



Editor choice paper

Selective hydrogenation of the C=O bond of ketones using Ni(0) complexes with a chelating bisphosphine

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ABSTRACT

The nickel complexes [(dippe)Ni(η^2 -O,C-benzophenone)] (**2**), [(dippe)Ni(η^2 -O,C-4-methylbenzophenone)] (**3**), [(dippe)Ni(η^2 -O,C-acetophenone)] (**4**), [(dippe)Ni(η^2 -O,C-acetone)] (**5**), [(dippe)Ni(η^2 -O,C-fluorenone)] (**6**), [(dippe)Ni(η^2 -O,C-di(2-pyridyl) ketone)] (**7a**), [(dippe)Ni(κ^2 -N,N-di(2-pyridyl) ketone)] (**7b**), [(dippe)Ni(κ^2 -O,O-2,2'-pyridil)] (**8**), [(dippe)Ni(κ^2 -O,O-benzil)] (**9a**), and [(dippe)Ni]₂(η^2 -O,C-benzil)] (**9b**) were prepared by the reaction of [(dippe)Ni(μ -H)]₂ (**1**) with the corresponding ketone or 1,2-diketone at room temperature. The structures of compounds **2**, **6**, **9a** and **9b** were confirmed by X-ray crystallography. The selective hydrogenation of the two types of substrates was undertaken using H₂, giving high conversions to the corresponding reduction products, either alcohols or alkanes. Tunable reaction conditions to promote the partial or total hydrogenation (hydrogenolysis) of the substrates are described.

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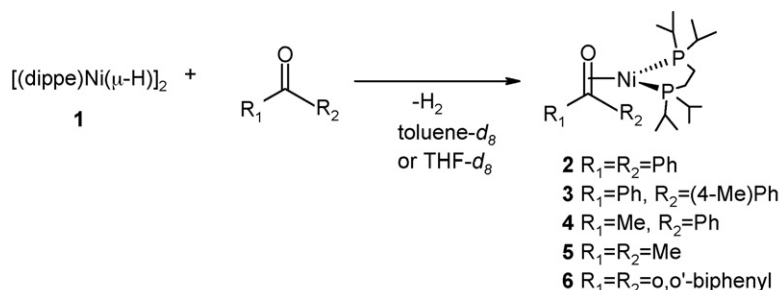
1. Introduction

A variety of organic substrates containing the CO group are important in synthesis since they can be transformed into many other different functional groups [1]. Partial and total reduction of the carbonyl group serve as important examples of these transformations as they give the corresponding alcohols or alkanes, but preparative methods that may drive these reactions selectively have been seldom optimized in the past. In the first case, the partial reduction has been observed to take place only when an excess of a conventional reducing agent such as LiAlH₄, NaBH₄, Al(OPrⁱ)₃, or EtSiH are used and the reaction is followed by a hydrolysis [2]. In the second case, Raney-nickel [3] as well as Wolff-Kishner and Clemmensen reductions [4] are typically used, although the tolerance to other functional groups in the target molecules is an issue that remains challenging.

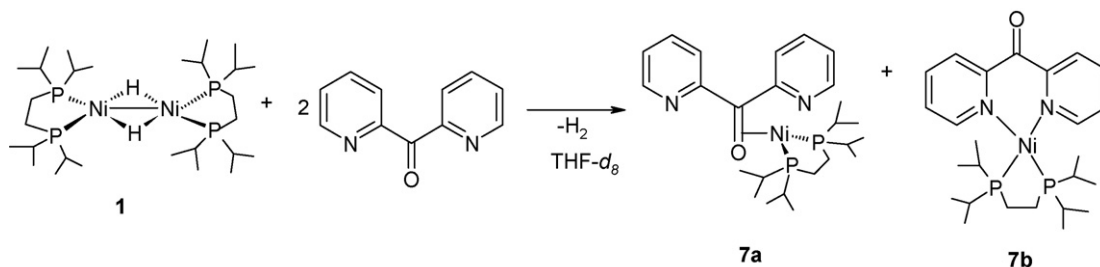
Industrially, large-scale processes that involve the catalytic hydrogenation of numerous organic functions are operated worldwide [5]. The metal catalysts and the processes in which they participate can be classified depending on the hydrogen source that is used. A first set of reactions can be described as *direct hydrogenations*

if molecular hydrogen is used as the reducing agent, whereas a second set can be described as *transfer hydrogenations* whenever an organic compound is used as the hydrogen source. A seminal contribution to the latter set was made by Noyori and co-workers who developed a homogeneous asymmetric transfer hydrogenation system employing complexes of the type [RuCl₂(P–P)(1,2-diamine)], where (P–P) is a chiral bisphosphine [6]. Currently, ruthenium is still the most widely used metal for this reaction [7], but similar reactivities have also been observed with other compounds using iridium [8] and rhodium [9]. Shvo's ruthenium catalyst has been used in a broad range of hydrogen transfer reductions, including carbonyl reductions [10]. Recently, Baratta et al. reported the use of osmium complexes with the formula, [OsCl₂P₂(Pyme)] (P = phosphine, Pyme = 1-(pyridin-2-yl)methanamine), as active catalysts for the reduction of ketones in basic alcohol media [11], and an effective iron-based catalyst was reported by Casey for the selective hydrogenation of aldehydes and ketones under mild conditions [12]. The use of nickel in homogeneous hydrogenation of ketones is relatively scarce; however, heterogeneous examples are rather common, but not always well understood [13]. With the aim of developing inexpensive and efficient catalysts, we herein disclose the use of bisphosphine-nickel(0) complexes which are active catalysts for the homogeneous hydrogenation of mono- and diketones, giving their corresponding alcohols or alkanes in high conversions and tunable conditions.

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Scheme 1. Formation of $[(\text{dippe})\text{Ni}(\eta^2\text{-C,O-ketone})]$ complexes **2–6**.



Scheme 2. Formation of $[(\text{dippe})\text{Ni}(\eta^2\text{-C,O-di-2-pyridyl ketone})]$ (**7a**) and $[(\text{dippe})\text{Ni}(\kappa^2\text{-N,N-di-2-pyridyl ketone})]$ (**7b**).

2. Results and discussion

2.1. Reactivity of $[(\text{dippe})\text{Ni}(\mu\text{-H})_2]$ **1** with monoketones

As has been reported previously, the nickel(I) dimer **1** can be used to cleave the C–C [14], C–S [15], and C–CN [16] bonds of a variety of substrates, following reductive elimination of H_2 and *in situ* generation of the reactive nickel(0) moiety, $[(\text{dippe})\text{Ni}^0]$. **1** has been found to react with monoketones at room temperature in toluene- d_8 and THF- d_8 solutions, allowing the formation of stable $\eta^2\text{-C,O}$ complexes with formula $[(\text{dippe})\text{Ni}(\eta^2\text{-C,O-ketone})]$ (**2–6**). Scheme 1 summarizes the reactions that take place.

Complexes **2–6** typically display two doublets in the range 60–72 ppm with P–P coupling constants in the range of 66–77 Hz in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The presence of the doublets is characteristic of two non-equivalent phosphorus atoms coordinated to a metal center, the magnitude of the coupling constants being indicative of $^2J_{\text{P-P}}$ through a Ni(0) center, i.e. $[(\text{P-P})\text{Ni}(\eta^2\text{-C,O-ketone})]$. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the same complexes exhibited a doublet of doublets in the range δ 82–87 for the carbon in the coordinated C=O bond, which appeared shifted to *high-field* when compared with the corresponding carbonyl signal in the free ketones (observed as a singlet in the region of δ 195–206). The changes in chemical shifts and multiplicities are consistent with coordination of the carbonyl moiety to nickel(0). It is worth noting that a different reaction outcome was observed in the reaction of **1** with di(2-pyridyl) ketone, which yielded two different products, the expected $[(\text{dippe})\text{Ni}(\eta^2\text{-O,C-di(2-pyridyl) ketone})]$ (**7a**) (70%) and the unexpected $[(\text{dippe})\text{Ni}(\kappa^2\text{-N,N-di(2-pyridyl) ketone})]$ (**7b**) (30%). The latter compound corresponds to a bis-*N,N* chelate complex whose structure is illustrated in Scheme 2. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum compound **7a** displayed two doublets at δ 63.9 and 72.4 with $^2J_{\text{P-P}} = 57.6$ Hz.¹⁶ **7b** exhibited a broad singlet centered at δ 116.7 arising from the equivalence in the phosphorus atoms coordinated to the nickel(0) center.

