Polyhedron 32 (2012) 30-34

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Catalytic properties of nickel bis(phosphinite) pincer complexes in the reduction of CO₂ to methanol derivatives

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ARTICLE INFO

Article history: Available online 4 May 2011

Keywords: Nickel Pincer complex Carbon dioxide Reduction Methanol Borane

ABSTRACT

A new nickel bis(phosphinite) pincer complex $[2,6-(R_2PO)_2C_6H_3]$ NiCl (L^RNiCl, R = cyclopentyl) has been prepared in one pot from resorcinol, ClP(C₅H₉)₂, NiCl₂, and 4-dimethylaminopyridine. The reaction of this pincer compound with LiAlH₄ produces a nickel hydride complex, which is capable of reducing CO₂ rapidly at room temperature to give a nickel formate complex. X-ray structures of two related nickel formate complexes L^RNiOCHO (R = cyclopentyl and isopropyl) have shown an "in plane" conformation of the formato group with respect to the coordination plane. The stoichiometric reaction of nickel formate complexes L^RNiOCHO (R = cyclopentyl, isopropyl, and *tert*-butyl) with catecholborane has suggested that the reaction is favored by a bulky R group. L^RNiOCHO (R = *tert*-butyl) does not react with PhSiH₃ at room temperature; however, it reacts with 9-borabicyclo[3.3.1]nonane and pinacolborane to generate a methanol derivative and a boryl formate species, respectively. The catalytic reduction of CO₂ with catecholborane is more effectively catalyzed by a more sterically hindered nickel pincer hydride complex with bulky R groups on the phosphorus donor atoms. The nickel pincer hydride complexes are inactive catalysts for the hydrosilylation of CO₂ with PhSiH₃.

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1. Introduction

Catalytic reduction of CO₂ to liquid fuels such as methanol and hydrocarbons is one of the key strategies to mastering carbon management [1]. Homogeneous systems of such a process are exceedingly rare in the literature [2-4], despite the widespread use of homogeneous catalysts in many other reactions. To make methanol or its derivatives in particular, from CO₂, one has to use an appropriate reagent to abstract one of the two oxygen atoms in CO₂. Successful examples have involved the use of boron- [5] or aluminum-based [6] frustrated Lewis acid-base pairs, largely due to the oxophilic nature of these reagents. Simple silanes [7,8] and boranes [9] may also be used, although a catalyst must be employed to facilitate the reduction. We have recently reported that in the presence of a catalytic amount of L^{tBu}NiH (Fig. 1), the reaction of CO₂ with HBcat affords CH₃OBcat along with catBOBcat as the oxygen-containing byproduct [9]. DFT calculations of our catalytic system have implied that the steric environment around the nickel center is critical to the efficiency of the catalysis [10]. The choice of reductant is also crucial; the same computational study

has predicted that, if $PhSiH_3$ is used instead, the reduction of CO_2 will not occur [10]. To validate these computational results, we report herein the synthesis of related nickel bis(phosphinite) pincer complexes with different sizes of alkyl groups on the phosphorus donor atoms, and the catalytic properties of these complexes in the reduction of CO_2 with various boranes and PhSiH₃.

2. Results and discussion

2.1. Synthesis of L^{cPe}NiH

We have previously prepared L^RNiH (R = tBu and iPr) through the reaction of L^RNiCl with LiAlH₄ in toluene [11]. Unfortunately, using the same approach for the synthesis of L^{Ph}NiH and L^{Me}NiH produced intractable products. It is likely that the smaller R groups do not provide enough steric protection to stabilize the hydride, or perhaps in these complexes the more exposed pincer P–O bonds are susceptible to cleavage by an adventitious base [12]. We were, however, able to isolate L^{cPe}NiH in 55% yield from the reaction between LiAlH₄ and L^{cPe}NiCl, which was obtained following a similar procedure described in the literature [13–17], or alternatively from a one-pot synthesis as shown in Scheme 1. The ¹H NMR spectrum of L^{cPe}NiH in C₆D₆ displays a characteristic hydride resonance at -7.88 ppm as a triplet (²J_{P-H} = 54.4 Hz), and the ³¹P{¹H} NMR spectrum exhibits a singlet at 199.66 ppm.



