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Nickel(II)-Dipyridylphosphine-Catalyzed Enantioselective Hydrosilylation of Ketones in Air

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Optically enriched secondary alcohols are highly valuable intermediates in organic synthesis, especially when their significance as chiral building blocks of numerous natural products, pharmaceuticals, and other biologically active molecules is taken into account.[1] The non-noble-metal-catalyzed enantioselective hydrosilylation of prochiral ketones represents a rewarding transformation towards chiral alcohols owing to the economic benefits and the operational simplicity of such methods.[2] Thus, in the past two decades, a variety of effective chiral transition-metal catalysts based on titanium,[3] zinc,[4] tin,[5] copper,[6,7] iron,[8,9] and cobalt[10] have been accordingly developed and applied in the asymmetric hydrosilylation of ketones with good to excellent enantioselectivities. Nickel-based catalysts have shown better activities in heterogeneous and some homogeneous reactions, such as hydrogenation and cross-coupling reactions, than other catalytic systems mediated by biologically relevant metals, for example, Fe, Cu, or Zn.[11] Also, nickel catalyst technology has played an important role in improving efficiency in a number of industrial processes.[11a] To our knowledge, although some achiral nickel catalysts have been exploited for the reduction of ketones,[12] there is no reported analogous non-racemic catalyst involving nickel precursors.

Recently, we described the use of a family of atropisomeric bipyridyldiphosphine ligands P-Phos (**L1a**, Table 1)[13] and its variants (**L1b** Tol-P-Phos, **L1c** Xyl-Phos)[14] for effecting the copper-mediated hydrosilylation of a diverse assortment of ketones[7,15] as well as conjugate reduction of β-(acylamino)acrylates[16] under ambient conditions in competitive levels of enantioselectivities and activities. Moreover, in the presence of $PhSiH_3$ as the hydride donor, the effectively enantioselective reduction of alkyl aryl ketones was also realized by using the cobalt(II)/Xyl-P-Phos catalyst system.[10c] It is noteworthy that the aforementioned hydrosilylation systems were air-stable, which underlined their practical viability and prompted us to investigate the catalytic properties of NiH nonracemically ligated by P-Phos family ligands in the relevant reduction reactions. Herein, we describe the first example of nickel-catalyzed stereoselective hydrosilylation of a selection of alkyl aryl ketones in air atmosphere in moderate to good yields and enantioselectivities.

We commenced our studies by examining the effects of various nickel precursors on the reduction of 4′-nitroacetophenone (**1a**, Table 1). By utilizing 5 mol% anhydrous NiF_2 and (*S*)-P-Phos ligand as well as two equivalents $PhSiH_3$ as the stoichiometric hydride source, the reaction proceeded in toluene in air atmosphere at 45 °C to only 23% conversion after 40 h to afford the desired alcohol (*S*)-**2a** in 79% *ee* (Table 1, entry 1). Consistent with the results obtained from our previous cobalt catalyst system,[10c] dramatic enhancements in both conversion (99%) and enantioselectivity (87% *ee*) were observed by adding 4 Å MS (30 mg) to the reaction mixture (0.2 mmol **1a**; Table 1, entry 2 vs. entry 1). Similar reaction outcomes were achieved in the case of $Ni(OAc)_2{\cdot}4H_2O$, which is easy to handle and less expensive, as a nickel source (Table 1, entry 3 vs. entry 2). Nonetheless, 17% and 77% conversions were obtained, respectively, when the hydrosilylation of 0.2 mmol **1a** was carried out in the presence of 4 Å MS (15 or 60 mg; Table 1, entries 4 and 5 vs. entry 3). In addition, other nickel(II) halides including $NiCl_2$, $NiBr_2$ and NiI_2 as well as $[Ni(acac)_2]$ (acac = acetylacetonate) showed poor to moderate activities (1–61% conv.; Table 1, entries 6–9 vs. entries 2 and 3). Moreover, as the data in Table 1, entries 10 to 16 indicated, the reaction was also strongly ligand-dependent. Among the various chiral diphosphine ligands screened, sterically more demanding ligands (*S*)-Tol-P-Phos (**L1b**, Table 1, entry 10) and (*S*)-Xyl-P-Phos (**L1c**, Table 1, entry 11) possessed comparative levels of activity and asymmetric induction with those of parent ligand (*S*)-P-Phos (Table 1, entry 3) under otherwise identical conditions. Moreover, when the reaction was conducted in nitrogen, the reaction rate was lower than in air (Table 1, entry 17 vs. entry 13). Finally, upon increasing the catalyst loading to 10 mol%, full conversion and 90% *ee* were attained at 30 °C by prolonging the reaction time to 64 h (Table 1, entry 18 vs. entry 3).