X-ray quality crystals for complex **2** were grown from a concentrated solution in benzene at room temperature. The ORTEP representation of this compound is presented in Fig. 1 and the

complete crystallographic and structure refinement data are summarized in Table 1. The geometry around the Ni center corresponds to square planar and shows a considerable lengthening of the η^2 -coordinated carbonyl group (1.343(2) Å) vs. that of the free ligand (1.223 Å) [17]. The NiCO plane is nearly coplanar with the NiP₂ plane (4.2°). The almost equidistant Ni–P1 and Ni–P2 bond lengths suggest that the Ni(dippe) fragment is symmetrically bonded. Similarly, an X-ray structure of fluorenone adduct **6** shows a lengthened C–O bond to 1.326(5) Å, compared with 1.222 Å in the free ketone (Fig. 2) [18], and the angle between the NiP₂ and NiCO planes is 3.0°. A closely related structure has been reported by Hillhouse and coworkers [19].

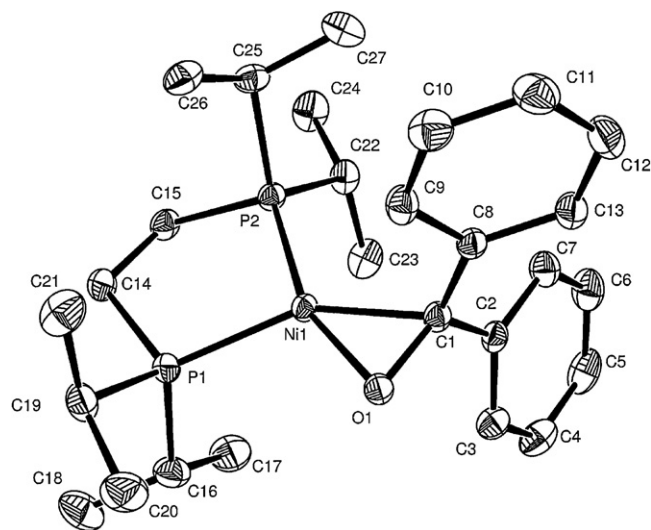


Fig. 1. ORTEP representation of **2** showing thermal ellipsoids at the 30% probability level. Selected bond distances (Å): O1–C1 (1.343(2)), Ni1–O1 (1.8549(11)), Ni1–C1 (1.9734(16)), Ni1–P1 (2.1722(5)), Ni1–P2 (2.1461(5)). Selected bond angles (deg): O1–Ni1–C1 (40.94(6)), O1–Ni1–P1 (109.42(4)), C1–Ni1–P1 (150.15(5)), O1–Ni1–P2 (159.21(4)), C1–Ni1–P2 (118.28(5)), P1–Ni1–P2 (91.267(18)).

Table 1
Summary of crystallographic data for compounds **2**, **6**, **9a** and **9b**.

Empirical formula	2	6	9a	9b
	P ₂ C ₂₇ H ₄₂ NiO	C ₂₇ H ₄₀ NiOP ₂	C ₂₈ H ₄₂ Ni O ₂ P ₂	C ₄₂ H ₇₄ Ni ₂ O ₂ P ₄
Formula weight	503.26	501.24	531.27	852.31
Temperature	193(2) K	193(2) K	173(2) K	100(2) K
Wavelength	0.71073 Å ³	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Trigonal	Orthorhombic	Monoclinic	Monoclinic
Space group	P3(2)	Pbca	C2/c	Cc
Unit cell dimen.	<i>a</i> = 10.1065(4) Å <i>b</i> = 10.1065(4) Å <i>c</i> = 22.9752(12) Å α = 90° β = 90° γ = 120°	<i>a</i> = 9.3568(5) Å <i>b</i> = 17.1854(9) Å <i>c</i> = 32.1948(16) Å α = 90° β = 90° γ = 90°	<i>a</i> = 27.766(3) Å <i>b</i> = 15.1846(16) Å <i>c</i> = 22.811(2) Å α = 90° β = 120.496(2)° γ = 90°	<i>a</i> = 15.063(3) Å <i>b</i> = 17.403(3) Å <i>c</i> = 17.427(3) Å α = 90° β = 106.155(3)° γ = 90°
Volume	2032.32(16) Å ³	5176.9(5) Å ³	8287.0(15) Å ³	4387.9(14) Å ³
Z	3	8	12	4
Density (calculated)	1.234 Mg/m ³	1.286 Mg/m ³	1.277 Mg/m ³	1.290 Mg/m ³
Absorption coefficient	0.850 mm ⁻¹	0.890 mm ⁻¹	0.840 mm ⁻¹	1.037 mm ⁻¹
F(000)	810	2144	3408	1832
Crystal size	0.20 mm × 0.26 mm × 0.28 mm	0.28 mm × 0.24 mm × 0.06 mm	0.152 mm × 0.132 mm × 0.082 mm	0.18 mm × 0.14 mm × 0.11 mm
θ Range for data collection	2.33–28.29°	2.37–28.31°	1.64–25.50°	1.83–25.03°
Index ranges	–13 ≤ <i>h</i> ≤ 7, –11 ≤ <i>k</i> ≤ 13, –30 ≤ <i>l</i> ≤ 30	–12 ≤ <i>h</i> ≤ 12, –22 ≤ <i>k</i> ≤ 22, –42 ≤ <i>l</i> ≤ 42	–33 ≤ <i>h</i> ≤ 33, –18 ≤ <i>k</i> ≤ 18, –27 ≤ <i>l</i> ≤ 27	–17 ≤ <i>h</i> ≤ 17, –20 ≤ <i>k</i> ≤ 20, –20 ≤ <i>l</i> ≤ 20
Reflections collected	13,360	59,661	39,094	20,872
Independent reflections	6371 [R(int) = 0.0172]	6420 [R(int) = 0.0816]	7669 [R(int) = 0.0836]	7732 [R(int) = 0.0545]
Completeness to theta	97.5%	99.6%	99.3%	99.8%
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-Squares on F ²	Full-matrix least-Squares on F ²
Data/restraints/parameters	6371/1/288	6420/0/287	7669/0/459	7732/2/398
Goodness-of-fit on F ²	1.035	1.253	1.017	0.861
Final R indices [I > 2σ(I)]	R1 = 0.0243, wR2 = 0.0547	R1 = 0.0887, wR2 = 0.1637	R1 = 0.0466, wR2 = 0.0987	R1 = 0.0616, wR2 = 0.1534
R indices (all data)	R1 = 0.0262, wR2 = 0.0554	R1 = 0.1149, wR2 = 0.1729	R1 = 0.0744, wR2 = 0.1088	R1 = 0.0705, wR2 = 0.1622
Largest diff. peak and hole	0.221 and –0.168 e Å ⁻³	0.829 and –0.941 e Å ⁻³	0.473 and –0.284 e Å ⁻³	2.139 and –0.605 e Å ⁻³

2.2. Reaction of [(dippe)Ni(μ-H)]₂ **1** with 1,2-diketones

The stoichiometric reaction of 2,2'-pyridil with **1** yielded Ni(CO)₄ as the main product (*caution, poisonous gas!*). The latter was obtained as a white crystalline powder at –78 °C. Its presence was accompanied by formation of decomposition products from compound **1**, as indicated in the ³¹P{¹H} NMR spectrum of the crude reaction mixture. The additional by-products present were characterized as [Ni(dippe)₂] (δ 52.5, s, 82%) and free dippe (δ 7.3, s,

14%). A minute amount of the nickel complex [(dippe)Ni(κ²-O,O-2,2'-pyridil)] (**8**) was also detected (δ 79.8, s, 1%). Use of 2 equiv. of 2,2'-pyridil resulted in the formation of **8** as the major product (Scheme 3), the structure of this complex is proposed in analogy to complex **9a** (*vide infra*).