Abbreviations: HBcat, catecholborane; DFT, density functional theory; tBu, *tert*-butyl; iPr, isopropyl; cPe, cyclopentyl; DMAP, 4-dimethylaminopyridine; 9-BBN, 9-borabicyclo[3.3.1]nonane; HBpin, pinacolborane; TON, turnover number.

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Fig. 1. Nickel bis(phosphinite) pincer hydride complexes (L^RNiH, where R indicates

Most catalytic systems for CO_2 reduction involve the insertion of CO_2 into a metal-hydrogen bond [18–20]. Studies of well-de-

fined nickel hydride systems have shown that nickel formate complexes are the insertion products [9,21–23], except in one case where a more stable hydridonickel cyanate complex was isolated

as a consequence of the ancillary ligand participating in the reaction [24]. Consistent with our previous observation of the reactivity of L^{tBu} NiH [9], the reaction of CO₂ with L^{iPr} NiH or L^{cPe} NiH at room temperature gives the analogous nickel formate complex as the sole product (Scheme 2). Although for the preparative scale reaction, the solution of L^{R} NiH was stirred under 1 atm of CO₂ for 1 h to ensure a full conversion, NMR studies of small-scale reactions suggested that the insertion was complete in several minutes. Both L^{iPr} NiOCHO and L^{cPe} NiOCHO were characterized by NMR spectroscopy, elemental analysis, IR spectroscopy, and X-ray crystallography. Of particular interest is the orientation of the formato groups in their crystal structures (Figs. 2 and 3), which show a relatively small dihedral angle between the least-squares plane de-

fined by P1, P2, C1, Ni atoms and the OC(O)H plane [11.3(5)° in

 L^{iPr} NiOCHO; 16.8(5)° (top structure) and 6.6(7)° (bottom structure) in L^{cPe} NiOCHO]. To accommodate the "in plane" conformation, the iPr and cPe groups are steered away from the OC(O)H moiety to

avoid the steric clash. In contrast, L^{tBu}NiOCHO contains a "perpen-

dicular" formato group in the solid-state structure with a much lar-

ger dihedral angle [73.8(3)°] between the P1-P2-C1-Ni plane and

the OC(O)H plane [9]. However, in the solution the rotation of

the Ni–O3 bond is expected to be rapid. Restricted bond rotation favoring the "in plane" conformer of L^RNiOCHO would render the

two phosphorus nuclei inequivalent. We found that within the

temperature range of 23 to -50 °C, the ³¹P {¹H} NMR spectra of

L^{iPr}NiOCHO and L^{cPe}NiOCHO in toluene-d₈ showed singlet reso-

The regeneration of L^RNiH from the reaction of L^RNiOCHO with

a reducing reagent would close a potential catalytic cycle for the

reduction of CO₂. To understand how the R groups influence the

reactivity of L^{R} NiOCHO, we examined the NMR-scale reactions of these complexes with 3 equivalents of HBcat in C₆D₆ (Scheme 3).

Under the same conditions (concentration and temperature), the

reaction of L^{tBu}NiOCHO is the fastest with quantitative formation

of CH₃OBcat within 10 min. Counterintuitive to the notion that a

2.3. Stoichiometric reaction of L^R NiOCHO (R = tBu, iPr, and cPe)

nances with no significant broadening.

2.2. Synthesis and structures of L^{iPr}NiOCHO and L^{cPe}NiOCHO

the substituents on the phosphorus atoms).

