



Hydroboration

Ni(bpy)(cod): A Convenient Entryway into the Efficient Hydroboration of Ketones, Aldehydes, and Imines

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Abstract: The catalytic hydroboration of ketones, aldehydes, and imines with pinacol borane and Ni(bpy)(cod) has been demonstrated in benzene at room temperature and low catalyst loadings (0.03–0.3 mol-%). Spectroscopic and structural evi-

dence support the formulation of Ni(bpy)(cod) as containing a Ni¹ cation and a bpy⁻⁻ ligand. The Ni(bpy)(cod) complex reacts quickly with ketonic substrates to form an adduct that appears to function as an entryway into catalytic activity.

Introduction

The development of new catalysts based on earth-abundant elements, especially first-row transition metals, is an area of great interest, both with regard to the potential for lower catalyst cost as well as harnessing new modes of reactivity. Despite these advantages, the development of catalysts based on these elements has lagged behind the development of catalysts based on precious metal analogs for several reasons. Often, these classes of catalysts are less efficient than their second-and third-row congeners and require higher catalyst loadings for comparable product yields.^[11] In contrast to platinum group elements, first-row transition metals exhibit a tendency to undergo one-electron redox changes, often resulting in different reactivities.

One strategy used to mitigate against the propensity for one-electron redox events involving first-row metals is the use of redox-active ligands that can act as electron reservoirs to enable multi-electron transformations. This has resulted in several examples of first-row transition metals that mimic catalytic behavior typically exhibited by platinum group metal complexes, such as proton^[2] and O₂ reduction,^[3] Negishi-type cross coupling,^[4] hydrazine disproportionation via nitrene transfer^[5]

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and alkene hydrogenation.^[6] We have initiated studies aimed towards the reduction of highly oxidized substrates of relevance

Reported catalytic reactivity of 1



Reported stoichiometric reactivity of 1



Scheme 1. Reported catalytic and stoichiometric reactivity of 1.^[9,10]

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to biomass-to-fuel conversion strategies, including the reduction of ketones via hydrodeoxygenation,^[7] using first-row transition metal catalysts supported by redox-active ligands. During our efforts, we became interested in the potential reductive reactivity of Ni(bpy)(cod) (**1**).

First reported by Mori et al. in 1970^[8a] and subsequently isolated and studied more thoroughly by Dinius and Schindler,^[8b,8c] 1 is known to exhibit both catalytic and stoichiometric reactivity towards a number of substrates (Scheme 1). Compound 1 will catalytically oligomerize unsaturated hydrocarbons,^[9a] cyclodimerize substituted cyclopropenes and norbornadiene,^[9a] dimerize propionaldehyde,^[9b] and alkylate anhydrides with alkylzinc reagents.^[9c] Stoichiometric reactivity of 1 includes the ring-opening of aziridines^[10a] and α -amino acid Ncarboxy anhydrides,^[10b] the dimerization of 1,4-substituted allenes,^[10c] coupling of CO with 1,2-diphenylacetylene,^[10d] and the reduction of CO₂ with both 1,4-dienes and aldehydes.^[10e,10f] The stoichiometric reactions shown in Scheme 1 result in formal oxidation of the nickel center. The addition of an external reductant such as pinacol borane to these reactions could promote release of the reduced substrate from the nickel center and regenerate the starting [Ni(bpy)] moiety, thus potentially creating a catalytic cycle. In particular, we postulated that the reported coordination of ketones and aldehydes to compound 1^[10e] could be exploited in a catalytic fashion.

Results and Discussion

Herein we present results that establish Ni(bpy)(cod) as an efficient precatalyst for the hydroboration of ketones, aldehydes, and imines; that suggest an alternative electronic structure description of **1**; and that also suggest a different mechanistic pathway for the observed hydroboration chemistry may be in operation.