In sharp contrast to 2,2'-pyridil, the equimolecular reaction of **1** with benzil yielded the complexes, [(dippe)Ni(κ²-O,O-benzil)] (**9a**) and [(dippe)Ni]₂(η²-C,O-benzil)] (**9b**) in a (1:1) ratio (Scheme 4). No decomposition or formation of Ni(CO)₄ was observed. The latter reaction is very susceptible to the stoichiometry employed, as the use of 2 equiv. of benzil resulted in the selective formation of **9a** over **9b**. A singlet for the diphosphine ligand was observed at δ 79.2 in the ³¹P{¹H} NMR spectrum for **9a**. The κ²-coordinated carbonyls were located as a triplet (³J_{C-P} = 3 Hz) at δ 145.2 by ¹³C{¹H} NMR spectroscopy. If an excess of **1** (1.5 equiv.) is used, the formation of **9b** was favored and a multiplet at δ 60.6 in the ³¹P{¹H} NMR spectrum was observed instead of the singlet described above for **9a**. The equivalent η²-coordinated carbonyls in **9b** were located at δ 93.6 in the ¹³C{¹H} NMR spectrum. Compound **9b** can be completely converted to **9a** by heating at 120 °C for 2 days in benzene-*d*₆ (Scheme 4).

Green crystals of **9a** suitable for X-ray diffraction were grown from a concentrated benzene solution at room temperature. The crystallographic and structure refinement data for this compound are also summarized in Table 1. The structure of **9a** shows a square planar geometry around the nickel(II) center as a result of formation of the κ²-O,O chelate (Fig. 3), with trans O–Ni–P geometries of O1–Ni1–P2 (176.35(7)°) and O2–Ni1–P1 (174.03(7)°). The NiP₂ plane and the Ni–O1–O2 plane lie at an angle of 4.5°. The C1–O1 (1.369(3) Å) and C2–O2 (1.363(3) Å) bond lengths appeared considerably longer than that of the same bond in the free ligand (1.21(2) Å),²⁰ due to reduction by the metal, along with the shortening of C1–C2 bond (1.364 vs 1.525 for the free ligand), both indicative of an alkenediolate moiety coordinated to the metal center.

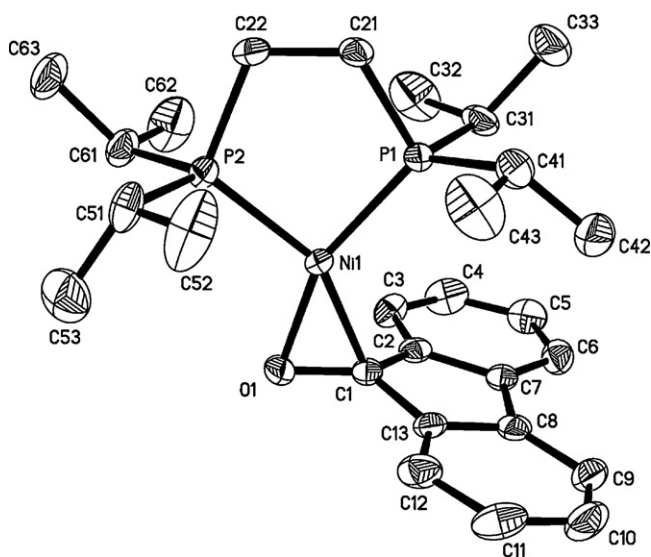
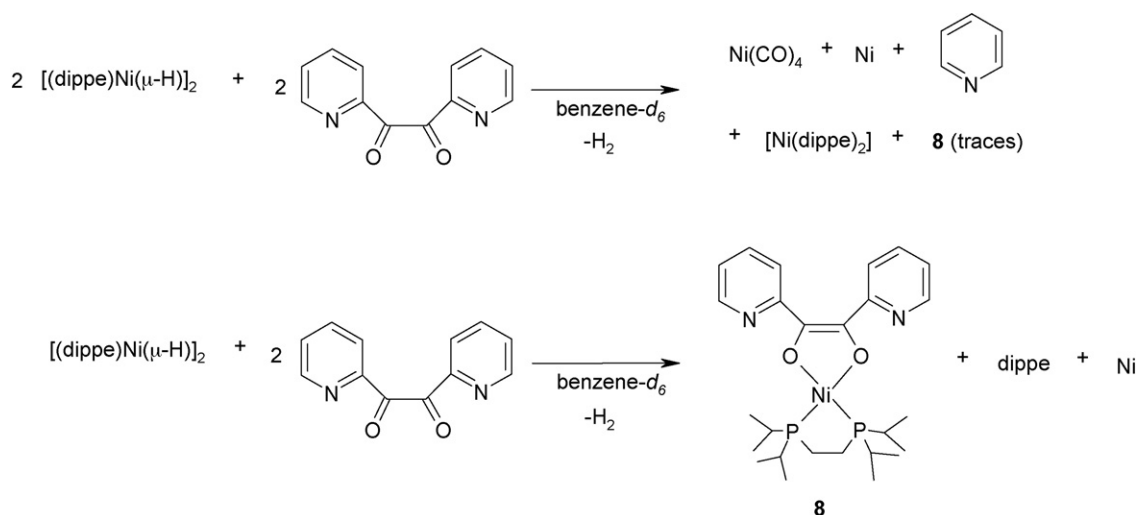


Fig. 2. ORTEP representation of **6** showing thermal ellipsoids at the 30% probability level. Selected bond distances (Å): O1–C14 (1.326(5)), Ni1–O1 (1.869(3)), Ni1–C1 (1.973(4)), Ni1–P1 (2.1436(11)), Ni1–P2 (2.1789(11)). Selected bond angles (deg): O1–Ni1–C1 (40.26(14)), O1–Ni1–P1 (156.36(9)), C1–Ni1–P1 (116.17(12)), O1–Ni–P2 (111.83(9)), C1–Ni–P2 (152.03(12)), P1–Ni–P2 (91.62(4)).



Scheme 3. Formation of [(dippe)Ni(η^2 -C,O-ketone)] complexes.

Orange crystals of complex **9b** were grown from a concentrated solution of benzene at room temperature and were also characterized by X-ray diffraction. The crystallographic and structure refinement data for **9b** are summarized in Table 1. The NiP₂ and NiCO planes are nearly coplanar (5.1–5.8°), consistent with square planar coordination as in **2** and **6** (Fig. 4). The O1–C15–C22–O2 (179.4°) and C16–C15–C22–C23 (176.9°) torsion angles indicate that both benzene moieties lie essentially in the same plane. Each carbonyl group appeared coordinated to a [(dippe)Ni⁰] fragment and thus, exhibited a mutually *anti* conformation. Also, they displayed similar C–O bond lengths (C15–O1, 1.347(8) Å; C22–O2, 1.357(8) Å) which are longer than those in benzil (1.21(2) Å) [20], although smaller than those encountered in **9a**. This lengthening is indicative of depletion of C–O bonding character as a result of back-donation from the [(dippe)Ni⁰] moieties.

2.3. Hydrogenation experiments

2.3.1. Stoichiometric reactions

The hydrogenations of benzophenone, di(2-pyridyl) ketone and benzil were performed in either toluene or THF solvent using 1 equiv. of **1** and 2 equiv. of mono-ketone, or 1 equiv. of **1** and 1 equiv. of the 1,2-diketone, under hydrogen (60 psi). The results obtained are summarized in Table 2.