 $L^{R}NiH + CO_{2} (1 atm) \xrightarrow{\text{toluene}} RT, 1h L^{R}NiOCHO$ R = iPr, 82%R = cPe, 77%

Scheme 2.

O PR₂



Fig. 2. ORTEP drawing of L^{ipr}NiOCHO at the 50% probability level. Hydrogen atoms (except the formate hydrogen) are omitted for clarity.

less sterically hindered nickel center would be more susceptible to the attack of HBcat and the subsequent insertion reactions, the reaction of L^{iPr} NiOCHO took 45 min to complete. Interestingly, the reaction of L^{cPe} NiOCHO finished within 10 min; however, the NMR yield of CH₃OBcat was merely 74%, implying a partial decomposition of the nickel complex (or L^{cPe} NiH, which is the intermediate during the reaction).

To expand the scope of reducing reagents that can be used for the reduction of CO₂, we focused on the stoichiometric reaction of L^{tBu}NiOCHO with other boranes and PhSiH₃ under similar reaction conditions (Scheme 4). 9-BBN behaves similarly to HBcat, reducing the nickel formate complex to L^{tBu}NiH and a methoxyboryl species [25] within 1 h. In contrast, even with a large excess of HBpin, only one equivalent of borane was consumed to yield L^{tBu-} NiH and presumably HCOOBpin on the basis of our previous study of similar reactions with HBcat [9]. While this type of boryl formate species is too unstable to be isolated, spectroscopic evidence to support its formation includes ¹H NMR resonances at 8.07 ppm (singlet) and 0.88 ppm (singlet) with an expected integration ratio of 1:12. DFT calculations have suggested that the reaction of L^{tBu}NiOCHO with PhSiH₃ should be sluggish at ambient temperature with a high kinetic barrier of 42.6 kcal/mol [10]. Consistent



Scheme 1.

Table 1



Fig. 3. ORTEP drawing of L^{cPe}NiOCHO at the 50% probability level. Hydrogen atoms (except the formate hydrogen) are omitted for clarity. Two independent molecules in the crystal lattice are shown.

$$L^{R}$$
NiOCHO + 3 HBcat $\frac{C_{6}D_{6}}{RT} L^{R}$ NiH + CH₃OBcat + catBOBcat

Scheme 3.

with the computational prediction, no appreciable reaction was observed when L^{tBu} NiOCHO was mixed with PhSiH₃ for 16 h.

2.4. Catalytic reduction of CO_2 with $L^R NiH$ (R = tBu, iPr, and cPe)

To compare the relative activity of $L^{R}NiH$ in catalyzing the reduction of CO_2 , we chose HBcat as the hydrogen source mainly for two reasons: (1) it has been established in the stoichiometric studies as an efficient reductant for the conversion of nickel formate complexes to a methanol derivative, and (2) the precipitation of catBOBcat from C_6D_6 is often a good indication of a nearly



Scheme 5.

Catalytic activity of nickel pincer hydride complexes in the reduction of CO₂.^a

Catalyst	Reductant	Time	TON
L ^{tBu} NiH	HBcat	45 min	100
L ^{iPr} NiH	HBcat	2 h	100
L _{cPe} NiH	HBcat	12 h	30
L ^{tBu} NiH	PhSiH ₃ ^b	48 h	0

^a Reaction conditions: L^RNiH (25 µmol), HBcat (2.5 mmol), and hexamethylbenzene (62.5 µmol) in 2 mL of C₆D₆ under 1 atm of CO₂ at room temperature.