Our initial efforts focused on the stoichiometric hydroboration of benzophenone with pinacol borane (Scheme 2). Reaction of 1 with one equivalent of benzophenone in benzene results in a rapid color change from dark purple to dark blue with concomitant precipitation of Ni(bpy)(Ph₂CO) (2, vide infra), which had been previously postulated as the likely reaction product.^[10e,10f,11] An equilibrium constant of $K_{eq} = 1.06$ can be derived from the free benzophenone and free 1,5-cyclooctadiene resonances, resulting in a free energy difference of -0.04 kcal/mol. Subsequent addition of one equivalent of pinacol borane to this solution results in an instantaneous color change back to a homogeneous dark purple. We identified the resulting formation of the hydroborated benzophenone product in quantitative yield and the regeneration of compound 1 in 88 % yield based on the amount of added pinacol borane, as established by ¹H NMR spectroscopy (Figure 1). The addition of pinacol borane to compound 1 resulted in no observable spectroscopic change (Figures S1 and S2), suggesting that compound 2 is likely formed prior to borane activation in the hydroboration of benzophenone.



Scheme 2. Stoichiometric hydroboration of benzophenone with pinacol borane using ${\bf 1}.$

The regeneration of **1** upon stoichiometric hydroboration of benzophenone suggested that **1** could be a competent precatalyst for the hydroboration of a variety of ketones and aldehydes. Compound **1** proved to be a highly active precatalyst, with 94 % conversion of benzophenone and pinacol borane into the hydroborated product within 30 min at room temperature. The process proceeds at 0.03 mol-% catalyst loading (turnover number \approx 3100 and turnover frequency \approx 6200 h⁻¹). Furthermore, the hydroboration of benzophenone was unaffected



Figure 1. ¹H NMR spectra of compound **1** (top, red), a 1:1 mixture of **1** and benzophenone (middle, green), and a 1:1:1 mixture of **1**, benzophenone, and pinacolborane (bottom, blue). Tri-*tert*-butylbenzene was used as an internal standard. Resonances are denoted as follows: **1** (\bullet), 1,5-cyclooctadiene (\ddagger), benzophenone (\blacksquare), hydroborated product (\blacktriangle), tri-*tert*-butylbenzene (\diamond).

1636



by the addition of excess Hg metal, consistent with a homogeneous species effecting catalysis.^[12] Encouraged by the observation of such efficient reactivity under mild conditions, we examined the substrate scope of hydroboration and the effect of catalyst loading using compound 1 under the conditions shown in Scheme 3. Hydroboration of benzophenone, benzaldehyde and acetophenone substrates proceeds readily in good to excellent yields (79-96 %) within 3 hours (Table 1, entries 1-8). In general, the inclusion of electron-donating groups such as methyl and methoxy substituents has no effect on substrate conversion or product yield for the benzophenone, acetophenone, and benzaldehyde substrates. Aryl-substituted imines are also reduced in excellent yields at room temperature, albeit at higher catalyst loadings (0.3 mol-%; Table 1, entries 9-11). In contrast, alkenes are unreactive towards hydroboration; accordingly, the hydroboration of neither 1-octene nor styrene occurs (Table 1, entries 12 and 13). Thus, compound 1 displays reactivity competitive with previously reported magnesium-,[13a] titanium-,^[13b,13c] gallium-,^[13d] aluminum-,^[13e] molybdenum-,^[13f] ruthenium,^[13g] germanium and tin,^[13h] and phosphine-containing^[13i] ketone and aldehyde hydroboration catalysts, and is one of the most efficient pre-catalysts reported to date for the catalytic hydroboration of imines.[14]



Scheme 3. Catalytic hydroboration of ketones, aldehydes, and imines with pinacol borane using 1.

The ability of bipyridine to display redox non-innocence during catalysis is established with respect to CO₂ reductions,^[15] and we questioned whether similar behavior might be in operation under the conditions shown in Scheme 3. Compound 1 has traditionally been assigned as a nickel(0) complex with a neutral bipyridine ligand on the basis of its ¹H NMR spectrum, whose features are in the range typical for diamagnetic compounds, as well as inferences made from the oxidation state of the Ni(cod)₂ precursor.^[10e,10f] An alternative formulation for **1** is a nickel(I) complex supported by a bipyridine anion radical. The first indication that compound 1 contains a reduced bipyridine ligand comes from its UV/Visible spectrum (Figure 2). The UV/ Visible spectra of both Ni(cod)₂ and bipyridine are featureless between 400 and 1100 nm (Figure S14), while the spectrum of 1 reveals intense bands at 298 nm and 568 nm and broad, overlapping bands between 700 and 1000 nm. Furthermore, the observed transitions are similar to those observed for other metal complexes supported by a bpy- ligand (Figure 2 and Table S4).[16]