As can be seen in Table 2, formation of the corresponding alcohol (partial hydrogenation product) or alkane (total hydrogenation product) depends on the reaction conditions. In particular, for benzophenone formation of diphenylmethanol was observed at 150 °C, although in low conversion (entry 1). Upon increasing the temperature to 250 °C, total reduction of the C=O bond was achieved, resulting in formation of diphenylmethane (entry 2). Using di(2-pyridyl) ketone, formation of the partial reduction product di-pyridin-2-yl-methanol (88%, entry 3) was observed after 12 h, longer reaction time (close to 100 h) allow the formation of the corresponding alkane (98%, entry 4). In the case of benzil (entry 5), heating to 150 °C for 12 h gave a mixture of products, whereas only 2-phenylacetophenone (100% yield) was observed after 48 h (entry 6; see also Scheme 5 *vide infra*). A thermal stability test at the different temperatures used was performed, and none of the ketone complexes exhibited any significant decomposition in the absence of H₂.

2.3.2. Catalytic hydrogenation reactions

Experiments were performed using a variety of reaction conditions, maintaining the concentration of the catalyst precursor **1**

constant at 2 mol%. The results obtained for this series of experiments are summarized in Table 3. Due to the relatively high temperatures used in some of the catalytic runs, selected experiments were performed using the mercury drop test to confirm the homogeneity of the system (see experimental section). No significant differences in conversions were observed, and the color of the solutions was always yellow at the end of each experiment. No black residues characteristic of metallic nickel or nanoparticles [21] of such metal were observed.

Hydrogenation of benzophenone at 250 °C under 60 psi of H₂ resulted in formation of a small amount of diphenylmethane (25%) after 72 h (Table 3, entry 1). Its yield was increased to 72% by heating the mixture to 270 °C (entries 2 and 3). Hydrogenation of acetophenone at 250 °C, resulted in almost complete formation of ethylbenzene as the sole product (98%), after 96 h (entry 4). The apparently greater reactivity observed for acetophenone can be attributed to the smaller steric hindrance of the methyl substituent as opposed to the phenyl rings. Reduction of 4-methylbenzophenone at 250 °C for 96 h or 270 °C for 72 h resulted in formation of tolylphenylmethane in 25 and 65% yield (entries 5 and 6 respectively), exactly as observed for benzophenone.

The presence of a heteroatom in the phenyl substituent as in the case of di(2-pyridyl) ketone apparently lowers the energy barrier required to promote hydrogenation of the carbonyl functionality. The efficient hydrogenation of di(2-pyridyl) ketone was achieved at a much lower temperature (150 °C, entries 7–10) than that required for the benzophenone analogs. This result suggests that the rate of hydrogenation of di(2-pyridyl) ketone may be affected by the presence of the pyridine ring which is known to coordinate to nickel(0) competitively with the carbonyl (see Scheme 2). The steric hindrance limitation that operates in the case of benzophenone is probably not a major issue for di(2-pyridyl) ketone. The presence of an adjacent carbonyl in a benzophenone related molecule such as benzil also resulted in a higher reactivity which also permitted hydrogenation at 150 °C (entries 11–13). Analysis of the product distributions (*vide infra*) suggests that the carbonyls acquire distinct electrophilic character in the molecule when only one of the two is coordinated to nickel(0), enabling partial or even total hydrogenation to be effected in just one of the two carbonyls (Scheme 5).

In the case of di(2-pyridyl) ketone, hydrogenation at 150 °C using 60 psi of H₂ yielded both the alcohol, di-pyridin-2-yl-methanol (86%), and the alkane, di-pyridin-2-yl methane (14%), after 12 h (entry 7). The ratio of products was maintained even after heating the vessel for 96 h (entry 8). A greater H₂ pressure (120 psi) showed only a slight increase in the corresponding alkane (35%) after 96 h

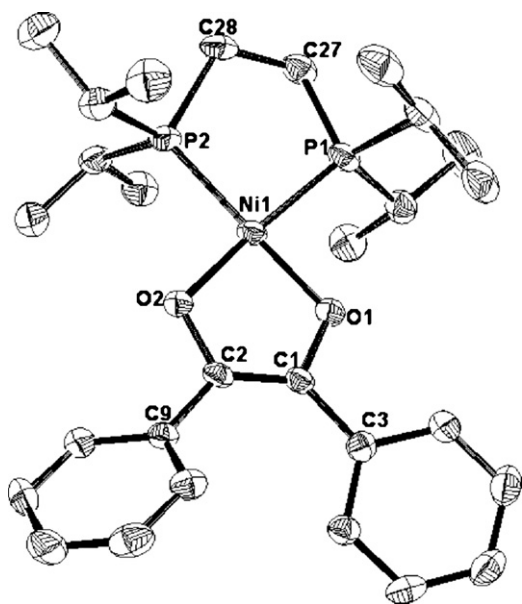


Fig. 3. ORTEP representation of **9a** showing thermal ellipsoids at the 50% probability level. Selected bond distances (Å): C1–O1 (1.369(3)), C2–O2 (1.363(3)), Ni1–O1 (1.832(2)), Ni1–O2 (1.851(2)), Ni1–P1 (2.1357(9)), Ni1–P2 (2.1508(9)), C1–C2 (1.364(4)). Selected bond angles (deg): O1–Ni1–P2 (176.35(7)), O2–Ni1–P1 (174.03(7)), P1–Ni1–P2 (89.38(4)), O1–Ni–O2 (87.62(9)).

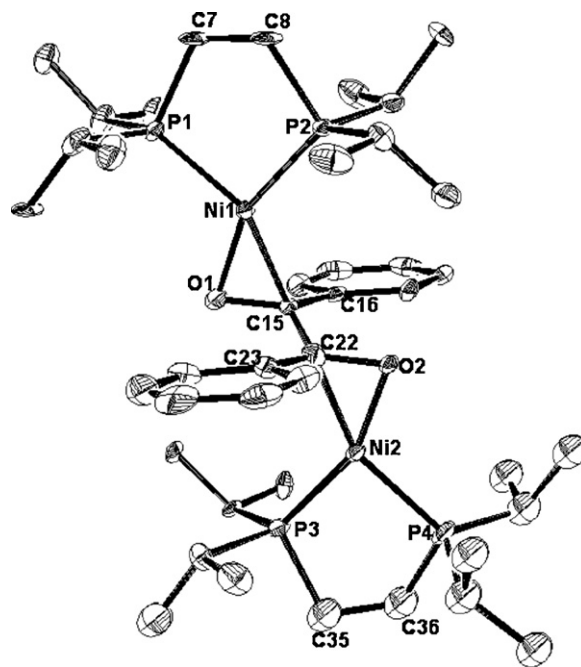
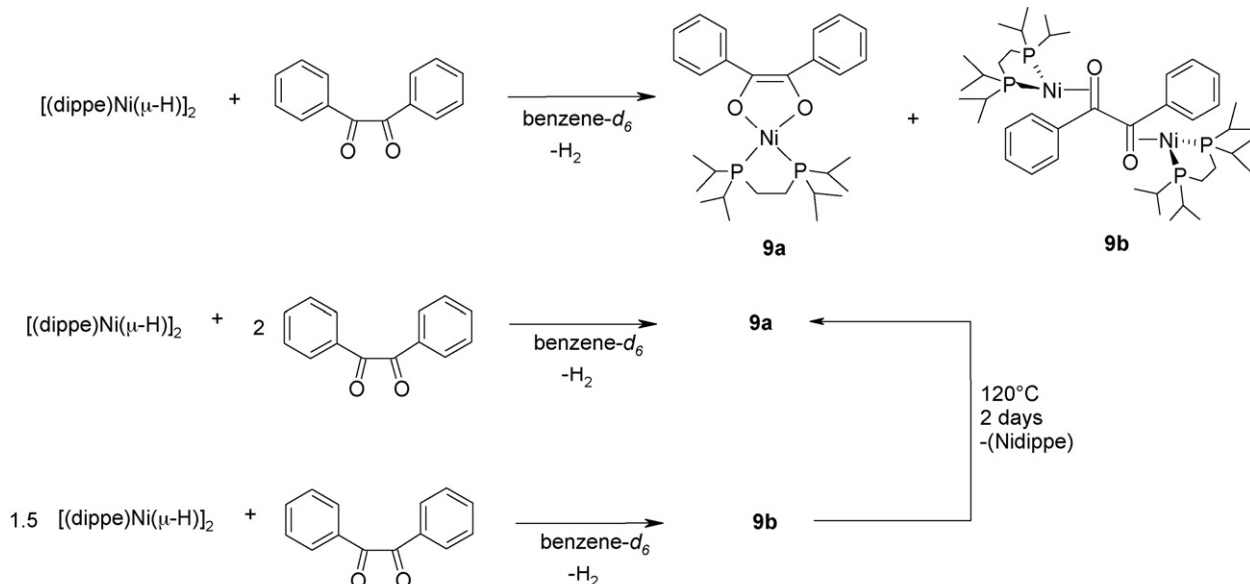