^b 7.5 mmol of PhSiH₃ was used.

complete reaction. In a typical catalytic study, HBcat and L^RNiH (with a ratio of 100:1) were mixed in C_6D_6 and then stirred under 1 atm of CO_2 (Scheme 5). Hexamethylbenzene was used as an NMR internal standard and the progress of the reaction was monitored by ¹H NMR spectroscopy. When L^{tBu}NiH was used as the catalyst, the reaction took 45 min to reach the maximum TON of 100 (based on B–H, Table 1). The less sterically bulky nickel hydrides proved to be less active catalysts. The same reaction catalyzed by L^{iPr}NiH required 2 h to complete, whereas the catalytic reaction with L^{cPe}NiH did not go to completion within 12 h, giving a TON of 30. Fully rationalizing the substituent effect on the catalytic activity is challenging due to the complexity of the reaction mechanism [9,10]. One explanation is that with a smaller R group, the interaction between L^RNiH and HBcat is more favorable, resulting in a lower concentration of the catalytically active species L^RNiH [9].

We also attempted to carry out catalytic hydrosilylation of CO_2 using PhSiH₃ as the reducing reagent and using L^{tBu}NiH as the catalyst (Table 1). Unfortunately, no reaction was observed at room temperature even after 48 h. This result is consistent with the stoichiometric reaction shown in Scheme 4 as well as the DFT studies [10].

3. Conclusions

We have synthesized a new nickel hydride complex bearing a bis(phosphinite) pincer ligand. This type of hydride complexes with variable sizes of substituents (R groups) on the phosphorus donor atoms undergoes rapid CO₂ insertion to give nickel formate complexes. Comparative studies of the stoichiometric reaction of these formate species with HBcat have demonstrated that the formation of CH₃OBcat, the final product of this process, is favored by bulky R groups. The outcome of the reaction is highly dependent on the reducing reagent that is used. The reaction of a nickel formate complex with 9-BBN produces a similar methanol derivative, albeit at a slower rate. In contrast, HCOOBpin is the reduced product when HBpin is provided as the hydrogen source. Consistent with previous DFT calculations, PhSiH₃ does not react with nickel



formate complexes at room temperature. The catalytic activity of nickel pincer hydride complexes for the reduction of CO_2 with HBcat correlates with the trend observed in the stoichiometric reaction of nickel formate complexes, i.e., more bulky R groups on the phosphorus atoms lead to a more reactive catalyst. The hydrosilylation of CO_2 with PhSiH₃ under similar catalytic conditions does not proceed at all.

4. Experimental

4.1. General considerations

Unless otherwise stated, all the organometallic compounds were prepared and handled under an argon atmosphere using standard glovebox and Schlenk techniques. Carbon dioxide (technical grade), boranes, and PhSiH₃ were purchased from commercial sources and used without further purification. Dry and oxygen-free solvents (THF, diethyl ether, toluene, and pentane) were collected from an Innovative Technology solvent purification system and used throughout the experiments. Methanol was degassed by bubbling argon through it for 15 min and then dried over molecular sieves (4 Å). Benzene- d_6 and toluene- d_8 were distilled from Na and benzophenone under an argon atmosphere. Both ¹H NMR and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance-400 MHz NMR spectrometer. Chemical shift values in ¹H NMR spectra were referenced internally to the residual solvent resonance (7.15 ppm for C_6D_6). The ³¹P{¹H} NMR spectra were referenced to an external 85% H₃PO₄ sample (0 ppm). L^{Me}NiCl [12], L^{Ph}NiCl [13], L^{iPr}NiH [11], L^{tBu}NiH [11], and L^{tBu}NiOCHO [9] were prepared as described in the literature.