The structural parameters of compound **1** were also investigated (Figure 3).^[17] The crystal structure of **1** reveals a nickel center located in a pseudo-tetrahedral environment, with Ni–N bond lengths measuring 1.9397(10) Å and 1.9319(9) Å, and Ni-C distances measuring between 2.0438(12) Å and 2.0640(12) Å.



Table 1. Catalytic hydroboration of ketones, aldehydes, and imines with 1.^[a]

Entry	Substrate	Catalyst loading	Time	Yield ^[b]
		[mol-%]	[h]	[%]
1		0.03	0.5	94
2	H ₃ C CH ₃	0.03	0.8	95
3	H ₃ CO OCH ₃	0.03	0.8	95
4	СН3	0.03	1.0	93
5	H ₃ CO CH ₃	0.03	1.0	91
6	O H	0.03	0.4	85
7	нзс Н	0.03	0.4	93
8	H ₃ CO	0.03	0.4	96
9	NH C	0.3	2.5	83
10	N ^{2CH} 3 H	0.3	2.5	89
11	N H	0.3	2.5	96
12		0.3	2.5	0
13	~~~//	0.3	2.5	0

[a] General conditions: [Pinacol borane] = 100 mm, [substrate] = 100 mm, [1] = 0.03 or 0.3 mm, C_6D_6 solvent, room temperature. [b] ¹H NMR yields using tritert-butylbenzene as an internal standard.

The internal C=C alkene bond lengths of the bound cyclooctadiene ligand are statistically identical to those found in Ni(cod)₂,^[18] however, the mean Ni–C bond length of 2.0528(12) Å is contracted in comparison to Ni(cod)₂ [2.117(3)– 2.130(9) Å], perhaps suggesting that the Ni center in **1** is oxidized.^[19] The contraction of the inter-pyridine C¹–C⁶ bond







Figure 2. UV/Visible spectra of 1 (black) and 1:1 mixture of Na/bipyridine (blue). Inset show spectra plotted on same scale. The spectra were recorded in benzene solvent.

length to 1.4578(15) Å {from 1.530(2) Å in Ni(bpy)- $(H_2O)_2(SO_4)^{[20a]}$ } is consistent with reduction of the bipyridine ligand, as are the observed contractions of the C¹–C², C³–C⁴, and C¹–N¹ bond lengths (see Table S2).^[16,20] However, as several groups have demonstrated, metrical parameters alone cannot rule out the possibility of extensive backbonding from a Ni⁰ center, thus necessitating the use of electronic structure calculations.^[21]



Figure 3. Molecular structure of **1**. Atoms in the bipyridine ring have been labelled for clarity. Ellipsoids shown at 50 % probability.

Attempting to model the electronic state of bpyNi(COD) computationally using the B3LYP functional, as has been demonstrated for a variety of Ni^[22] and Fe^[20d,23] complexes, results in a stable broken symmetry BS(1,1) solution (Figure S18) that is energetically (-1.5 kcal/mol) and structurally indistinguishable from the closed-shell state. Given the potential multi-reference character of 1 and because DFT can misidentify BS solutions^[24] we turned to the CASSCF method. The potential redox activity of bipyridine-type ligands has recently been studied using multi-reference methods, with the authors using the soft criterion of significant electron occupation of the metal-ligand anti-bonding orbital as the indicator of ligand reduction.^[24b] As the CSF weights of 1 fall between what is attributed to ligand reduction vs. π -back-donation, the CASSCF wavefunction of **1** was further analyzed using localization followed by calculation of the configurational interaction (CI) coefficients for the localized orbitals.^[25] This results in two frontier orbitals that are Niand bipyridine-based (Figure 4). The latter orbital has a weighted occupation of 94 % singly occupied, which supports the bipyridine ligand being best considered as monoanionic in **1**.



