresses a broad substrate scope, covering alkyl-, aryl-, and aryl, alkyl- ketones. The transfer hydrogenation of C=O bonds using ethanol as the hydrogen donor and solvent proceeded with high conversion and selectivity. Current investigations are underway on further mechanistic details and the development of the enantio-selective version of this transfer hydrogenation.

## 4. EXPERIMENTAL SECTION

Unless otherwise noted, all manipulations were performed using standard Schlenk techniques in an inert-gas/vacuum double manifold or under an argon atmosphere (Praxair 99.998) in an MBraun UniLab glovebox (<1 ppm $H_2O$ and $O_2$). All liquid reagents were purchased as reagent grade and were degassed before use. All ketones and $[Ni(COD)_2]$ were purchased from Aldrich and stored in a glovebox for their use. The nickel (I) complexes $[(P\text{-}P)Ni(\mu\text{-}H)]_2$ (P-P = chelating phosphine ligand) were prepared from a *n*-hexane slurry of $[(P\text{-}P)NiCl_2]$ using Super-Hydride ($LiHBEt_3$), according to the reported procedure.[19] The solvents were dried using standard techniques and stored in the glovebox before use. Deuterated solvents were purchased from

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Cambridge Isotope Laboratories and were stored under 4 Å molecular sieves for 24 h before use. NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer unless otherwise noted. $^{1}H$ NMR spectra (δ parts per million) are reported relative to the residual protio-solvent. $^{13}C\{^{1}H\}$ spectra give the characteristic carbon signal of each solvent. $^{31}P\{^{1}H\}$ NMR chemical shifts (δ parts per million) are reported relative to external 85% $H_3PO_4$. Coupling constants (*J* values) are given in Hz. The following abbreviations are used for the NMR data: s = singlet; d = doublet; t = triplet, m = multiplet and br=broad. GC-MS determinations were performed using an Agilent Technologies G3171A equipped with a column: 5 % phenylmethylsilicone, 30 m * .25 mm * .25 μm. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of the reduction products were obtained in $CDCl_3$. Catalytic experiments were carried out in a 100 mL stainless steel Parr, T315SS reactor. Elemental analyses (EAs) were also performed by USAI-UNAM using a PerkinElmer microanalizer 2400. EA where determined at USAII-FQ-UNAM.

**4.1. Preparation [(dippe)Ni(COD)] (c):** A yellow solution of $[Ni(COD)_2]$ (0.109 mmol, 30 mg) in dried THF (3 mL) was added to dippe [1,2-bis(diisopropylphosphino)ethane] (0.109 mmol, 28 mg). After the dippe was dissolved, the solution was stirred for 30 minutes at room temperature. The solvent was evaporated and further dried for six hours under vacuum to yield a brown solid. Yield: 37.4 mg (89 %). $^{1}H$ NMR (300 MHz, THF-$d_8$, r.t.): δ = 4.12 (s, H(**b**), H(**b'**), CH-COD), 2.11 (m, H(**a**), H(**a'**), $CH_2$-COD), δ = 1.97 (m, H(**e, e'**) P-$CH_2$), 2.01-0.5 (m, H(**c, c'**), H(**d, d'**), *i*Pr: CH, $CH_3$). $^{31}P\{^{1}H\}$ NMR (121.32 MHz, THF-$d_8$, r.t.) δ = 70.18 (s).

**4.2. Preparation [(dippe)$_2$Ni] (d):** Similarly to the preparation for compound **c** (*vide supra*), the reaction between $[Ni(COD)_2]$ (0.109 mmol, 30 mg) in dried THF (3 mL) was added to the liquid dippe: [1,2-bis(diisopropylphosphino)ethane] (0.218 mmol, 57.22 mg). After the dippe had dissolved, the solution was stirred for 30 minutes at room temperature. The solvent was then

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evaporated and dried for six hours under vacuum to obtain a brown solid. Yield: 58.54 mg (92 %). $^{1}$H NMR (300 MHz, THF-$d_8$, r.t.): δ = 1.97 (m, H(**a, a'**) P-$CH_2$), 2.01-0.87 (m, H(**b, b'**), H(**c, c'**), *i*Pr: CH, $CH_3$). $^{31}P\{^{1}H\}$ NMR (121.32 MHz, THF-$d_8$, r.t.). δ = 53.96 (s).