Fig. 4. ORTEP representation of **9b** showing thermal ellipsoids at the 50% probability level. Selected bond distances (Å): C15–O1 (1.37(8)), Ni1–C15 (1.999(6)), Ni1–O1 (1.872(5)), Ni1–P2 (2.127(19)), Ni1–P1 (2.171(2)), C22–O2 (1.357(8)), Ni2–C22 (1.983(7)), Ni2–O2 (1.848(5)), Ni2–P4 (2.168(2)), Ni1–P3 (2.124(2)), Ni2–P4 (2.168(2)), Ni2–O2 (1.848(5)), Ni2–C22 (1.983(7)), C22–O2 (1.357(8)). Selected bond angles (deg): P1–Ni1–P2 (92.02(8)), O1–Ni1–C15 (40.6(2)), O1–Ni1–P1 (111.16(18)), C15–Ni1–P2 (115.93(18)), P1–Ni1–O1 (156.31(17)), P3–Ni2–P4 (91.42(8)), O2–Ni2–C22 (41.3(2)), O2–Ni2–P4 (111.58(18)), C22–Ni2–P3 (115.4(2)), C22–Ni2–P4 (152.5(2)), O2–Ni2–P3 (156.67(17)).

(entry 9). Heating the mixture for a longer time (216 h) significantly improved the yield of di-pyridin-2-yl methane (70%, entry 10).

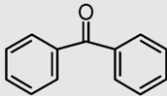
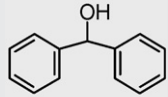
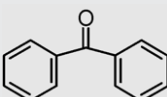
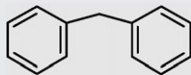
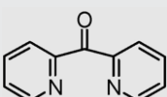
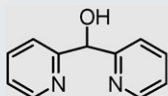
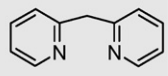
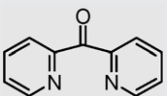
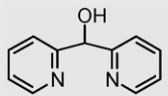
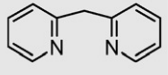
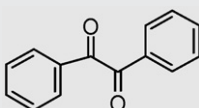
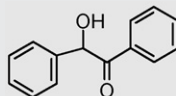
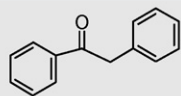
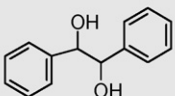
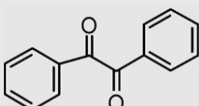
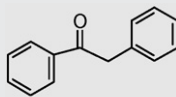
In the case of benzil, catalytic hydrogenation at 150 °C resulted in formation of 2-phenylacetophenone in low yield (2%) after 96 h. An increase of H₂ pressure to 250 psi resulted in complete conversion of this substrate, producing a mixture of three hydrogenation products (benzoin, 60%; 2-phenylacetophenone, 17%; and hydrobenzoin, 23%; entry 12). An increase in the H₂ pressure and reaction time showed little variation in the composition of products other than small changes in their relative ratios. This latter reaction demonstrates that both 2-phenylacetophenone and hydrobenzoin are produced in successive stages of the hydrogenation process starting from benzoin (Scheme 5).

In light of the distribution of products that were obtained in the case of benzil hydrogenation, it is possible that a reversible β-H elimination route competing with the overall hydrogenation process to form hydrobenzoin might be operating. This possibility was examined by exploring the separate reactivity of benzoin and hydrobenzoin in the presence of **1**. In the case of benzoin, the formation of two nickel(0) complexes, not isolated, were observed after mixing in benzene-*d*₆ at room temperature and after stirring



Scheme 4. Reactions of **1** with benzil.

Table 2
Stoichiometric hydrogenation of ketones using **1** as precursor.

Entry	T (°C)	Time (h)	Substrate	Product(s) ^e
1 ^{a,b}	150	96		 6%
2 ^{a,b}	250	96		 >99%
3 ^{a,d}	150	12		 88%  12%
4 ^{a,d}	150	96		 2%  98%
5 ^{c,d}	150	12		 15%  51%  34%
6 ^{c,d}	150	48		 100%

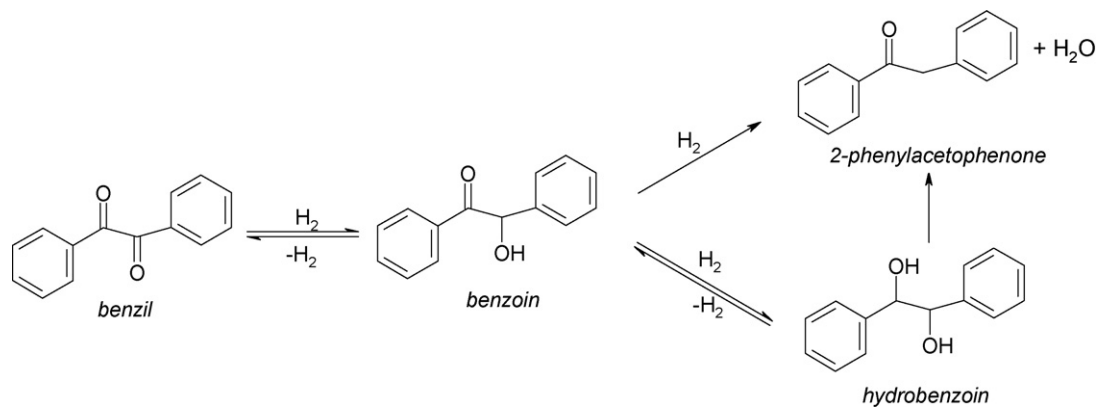
^a Ketone/precursor = 2/1.

^b THF as solvent (15 mL).

^c 1,2-Diketone/precursor = 1:1.

^d Toluene as solvent (15 mL).

^e The reactions were carried out using a Parr reactor. All conversions were determined by GC-MS and ¹H NMR.



Scheme 5. Benzil hydrogenation.

Table 3
Catalytic hydrogenation of ketones using 2% **1** as catalyst precursor.

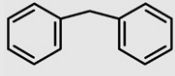
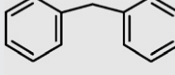
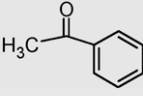
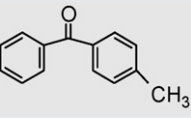
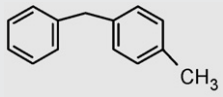
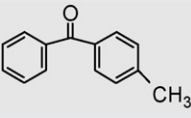
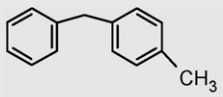
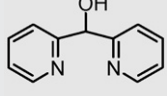
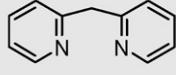
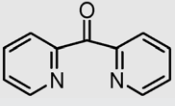
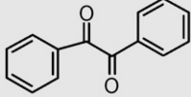
Entry	Substrate	T (°C)	P (psi)	Time (h)	Product(s) ^e
1 ^{a,b}		250	60	72	 25%
2 ^{a,b}		270	60	72	 65%
3 ^{a,b}		270	60	96	 72%
4 ^{a,b}		250	60	96	 98%
5 ^{a,b}		250	60	96	 25%
6 ^{a,b}		270	60	72	 65%
7 ^{a,d}		150	60	12	 86%  14%
8 ^{a,d}		150	60	96	 80%  20%
9 ^{a,d}		150	120	96	 65%  35%
10 ^{a,d}		150	120	216	 30%  70%
11 ^{c,d}		150	60	96	 2%

Table 3 (Continued)

12 ^{c,d}		150	250	96	 60% 17% 23%
13 ^{c,d}		150	480	120	 35% 24% 41%

^a 2% mol of catalytic precursor.