Further investigations demonstrated that both silanes and solvents had pronounced influences on the reaction activities. For instance, by selecting Ph_2SiH_2, Ph_3SiH, PMHS

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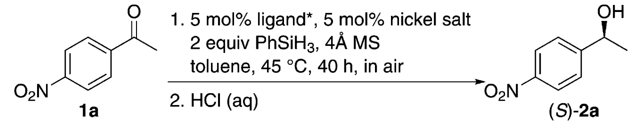
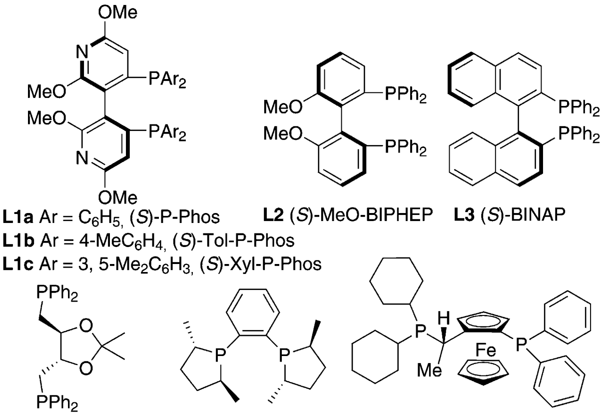
Table 1. Selected optimization of conditions for the nickel-catalyzed asymmetric hydrosilylation of 4′-nitroacetophenone **1a** in air.[a]



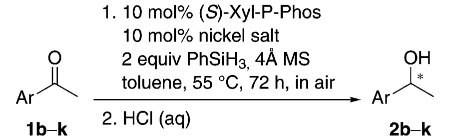
Entry	Nickel salt	Ligand	Conv. [%][b]	*ee* [%][c]
1[d]	NiF_2	**L1a**	23	79
2	NiF_2	**L1a**	99	87
3[e]	$Ni(OAc)_2{\cdot}4H_2O$	**L1a**	98	87
4[f]	$Ni(OAc)_2{\cdot}4H_2O$	**L1a**	17	81
5[g]	$Ni(OAc)_2{\cdot}4H_2O$	**L1a**	77	85
6	$NiCl_2$	**L1a**	61	80
7	$NiBr_2$	**L1a**	3	n.d.[h]
8	NiI_2	**L1a**	<1	n.d.
9	$Ni(acac)_2$	**L1a**	26	71
10	$Ni(OAc)_2{\cdot}4H_2O$	**L1b**	99	84
11	$Ni(OAc)_2{\cdot}4H_2O$	**L1c**	97	88
12	$Ni(OAc)_2{\cdot}4H_2O$	**L2**	90	34
13	$Ni(OAc)_2{\cdot}4H_2O$	**L3**	47	76
14	$Ni(OAc)_2{\cdot}4H_2O$	**L4**	5	23
15	$Ni(OAc)_2{\cdot}4H_2O$	**L5**	3	2
16	$Ni(OAc)_2{\cdot}4H_2O$	**L6**	10	15
17[i]	$Ni(OAc)_2{\cdot}4H_2O$	**L3**	18	77
18[j]	$Ni(OAc)_2{\cdot}4H_2O$	**L1a**	99	**90**