**4.3. Preparation [(dcype)Ni(COD)] (e):** The nickel (0) complex [(dcype)Ni(COD)] was prepared following the method of Freund *et al*.[21] Solid dcype (101 mg, 0.24 mmol) was added in one portion to a yellow solution of [$Ni(COD)_2$] (66 mg, 0.24 mmol) that was stirred in THF (3 mL) at room temperature. After dissolution of the dcype, the yellow reaction mixture was stored for two days at -28 ºC. Then, the formed yellow crystals were isolated by decantation, washed with hexanes (6 mL), and dried for six hours under vacuum. Yield: 115 mg (82 %). The resulting solid was analyzed by NMR spectroscopy: $^{1}$H NMR (300 MHz, THF-$d_8$, r.t.): δ = 4.3 (s, H(**b**), H(**b'**), CH-COD), 2.53 (m, H(**a**), H(**a'**), $CH_2$-COD), 2.01-1.83 (m, H(**c, c'**), H(**d, d'**), Cy: CH, $CH_2$), 1.62 (m, H(**e, e'**) P-$CH_2$). $^{31}P\{^{1}H\}$ NMR (121.32 MHz, THF-$d_8$, r.t.) δ = 60.

**4.4. Preparation [$(dcype)_2Ni$] (f).** Similar to the preparation of compound (**d**), the reaction between [$Ni(COD)_2$] (0.109 mmol, 30 mg) in THF (3 mL) was added to a solid dcype [1,2-bis(dicyclohexylphosphino)ethane] (0.218 mmol, 92.18 mg). After the dcype was dissolved, the solution was stirred for 30 minutes at room temperature. The solvent was then evaporated and dried for six hours under vacuum to produce a brown solid. Yield: 77.88 mg (79 %). $^{1}$H NMR (300 MHz, THF-$d_8$, r.t.): δ = 2.41-1.05 (m, H(**a, a'**), H(**b, b'**) $CH_2$, CH-Cy), 1.62 (m, H(**c, c'**) P-$CH_2$). $^{31}P\{^{1}H\}$ NMR (121.32 MHz, THF-$d_8$, r.t.) δ = 43.8.

**4.5. Preparation [(dippe)Ni($\eta^2$-C,O-Acetophenone)] (3):** A brown solution of [(dippe)Ni(COD)] (0.145 mmol, 62.23 mg) in THF (5 mL) was added to acetophenone ($C_8H_8O$) (0.145 mmol, 17.40 mg). The resulting dark brown reaction mixture was heated to 100 ºC and

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stirred during 1 d. The solvent was then evaporated and dried during six hours to give a brown solid. Yield: 46.04 mg (72 %). NMR spectroscopy: $^{1}$H NMR (300 MHz, THF-$d_8$, r.t.): δ = 7.97 (d, H(**b**), H(**b'**) CH-Ph), 7.54 (t, H(**d**), CH-Ph), 7.44 (t, H(**c, c'**), CH-Ph), 2.53 (s, H(**a)** $CH_3$), 2.2-0.5 (m, H(**e, e'**), H(**f, f'**), H(**g, g'**) dippe: CH, $CH_2$, $CH_3$). $^{31}$P{$^{1}$H} NMR (121.32 MHz, THF-$d_8$, r.t.) δ = 70.20 (d, $^{2}J_{P\text{-}P}$ = 70.36 Hz), δ = 66.50 (d, $^{2}J_{P\text{-}P}$ = 70.36 Hz), selected IR: ν (C=O) 1658.39 cm $^{-1}$.

**4.6. Preparation [(dippe)Ni(η$^2$-C,O-4-Fluoroacetophenone)] (4):** Similar to the preparation of compound **(3)** (*vide supra*), a brown solution of [(dippe)Ni(COD)] (0.108 mmol, 46.56 mg) in THF (5 mL) was added to a liquid 4-Fluoroacetophenone ($C_8H_7FO$) (0.108 mmol, 15 mg). The resulting dark brown reaction mixture was heated to 100 ºC and stirred for 1 d. The solvent was then evaporated and dried for six hours under vacuum to produce a brown solid. Yield: 39.42 mg (72 %). Anal. Calcd. for (**4**), $C_{22}H_{39}NiOP_2F$: C, 57.5; H, 8.5; O, 3.5. Exp: C, 57.3; H, 8.6; O, 3.5. NMR spectroscopy: $^{1}$H NMR (300 MHz, THF-$d_8$, r.t.): δ = 7.19 (t, H(**b**), H(**b'**) CH-Ph), 6.76 (t, H(**c**), H(**c´**) CH-Ph), 2.52 (s, H(**a)** $CH_3$), 1.48-0.43 (m, H(**d, d'**), H(**e, e'**), H(**f, f'**) dippe: CH, $CH_2$, $CH_3$). $^{31}$P{$^{1}$H} NMR (121.32 MHz, THF-$d_8$, r.t.) δ = 70.20 (d, $^{2}J_{P\text{-}P}$ = 70.36 Hz), δ = 66.40 (d, $^{2}J_{P\text{-}P}$ = 70.36 Hz), selected IR: ν (C=O) 1683.82 cm $^{-1}$.