^b THF as solvent (15 mL).

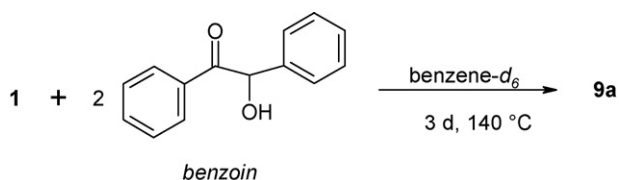
^c 4% mol of catalytic precursor.

^d Toluene as solvent (15 mL).

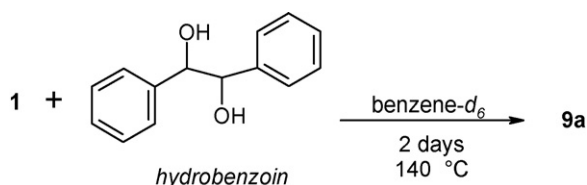
^e The reactions were carried out using a Parr reactor. All yields were quantified by GC–MS and ¹H NMR.

for 4d at room temperature: ³¹P{¹H} NMR: δ 69.4 (d, $J=62.6$ Hz); 66.13 (d, $J=62.6$ Hz) and δ 68.9 (d, $J=68.1$ Hz); 63.9 (d, $J=68.1$ Hz). A complete transformation into **9a** was observed to take place after 3 days while heating the mixture at 140 °C. Scheme 6 summarizes these reactions.

A similar examination of potential secondary reactions was performed using a benzene-*d*₆ solution of hydrobenzoin in the presence of **1**. Reaction took place after heating at 140 °C, resulting ultimately in the formation of **9a** within a period of 2 d (Scheme 7), and also confirmed the hypothesis of a competing β -H elimination process taking place in the hydrobenzoin produced in the catalytic hydrogenation process.



Scheme 6. Reactivity of benzoin with **1**.



Scheme 7. Reactivity of hydrobenzoin with **1**.

3. Conclusions

The current report shows an active system for the selective hydrogenation of ketones with the use of a cheap metal. Conversions were found to be high in general, producing either the alcohol or corresponding alkane. The selectivity for these can be tuned in certain cases, which makes the hydrogenation process synthetically attractive. In the case of diketones such as benzil, a β -H elimination process was found to play an important role competing with the hydrogenation route, thereby rendering the benzil hydrogenation a product-inhibited process. Studies are underway to probe the application of related type of catalysts to the ones disclosed herein for the enantioselective hydrogenation of ketones while using asymmetric diphosphine ligands.

4. Experimental

4.1. General methods

Unless otherwise noted, all manipulations were performed using standard Schlenk techniques in an inert-gas/vacuum double manifold or under argon atmosphere in an MBraun glovebox (<1 ppm H₂O and O₂). Benzophenone, acetophenone, 4-methylbenzophenone, di-2-pyridyl ketone, benzil and 2,2'-pyridyl-ketone were purchased from Aldrich and were used as received. The nickel(I) dimer, [(dippe)Ni(μ -H)]₂ (**1**), was prepared from an *n*-hexanes slurry of [(dippe)NiCl₂] [22] using Super-hydride (LiHBET₃), similar to the literature procedure.^{15a} Solvents were purchased from J.T. Baker (reagent grade) and were additionally dried and distilled from sodium/benzophenone ketyl. *n*-Hexanes and ethyl acetate for chromatographic separation of reduction products were used without further purification. NMR spectra of complexes and products were recorded at room temperature on a 300 MHz Varian Unity spectrometer unless otherwise noted. Deuterated

solvents for NMR experiments were purchased from Cambridge Isotope Laboratories and were stored over 3 Å molecular sieves in the glovebox for at least 24 h before use. All complexes were handled under argon using thin wall (0.38 mm) WILMAD NMR tubes with J Young valves. ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts (δ , ppm) are reported relative to either the residual protiated solvent or deuterated carbon resonances of the solvent, respectively. $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts (δ , ppm) are reported relative to external 85% H_3PO_4 . ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the reduction products were obtained in CDCl_3 . Elemental analyses were carried out by USAI-UNAM using an EA 1108 FISONs Instruments analyzer, reproducible elemental analyses could not be obtained due to few samples high instability (**9a** and **9b**). A Bruker APEX CCD diffractometer with monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was used for X-ray structure determinations.

Hydrogenation experiments were conducted in a 300 mL stainless steel Parr Series 4560 Bench Top Mini Reactor or alternatively in a 100 mL stainless steel Parr Series 4590 Micro Bench Top reactor vessel. The mixtures were charged into the vessels in the glovebox. The respective nickel(0) catalysts were prepared *in situ* from **1**. All hydrogen used in this work was supplied by Praxair in high purity grade (99.998%). The hydrogenation products were quantified by ^1H NMR spectroscopy. Product identification was made by direct comparison of their ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra and melting points with commercially available materials.

4.2. Preparation of [(dippe)Ni(η^2 -O,C-benzophenone)] (**2**)

The reaction of dark red **1** (0.050 g, 0.078 mmol) with benzophenone (0.028 g, 0.156 mmol) in 1 mL toluene- d_8 yielded monocoordinated nickel(0) complex [(dippe)Ni(η^2 -O,C-benzophenone)] (**2**). Immediate effervescence due to reductive elimination of H_2 was observed after mixing. The resulting solution was analyzed by NMR spectroscopy: ^1H , δ 8.1 (d, 4H, CH), 7.1 (m, 2H, CH), 7.2 (m, 2H, CH), 1.9–1.4 (m, 4H, CH), 1.3–0.8 (m, 4H, CH_2), 0.8–0.4 (m, 24H, CH_3). $^{13}\text{C}\{^1\text{H}\}$, δ 149.4 (dd, $^3J_{\text{C-P}}(\text{trans}) = 5.4$, $^3J_{\text{C-P}}(\text{cis}) = 1.5$, C), 132.4 (s, CH), 130.5 (s, CH), 128.3 (s, CH), 86.2 (d, $^2J_{\text{P-P}} = 22.2 \text{ Hz}$, C), 25.9 (d, $J_{\text{C-P}} = 22.1 \text{ Hz}$, CH), 24.5 (d, $J_{\text{C-P}} = 24 \text{ Hz}$, CH), 22.9–22.3 (m, CH_2), 20.4 (s, CH_3), 19.2 (s, CH_3), 18.1 (s, CH_3). $^{31}\text{P}\{^1\text{H}\}$, δ 71.9 (d, $^2J_{\text{P-P}} = 66 \text{ Hz}$), 61.4 (d, $^2J_{\text{P-P}} = 66 \text{ Hz}$). Slow evaporation of toluene at r.t. in the dry box allowed the crystallization of pure product. Anal. Calcd. (%) for $\text{C}_{27}\text{H}_{42}\text{NiOP}_2$: C, 64.43; H, 8.41. Found: C, 64.31; H, 8.44. 91% Yield.