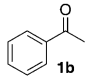
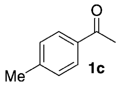
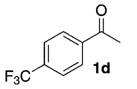
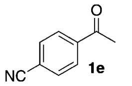
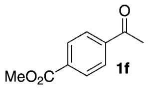
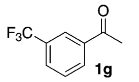
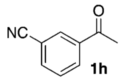
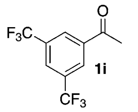
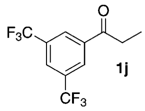
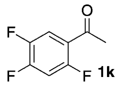
[a] Reaction conditions: 33.0 mg substrate, substrate concentration 0.2 M in toluene; 30 mg 4 Å MS added unless otherwise noted. [b] The conversions were determined by NMR spectroscopy and GC analysis. [c] The *ee* values were determined by chiral GC analysis. The absolute configuration was determined by comparing the retention times with known data. [d] The reaction was carried out in the absence of 4 Å MS. [e] 68 % conversion and 86 % *ee* were obtained in the presence of 1.2 equiv $PhSiH_3$. 99 % conversion and 88 % *ee* were obtained in the presence of (*R*)-**L1a**. [f] 15 mg 4 Å MS were added. [g] 60 mg of 4 Å MS were added. [h] n.d. = not determined. [i] N_2 atmosphere. [j] 10 mol % Ni salt and 10 mol % ligand were used; reaction temperature 30 °C, reaction time 64 h, 95 % isolated yield.



L1a Ar = C_6H_5, (*S*)-P-Phos
L1b Ar = 4-MeC_6H_4, (*S*)-Tol-P-Phos
L1c Ar = 3, 5-$Me_2C_6H_3$, (*S*)-Xyl-P-Phos
L2 (*S*)-MeO-BIPHEP
L3 (*S*)-BINAP
L4 (*S*,*S*)-DIOP
L5 (*S*,*S*)-Me-Duphos
L6 (*S*)-(*R*)-Josiphos

Table 2. Nickel(II)-catalyzed asymmetric hydrosilylation of ketones using (*S*)-Xyl-P-Phos in air.[a]



Entry	Ketones	Nickel salt	Yield [%][b]	*ee* [%][c]
1	 **1b**	$Ni(OAc)_2{\cdot}4H_2O$	<5	n.d.
2		NiF_2	<5	n.d.
3	 **1c**	$Ni(OAc)_2{\cdot}4H_2O$	<5	n.d.
4		NiF_2	<5	n.d.
5	 **1d**	$Ni(OAc)_2{\cdot}4H_2O$	91	80 (*S*)
6[d]	 **1e**	NiF_2	87	82 (*S*)
7[d]	 **1f**	$Ni(OAc)_2{\cdot}4H_2O$	71	73 (*S*)
8	 **1g**	NiF_2	34	71 (*S*)
9[d]	 **1h**	NiF_2	42	61 (−)
10[e]	 **1i**	$Ni(OAc)_2{\cdot}4H_2O$	97	87 (*S*)
11	 **1j**	NiF_2	78	86 (−)
12	 **1k**	NiF_2	68	67 (−)

[a] Substrate concentration 0.10–0.15 M in toluene. [b] Yield of isolated product. [c] The *ee* values were determined by chiral HPLC or GC analysis. The absolute configuration was determined by comparing the retention times with known data. [d] The reduction of the functional groups on the phenyl ring was not observed. [e] Reaction temperature 45 °C.

(poly(methyl hydrosiloxane)), $(EtO)_3SiH$, or $(EtO)_2MeSiH$ as the stoichiometric hydride donor, lower conversions or almost no reaction were detected. Besides, toluene was a much better solvent for the reaction than, for example, CH_2Cl_2, 1,4-dioxane, THF, and CH_3CN.