4.2. One-pot synthesis of L^{cPe}NiCl

Under an argon atmosphere, 60 mL of THF was added to a Schlenk flask containing resorcinol (550 mg, 5.0 mmol), DMAP (1.28 g, 10.5 mmol), anhydrous NiCl₂ (648 mg, 5.0 mmol), and chlorodicyclopentylphosphine (2.1 mL, 10.5 mmol). The resulting mixture was refluxed for 16 h to give a deep brown solution along with a purple/green precipitate, which was filtered through a short column packed with silica. The filtrate was concentrated by reducing the volume under vacuum to 5 mL, followed by the addition of anhydrous diethyl ether (ca. 10 mL) until a precipitate formed. The solid was collected by gravity filtration and dried under vacuum to give an orange/yellow powder (2.10 g, 78% yield). ¹H NMR (400 MHz, C₆D₆, δ): 1.14-1.19 (m, CH₂, 16H), 1.34-1.41 (m, CH₂, 16H), 2.15–2.20 (m, PCH, 4H), 6.57 (d, ArH, ³J_{H-H} = 8.0 Hz, 2H), 6.86 (t, ArH, ${}^{3}J_{H-H}$ = 8.0 Hz, 1H). ${}^{31}P{}^{1}H$ NMR (162 MHz, C₆D₆, δ): 175.35 (s). Anal. Calc. for C₂₆H₃₉O₂P₂NiCl: C, 57.86; H, 7.28; Cl, 6.57. Found: C, 57.67; H, 7.25; Cl, 6.46%.

4.3. Synthesis of L^{cPe}NiH

Under an argon atmosphere, the suspension of L^{CPe}NiCl (200 mg, 0.37 mmol) and LiAlH₄ (222 mg, 5.55 mmol) in 30 mL of toluene was stirred at room temperature for 24 h. The resulting mixture was filtered through a short plug of Celite to give a yellow solution. Removal of the solvent under vacuum yielded the crude product as a yellow solid, which was subjected to further purification by washing it with a small amount (1 mL × 2) of methanol (102 mg, 55% yield). ¹H NMR (400 MHz, C₆D₆, δ): -7.88 (t, NiH, ²J_{P-H} = 54.4 Hz, 1H), 1.36–1.40 (m, CH₂, 8H), 1.60–1.63 (m, CH₂, 8H), 1.77–1.79 (m, CH₂, 8H), 1.91–1.98 (m, CH₂, 8H), 2.31–2.39 (m, PCH, 4H), 6.87 (d, ArH, ³J_{H-H} = 7.6 Hz, 2H), 7.05 (t, ArH, ³J_{H-H} = 7.6 Hz, 1H). ³¹P{¹H} NMR (162 MHz, C₆D₆, δ): 199.66 (s). Anal. Calc. for C₂₆H₄₀O₂P₂Ni: C, 61.81; H, 7.98. Found: C, 61.12; H, 8.10%.

4.4. Synthesis of L^{iPr}NiOCHO

At room temperature, a stream of CO₂ was bubbled through the solution of L^{iPr}NiH (200 mg, 0.50 mmol) in 20 mL of toluene for 1 h. Subsequent evaporation of the solvent under vacuum yielded L^{iPr}NiOCHO as a yellow powder (183 mg, 82%). X-ray-quality crystals of L^{iPr}NiOCHO were obtained by cooling a saturated pentane solution of the complex to $-30 \,^{\circ}$ C. ¹H NMR (400 MHz, C₆D₆, δ): 1.16–1.21 (m, PCH(CH₃)₂, 12H), 1.30–1.36 (m, PCH(CH₃)₂, 12H), 2.25–2.30 (m, PCH(CH₃)₂, 4H), 6.53 (d, ArH, ³J_{H-H} = 7.6 Hz, 2H), 6.85 (t, ArH, ³J_{H-H} = 7.6 Hz, 1H), 8.34 (s, NiOCOH, 1H). ³¹P{¹H} NMR (162 MHz, C₆D₆, δ): 183.29 (s). IR (in toluene, cm⁻¹): 1605 (C=O). Anal. Calc. for C₁₉H₃₂O₄P₂Ni: C, 51.27; H, 7.25. Found: C, 51.49; H, 7.19%.