4.3. Preparation of [(dippe)Ni(η^2 -O,C-4-methyl-benzophenone)] (**3**)

A toluene- d_8 solution (1 mL) of **1** (0.050 g, 0.078 mmol) was reacted with 4-methylbenzophenone (0.028 g, 0.156 mmol) at room temperature, resulting in formation of the monocoordinated nickel(0) complex [(dippe)Ni(η^2 -O,C-4-methyl-benzophenone)] (**3**). Effervescence resulting from reductive elimination of H_2 was observed immediately after mixing. Slow evaporation of toluene at r.t. in the dry box allowed the crystallization of the pure product. Anal. Calcd. (%) for $\text{C}_{28}\text{H}_{44}\text{NiOP}_2$: C, 65.01; H, 8.57. Found: C, 64.96; H, 8.60. 92% Yield. NMR in toluene- d_8 : ^1H , δ 8.1 (m, 4H, CH), 7.8–7.4 (m, 1H, CH), 7.4–6.8 (m, 4H, CH), 2.1 (s, 3H, CH_3), 1.9–1.4 (m, 4H, CH), 1.3–0.8 (m, 4H, CH_2), 0.8–0.4 (m, 24H, CH_3). $^{13}\text{C}\{^1\text{H}\}$, δ 149.7 (d, $^3J_{\text{C-P}} = 1.3 \text{ Hz}$), 146.0 (d, $^3J_{\text{C-P}} = 1.4 \text{ Hz}$), 143.0 (s, C), 130.0 (s, CH), 25.9 (d, $J_{\text{C-P}} = 22.1 \text{ Hz}$, CH), 24.5 (d, $J_{\text{C-P}} = 24 \text{ Hz}$, CH), 22.0 (s, CH_3), 22.9–22.3 (m, CH_2), 20.4 (s, CH_3), 19.2 (s, CH_3), 18.1 (s, CH_3). $^{31}\text{P}\{^1\text{H}\}$, δ 71.7 (d, $^2J_{\text{P-P}} = 66.7 \text{ Hz}$), 61.7 (d, $^2J_{\text{P-P}} = 66.7 \text{ Hz}$).

4.4. Preparation of [(dippe)Ni(η^2 -O,C-acetophenone)] (**4**)

Similar to the above described preparations for compounds **2** and **3**, the reaction **1** (0.050 g, 0.078 mmol) with ace-

tophenone (0.028 g, 0.156 mmol) in toluene- d_8 solution (1 mL) yielded [(dippe)Ni(η^2 -O,C-acetophenone)] (**4**). Anal. Calcd. (%) for $\text{C}_{22}\text{H}_{40}\text{NiOP}_2$: C, 59.89; H, 9.13. Found: C, 59.72; H, 9.14. 92% Yield. NMR in toluene- d_8 : ^1H , δ 7.7 (m, 2H, CH), 6.8–7.2 (m, 3H, CH), 1.9 (s, 3H, CH_3), 1.8–1.4 (m, 4H, CH), 1.3–0.8 (m, 4H, CH_2), 0.8–0.4 (m, 24H, CH_3). $^{13}\text{C}\{^1\text{H}\}$, δ 153.6 (d, $^3J_{\text{C-P}}(\text{trans}) = 4.6$, $^3J_{\text{C-P}}(\text{cis}) = 1.9$, C), 133.0 (s, CH), 82.2 (d, C), 25.9 (d, $J_{\text{C-P}} = 22.1 \text{ Hz}$, CH), 24.5 (d, $J_{\text{C-P}} = 24 \text{ Hz}$, CH), 22.9–22.3 (m, CH_2), 20.4 (s, CH_3), 19.2 (s, CH_3), 18.1 (s, CH_3). $^{31}\text{P}\{^1\text{H}\}$, δ 68.4 (d, $^2J_{\text{P-P}} = 70.4 \text{ Hz}$), 64.1 (d, $^2J_{\text{P-P}} = 70.4 \text{ Hz}$).

4.5. Preparation of [(dippe)Ni(η^2 -O,C-acetone)] (**5**)

Reaction of **1** (0.050 g, 0.078 mmol) with an excess of acetone (20 mL) yielded [(dippe)Ni(η^2 -O,C-acetone)] (**5**). The reagents were mixed at room temperature, adding **1** to acetone, and the excess of acetone was eliminated by high vacuum evaporation at -78°C . Slow evaporation of solvent at r.t. in the dry box allowed the crystallization of a waxy residue which was further dried under vacuum. Re-crystallization from hexanes of the remaining residue at -30°C gave an analytically pure solid. Anal. Calcd. (%) for $\text{C}_{17}\text{H}_{37}\text{NiOP}_2$: C, 53.43; H, 9.75. Found: C, 53.31; H, 9.77. 85% Yield. NMR (toluene- d_8): ^1H , δ 1.5 (dd, 6H, CH_3), 1.6–0.8 (m, 8H, CH and CH_2), 0.8–0.4 (m, 24H, CH_3). $^{13}\text{C}\{^1\text{H}\}$, δ 82.7 (d, $^2J_{\text{C-P}} = 29.6$), 31.5 (d, CH_3), 25.9 (d, $J_{\text{C-P}} = 22.1 \text{ Hz}$, CH), 24.5 (d, $J_{\text{C-P}} = 24 \text{ Hz}$, CH), 22.9–22.3 (m, CH_2), 20.4 (s, CH_3), 19.2 (s, CH_3), 18.1 (s, CH_3). $^{31}\text{P}\{^1\text{H}\}$, δ 71.9 (d, $^2J_{\text{P-P}} = 66 \text{ Hz}$), 61.4 (d, $^2J_{\text{P-P}} = 66 \text{ Hz}$).

4.6. Preparation of [(dippe)Ni(η^2 -O,C-fluorenone)] (**6**)

9-Fluorenone (38 mg, 0.021 mmol) and 25 mg **1** were combined in 10 mL THF at r.t. The solvent was removed under vacuum and the product **6** recrystallized from pentane. Anal. Calcd. (%) for $\text{C}_{27}\text{H}_{44}\text{NiOP}_2$: C, 64.70; H, 8.04. Found: C, 63.97; H, 8.07. NMR (toluene- d_8): ^1H , δ 0.27 (dd, 6H, CH_3), 0.67 (dd, 6H, CH_3), 1.12 (m, 4H, CH), 1.37 (dd, 6H, CH_3), 1.44 (dd, 6H, CH_3), 1.56 (m, 2H), 2.18 (m, 2H), 7.11 (t, 2H), 7.17 (t, 2H), 7.66 (d, 2H), 7.68 (d, 2H). $^{31}\text{P}\{^1\text{H}\}$, δ 72.48 (d, $^2J_{\text{P-P}} = 55 \text{ Hz}$), 81.40 (d, $^2J_{\text{P-P}} = 66 \text{ Hz}$).

4.7. Generation of [(dippe)Ni(η^2 -O,C-di(2-pyridyl) ketone)] (**7a**) and [(dippe)Ni(κ^2 -N,N-di(2-pyridyl) ketone)] (**7b**)

Complex **1** (0.030 g, 0.046 mmol) was reacted with di(2-pyridyl) ketone (0.017 g, 0.092 mmol). The reagents were mixed at room temperature, adding the di(2-pyridyl) ketone to a dark red THF- d_8 solution (1 mL) of **1**. Anal. Calcd. (%) for $\text{C}_{25}\text{H}_{40}\text{N}_2\text{NiOP}_2$: C, 59.44; H, 7.97; N, 5.54. Found: C, 57.84; H, 7.98; N 5.13. FAB $^+$ 505.2. The mixture was analyzed by NMR at room and low temperature. The signals correspond to [(dippe)Ni(η^2 -O,C-di(2-pyridyl) ketone)] (**7a**) (70%) are: ^1H (r. t.), δ 8.3 (m, 2H, CH), 8.0 (m, 2H, CH), 7.4 (m, 2H, CH), 6.9 (m, 2H, CH), 2.1 (m, 4H, CH_2), 1.4–0.4 (m, 28H, CH and CH_3). $^{13}\text{C}\{^1\text{H}\}$, δ 168.0 (s, C), 135.0 (s, CH), 121.5 (s, CH), 118.6 (s, CH), 86.5 (s, C), 22.5–17.5 (m, CH, CH_2 , CH_3). $^{31}\text{P}\{^1\text{H}\}$ (r. t.): δ 72.4 (d, $^2J_{\text{P-P}} = 57.6 \text{ Hz}$), 63.9 (d, $^2J_{\text{P-P}} = 5.6 \text{ Hz}$) $^{31}\text{P}\{^1\text{H}\}$ (-90°C): δ 80.1 (d, $^2J_{\text{P-P}} = 57.6 \text{ Hz}$), 68.6 (d, $^2J_{\text{P-P}} = 5.6 \text{ Hz}$). The signals of [(dippe)Ni(κ^2 -N,N-di(2-pyridyl) ketone)] (**7b**) (30%) are: ^1H (-90°C), δ 9.4 (m, 2H, CH), 8.7 (m, 2H, CH), 8.2 (m, 2H, CH), 7.2 (m, 2H, CH), 2.4–0.6 (m, 32H, CH, CH_2 and CH_3). $^{31}\text{P}\{^1\text{H}\}$ (r. t.): δ 116.7 (s, br) $^{31}\text{P}\{^1\text{H}\}$ (-90°C): δ 100.0 (s).