With the aforementioned preferred conditions in hand, we set out to establish the general utility of this nickel-catalyzed protocol for the enantioselective hydrosilylation of a selection of aryl alkyl ketones **1b**–**1k** in air, and the representative results of these studies are summarized in Table 2. Our previous studies on the cobalt-catalyzed asymmetric hydrosilylation of aryl alky ketones indicated that the electronic nature of the substituents on the phenyl ring of the ketonic substrates had a dramatic effect on the reaction activities, and the substrates bearing an electron-withdrawing aryl group reacted favorably to give higher yields and enantioselectivities. Interestingly, a similar phenomenon was again observed in the present nickel catalyst system. As illustrated in Table 2, entries 1 to 4, under a given set of reaction conditions, the reduction of either acetophenone (**1b**) or 4′-methylacetophenone (**1c**) was found to be rather sluggish (<5 % yield) irrespective of the use of $Ni(OAc)_2{\cdot}4H_2O$ or NiF_2 as the catalyst precursor. Whereas, transformation of aryl alkyl ketones possessing electron-withdrawing substituents proceeded to provide the corresponding alcohols in 34–97 % yield and 61–87 % *ee* (Table 2, entries 5–12). The exact role of the electronic nature of the substituents on the phenyl ring of the ketonic substrates for the reaction reactivities remains unclear at this stage. It appeared that in the final step of the catalytic cycle, the nickel alkoxide intermediate [{(Ar)(R)C(H)O}NiL*(OAc)] undergoes σ-bond metathesis with $PhSiH_3$ between Ni−O and Si−H bonds to afford the silyl ether and regenerate active species nickel hydride [(AcO)NiHL*] (L* = (*S*)-**1c**). This is postulated to be the rate limiting step, and the electron-withdrawing groups on the nickel alkoxide might be favorable for the transmetalation between nickel and silicon.[7f,17]

In addition, the outcomes of the reaction depended on the positioning of the substituents on the arene ring of ketones. Substrates with a *para*-substituted electron-deficient aryl groups (**1a**, **1d–1f**) reacted favorably to afford the desired alcohols with higher enantiopurity in better yields (73–90 % *ee*, 71–99 % yield; Table 1, entry 17 and Table 2, entries 5–7) when compared to the substrates with *meta*-substitution (**1g** and **1h**; Table 2, entries 8 and 9). Furthermore, several other aryl alkyl ketones containing two or three electron-withdrawing substituents (**1i–1k**) also underwent effective and stereoselective hydrosilylation in air (Table 2, entries 10–12).

In conclusion, with appropriate amounts of 4 Å MS as additives, the Ni^{II}-catalyzed stereoselective hydrosilylation of a variety of electron-deficient aryl alkyl ketones was realized for the first time in the presence of catalytic amounts of nickel(II) salt and enantiomerically pure (*S*)-Xyl-P-Phos ligand as well as the stoichiometric hydride source $PhSiH_3$ with moderate to good enantioselectivities (up to 90 % *ee*). Noticeably, the reactions can be carried out in air atmosphere without special precautions, which highlights the practical potential of this protocol. Studies aimed at expanding the scope of the present catalyst system and investigating mechanistic features relevant to the above factors are underway in our laboratory.

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Keywords: asymmetric catalysis · hydrosilylation · ketones · nickel · P ligands

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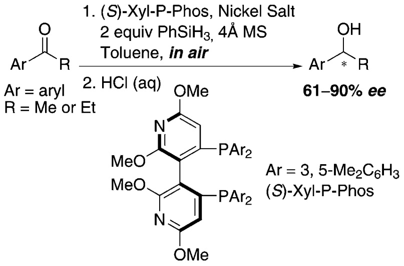
Out of thin air: Catalytic amounts of nickel(II) salt and non-racemic dipyridylphosphine ligand, as well as the stoichiometric hydride source $PhSiH_3$, formed an effective catalyst system for the Ni^{II}-catalyzed asymmetric hydrosilylation of a diverse range of electron-deficient aryl alkyl ketones with enantioselectivities up to 90 % *ee*. The practical potential of the protocol was evinced by its good air-stability.



Asymmetric Catalysis

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Nickel(II)-Dipyridylphosphine-Catalyzed Enantioselective Hydrosilylation of Ketones in Air