4.5. Synthesis of L^{cPe}NiOCHO

At room temperature, a stream of CO₂ was bubbled through the solution of L^{cPe} NiH (100 mg, 0.20 mmol) in 20 mL of toluene for 1 h. Subsequent evaporation of the solvent under vacuum yielded L^{cPe} NiOCHO as a yellow powder (85 mg, 77% yield). X-ray-quality crystals of L^{cPe} NiOCHO were obtained by cooling a saturated pentane solution of the complex to $-30 \degree C$. ¹H NMR (400 MHz, C₆D₆, δ): 1.38–1.42 (m, *CH*₂, 8H), 1.60–1.76 (m, *CH*₂, 12H), 2.00–2.10 (m, *CH*₂, 12H), 2.55–2.60 (m, PCH, 4H), 6.56 (d, ArH, ³J_{H-H} = 7.6 Hz, 2H), 6.86 (t, ArH, ³J_{H-H} = 7.6 Hz, 1H), 8.39 (s, OCHO, 1H). ³¹P{¹H} NMR (162 MHz, C₆D₆, δ): 173.31 (s). IR (in toluene, cm⁻¹): 1605 (C=O). Anal. Calc. for C₂₇H₄₀P₂O₄Ni: C, 59.04; H, 7.34. Found: C, 59.06; H, 7.48%.

4.6. X-ray structure determinations

Crystal data collection and refinement parameters are summarized in Table 2. Intensity data were collected at 150 K on a Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu K α radiation, λ = 1.54178 Å. The data frames were processed

Table 2	
Summary of the crystallographic data	a.

	L ^{iPr} NiOCHO	L ^{cPe} NiOCHO
Formula	C ₁₉ H ₃₂ O ₄ P ₂ Ni	C ₂₇ H ₄₀ O ₄ P ₂ Ni
Formula weight	445.10	549.24
Т (К)	150(2)	150(2)
λ (Å)	1.54178	1.54178
Lattice	triclinic	triclinic
Space group	$P\bar{1}$	ΡĪ
Unit cell dimensions		
a (Å)	8.1207(2)	8.6624(2)
b (Å)	10.0328(2)	14.8388(2)
<i>c</i> (Å)	13.7821(3)	20.8500(3)
α (°)	99.432(1)	83.670(10)
β (°)	99.873(1)	87.601(1)
γ (°)	93.002(1)	89.795(1)
$V(Å^3)$	1087.54(4)	2661.38(8)
Ζ	2	4
$ ho$ (g cm $^{-3}$)	1.359	1.371
μ (mm ⁻¹)	2.844	2.433
θ (°)	3.31-67.90	2.13-67.60
No. reflections collected	9221	22268
No. unique reflections	3743	9101
R _{int}	0.0256	0.0536
No. variable parameters	243	622
$R_1 \left[I > 2\sigma(I) \right]^a$	0.0352	0.0518
$wR_2 [I > 2\sigma(I)]^b$	0.0894	0.1227
R_1 [all data] ^a	0.0447	0.0852
wR_2 [all data] ^b	0.0954	0.1394
Goodness-of-fit (GOF) on F ²	1.027	0.997

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|.$

^b wR₂ = { $\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2$ }^{1/2}.

using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters. For L^{cPe}NiOCHO, two independent molecules crystallize in the lattice. A suitable two-component disorder model is applied for C25B/C25C (Fig. 3, bottom structure). Additional disorder was observed in other cyclopentyl C-atoms; however, reasonable multi-component disorder models were not obtained. The crystallographic data for L^{iPr}NiOCHO and L^{cPe}NiOCHO have been deposited with the Cambridge Crystallographic Data Centre (CCDC-816918 and 816919).

4.7. Stoichiometric reaction of L^RNiOCHO with HBcat

A screw-cap NMR tube was charged with L^{tBu}NiOCHO or L^{iPr}NiOCHO (25 μ mol), hexamethylbenzene (internal standard, 1.0 mg, 6.1 μ mol), and 0.6 mL of C₆D₆. To this solution, HBcat (8.1 μ L, 75 μ mol) was added via a microliter syringe and the reaction was monitored by ¹H and ³¹P{¹H} NMR spectroscopy. The NMR yield was calculated by comparing the integration of CH₃OB-cat methyl resonance (3.34 ppm) with that of the internal standard (2.12 ppm). Because the ¹H NMR resonances of L^{cPe}NiOCHO overlap with that of hexamethylbenzene, for the study of L^{cPe}NiOCHO, hexamethyldisilane (0.07 ppm) was used as the NMR internal standard. Control experiments showed that neither hexamethylbenzene nor hexamethyldisilane interfered with the reactions.