**4.7. Preparation [(dippe)Ni(η$^2$C,O-2-furyl-Methyl-Ketone)] (5):** Similar to the preparation of compound **(3)** (*vide supra*), a brown solution of [(dippe)Ni(COD)] (0.109 mmol, 46.71 mg) in THF (5 mL) was added to a liquid 2-furyl-Methyl-Ketone ($C_6H_6O$) (0.109 mmol, 12 mg). The resulting dark brown reaction mixture was heated to 100 ºC and stirred for 1 d. Then, the solvent was evaporated and dried for six hours under vacuum to produce a brown solid. Yield: 35.26 mg (75 %). Anal. Calcd. for (**5**), $C_{20}H_{38}NiO_2P_2$: C, 55.7; H, 6.9; O, 7.4. Exp: C, 56.0; H, 6.8; O, 7.2.

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$^{1}$H NMR (300 MHz, THF-$d_8$, r.t.): δ = 7.25 (br, H(**d**), CH-furyl), 7.17 (d, H(**b**), CH-furyl), 6.56 (br, H(**c**) CH-furyl), 2.38 (s, H(**a**) $CH_3$), 2.2-0.6 (m, H(**e, e'**), H(**f, f'**), H(**g, g'**) dippe: CH, $CH_2$, $CH_3$). $^{31}$P{$^{1}$H} NMR (121.32 MHz, THF-$d_8$, r.t.) δ = 69.8 (d, $^{2}J_{P-P}$ = 69.15 Hz), δ = 68.9 (d, $^{2}J_{P-P}$ = 69.15 Hz), selected IR: ν (C=O) 1675.82 cm $^{-1}$.

**4.8. Preparation α-Methylbenzyl alcohol (2a):** The reaction was made in a 100 mL Parr reactor typically charged with an amount of [(dcype)Ni(COD)] (0.022 mmol, 12.94 mg), $C_8H_8O$ = Acetophenone **1a** (1.1 mmol, 130.8 mg) and ethanol (119.88 mmol, 7 mL). The solution was heated with vigorous stirring at 130 ºC for 36 h (entry 1, **Table 3**). After this time, the reactor was opened in a well-vented hood prior to workup. Orange or yellow colored solutions were formed. During the reaction monitoring, yields and conversions were determined by GC-MS chromatography. Afterwards, the solvent was evaporated under vacuum, and the product was characterized by $^{1}$H and $^{13}$C{$^{1}$H} NMR. $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 7.32 (H(**d, d'**), (H(**e, e'**), (H(**f**), CH-Phenyl), 4.85 (m, $J_{H-H}$ = 6 Hz, H(**b**), CH), 3.63 (br, H(**a**), OH), 1.44 (H(c), $CH_3$). $^{13}$C{$^{1}$H} NMR (75.36 MHz, THF-$d_8$, r.t.): δ = 146.11 (s, C(**c**), **C**-Phenyl), 128.42 (s, C(**f**), CH-aromatic), 127.30 (s, C(**e**), CH-aromatic), 125.48 (s, C(**d**), CH-aromatic), 70.13 (s, C(**a**), **C**H-OH), 25.25 (s, C(**b**), $CH_3$).

**4.9. Catalytic Studies.** All reactions were made in a 100 mL Parr reactor typically charged with [(dcype)Ni(COD)] (0.022 mmol) and the corresponding ketone (1.1 mmol), [(dcype)Ni(COD)] (0.022 mmol) and ethanol (119.88 mmol, 7 mL). The solution was heated with vigorous stirring at 130 ºC for the corresponding reaction time. After this, the reactor was opened in a well-vented hood prior to workup. Orange or yellow colored solutions were formed. During the reaction monitoring, yields and conversions were determined by GC-MS chromatography. Products and

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intermediates were characterized by $^{1}H$ NMR and $^{13}C\{^{1}H\}$ NMR after column chromatography purification using n-hexanes/THF mixtures using a silica gel.

**4.10. Mercury Drop Test.** Following the procedure described in **Table 2** (entry 4 and 7), these reactions were prepared, and one drop of elemental Hg was added to the reaction mixture. At the end of each run, the corresponding solution was filtered over celite and analyzed by CG-MS.

## ASSOCIATED CONTENT

- **Supporting Information available.** Includes complete experimental procedures, selected IR, NMR spectra, and GC-MS determinations of all products. This material is available free of charge via the Internet.

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## ACKNOWLEDGMENTS

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