4.8. Preparation of [(dippe)Ni(κ^2 -O,O-2,2'-pyridil)] (**8**)

Complex **1** (0.030 g, 0.046 mmol) was reacted at room temperature with 2,2'-pyridil (0.019 g, 0.092 mmol) in benzene- d_6 (1 mL). After mixing, an effervescence corresponding to H_2 reductive elimination and a black powder (metallic nickel) were observed. Cooling the sample to -70°C allowed the precipitation of $\text{Ni}(\text{CO})_4$. The

mixture was examined by NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ shows two signals, the first at δ 79.9 (s) corresponding to the complex $[(\text{dippe})\text{Ni}(\kappa^2\text{-O},\text{O}-2,2'\text{-pyridil})]$ (**8**), and the second for free dippe at δ 7.3 (s). The formation of $\text{Ni}(\text{CO})_4$ was corroborated by comparison of the corresponding IR spectra with an authentic sample.

4.9. Generation of $[(\text{dippe})\text{Ni}_2(\eta^2\text{-O},\text{C-benzil})]$ (**9a**) and $[(\text{dippe})\text{Ni}(\kappa^2\text{-O},\text{O-benzil})]$ (**9b**)

Complex **1** (0.030 g, 0.046 mmol) was dissolved in benzene- d_6 (1 mL) at room temperature and benzil added (0.010 g, 0.046 mmol). The crude mixture was examined by NMR spectroscopy, showing the formation of two compounds by $^{31}\text{P}\{^1\text{H}\}$ spectroscopy. A multiplet centered at δ 60.6 was assigned to $[(\text{dippe})\text{Ni}_2(\eta^2\text{-O},\text{C-benzil})]$ (**9a**), and a singlet at δ 79.2 was assigned to $[(\text{dippe})\text{Ni}(\kappa^2\text{-O},\text{O-benzil})]$ (**9b**) (benzene- d_6). Complexes (**9a**) and (**9b**) were separated by a short column (silica gel, hexane/THF (80:20) as eluent) and were characterized separately. **9a** Anal. Calcd. (%) for $\text{C}_{28}\text{H}_{42}\text{Ni}_2\text{O}_2\text{P}_2$: C, 63.3; H, 7.96. Found: C, 61.62; H, 7.80. FAB^+ 531. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8): δ 83.7 (s); ^1H NMR (THF- d_8): δ 7.4 (d, 4H, CH), 6.9 (t, 4H, CH), 6.8 (t, 2H, CH), 1.5 (dd, 12H, CH_3), 2.2 (m, 4H, CH), 1.7 (d, 4H, CH_2), 1.3 (dd, 12H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 145 (t, C, $J_{\text{C-P}} = 3$ Hz), 142.5 (s, C), 127.9 (s, CH), 127.4 (s, CH), 123.6 (s, CH), 25.3 (d, CH), 20.9 (t, CH_2 , $J_{\text{C-P}} = 20$ Hz), 19.4 (s, CH_3), 18.7 (s, CH_3). **9b** Anal. Calcd. (%) for $\text{C}_{42}\text{H}_{74}\text{Ni}_2\text{O}_2\text{P}_4$: C, 59.18; H, 8.74. Found: C, 57.34; H, 8.55. FAB^+ ($-\text{Ni}(\text{dippe})$) 530. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8): δ 60.6 (m); ^1H NMR (THF- d_8): δ 8.3 (d, 4H, CH), 6.9 (t, 4H, CH), 6.7 (t, 2H, CH), 1.9 (m, 8H, CH), 1.5–0.8 (m, 56H, CH_2 and CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 150.9 (s, C), 129.1 (s, CH), 126.9 (s, CH), 122.2 (s, CH), 93.6 (s (br), C), 25 (t, CH_2), 22–18 (m, CH, CH_3).

4.10. Reactivity of **1** with benzoin and hydrobenzoin

To a benzene- d_6 (1 mL) solution of **1** (0.078 mmol, 0.050 g) was added either benzoin (0.156 mmol, 0.033 g) or hydrobenzoin (0.078 mmol, 0.017 g). The solutions were stirred in the glovebox as H_2 was vented. The resulting red-brown solutions were transferred into an NMR tube with a J. Young valve and analyzed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. For $\text{Ni}(0)$ intermediates at: $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 69.4 (d, $J = 62.6$ Hz); 66.13 (d, $J = 62.6$ Hz) and δ 68.9 (d, $J = 68.1$ Hz); 63.9 (d, $J = 68.1$ Hz).

4.11. Hydrogenation reactions: Stoichiometric conditions

Reactor vessels were charged in separate runs with a constant amount of **1** (0.078 mmol, 0.050 g) and the corresponding monoketone (0.16 mmol) or 1,2-diketone (0.078 mmol): benzophenone (0.029 g), di(2-pyridyl) ketone (0.029 g), or benzil (0.016 g) using toluene or THF (15 ml). Each mixture was heated under vigorous stirring at the temperature and time indicated in Table 2. The reactor vessels were allowed to cool down to room temperature and opened in a well-vented hood prior to work-up. The yellow crude solution was regularly filtered over celite and then analyzed by GC–MS using an aliquot of the filtrate. The latter was dried and re-dissolved in CDCl_3 for ^1H NMR analysis. The organic products were characterized by comparison with authentic samples of each obtained from commercial sources.

Toluene- d_8 solutions of complexes **2**, **3** and **4** were heated from room temperature up to 250 °C, none of them exhibited any significant decomposition, monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$. All other compounds used in catalytic experiments were heated from room temperature up to 150 °C, with the same result.

4.12. Hydrogenation reactions: catalytic conditions

Reactor vessels were charged in separate runs with a constant amount of **1** (0.015 mmol, 0.010 g) and the corresponding mono-

ketone or 1,2-diketone (0.78 mmol): benzophenone (0.142 g), acetophenone (0.094 g), 4-methylbenzophenone (0.153 g), di(2-pyridyl) ketone (0.142 g) and benzil (0.164 g), dissolved in toluene or THF (15 ml). The resulting solutions were heated with vigorous stirring at the temperatures and times indicated in Table 3, after which the vessels were cooled down and opened in a well vented hood prior to work-up. Yellow solutions were typically recovered from the vessels after reaction. These were filtered over celite and analyzed by GC–MS following the above-described procedure.

4.13. Mercury drop experiments

Following the above described procedure; additionally adding two drops of elemental Hg to the reaction mixture. After reaction completion, the solution was filtered and analyzed by GC–MS: no significant difference in conversion between these experiments and those in the absence of mercury was observed, indicating that heterogeneous $\text{Ni}(0)$ is not involved. The procedure was performed in all the optimized conditions such as entries 5, 6 in Table 2 and entries 3, 4, 6, 8, 10, 12, 13 in Table 3. Mercury was always visible at the end of each experiment, immersed in the yellow solutions and no black residues were observed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.05.026.

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