4.8. Stoichiometric reaction of L^{tBu}NiOCHO with boranes

A screw-cap NMR tube was charged with L^{tBu} NiOCHO (12.5 mg, 25 µmol), hexamethylbenzene (internal standard, 2.0 mg, 12.5 µmol), and 0.6 mL of C₆D₆. To this solution, 9-BBN or HBpin (75 µmol) was added via a microliter syringe and the reaction was monitored by ¹H NMR and ³¹P{¹H} spectroscopy. After 1 h reaction with 9-BBN, L^{tBu} NiH was the only nickel species observed by ³¹P{¹H} spectroscopy. The boron-containing products were identified as the known *B*-methoxy-9-BBN [25] and a borate ester [26]. The reaction of HBpin led to the quantitative formation of L^{tBu} NiH and HCOOBpin within 15 min.

4.9. Attempted stoichiometric reaction of L^{tBu}NiOCHO with PhSiH₃

A screw-cap NMR tube was charged with L^{tBu} NiOCHO (12.5 mg, 25 µmol), PhSiH₃ (3.2 µL, 25 µmol), and 0.6 mL of C₆D₆. The progress of the reaction was monitored by ¹H and ³¹P{¹H} NMR spectroscopy. No appreciable reaction was observed within 16 h.

4.10. Catalytic hydroboration of CO₂ with L^RNiH

Under an argon atmosphere, a flame-dried 50 mL Schlenk flask was charged with L^{R} NiH (25 µmol), HBcat (272 µL, 2.50 mmol), and 2 mL of C₆D₆. To this solution, hexamethylbenzene (10.0 mg, 62.5 µmol) was added as an internal standard. The mixture was degassed by a freeze–pump-thaw cycle and placed under 1 atm of CO₂. At different time intervals, a small portion of the clear liquid layer (*ca.* 0.6 mL) was withdrawn from the flask and transferred into a J. Young NMR tube under an argon atmosphere. From the ¹H NMR spectrum of the aliquot, turnover number (TON) was calculated by comparing the integration of CH₃OBcat methyl resonance (3.34 ppm) with that of the internal standard (2.12 ppm).

4.11. Attempted catalytic hydrosilylation of CO₂ with L^{tBu}NiH

Under an argon atmosphere, a flame-dried 50 mL Schlenk flask was charged with L^{tBu} NiH (12.5 mg, 25 µmol), PhSiH₃ (953 µL, 7.50 mmol), and 2 mL of C₆D₆. The mixture was degassed by a freeze–pump-thaw cycle and placed under 1 atm of CO₂. After 24 h, a small portion of the clear liquid layer (*ca.* 0.6 mL) was transferred into a J. Young NMR tube under an argon atmosphere. The ¹H NMR spectrum of the solution showed the unreacted PhSiH₃ with no evidence of forming a methanol derivative.

Acknowledgments

We thank the National Science Foundation (CHE-0952083) and the donors of the American Chemical Society Petroleum Research Fund (49646-DNI3) for support of this research. S. Chakraborty is grateful to the University of Cincinnati URC for a graduate student research fellowship. X-ray data were collected on a Bruker SMART6000 diffractometer which was funded through an NSF-MRI Grant (CHE-0215950).

Appendix A. Supplementary data

CCDC 816918 and 816919 contain the supplementary crystallographic data for L^{iPr}NiOCHO and L^{cPe}NiOCHO. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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