Figure 4. Ruedenberg-localized frontier molecular orbitals showing Ni (left) and bipyridine (right) character.

The characteristic spectral features of the bpy- species in Figure 2 disappear upon the addition of benzophenone, benzaldehyde, or benzophenone imine to solutions of 1 (Figure S15).^[10e] These UV/Vis results suggest that the reaction between 1 and R₂CO results in oxidation of the bipyridine ligand, loss of cod, and reduction of the Ni¹ ion. Hence, 2 is best described as containing a neutral bipyridine ligand. DFT calculations suggest that 2 contains a Ni⁰ center with substantial interaction with the benzophenone ligand, with both RKS, UKS, and broken symmetry approaches converging to a closed-shell, Ni⁰ species (Figure S18).^[26] In support of this interpretation, the formal reduction of the nickel center, in this case to a Ni⁰ oxidation state, upon the binding of a π -acid such as benzophenone has experimental precedent.^[27] The computed electronic structure of 2 implies that the bipyridine redox activity likely does not contribute to the catalytic activity seen when 1 is used as a precatalyst.

A generally accepted mechanism for the hydroboration of ketones, aldehydes, and imines is shown in Scheme 4.^[28] A key feature of previously proposed mechanisms is the direct interaction of the catalyst with the borane substrate to form a metal hydride species, prior to activation of the ketonic substrate. In contrast, the experimental data presented herein highlights the possibility for another catalytic pathway that proceeds via the nickel-ketone adduct. In this alternative mechanism, compound 2 could be the active catalytic species under the reaction conditions. Hydroboration of benzophenone proceeds smoothly to completion with a catalytic amount of pre-formed and crystallographically characterized Ni(^{tBu}bpy)(benzophenone)^[29] within 30 min. Thermodynamic calculations support the essentially thermoneutral reaction between benzophenone and 1 with a calculated free energy of 2.6 kcal/mol (vs. an experimental value of -0.04 kcal/mol, vide supra). While the experimental data point to the likelihood of 2 being a catalytically active species, the possibility of a nickel hydride intermediate cannot be conclusively dismissed on the basis of thermodynamic arguments.





DFT calculations indicate that the net dissociation of benzophenone from **2** and subsequent oxidative addition of pinacol borane^[30] is only 8.3 kcal/mol uphill in energy (Scheme 5).



Scheme 4. Comparison of previously proposed mechanism for transitionmetal catalyzed hydroboration of alkenes/ketones (top) and the observed reactivity for the hydroboration of ketonic substrates using **1** as a pre-catalyst (bottom).

Ni(bpy)(cod) + Ph₂CO \longrightarrow Ni(bpy)(Ph₂CO) + cod $\Delta G = 2.6$ kcal/mol **1 2**

Ni(bpy)(Ph₂CO) + pinBH
$$\longrightarrow$$
 Ni(bpy)(Bpin)(H) + Ph₂CO $\Delta G = 8.3$ kcal/mol 2

Scheme 5. Calculated free energies for the reaction of benzophenone and pinacol borane with compound **1**.

Conclusion

Compound 1 provides an extremely efficient entryway into the hydroboration of ketones, aldehydes, and imines. In contrast to previously reported assignments, 1 is best described as containing a Ni¹(bpy⁻) fragment. However, the likely catalytic species, compound 2, contains a neutral bipyridine ligand. Both the observation of 2 in stoichiometric experiments and the ability of 2 to efficiently catalyze the hydroboration of benzophenone suggest the possibility of a mechanism for ketone hydroboration that differs from currently accepted pathways. Further mechanistic investigations exploring this possibility and examining the electronic state of the catalytically active species are currently underway.

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- [30] Several putative Ni(bpy)(H)(pin)species of differing geometries and spin states were computationally examined; see the Supporting Information for details. The lowest energy structure is included in the thermodynamic calculations described in Scheme 5 and is best described as a square-planar geometry with a singlet ground state.

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